ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

MIGRATION OF DIPROPYLENE AND TRIPROPYLENE GLYCOL DIACRYLATE FROM PACKAGING MATERIALS AND SCREENING OF POTENTIAL RISKS IN PAPER PACKAGINGS

M.Sc. THESIS

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JANUARY 2013

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

AMBALAJLARDAN DİPROPİLEN GLİKOL DİAKRİLAT VE TRİPROPİLEN GLİKOL DİAKRİLAT MİGRASYONUNUN BELİRLENMESİ VE KAĞIT AMBALAJLARDA POTANSİYEL RİSKLERİN TARANMASI

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OCAK 2013

Havvana Tuba Yavuz, a **M.Sc.** student of ITU **Institute of Science Engineering and Technology** student ID **506101509**, successfully defended the **thesis** entitled **''MIGRATION OF DIPROPYLENE AND TRIPROPYLENE GLYCOL DIACRYLATE FROM PACKAGING MATERIALS AND SCREENING OF POTENTIAL RISKS IN PAPER PACKAGINGS**", which he/she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Beraat ÖZÇELİK** İstanbul Technical University	.....
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To my family,

FOREWORD

First of all, I would like to express my special thanks and gratitude to my supervisor and mentor, Prof. Dr. Beraat ÖZÇELİK who helped me in countless ways, educated me in the scientific and academic field, and supervised me to carry out this study. This master thesis was carried out in Institute of Chemical Technology Prague as a part of Erasmus Student Exchange Programme. I would like to express my deep appreciation and thanks for my supervisor in Czech Republic, Assoc.Prof. Jaroslav Dobias, for his valuable advices and guidance during this study.

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January 2013

Havvana Tuba Yavuz
(Food Engineer)

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ABBREVIATIONS

ADI	: Acceptable Daily Intake
BP	: Benzophenone
BBP	: Benzylbutylphthalate
BHT	**:** Butylated Hydroxytoluen
DEHA	: Bis (2-ethylhexyl) adipate
DEHP	: Di(2-ethylhexyl) phthalate
DEAB	: 4,4-bis (diethylamino) benzophenone
DBP	: Dibutylphthalate
DiBP	: Diisobutylphthalate
DiNP	: Diisononylphthalate
DiDP	: Diisodecylphthalate
DiPN	: Diisopropylnaphthalene
DIPN	: Diisopropylnaphthalene
DMAB	: 4,4-bis(dimethylamino) benzophenone
DPGDA	: Dipropylene Glycol Diacrylate
EB	: Electron beam
EB	: Electron beam
EtOH	: Ethanol
FDA	: Food and Drugs Administration
GC/MS	: Gas Chromatography-Mass Spectrometry
HS-SPME	: Head Space Solid Phase Microectraction
LDPE	: Low density polyethylene
LD_{50}	: Lethal Dose,%50
PAAs	: Primary aromatic amines
PAH	: Polycyclic aromatic hydrıcarbons
PL	: Positive List
SIM	: Selected Ion Mode
SML	: Specific migration limit
SCF-L	: Scientific Committee of Food list
TBC	: Tributyl acetylcitrate
TDI	: Tolerable Daily Intake
TSCA	: Toxic Substances Control
TPGDA	: Tripropylene Glycol Diacrylate
UV	: Ultraviolet

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MIGRATION OF DIPROPYLENE AND TRIPROPYLENE GLYCOL DIACRYLATE FROM PACKAGING MATERIALS AND SCREENING OF POTENTIAL RISKS FOR PAPER PACKAGINGS

SUMMARY

Paper is widely used as primary, secondary and tertiary packaging in food industry. It may endanger health due to migration risk of its constitute into foods. Concerns for potential risks of paper packagings contacted with food increase due to the lack of special regulatory reguirement about paper and paper board especially the printing inks used for packaging material. Therefore, more research is necessary to determine potential hazardous substances that may migrate from food packaging into food.

The aim of this study was (i) to investigate the occurence of residual dipropylene and tripropylene glycol diacrylates (DPGDA, resp. TPGDA) in the stick paper packages of crystaline sugar and in the packaged sugar which had been complained about unpleasant smell (ii) to study migration of DPGDA and TPGDA from packaging materials made of paper coated with LDPE into 10% and 90% ethanol iii) to study migration of DPGDA and TPGDA from packaging materials into different simulant (iv) to study risk assesment of paper packagings supplied from manufacturers in Czech Republic.

Three kinds of commercially produced sugar packages were tested for DPGDA and TPGDA content using GC-MS technique. The residual DPGDA was found in two from three tested commercial packages in concentrations 443 and 4 mg/kg, the residuals of TPGDA were identified in all tested packages in levels 40, 52 and 222 mg/kg. Even the packaged sugar was unacceptable for consumption in all cases due to unpleasant smell, only in the product from the package containing 443±11mg/kg of DPGDA and 40±3 mg/kg of TPGDA the content of DPGDA could be quantified on the level 0.2±0.04 mg/kg, in other two samples diacrylates content was lower than the detection limit of used analytical method.

The migration of both diacrylates into 10% ethanol and 95 % ethanol simulants from paper packaging materials laboratory contaminated with known amount of diacrylates was also studied at 40 °C. The results of the migration of DPGDA and TPGDA from papers with different thickness into simulants through LDPE layer showed that the transfer of both substances is quite rapid, the equilibrium state was reached within 15 hours. The tested packaging materials contained 4.1 ± 0.2 mg/dm^2 of DPGDA and 4.3 ± 0.4 mg/dm^2 mg/kg of TPGDA. The maximal extent of DPGDA transfer into 10 % ethanol corresponds up to 1-2 % of the substance amount presented in both of the packaging materials, the percentages of the migration of TPGDA ranged from 7% to 38% depending on packaging material thickness. The extent of diacrylate migration into 95 % ethanol was higher, i.e. 12% -30% for

DPGDA and 34% - 73% for TPGDA. The results confirmed that LDPE coating should not be seen as a complete barrier against diacrylates migration from packaging materials into food. Even the LDPE layer of one of the packagings was about twice thicker,the higher levels of migration both DPGDA and TPGDA were found for thicker packaging compared with thinner one. This surprising result can be caused by the different quality of LDPE coating on both packaging.

