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Migration of toluene through different plastic laminated films into food simulants

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ABSTRACT

Laminated films are generally prepared from two or more monolayer films bonded using adhesives, such that the printing ink and adhesives are located between the films. Although the organic solvents in the adhesive, printing ink, and diluter are not in direct contact with the food, they may migrate through the films under certain conditions, potentially threatening human health. In this study, gas chromatography was used to analyze the migration rate of residual toluene from laminated films into four food simulants, namely isooctane, 50% ethanol, 3% acetic acid, and 10% ethanol. The effect of different parameters on toluene migration was characterized for internal films prepared with either low density polyethylene (LDPE) or cast polypropylene (CPP). The migration rate varied markedly with the temperature, with higher temperatures leading to accelerated migration into the simulants. The toluene levels in the simulants plateaued after a certain time period. Isooctane was the simulant into which toluene migrated the fastest. CPP films proved more efficient barriers than those prepared with LDPE. Within a certain range, increasing the initial toluene content in the laminated films had almost no observable effect on its migration rate.

1. Introduction

Plastic films are mechanically strong and chemically stable and thereby play an important role in food packaging. Laminated films are prepared from two or more films bonded using adhesives, so that the beneficial properties of both may be utilized simultaneously and provide an optimal and flexible packaging material for food preservation. These laminated films significantly increase the shelf life of various packaged foods such as fish, meat, cheese, sausage, poultry, beverages, and sauerkraut.

Low density polyethylene (LDPE) and cast polypropylene (CPP) films form effective moisture barriers and provide good heat sealing. In laminated films (Twede & Goddard, 1998), they are widely used for the inner layer, which is in direct contact with the food. In industry, plastic composite films are prepared either by extrusion or dry lamination (Torres, Guarda, Moraga, Romero, & Galotto, 2012), with the latter being the simpler, less expensive, and therefore most widely used process, accounting for more than 70% of all composite film production. In dry lamination, a single-layer film is coated with an adhesive that is then evaporated in a drying oven. The coated film is then laminated onto another single-layer film at high temperature and pressure. The substances used for printed lamination films—printing inks, adhesives, and organic solvents—which are located between the two layers, may nonetheless migrate through the latter and into the foodstuffs (Dong, Li, & Zhang, 2011; Katan, 1996; Reinas, Oliveira, Pereira, Machado, & Pocas, 2012).

The two solvents most often used for the ink and adhesives are toluene and ethyl acetate. Toluene is one of the most widely used aromatic solvents but is a known carcinogen and teratogen (Bowen & Hannigan, 2013). It is toxic furthermore to the liver and to the hematological and immune systems. The migration of solvents such as toluene from wrapping into food therefore affects not only the taste and quality of the latter, but is also a potential health hazard.

The diffusion of chemical substances through plastic films is a very complex process that depends on several factors such as the

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concentration of the substances in the packaging and the food, the fat content of the latter, the temperature, and the storage time (Bhuni, Sablani, Tang, & Rasco, 2013). The migration process can be divided into four major steps: the sorption of the compounds at the plastic–food interface, the diffusion of chemical compounds through the polymers, the desorption of the diffused molecules from the polymer surface, and the diffusion of the compounds in the food (Coltro et al., 2014; Ferrara, Bertolodo, Scoponi, & Ciardelli, 2001).

Previous studies have highlighted the presence of many compounds in the different laminated films on the market, 66% of which migrated into the simulant Tenax (a solid food simulants), with toluene in particular reaching 1.2 mg/kg (Vera, Canellas, & Nerín, 2014). A study of the migration of alkylbenzenes from offset printing inks into hamburger rolls found 2 mg/kg alkylbenzenes therein. (Aurela, Ohra-aho, & Söderhjelm, 2001). Goulas (2001) showed that the overall migration from five-layer coextruded packaging films into aqueous food simulants was 2.3–15.9 mg/L. Elsewhere, Meng et al. have characterized the risk of food contamination arising from the migration of alkylbenzenes from paper and plastic packaging materials into food (Meng, Liao, Sun, Liao, & Liu, 2007).

