Determination of antioxidant migration levels from polyethylene films into legumes

Polietilenden baklagillere geçen antioksidanların saptanması

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ABSTRACT
Polyethylene packaging is a widely used packaging material in a wide range of foods such as bread, pulses, and meat products. These materials, which are produced in the form of small granules, are produced with different techniques depending on their usage area. Methods such as extrusion, blow molding and molding are the most frequently used of these production forms. As a result of some studies, it has been determined that some additives used during the production and called as masterbatch have a contact with food and they pass through food and beverages in this way. In this study, polyethylene samples containing 1000 ppm and 3000 ppm of Irganox 1010 (pentaerythritoltetraakis(3-(3,5-di-tbutyl-4-hydroxyphenyl) propionate) and Irganox 1076 (octadecyl 3-(3,5-di-tbutyl-4-hydroxyphenyl) propionate) were prepared. Then, five different legume samples (rice, cracked wheat, corn, white beans, and chickpea) were sandwiched between two circular pieces of polyethylene films, with the contact layer facing the sample. Samples were stored at two different temperatures (4 ºC and 25 ºC) for 30 days. Migration quantities were determined using GC-MS and comparative evaluations were made. Migration amounts from polyethylene samples containing 1000 ppm Irganox 1010 at 4 ºC are between 364-642 ppb, while migration amounts from polyethylene samples containing 1000 ppm Irganox 1010 are between 407 and 682 ppb. In these conditions, the highest migration was 682 ppb from 3000 ppm polyethylene to cracked wheat in 30 days, while the lowest migration was 364 ppb from 1000 ppm polyethylene to white beans in 10 days. Transitions from polyethylene samples containing 1000 ppm Irganox 1010 at 25 ºC are in the range of 423 - 827 ppb, and the migration amounts from polyethylene samples of 3000 ppm are in the range of 512 - 848 ppb. In these conditions, the highest migration was 848 ppb from 3000 ppm polyethylene to cracked wheat in 30 days, while the lowest migration was 423 ppb from 1000 ppm polyethylene to white beans in 10 days.

Key Words: Polyethylene packaging, Irganox 1010, Irganox 1076, Migration, Legume.

ÖZ
Polietilen paketleme, ekmek, baklâyat ve et ürünlerleri gibi çok çeşitli gıdalarda yaygın olarak kullanılan bir ambalaj malzemesidir. Kuçük granüllü formunda üretilen bu malzemeler kullanımlarını bağlı olarak farklı tekniklerle üretilmektedir. Ekstrüzyon, şişirmeli kalıplama ve kalıplama gibi yöntemler bu üretim formlarında en sık kullanılanlardır. Bazı çalışmalar sonucunda, üretim sırasında kullanılan ve “masterbatch” olarak adlandırılan bazı katkı maddelerinin gıda ile temas ettiğini ve bu şekilde yiyecek ve içeceklerde geçtiğini tespit edilmiştir. Bu çalışmada, 1000 ppm ve 3000 ppm Irganoks 1010 ve Irganoks 1076 içeren polietilen örnekler hazırlanı. Daha sonra, beş farklı baklagil numunesi (pirinç, bulgur, msir, kuru fasulye ve nohut) iki dairesel polietilen film parçası arasına yerleştirildi. Elde edilen sonuçlara göre Irganox 1010’un 4 ºC'de 1000 ppm’lik polietilen numunelerinden geçenkeßen migrasyon miktari 362-644 ppb, 3000 ppm’lik polietilen numunelerinde geçenkeßen migrasyon miktarı ise 407-682 ppb.
**Introduction**

Plastic is a material consisting of any of synthetic or semi-synthetic organic compounds that can be molded into soft and solid objects. Plastic materials have become the most important commercial materials today because they are light, inexpensive, and easy to process and have many different uses. Because of these properties, it is frequently used in food packaging.

Polyolefins, together with the two most popular types, polypropylene and polyethylene, are the largest thermoplastic group since they can be used in a wide variety of applications. Polyolefins are polymers which consist of simple olefins such as ethylene, propylene, butene, isoprene or pentene, and copolymers thereof. Easy process ability, low cost, good chemical and physical properties make them the best choice for a wide range of plastic applications (Peacock, 2000). Antioxidants are used to increase the resistance of polyolefin containing materials to high temperature and UV light. When polyolefins are used in food packaging, these compounds or their degradation products may be transferred from plastics to foodstuffs during processing or storage. This situation may pose a risk to human health. Al-Malaika reviewed the effect of some of the parameters on the leaching of antioxidants in the human environment. Migration of antioxidants from packaging material to food product is determined by the interaction of a number of physical and chemical parameters, including the nature of the polymer and the food product; the molecular weight, volatility, and solubility of the antioxidant; temperature, light, irradiation and duration of contact with the food product. It provides important information about determination of antioxidant contents of polyolefinic materials, their potential migration and plastic quality measurements (Al-Malaika, 2004).