The migration tests into food stimulants (10% and 95% ethanol, 3% acetic acid and olive oil) at 40 °C for 10 days were made using GC-MS method for diacrylate determination. The highest migration was obtained into 95% ethanol for DPGDA and TPGDA 102 $\mu g/dm^2$, 42± $\mu g/dm^2$ respectively. Migration into 95% ethanol was significantly different from migration into other simulants for both diarylates ($p<0.05$).

20 different paper food packaging materials provided from the manufacturers in Czech Republic. The main aim of this study was to screen paper packaging materials commercially used in Czech Republic to obtain objective data for risk assesment of possible hazardous contaminants in paper packaging. All packaging samples were extracted with diethylether and analyzed by GC/MS. It is revealed that unprinted paper board packagings has almost no peak on chromatogram. It is found that most of the packagings had high peaks due to plasticizer, either phthalates or adipates, and also the hydrocarbon contents varied considerably. The identified substances included in EU positive list of monomers and/or additives for food contact materials are triacetin, o-Phthalic Acid, 1,2-Benzenedicarboxylic acid, diisooctyl ester, Dibutyl phthalate, 2,6-Di-tert-butyl-p-cresol (BHT), Phthalic anhydride. It is clearly found that most of the substances are not included in the EU positive list of monomers and/or additives for food contact polymer and there is no special legislation about these substances.

AMBALAJLARDAN DİPROPİLEN GLİKOL DİAKRİLAT VE TRİPROPİLEN GLİKOL DİAKRİLAT MİGRASYONUNUN BELİRLENMESİ VE KAĞIT AMBALAJLARDA POTANSİYEL RİSKLERİN DEĞERLENDİRİLMESİ

ÖZET

Kağıt, birincil, ikincil ve üçüncül ambalaj olarak gıda sanayinde yaygın olarak kullanılmaktadır. Gıda ile temas halindeki ambalajlar içeriğindeki bileşenlerin gıdaya geçişi riski nedeniyle insan sağlığını açısından tehlike oluşturabilir. Kağıt ambajlar ve özellikle de ambalaj materyallerinde kullanılan mürekkepler hakkında spesifik bir regülasyonun bulunmaması nedeniyle gıda ile temas halindeki kağıt ambalajların potensiyel riskleri hakkındaki endişeler son yıllarda artmıştır. Bu nedenle ambalajdan gıdaya geçebilecek potensiyel tehlikelerin belirlenmesi üzerine daha çok bilimsel çalışmaya ihtiyaç duyulmaktadır.

Yapılan çalışmada amaç; (i) istenmeyen koku nedeniyle müşteri şikayeti alan dört gramlık şeker ambalajlarında ve ambalajlı şekerde, istenmeyen kokuya neden olan dipropilen glikol diakrilat (DPGDA) ve triproplen glikol diakrilat (TPGDA) miktarlarının belirlenmesi (ii) farklı kalınlıktaki düşük yoğunluklu polietilen (LDPE) kaplı kağıt ambalajlardan 10% ve 90% etanol içerisine, DPGDA ve TPGDA migrasyonun belirlenmesi (iii) Ambalaj materyallerinden farklı simulantlara DPGDA ve TPGDA geçişinin belirlenmesi (iv) Çek Cumhuriyetinde farklı üreticilerden elde edilen kağıt ambalajlarda risk değerlendirmesi yapılmasıdır.

Çalışmanın ilk bölümünde, ticari olarak üretilmiş ve kötü koku nedeniyle analizlenen üç farklı şeker ambalajında DPGDA ve TPGDA miktarları gaz kromatografisi-kütle spektrometresi (GC-MS) kullanılarak tespit edilmiştir. Analizlenen şeker ambalajların sadece 2 tanesinde DPGDA konsantrasyonu 443 ve 4 mg/kg olarak belirlenirken, tüm ambalajlardaki TPGDA miktarı 40, 52 ve 222 mg/kg olarak tespit edilmiştir. İstenmeyen koku nedeniyle diakrilate içeren şekerlerin tüketimi uygun bulunmazken, 443±11mg/kg DPGDA ve 40±3 mg/kg TPGDA içeren ambalajdan şekere geçen DPGDA miktarının 0.2±0.04 mg/kg olduğu tespit edilmiştir. Ambalajdan şekere geçen DPGDA ve TPGDA geçişini belirlemek amacıyla, şeker numuneleri katı-faz mikroekstraksiyon (SPME) yöntemleri ile ekstre edilmiş ve gaz kromatografisi-kütle spektrometresi (GC-MS)'nde tanımlanmıştır. Diğer ambalaj örneklerinden şekere geçiş, örneklerdeki miktarın dedeksiyon sınırının altında olması nedeniyle belirlenememiştir.

Laboratuvar koşullarında hazırlanan ve her iki diakrilattan bilinen miktarda içeren farklı kalınlıktaki LDPE kaplı kağıt ambajlardan 10% etanol ve 95% etanole 40 °C

sıcaklıktaki geçiş takip edilmiştir. Farklı kalınlıktaki iki kağıt ambalajdan simulantlara DPGDA ve TPGDA migrasyonu sonuçları, migrasyonun oldukça hızlı gerçekleştiğini ve 15 saatin sonunda dengeye ulaştığını göstermektedir. Çalışmada kullanılan ambalaj materyalleri 4.1 ± 0.2 mg/dm^2 DPGDA ve 4.3 ± 0.4 mg/dm^2 TPGDA içermektedir. Ambalajlardan 10% ethanol içerisine maksimum DPGDA geçişi, ambalaj içesindeki miktarının yüzde 1-2' si kadarken, TPGDA geçişi ambalaj kalınlığına baglı olarak yüzde 7 ile 38 olarak değişmektedir. Diakrilatların yüzde 95 etanole geçişinin yüksek olduğu belirlenmiştir. Ambalajda bulunan DPGDA 'nın 12% -30% 'nun yüzde 95 ethanole geçtiği tespit edilirken, TPGDA'nın 34% - 73% 'nün geçtiği belirlenmiştir. Sonuçlar, LDPE kaplamanın tamamen bariyer özelliği göstermediğini göstermektedir. Ayrıca, kalın LPDE kaplı kağıt ambalajdan migrasyonun her iki diakrilat ve simulant için ince kaplamaya kıyasla daha fazla olması, geçişte polietilen kalitesinin önemli bir etken oldugunu göstermektedir.