According to European Union (EU) regulations, the quality of food packaging materials is assessed mainly via two migration indexes: the overall migration limit (OML) and the specific migration limit (SML). The regulations state that plastic packages should not transfer their constituents to food simulants in quantities exceeding the OML, namely 10 mg in total per dm^2 of food contact surface (mg/dm^2). Furthermore, the contents in the food of particular packaging constituents should be below 60 mg/kg, the SML (Reg 10/2011). Furthermore, all food-contact materials need to follow European Commission Regulation 1935/2004 (Reg 1935/2004), which states that substances migrating into food should not be harmful to humans. Furthermore, benzene derivatives are strictly prohibited in foodstuffs, both in Europe and the United States. The EU has no specific regulations concerning adhesives or ink in plastic laminated films. Nonetheless, such limits have been included in the corporate standards of certain companies. For example, Coexpan ensures that the total amount of solvent residues transferred into its wrapped foodstuffs does not exceed 20 mg/m^2 (Mao, Zheng, Yu, Jiang, & Chen, 2008).

In the People's Republic of China (PRC), the General Administration of Quality Supervision, Inspection and Quarantine has published Review Guidelines for the Manufacturing License of Food-Grade Plastic Package, Container, Tools and Other Products, which states that the total amount of solvent residues in plastic laminated film (pouch) products should be less than 10 mg/m^2 in general, and less than 2 mg/m^2 for benzene derivatives (AQSIQ, 2006). The national standard GB/T 10004-2008 specifies the acceptable level of solvent residues in food-grade laminated films. The total solvent content should be less than 5.0 mg/m^2 and no benzene derivatives should be detected (AQSIQ, 2008). However, this standard only considers three types of laminated film whereas more than 20 of these are currently in use on the market, with their own specific company standards that may differ in terms of their residual solvent limits. Indeed, rather than banning it completely, some companies only require benzene derivative contents to be less than 2 mg/m^2. Clearly, although efforts are being made in the PRC to resolve problems related to solvents in food-grade laminated films, the many factors that can affect solvent migration into food mean that systematic studies thereof are currently lacking.

In this study, two plastic laminated films prepared with different inner layers were chosen to study the effects, among others, of temperature, simulants, time and inner layer materials on migration. In view of reducing the hazards associated with toluene ingestion, the results presented herein provide a scientific basis for future regulations concerning the migration of toluene from laminated films into foodstuffs.

2. Materials and methods

2.1. Reagents

Chromatography grade toluene, isooctane, anhydrous ethanol, and acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd, Shenyang, PRC. Ultrapure water was prepared using a Milli-Q filtration system.

According to relevant EU rules and regulations, as well as for practical reasons, migration tests were conducted on the films in contact with the following four food simulants (Reg 10/2011; Directives 82/711/EEC & 85/572/EEC).

Simulant A: isooctane;
Simulant B: ethanol 50% (v/v) aqueous solution (Milli-Q water);
Simulant C: ethanol 10% (v/v) aqueous solution (Milli-Q water);
Simulant D: acetic acid 3% (w/v) aqueous solution (Milli-Q water).

2.2. Samples

Two compositions were used for the printed laminate samples, namely biaxial oriented propylene (BOPP)/LDPE and BOPP/CPP, with BOPP forming the outer layer and LDPE or CPP the inner one in direct contact with the food. The samples were provided by Shenyang Bafang Plastic Packaging Co., Ltd. The laminated films were heat-sealed into pouches.

In this study, four types of laminated film samples were prepared, namely:

LDPE30: a BOPP/LDPE bilayer film with a 30 μm thick LDPE (inner) layer;
LDPE50: a BOPP/LDPE bilayer film with a 50 μm thick LDPE layer;
CPP30: a BOPP/CPP bilayer film with a 30 μm thick CPP layer;
CPP50: a BOPP/CPP bilayer film with a 50 μm thick CPP layer.

The effect of the initial toluene concentration on its migration rate through different laminated films was investigated. The initial toluene contents of samples in groups A, B, and C were 1.371–1.402 mg/m^2, 2.407–2.593 mg/m^2, and 3.612–3.708 mg/m^2, respectively (Table 1).

2.3. Migration tests

According to EU regulation No 10/2011, isooctane, 50% ethanol, 10% ethanol and 3% acetic acid were selected as food simulants with a surface-to-volume ratio of 1 dm^2/20 mL (Reg 10/2011), and single-surface migration tests were performed within the pouches. The food simulants were packed into the pouches and then

Table 1
Initial toluene contents of the different laminated films (n = 3).

Sample	Initial content ± SD (mg/m^2)		
	A	B	C
LDPE30	1.373 ± 0.021	2.561 ± 0.029	3.612 ± 0.025
LDPE50	1.402 ± 0.010	2.593 ± 0.037	3.708 ± 0.036
CPP30	1.371 ± 0.017	2.407 ± 0.028	3.669 ± 0.021
CPP50	1.381 ± 0.014	2.586 ± 0.030	3.645 ± 0.033