The most commonly used antioxidants to ensure long-term thermal stability of polyolefins are Irganox 1010 (pentaerythritoltetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate) and Irganox 1076 (octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate). U.S. Food and Drug Administration (U.S. FDA) has set the tolerable daily intakes of Irganox 1010 and Irganox 1076 at 0.115 mg/kg body weight/day (U.S. FDA, 2015). The specific migration limit for Irganox 1010 and Irganox 1076 in food or food simulant was set at 6 mg/kg food by the EU Commission (European Commission, 2003).

In the literature, there are many studies on the migration of antioxidants from polyolefinic materials into the various foods (Marcato et al., 2003; Burman et al., 2005; Dopico – Garcia et al., 2007; Galotto et al., 2011; Reinas et al., 2012; Karaca and Taşdemir, 2014; Coltro et al., 2014; McCombie et al., 2016; Vera et al., 2018). In these studies, commercial packaging materials were used to examine migration of the antioxidants. Cereals and legumes are widely consumed foods that help to sustain two-thirds of the worlds’ population. Legumes are sold in polyethylene packaging. There is no study on the determination of antioxidant migration levels from polyethylene films into legumes in the literature.

In this study, migration levels of Irganox 1010 and Irganox 1076 from polyethylene packages into legumes such as rice, cracked wheat, corn, white beans, chickpea at two different temperatures (4 °C and 25 °C) and different storage times (10, 20, 30 days) were determined.
Materials and Methods

Reagents and Standards

The studied migrants Irganox 1010 and Irganox 1076 were supplied from BASF Co. (Charlotte, USA). All chemicals were obtained from Merck (Darmstadt, Germany). All chemicals used were of analytical reagent grade and were at least 99.5% pure.

Preparation of Masterbatch Forms

The antioxidants in fine powder form were homogeneously mixed with pure granular low density polyethylene, then melted and re-granulated. Masterbatch production machine is used for this. It is a GS- mach GSD-150 model single-screw extruder with a screw diameter of 25 mm and length of 40 L/D. Masterbatchs are prepared to be 10% antioxidant + 90% polyethylene (w/w).

Masterbatch and Polyethylene Granule Filling

The masterbatch produced in granule form and the pure low density polyethylene (H2-8 code product) raw material from PETKİM were filmed in the extrusion machine as a single layer pipe with a thickness of 60 µm and a width of 30 cm. Fong Kee single-screw extruder (L=400 mm and L/D=20) was used. The screw speed was 90 rpm at the constant temperature profile of 190 ºC. The blow up ratio and draw down ratio were 2.5 and 23, respectively. Corona treatment has not been applied to the product since it is not necessary. Polyethylene films containing 1000 ppm and 3000 ppm of Irganox 1010 and Irganox 1076 were prepared according to the information provided in the European Union practical guide for plastic packaging (European Commission, 2003). Polyethylene films are shown in Fig.1.

Migration Tests

Legume samples were sandwiched between two circular pieces of plastic, with a total surface area of 0.565 dm² (2 discs of 0.283 dm² each). Then, these sets were placed in 6 cm diameter petri dishes and stored at two different temperatures (4 ºC and 25 ºC) for 30 days according to the standard migration conditions of the US FDA (US FDA, 2015). The system used is shown schematically in Fig. 2.

Quantification of Migrant in the Legumes

The migrants from the legumes were extracted with 5 ml isoctane for 2 h. The legume samples were shaken in a vortex every 20 min to enhance extraction. Solid phase was separated by centrifugation at 4500 rpm for 5 min. Quantification was carried out using a Shimadzu QP2010-Ultra model gas chromatography – mass
spectrometer. Calibration curves with 5 standards up to 1400 ng ml\(^{-1}\) for Irganox 1076 (correlation coefficient 0.9985) and Irganox 1010 (correlation coefficient 0.9999). The limits of detection were determined to be 40 ng ml\(^{-1}\) for Irganox 1076 and 20 ng ml\(^{-1}\) for Irganox 1010. Carbowax 20 M (30 m x 0.25 mm; 0.25 µm) column was used. The oven was held at an initial temperature of 50 ºC for 5 min, then increased to 200 ºC at the rate of 10 ºC per minute, the end temperature of 200 ºC held for 20 minute. All analyses were repeated three times for each sample.