Kağıt ambalajlardan farklı gıda simulantlarına (%10, %50 and %95 etanol ,%3 asetik asit ve zeytinyağı) 40 °C 'de 10 gününün sonunda gerçekleşen diakrilat migrasyonu GC-MS kullanılarak belirlenmiştir. En yüksek migrasyon %95 etanolde, DPGDA için 102 µg/dm^2 ,TPGDA için ise 42± µg/dm^2 olduğu tespit edilmiştir. Her iki diakrilat için %95 etanole geçişin diğer simulantlara oranla önemli ölçüde farklı olduğu tespit edilmiştir ($p<0.05$).

Çalışmanın son bölümünde, Çek Cumhuriyeti'nde farklı ambalaj üreticilerinden 20 adet kağıt ambalaj temin edilmiştir. Bu çalışmada amaç, kağıt ambalajlarda bulunması muhtemel tehlikeli kontaminantların, farklı ambalajlarda tarama yapılarak tespit edilmesidir. Bütün kağıt ambalajlar dietileter ile ekstrakte edilerek GC/MS kullanılarak analizlenmiştir. Yapılan çalışmada, baskısız ambalaj ekstraklarının kromatogramlarında neredeyse hiç pike rastlanmamıştır. Ambalajların çoğunda yüksek piklere neden olan kontaminantların plastikleştiriciler, fitalat yada adipatlar ve farklı hidrokarbonlar olduğu belirlenmemiştir. Ambalajlarda tespit edilen miristik asit,o-fitalik asit, diisooktil ester, dibütil fitalat, 2,6-Di-tert-butyl-p-cresol (BHT) ,stearik asit ve fitalik anhidrit Avrupa Birliği regulasyonlarında gıdalarla temas halindeki plastik malzemeler için oluşturulmuş düzenlemede (EU 1935/2004, Annex I) monomer ve katkı maddeleri için belirlenen positif listede yer almaktadır. Tespit edilen diğer maddeler için toksikolojik datalar dışında herhangi bir limit bulunmamaktadır

1. INTRODUCTION

Packaging plays an important role to provide quality and safety of food by protecting it from physical, chemical, and microbiological risks. However, packaging material can be endanger for human health itself. Therefore, packaging has become an essential part in food industry. Significant growth has been seen in food packaging development because of the increase in demand of food industry in the past decades. Many types of additives (antioksidans, plasticiser, stabilizers, lubricants,) have been used and developed to obtain better packaging materials performance during processing or in usage. Nevertheless concern about the packaging materials and additives has increased recently due to the risk of migration of these substances from packaging materials to food (Lau and Wongs, 2000).

Quality of packaging materials poses one of crucial problems of food precessing. The packaging materials in contact with food should comply with existing regulation,e.g. harmonized European legislation, national legislation etc. Council Directive 89/109/EEC that covers all food contact materials indicates hazardous substances for human health must not be transferred from the packaging into food. There are some specific regulation, especially for plastics (2002/72/EU and its 5 amendments), which indicates the exact amounts and types of additives which can be used for production of plastics. Additionally, limitations about some addivites are defined in the positive lists in these regulations (Anon., 2009a).

Paper which is widely used as primary, secondary and tertiary packaging is perceived as safe and healthy by consumers because of natural origin from wood. However, chemical hazards such as additives added during manufacture to improve paper characteristic must be taken in consideration. Components of printing inks, coatings or adhesives could migrate into the packaged food in consequence of extraction by food, penetration through polymer layer and evaporation during storage (Sun Chemical, 2007).

Although there is increasing concern about safety of food packaging, specific EU (European Union) directive about paper and board in contact with foodstuffs is not present so far. Compared with polymer packaging material there is still lack of objective information about migration parameters of fiber based food contact materials. In the literature, there are many research regarding to the safety assessment of plastic materials contacted with food and it has been studied extensively for several decades, while concerns about fiber based food contact materials has increased and extensive research has been performed only for the last ten years (Jickells et al.2005; Nerin, 2004; Papilloud and Baudraz, 2002). There is much more specific legislation on plastic materials than that on fiber-based materials. In consideration of recent scientific results, recommendations for fiber based food contact materials have been carried out and there is still need more scientific evaluations to build up future recommendation and legislation (Aulera, 2001). The present situation can be characterized by the statement of The Advisory Forum of EFSA (AF) (2011a):

''While plastics are covered by a specific regulation, with positive lists of substances, crises were originating from non-plastic parts of FCM, e.g. coatings, paper and board, adhesives, printing inks and rubber. These materials are not covered by a specific regulation and thousands of substances used to manufacture them have not been evaluated at the EU level for their safety''.

In this study, migration of the diacrylates through paper packaging into simulants was examined. Acrylate monomers and oligomers are the most popular chemicals used for the chemistry used in the UV&EB curing of inks. Consumers have complainted about packed sugars which were produced in Czech Republic because of bad odours in sugar box. Some samples were sent by company to the laboratory at Institute of Chemical Technology, Prague to determine which compound causes bad odour in sugar packaging. It was clearly found that diacrylates leaded to unpleasant odour in sugar packaging and there is no regulatory restriction for amount of diacrylates used in food packaging. Therefore, determination of migration of diacrylates from food packaging into different simulants was decided as an important issue to understand whether diacrylates have migration risk for food products. The second part of the study includes risk assessment of potential migrants in paper

packaging used in food industry in Czech Republic. 20 different paper food packagings were analysed to determine which type of compounds they have and which of them has risk of migration into food.

2. LITERATURE REVIEW

2.1 Role of Packaging Materials

Packaging is a specisific material which protects the products from environmental effects and damages by covering them, provides easy transport and also informs consumer about the definition of products. Packaging materials should provide industry requirements, consumer desires and food safety (Marsh and Bugusu, 2007).

Packaging materials are generally used as primary, secondary and tertiary packaging. Primary packaging is a package which is directly contacted with food material and also called sales packaging. Secondary packaging is a packaging which contains a number of primary packagings, is not directly contacted with food. Tertiary packaging covers number of secondary packaging and is generally used to provide easy transport and handling. Different types of packaging materials are used as a food packaging material. The main packaging materials are showed on the Table 2.1. (Barnes *et al*., 2007; Arıkan, 2010)

Table 2.1 : The main packaging materials, packages and raw materials of packages (Barnes *et al*., 2007)

Packaging Material	Raw Material	Package
Glass	Silica	Bottle, jar
Paper/board	Celulose	Paper packaging, paper board box, corrugated fiberboard
Metal	Aluminium, iron, tin	Canned, closure, tin, aluminium foil
Plastic	Polimer (low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polysterene (PS), polyvinilyl chloride (PVC) polyethylene terephthalate (PET))	Flexible Packaging, rigid packaging
Wood	Tree	Paddle, box

2.2 Interaction Between Packaging Materials and Food

There are many interactions which occur between packaging, food and environment. Concerning safety of food package, migration, sorption and permeation belong to the most important from these interactions.

According to literature some definitions of these interactions (see Figure 2.1.) are described below (Hernandez and Giacin, 1997; Aurela, 2001);

- Migration is the transfer of low-molecular-weight compounds from packaging materials to packaged food.
- Sorption is the absorption of food components by packaging materials. It includes the transfer of molecules from the product into the package.
- Permeation is the transfer through the package of molecules from the product to the environment or from the environment to the product

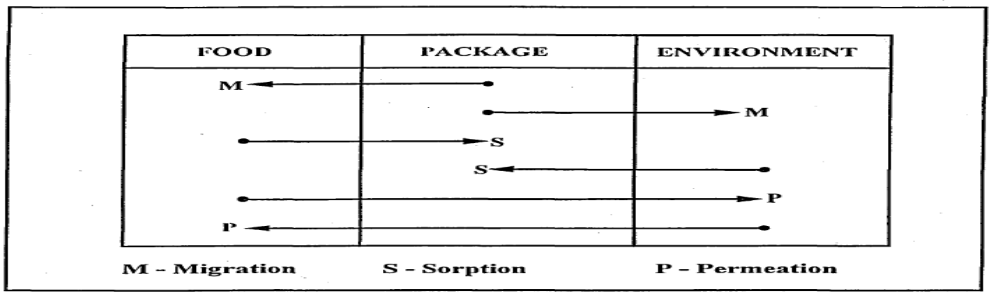


Figure 2.1 : The system of migration, sorption and permeation (Gnanasekharan,1997)

2.2.1 Migration Mechanism

One of the main mechanisms of the migration is diffusion concerning the safety and quality of the packaged food. Diffusion is mass transfer of the components from regions of high concentration to regions of low concentration and it increases because of concentration difference. It may occur within the food and within the packaging material contact with food (Aulera, 2001). Even though the migration of chemical compounds from packaging material into food is mostly undesirable, it is unavoidable. Migration of compounds into food can be classified into three types according to diffusion coefficient. In the first case, migration is negligible (generally diffusion coefficient $D<10^{-16}$ m^2/s). In the second case, diffusion coefficient is

constant and the rate of mass transfer does not depend on the presence and type of food so it is called spontaneous migration. In the third type, which is much more common, migration is controlled by food contact, and the migrants are extracted (leached) by food. In this case the level of migration is significant (generally $D>10^{-13}$ m^2/s). Due to dissolving of food constituents in package contact layer the multiphase system created by differently solvated layers of polymer forms. It results in nonconstant value of diffusion quotient and in the fact that the course of migration of food components from packaging material into food does not obey Fick´s law. The wide variability of formed multiphase systems cause mathematical modeling of migration quite difficult and so the migration tests are still the main way for the evaluation of packaging materials safety (Gnanasekharan, 1997; Aurela, 2001).

The mass transfer from the packaging material to the food can have deteriorative effects on food including sensory aspects. Moreover migration of toxic compounds from packaging to the food is a serious risk to food safety. The issues indicated below should be taken in consideration to understand the risk and control mechanism of migration (Lau and Wong, 2000);

- Identification of the potential migrants in packaging material in contact with food and determination of their potential toxicological data.
- Quantificaiton of substances such as additives, monomers etc.i n food contact material and determination of their level of migration into food
- Determination of the factors concerning the migration of contaminants
- Determination of the maximum intake of contaminants originating in food contact material and estimation of health risk.

2.3 Mathematical Modelling (Migration Modelling)

Mathematical models have great use as substitution for experimental study of actual process and it gives idea about physical processes of practical cases. Models which demostrate mass transfer of additives and contaminants from packaging material to foods simulants are valuable tools for manufacturer and regulators. Migration modeling has been studied for years and it is still in progress of development with aim of decreasing the number of migration tests which is expensive and time

consuming. Additionally, mathematical modelling provides information to enforce legislations about risk evaluation of migrants. Furthermore, a better understanding of the migration process will make a great contribution controlling and limiting chemical contamination of food from packaging materials (Helmroth et al.2002; Aulera, 2001).

Migration of chemical substances is a diffusion process depending on both kinetic and thermodynamic parameters and can be described by diffusion mathematics derived from Fick's Law. The mathematical equations explain diffusion mechanism as a function of time, temperature, thickness of the material, amount of chemical in the material, partition coefficient and diffusion coefficient. The diffusion coefficient

represents the migration rate and the partition coefficient represents the ratio of the migrant concentration in the packaging to the migrant concentration in the food simulant at equilibrium. Thermodynamic factors (solubility, partition coefficient) indicate distribution of migrant at equilibrium. The kinetic factors (diffusion coefficiency) give an idea about migration velocity so these factors demostrate how fast the migration process is. In some cases, the migrant has a higher affinity for the food than for the packaging material however migration may occur at a slow rate. Therefore, if enough time is given, it may migrate extensively into food (Helmroth *et al*.2002; Barnes *et al*, 2007).

The modeling of migration from fiber materials has drowned attenttion recent years whereas migration from paper and board has been studied much less than migration from plastics. There is a a large database of the diffusion constants of additives in polyolefins and assumed partition coefficients for modelling studies of plastic materials. A similiar approach is used to fiber materials and for the study of functional barriers, for example plastic-coated board (Aulera, 2001).

The migration mechanism from fiber based materials is different from the migration sytem in plastics because paper and paper board have heteregeneous, open and pores structures consisting of cellulosic fibres and air pores. Therefore migration through paper consists of adsorption and desorption of migrant on the fiber, transfer across the fiber and diffusion on the pores. There are few studies about development of

predictive migration models for fiber based material due to restrictions result from its non homogeneity (Pocaz, 2011).