**Results and Discussion**

The amounts of migrants passing to the legumes contacted at 25 ºC and 4 ºC for 10 days, 20 days and 30 days with PE samples prepared to contain 1000 ppm and 3000 ppm from Irganox 1076 are given in Table 1 and Table 2, respectively. It is observed that the migration levels of Irganox 1076 into legumes increased with increasing antioxidant content of polyethylene packages and storage time. It is thought that as the contact time increases, the migration value approaches towards an equilibrium value.

Irganox 1076 concentrations were found ranging from 350.83 – 1702.20 µg kg\(^{-1}\) and 222.34 – 1108.48 µg kg\(^{-1}\) in the legume samples during 30 days of storage at 25 ºC and 4 ºC, respectively. The highest Irganox 1076 concentrations were determined in rice and cracked wheat, while the lowest Irganox 1076 concentration was determined in chickpea. These results are consistent with the contact time, the concentration of the migrant in the polyethylene and the size of the contact surface with the pulses. It is seen that the migration in all the legumes kept at 4 ºC is lower than those kept at 25 ºC. Migration of Irganox 1076 to legumes stored at 4 ºC for 30 days was found to be 25-40 % less than those stored at 25 ºC.

Table 1. Migration data depending on storage time at 25 ºC for Irganox 1076

| Legumes         | Amount of Irganox 1076 Miktari (mg kg\(^{-1}\)) | The amount of migrants passing to the legumes (µg kg\(^{-1}\)) | Tenth day 10.gün | Twentieth day 20.gün | Thirtieth day 30.gün |
|-----------------|-----------------------------------------------|------------------------------------------------------------|------------------|---------------------|---------------------|
| Rice            | 1000                                         | 1405.52 ± 1.0                                              | 1498.32 ± 1.0    | 1548.16 ± 1.0       |
| Pirinç          | 3000                                         | 1523.80 ± 1.0                                              | 1644.83 ± 1.0    | 1702.20 ± 1.0       |
| Rice            | 1000                                         | 808.26 ± 0.7                                               | 902.12 ± 0.7     | 953.30 ± 0.8        |
| Pirinç          | 3000                                         | 939.09 ± 0.9                                               | 1068.20 ± 1.0    | 1125.60 ± 1.0       |
| Cracked wheat   | 1000                                         | 652.75 ± 0.6                                               | 778.52 ± 0.6     | 833.14 ± 0.7        |
| Bulgur          | 3000                                         | 701.56 ± 0.6                                               | 824.16 ± 0.7     | 886.98 ± 0.7        |
| Corn            | 1000                                         | 587.16 ± 0.6                                               | 698.16 ± 0.6     | 748.32 ± 0.6        |
| Misir           | 3000                                         | 690.30 ± 0.6                                               | 801.24 ± 0.7     | 856.13 ± 0.7        |
| White beans     | 1000                                         | 350.83 ± 0.5                                               | 467.63 ± 0.5     | 507.51 ± 0.5        |
| Kuru fasulye    | 3000                                         | 371.72 ± 0.5                                               | 498.32 ± 0.5     | 549.85 ± 0.5        |
| Chickpea        |                                              |                                                            |                  |                     |
| Nohut           |                                              |                                                            |                  |                     |
Table 2. Migration data depending on storage time at 4 ºC for Irganox 1076

| Legumes | Amount of Irganox 1076 (mg kg\(^{-1}\)) | The amount of migrants passing to the legumes (µg kg\(^{-1}\)) |
|---------|----------------------------------------|--------------------------------------------------------|
|         | Tenth day 10.gün | Twentieth day 20.gün | Thirtieth day 30.gün |
| Rice    | 1000    | 802.50 ± 0.7 | 890.48 ± 0.7 | 942.26 ± 0.8 |
| Pirinç  | 3000    | 933.00 ± 0.8 | 1052.24 ± 1.0 | 1108.48 ± 1.0 |
| Cracked wheat Bulgur | 1000    | 569.18 ± 0.6 | 659.54 ± 0.6 | 710.44 ± 0.6 |
| Cracked wheat Bulgur | 3000    | 700.98 ± 0.8 | 826.52 ± 0.7 | 888.32 ± 0.7 |
| Corn Misir | 1000    | 514.36 ± 0.5 | 603.56 ± 0.6 | 652.16 ± 0.6 |
| Corn Misir | 3000    | 568.44 ± 0.5 | 658.80 ± 0.6 | 710.50 ± 0.6 |
| White beans Kuru fasulye | 1000    | 426.19 ± 0.5 | 513.46 ± 0.5 | 561.85 ± 0.5 |
| White beans Kuru fasulye | 3000    | 548.25 ± 0.5 | 638.66 ± 0.6 | 689.60 ± 0.6 |
| Chickpea Nohut | 1000    | 222.34 ± 0.3 | 312.52 ± 0.5 | 363.48 ± 0.5 |
| Chickpea Nohut | 3000    | 256.48 ± 0.3 | 344.15 ± 0.5 | 395.72 ± 0.5 |

Table 3. Migration data depending on storage time at 25 ºC for Irganox 1010

| Legumes | Amount of Irganox 1010 (mg kg\(^{-1}\)) | The amount of migrants passing to the legumes (µg kg\(^{-1}\)) |
|---------|----------------------------------------|--------------------------------------------------------|
|         | Tenth day 10.gün | Twentieth day 20.gün | Thirtieth day 30.gün |
| Rice    | 1000    | 518.70 ± 0.5 | 642.62 ± 0.6 | 693.44 ± 0.6 |
| Pirinç  | 3000    | 647.64 ± 0.6 | 758.22 ± 0.6 | 800.50 ± 0.7 |
| Cracked wheat Bulgur | 1000    | 656.14 ± 0.6 | 782.15 ± 0.6 | 827.58 ± 0.7 |
| Cracked wheat Bulgur | 3000    | 680.11 ± 0.6 | 800.30 ± 0.7 | 848.12 ± 0.7 |
| Corn Misir | 1000    | 470.49 ± 0.5 | 590.35 ± 0.6 | 632.14 ± 0.6 |
| Corn Misir | 3000    | 556.32 ± 0.5 | 670.20 ± 0.6 | 710.22 ± 0.6 |
| White beans Kuru fasulye | 1000    | 423.67 ± 0.5 | 544.20 ± 0.5 | 608.12 ± 0.6 |
| White beans Kuru fasulye | 3000    | 512.20 ± 0.5 | 640.12 ± 0.6 | 700.26 ± 0.6 |
| Chickpea Nohut | 1000    | 485.37 ± 0.3 | 600.18 ± 0.6 | 642.30 ± 0.6 |
| Chickpea Nohut | 3000    | 560.82 ± 0.5 | 668.42 ± 0.6 | 712.10 ± 0.6 |

The amounts of migrants passing to the legumes contacted at 25 ºC and 4 ºC for 10 days, 20 days and 30 days with PE samples prepared to contain 1000 ppm and 3000 ppm from Irganox 1010 are given in Table 3 and Table 4, respectively. Irganox 1010 concentrations were found ranging from 423.67 – 848.12 µg kg\(^{-1}\) in the legume samples during 30 days of storage at 25 ºC. The highest Irganox 1010 concentration was determined in cracked wheat, while the lowest...
Irganox 1010 concentration was determined in white beans. Irganox 1010 concentrations were found ranging from 364.58 – 682.20 µg kg\(^{-1}\) in the legume samples during 30 days of storage at 4 ºC. Similarly, the highest Irganox 1010 concentration was determined in cracked wheat, while the lowest Irganox 1010 concentration was determined in white beans. Migration of Irganox 1010 to legumes stored at 4 ºC for 30 days was found to be 15-25 % less than those stored at 25 ºC.

Many factors need to be controlled to ensure that food is delivered to the consumer in a healthy manner. These factors start with the production process of food and continue with packaging and sales. One of the most important factors is packaging. Although packaging materials are compatible with food and are not intended to interact with food, it is also known that there is no practically inert packaging. In this case, the most important criterion is the physical contact and chemical interactions between foods and packaging material.

Irganox 1010 and Irganox 1076 are the most widely used additives in polyethylene packages. Although there are some studies on the migration of these additives in the literature (Chang et al., 2019; Dopico – Garcia et al., 2003; Dopico – Garcia et al., 2007; Galotto et al., 2011; Beldi et al., 2012), there is no study on the migration from polyethylene packages containing controlled amounts of additives into the foods.

**Conclusion**

In this study, the controlled forms and contents of the polyethylene packages containing Irganox 1010 and Irganox 1076 were contacted with solid legumes at different temperatures and times and the migration amounts were measured. Migration levels of both Irganox 1076 and Irganox 1010 into legumes increased with increasing antioxidant content of polyethylene packages and storage time. Furthermore, it has been determined that migrations occurring in refrigerated samples are less than samples stored at room temperature. Thus, temperature has similar impact on the migration of both Irganox 1010 and Irganox 1076.
1076 and Irganox 1010 when migrating into the same matrix.

Specific migration levels were established at 6 mg/kg for Irganox 1076 and Irganox 1010 by European legislation. The determined concentrations of Irganox 1076 and Irganox 1010 did not exceed its specific migration limit. As a result, we can say that these antioxidants are not a risk factor for human health at the present time.

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Compliance with Ethical Standards

Conflict of Interest: The authors declare that they have no conflict of interest.

Ethical approval: For this type of study formal consent is not required.

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