2.4 Parameters of Migration

There are several parameters which affect the rate of migration from food contact material into food. Parameters can be summarised as (Pocaz et al.2011; Barnes et al. 2007) :

- Direct or indirect contact of packaging material to the food
- Characteristics of material contacted with food (such as characteristics for paper : thickness, porosity, lignin and recycled fibre content in used pulp);
- The chemical nature of migrant (vapour pressure, polarity, molecular size and structure, etc.)
- The nature of food or stimulant contacted with material
- The initial concentration of the migrant in the material
- Time and temperature of contact.
- The substance contacted with material (food or stimulant)

One of the important parameters which affect migration is the nature and extent of any contact between food and packaging. Physical properties of food and the size and shape of the package in contact with food are critical parameters. If the mass ratio of surface area to food is high, migration risk increases .The nature of the food is another critical factor because of their compatibility with packaging material and the solubility. For example; fats and oil in food interact with plastic material in packaging and cause swelling of plastic and leaching of chemicals from that plastic. Therefore it is important to choose right combination of packaging material and food type (Barnes *et al.* 2007).

Moreover, the level of migration depends strongly on the affinity of migrant and packaged food product. As it has been demostrated in Table 2.2 foodstuff can be seperated into 5 principal groups as aqueous, acidic, alcoholic, fatty and dry.

Table 2.2 : Type of chemicals which have high affinity for different food categories (Barnes *et al.* 2007)

Type of the food	Nature of Substances
Acidic foods, aqueous foods and low alcohol beverages	Polar organic chemicals, salts, metals
Fatty food, distilled spirits	Non-polar, lipophilic organic substances
Dry foods	Low molecular weight, volatile substances

In addition, the presence of a barrier layer (functional barrier) is an another factor which affect migration. It generally prevents migration between packaging material and food. If the functional barrier of packaging material is located between printings and packaged product, migration is prevented or significantly retarded. Besides, the migration from packaging material is accelerated by heat. If the temperature increases, migration will occur faster (Barnes *et al.* 2007).

2.5 Migration into Food Simulant

Food simulants may be used for migration test of packaging materials instead of actual food stuff by reason of complex analyses of real foods. Migration test for stimulants is simpler due to known composition of food stimulants. Liquid or solid substances which have similar contaminant extraction capacity to the food stuff can be used as a food stimulant (Tiggelman, 2012). Food simulants which represent different basic type of foodstuff are defined in Commission Regulation (EU) No. 10/2011 on plastic materials and articles intended to come into contact with food (see Table 2.2). Food simulants A, B and C represent hydrophilic and they are able to extract hydrophilic substances. Food simulants D1 and D2 are used for liphophilic foods and they are able to extract non polar substances. Food simulant E is used for testing specific migration into dry foods (Regulation no. 10/2011)

Table 2.3 : Food simulants and their corresponding food types (Commission Regulation (EU) No. 10/2011)

Food Simulant	**Abbreviation in Regulation**	**Applications**
10% (v/v) Ethanol	A	Aqueous food (pH > 4,5) Alcoholic foods (alcohol content < 10%)
3% (w/v) Acetic Acid	B	Acidic foods (pH < 4,5)
20% (v/v) Ethanol	C	Alcoholic foods containing up to 20% alcohol
50% (v/v) ethanol	D1	Dairy products, alcoholic foods (alcohol content >20%)
Vegetable oil	D2	Fatty foods
Poly(2,6-diphenyl)-p-phenylene oxide [Tenax®]	E	Dry foods

2.6 Migration into Food Simulant

2.6.1 Safety assesment of paper packagings

Risk assesment should be carried out for paper and paper board due to its specific nature. Firstly, the chemicals used during paper making process are critical to obtain specific properties of paper grades. There are two categories of chemicals added and should be taken in consideration to evaluate risk assesment (Anon., 2010):

- Functional additives which are added to obtain some technical properties of the paper and board and stay in it.
- Process chemicals or processing aids that are used to improve the efficiency of the papermaking process.

On the otherhand, risk assesment of paper and board for food contacts should be different from plastics which most of the regulation focus on (Anon., 2010). For instance:

- Paper and board materials are mainly used for dry foods. If they should be intended for foodstuffs of higher water activity, it must be impregnates with hydrophobic agents.
- Manufacturing process of paper and board is completely different compared to plastics.
- Nature of the paper and board quite different from plastics. It has natural polymer mainly based on cellulose.
- Standard migration test methods which are used for plastics are not easily applicable or not suitable to test paper and boards.

When all these reasons take in consideration, it is clearly seen that regulation and control of paper and board for food contact using the plastic approach with control of numerous specific migration limits does not seem to be the most suitable for paper (Anon., 2010).

2.6.2 Existing EU legislations

The Regulation (EC) No 1935/2004 (EC 2004) is the framework EU legislation that covers all food contact materials and articles. According to this framework;

- Food contact materials shall not endanger human health,
- Food contact materials shall not cause an unacceptable change in the composition of the food,
- Food contact materials shall not cause deterioration in the organoleptic characteristics of food (Pastorelli *et al*., 2008).

The Commission Regulation (EC) No 2023/2006 (EC 2006) states that all food contact materials have to be manufactured in accordance with good manufacturing practice. Concerning different types of food contact materials currently the harmonized legislation exists only for few of them, i.e. plastics (EC 2011), recycled plastics (EC 2008), ceramics (EC 1984), active and intelligent materials (EC 2009) and regenerated cellulose (EC 2007), while the quality of other 13 mentioned in

Annex 1 of the Regulation no. 1935/2004 including paper and board is still controlled on the base of the national legislation of EU member states(Aulera, 2001).

Plastics Regulation (EU) No. 10/2011 covers plastic food contact materials and articles and contains a positive list of component monomers and additives, specifies global and specific migration limits as well as standard conditions for migration testing. Concerning printing inks directive no 2007/42/EC relating to materials and articles made of regenerated cellulose film states that the printed surface of regenerated cellulose film must not come into contact with food. Existing EU regulations for food contact materials have been shown in Table 2.4.

Tablo 2.4 : Existing EU regulations for food contact materials (European Commision, 2013)

	Regulation No	**Name of regulation**
All food contact materials and articles	(EC) No. 1935/2004	Framework Regulation on materials and articles intended to come into contact with food
	(EC) No. 2023/2006	Good manufacturing practice for materials and articles intended to come into contact with food
Legislation on specific materials	Regulation EU 1282/2011	Plastic materials and articles intended to come into contact with food:
	2002/72/EC	Principle directive for plastic materials and articles intended to come into contact with food
	(EC) No. 450/2009	Active and intelligent materials and articles intended to come into contact with food
	EC 282/2008	Recycled plastic materials and articles intended to come into contact with foods
	Directive 2007/42/EC	Materials and articles made of regenerated cellulose film intended to come into contact with foods
	Directive 84/500/EEC	Approximating EU countries' laws on ceramic articles intended to come into contact with foods

Tablo 2.4: List of Existing EU regulations for food contact materials (European Commision, 2013) (continuing)

Legislation on specific substances	Regulation 1895/2005/EC	Restricting use of certain epoxy derivatives in materials and articles intended to come into contact with food
	Directive 93/11/EEC	Release of N-nitrosamines and N-nitrosatable substances from rubber teats and soothers
	Regulation EU 321/2011	Restricting Bisphenol A use in plastic infant feeding bottles
	Regulation EU 284/2011	Import procedures for polyamide and melamine plastic kitchenware from China and Hong Kong

2.6.3 Potential migrants in paper based packaging materials

Migration from paper and paper board has not been studied as much as migration from plastic materials. There are several scientific researches about migration of organic substance such as phthalates, diisopropylnaphthalene, n-dibutylphthalate, trimethyldiphenylmethane, perfluorochemicals, benzophenone and derivatives, 3-chloro-1,2-propanediol (3-MCPD), mineral oils and inorganic substances from paper and paper board in to food stuff or simulants (Zhang et al. 2008; Sturaro et al. 2006; Begley et al., 2005; Pastorelli et al. 2008 ; Pace et al.2010; Biedermann et al. 2010)

In several studies, kinetics of migration and modelling of potential contaminant has been performed in paper an boards aganist food or simulants (Poças et al.2011;Triantafyllou et al. 2005; Nerín and Asensio 2004; Choi et al. 2002). Additionally, effect of different barriers factors affecting migration using different contaminants has been studied (Song et al. 2003; Choi et al. 2002).

Many researchers report that migration of substance from paper packaging to food stuff has been executed. Boccacci et al.(1999) report that migration of diisopropylnaphthalene (DIPN) to dry food (rice, pasta, maize flour) from cardboard occured after three days at ambient temperature. In this study, it showes that volatile substances in food contact material can migrate in to food through gas phase (Boccacci et al.,1999). It is also studied that migration of benzophenone from cardboard which was used as a secondary packaging to food stuff was investigated and it is indicated that there can be migration to foods even where the foodstuff is packaged in plastic wrap as a primary package (Anderson and Castle, 2002). Another

suspicious result was obtained by Aulera et. Al. (1999) that 74% of DIBP and 57% of DBP in packaging material migrated into sugar.

One of the fundamental issues concerning safety assesment of paper packaging is the use of recycled fibre. It has been proved that concentration of chemical which has ability to migrate into food is more significant for recycled paper compare to virgin paper (Tiggelman,2012). In the litrature, it is indicated that aldehydes, alkanes, ketones, phthalates, hydrocarbons, printing inks, volatiles have been detected in recyled paper (Triantafyllou et al.2002).

Table 2.5 shows the most common migrants with ability to migrate from paper and board packaging and their migration limits by the plastic regulation. According to Tiggelman (2012) printing inks or rather their components pose one of the main risks. Although printed surface of the packaging is generally not in direct contact with the food itself, it may cause a risk of migration in absence of a suitable barrier. Additionally these printing inks may also cause a risk because of recycling and subsequent production of food packages from recycled fibre (Tiggelman,2012).

Table 2.5 : Potential contaminanats in paper and board for food contact (Tiggelman,2012)

Compounds	Limit in food (SML)(mg/kg) (*)	Content in paper&board	Source of contamination
Cadmium	-	0.002 mg/dm^2	Inks (Anon.,2002)
Lead	-	0.003 mg/dm^2	Inks (Anon.,2002)
mercury	-	0.002 mg/dm^2	Inks (Anon.,2002)
Pentachlorophenol	-	0.15 mg/kg	Biocide (Anon,2002)
Azo colourant	-	0.1 mg/kg	
Primary aromatic amines(PAAs)	<0.01		Overprint varnishes;polyerthane adhesives (Ash and Ash,2008)
Dyes and colourants	-	No bleeding	
Flourescent whitening agents (FWAs)	-	No bleeding	
Formaldeyde	-	1 mg/dm^2	Dry strength resins and crosslinkers (Tiggelman,2012)
Polycyclic aromatic hydrıcarbons (PAH)	0.01	0.0016 mg/dm^2	
Dibutylphthalate(DBP)	0.3		Plasticiser,additive in adhesives or printing inks (Zhang et. Al, 2008)

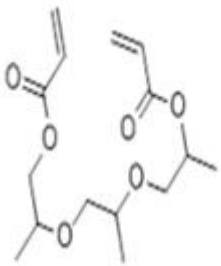
Table 2.6: Contaminants in paper and board for food contact (Tiggelman, 2012) (continuing)

Diisobutylphthalate(DiBP	1.0		Plasticiser, a component in adhesives (Ash and Ash,2008)
Sum of DBP+DiBP	1.0	0.17 mg/dm^2	
Di(2-ethylhexyl) phthalate (DEHP)	1.5		Plasticiser in adhesives, component in defoamers (Ash and Ash,2008)
Benzylbutylphthalate(BBP)	30	5	
Diisononylphthalate (DiNP)	9	1.5	Hot-melt adhesives
Diisodecylphthalate (DiDP)	9	1.5	
4,4-bis (diethylamino) benzophenone (DEAB)	0.01	0.0016	UV-cure ink photoinitiators (Ash and Ash,2008)
Benzophenone (BP)	0.6	0.1	UV-cure ink photoinitiators, wetting agent for pigments, reactive solvent in inks
Sum: BP + hydroxybenzophenone+ 4-methylbenzophenone	0.6	0.1	
Diisopropylnaphthalene (DiPN)	-	As low as technically feasible	Solvent in manufacture of carbonless and thermal copy paper (Zhang et. Al, 2008)
Bisphenol A	0.6	0.1	Epoxy-phenolic resins used as binders in printing inks

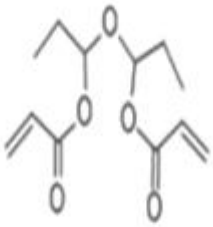
(*) SML according to tha Regulation (EU) No. 10/2011

2.6.4 Diacrylates in packagings

The type of acrylates used by companies in industry is frequently called multifunctional acrylates and can be divided into two main groups as an stenomeric and eurymeric acrylates. TPGDA and DPGDA are classified as a stenomeric acrylates with low molecular weight and are often called "diluents" or "monomers" by the industry (Anon., 2011b). TPGDA and DPGDA are defined as an energy curing monomers which is used for packaging ink and applied to the non-food contact surface (Anon., 2009b). Figure 2.2 shows the structure and toxicological data of both diacrylates.



1) **DPGDA** – acute toxicity: oral (rat) LD50 =4600 mg/kg, dermal (rabbit)LD50≥2000 mg/kg



2) **TPGDA** – acute toxicity: oral (rat) LD50 >2000 mg/kg

Figure 2.2 : Structure and toxicological data of 1) DPGDA and 2) TPGDA

To the best of our knowledge, there is no information about migration of diacrylates from packaging material into food or simulant and also no spesific regulation about diacrylates in food contact materials. Harmonised classification and labelling for certain hazardous substances are listed in Regulation (EC) No.1272/2008 (Annex VI). The acrylates widely used in the Ultraviolet (UV)/Electron beam (EB) industry are not listed in Regulation (EC) No.1272/2008. Besides acrylates have not registered under Regulation (EC) No. 1907/2006 which ensure a high level of protection of human health and the environment. Therefore companies have taken into consideration the available toxicological data for each substances and agreed voluntarily on a common, harmonized labelling (Anon., 2011b).

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Chemicals

Diphentyl phthalate and n-dibutylphthalate (DBP), bis (2-ethylhexyl) adipate (DEHA), bis(2-ethylhexyl) phthalate, triacetin, tri(2-Ethylhexyl) trimellitate, tripropylenglycol-diacrylate (TPGDA) were obtained from Sigma-Aldrich (Steinheim, Germany). Dipropylene glycol diacrylate (DPGDA) was purchased from TCI (Chuo-Ku, Tokyo, Japan). Methanol, diethyl ether, acetic acid, ethanol was HPLC analytical grade from Sigma-Aldrich (Steinheim, Germany).

3.1.2 Samples

All the papers used for the experiments were supplied from packaging companies in Czech Republic. Table 3.1 shows the types of packaging materials analysed for diacrylates migration. P1, P2, P3 were original sugar packagings. Film A and Film B were unprinted papers coated with low density polyethylene (LDPE) the thickness of polymer layer was 57 µm and 86 µm, respectively.having different thickness, they were laboratory prepared packagings spiked with diacrylates

Table 3.1 : List of packaging materials analysed for diacrylate migation

Codes	Samples
P1	Original sugar package
P2	Original sugar package
P3	Original sugar package
Film A	Unprinted Paper Coated with LDPE (57 µm)
Film B	Unprinted Paper Coated with LDPE (86 µm)

Additionally, 20 different packagings which were obtained from manufacturers in Czech Republic, were analysed with regard to identify possible migrants into packaged food.

3.2 Equipments

A Hewlett-Packard 6890 Series GC system equipped with an auto-inject tor and HP 5973 mass-selective detector (Figure 3.1.) (Agilent Technologies Inc., Palo Alto, USA) were used for the gas chromatography-mass spectrometry (GC-MS) analysis. Chromatographic separations were performed using a DB-5MS capillary column(30x0,25 mm i.d.,0,25 µm film-J&W Scientific Inc. Foldom, USA).

Solid phase microextraction (SPME) was adopted with GC/MS(Agilent Technologies, Palo Alto, USA) (Figure 3.1.) was used to identify and quantify diacrylates in sugar. The diacrylates absorbed onto the SPME fiber (100 µm polydimethylsiloxane fibre (Supelco Inc., Belefonte, USA)). Chromatographic separations were performed using a DB-5MS capillary column (30x0,25 mm i.d.,0,25 µm film-Agilent Technologies, USA). Water was purified with a Milli-Q water purification system from Millipore (USA). Shaking Water Bath (GFL 1003/14 liters) and heating oven (Binder E28) were used in this study.

3.3 Methods

3.3.1 Sensory analysis of sugar packaging materials

3 different sugar packaging materials were used for sensory analysis. Analysis was performed according to Robinson test. 6 dm^2 of sugar packaging materials were cut and put in the three different glass bottles (250 ml) which was covered with aluminium foil. Empty flask with zero odour was also prepared. The jars were stored for a period of 24 hours. Panel consisting of 6 assessors was performed to evaluate the odour of the air in the jars. A scale from 0 to 4 was used to evaluate the intensity of the odour. Scale of the test is shown below;

a) 0 = no perceptible odour;

b) 1 = odour just perceptible (difficult to define);

c) 2 = weak odour;

d) 3 = clear odour;

e) 4 = strong odour.

The median of all individual values was calculated.

3.3.2 Extraction of diacrylates from paper packagings

P1, P2, P3 were used to determine diacrylates in paper. The spiked papers (Film A and Film B) which were used for the coarse study of diacrylates were analysed as well. Sample of packaging material (2.5 gr) was cut into pieces and extracted in the erlenmayer with 50 ml 95% ethanol at 40 °C over night. Ethanol extracts were analysed directly by gas chromatography as described in the following chapter.

3.3.3 Determination of diacrylates

In packaged sugar the diacrylates were determined by GC-MS technique using solid phase micro extraction method for diacrylates isolation. The procedure was as it follows: 100 μm polydimethylsiloxane fibres were inserted into the headspace. 10 ml vial filled with 1,5 gr of sugar and extracted under agitation for 10 min at 40°C. The fibre with sorbed analytes were inserted into the gas chromatography (GC 6890N), equipped with a mass detector (MS 5973) and column DB-5MS (30 m × 0.25 mm i.d. × 0.25 um film thickness) (Papilloud and Baudraz, 2002). Analyses conditions:

- GC inlet: temperature 240°C and desorption time 6 min, splitless mode.
- Carrier gas (He) flow rate 1.2 ml/min.
- Oven temperature program: 60°C (for 2 min), temperature increasing 10°C/min to 250°C (for 3 min).
- Detection in single ion mode (SIM), followed ion m/z 113, 55 (Papilloud and Baudraz, 2002.

Same method was used for GC/MC analysis of paper extracts as well. In this case, 1 μl of solution was injected into a gas chromatograph coupled with a mass spectrometry detector.

Potential migrants in 20 different paper packagings were determined by GC-MS technique at following conditions:

- Electron impact ionisation 70 eV,
- GC inlet: temperature 300°C (70°C for 5 minutes, increase 15 °C/min to 300°C, 300°C to the analysis end. Injection - 1 μl using split 1 : 100
- Carrier gas (He) flow rate 0.6 ml/min,

- Linear speed 28.9 cm/s.

Identification of separated substances consisted in comparison of obtained mass spectra with the spectrum library of used chromatography software (NIST MS Search 2.0).

A B

Figure 3.1 : A) GC system equipped with an auto-injector and HP 5973 mass-selective detector (Agilent Technologies, Palo Alto, USA), **B)** Solid phase microextraction (SPME) adopted with GC/MS(Agilent Technologies, Palo Alto, USA)

3.3.4 Determination of diacrylates migration

Migration test was achieved by using only sugar packaging, P1. Tests were performed using commercial migration cells (EN 1186-1:2002) (see Fig.3.2) having 1,92 dm^2 surface area in a single contact with food simulants. Migration of diacrylates from the paper packaging into 10% ethanol, 95% ethanol, 50% ethanol, 3% acetic acid and olive oil. The sample was placed on the bottom plate of the tested cell with the polyethylene surface up. Then the migration cell was filled with 100 ml of simulant solvent, the cell was closed with a teflon stopper and stored for 10 days at 40°C.

Figure 3.2 : Commercial migration cell used in the test.

3.3.5 Determination of diacylates in packed sugar

Sugar from several packages was emptied into glass jar and mixed carefully. Two replicates of 1,5 g were taken for analysis. Diacrylates were determined using procedure described in chapter 3.3.3. Figure 3.3 shows the sugar bags used for analyses.

Figure 3.3 : Tested paper bags(P1) containing 4 g of crystalline sugar

3.3.6 Migration from laboratory prepared packaging materials

The unprinted papers described in chapter 3.1.2 (Film A, Film B) were used for preparation of pouches, the papers were cut into sheets 30x10 cm size and sealed with sealing machine. Figure 3.4. shows the prepared pouches in laboratory. Films were spiked by manual spraying using plastic spray. The outer layer of pouches was spiked with solution containing diacrylates (TPGDA and DPGDA) of 16 mg/ml

each. Initial concentration of diacrylates spiking in this study 4,5 mg/dm². After 15 min drying, the samples were ready for use. 10% percent ethanol and 95% ethanol were choosen as a simulant. Pouches were filled with 25 ml simulant for the migration test which was carried out at 40°C. Pouches were shaken and 1 ml sample was taken periodically to determine the level of diacrylate migration using gas chromatography technique decribed in the chapter 3.3.3.

Figure 3.4 : Laboratory prepared packaging samples

3.3.7 Screening for potentially hazardous substances in paper packagings

Packaging materials listed in chapter 3.2.1 were extracted with diethyether and analyzed by using gas chromatography technique decribed in the chapter 3.3.3. 1 dm^2 of tested sample was extracted with diethyl ether (50 ml) in Soxtec^{TM} 2043 extractor (Foss Analytical, DK) for two hours. Diethyl ether extract was evaporated to dryness at 40 °C using a vacuum evaporator and redissolved in 2 ml of diethyl ether. 1 µl of this solution was injected into a gas chromatograph and analysed using GC technique decribed in the chapter 3.3.3.

The quantification of selected important chemicals was done using dipentyl phthalate as the inner standard. The method which was used for screening of paper packages is also used for quantification of selected compounds in paper packages. Packaging samples were extracted with diethylether as described above (3.2.4.). Phthalates were determined in the diethyether extracts by GC/MS. The amount of dibutyl phthalate (DBP),Triacetin, DEHA, TBC(Tributyl acetylcitrate) ,dipentyl phthalate (internal standart), ethyleneglycol mono(2-ethylhexyl)ether were determined in paper packagings.

3.3.8 Statistical analyses

All analyses were performed in two replications. Data were subjected to statistical analysis using SPSS software (version 16 for Windows XP, SPSS Inc.) for the Analysis of Variance (ANOVA). Duncan's New Multiple Range Test was used to analyze differences between samples.

4. RESULTS AND DISCUSSION

4.1 Sensory Analysis

The odour of the air in the jars was estimated by a panel consisting of 6 assessors. The intensity of the odour is evaluated on a scale from 0 to 4 to test the organoleptic properties of sugar packaging materials. Table 4.1 shows that the result of sensory analysis for 3 sugar packagings.

Table 4.1 : Sensory analysis results of packaging samples

Packaging Samples	**Intensity (Mean Value)**	**Comment**
P1	3,5	Between clear and strong odour
P2	2	Weak odour
P3	3	Clear odour

It is found that P1 has a strong odour according to sensory evaluation of assessors. Additionally, P3 has clear odour and P2 has weak odour for panelists.

4.2 Diacrylates in Sugar Packagings

Three different unused sugar packagings were analysed for diacrylates content. The typical results are presented in Fig.4.1. which shows the results obtained for P1. It is obvious that in addition to DPGDA and TPGDA, sugar packagings contained antioxidant (BHT), unidentified acrylic derivatives and hydrocarbons. Table 4.2 illustrates the DPGDA and TPGDA concentrations found in tested packaging materials. DPGDA in the packaging materials P1 and P2 in the levels 443 mg/kg and 4 mg/kg respectively. The concentration of DPGDA in the packaging material P3 was too low, below the limit of detection of used method. TPGDA was found in all tested packaging materials P1, P2 and P3 in concentrations 40 mg/kg, 52 mg/kg and 222 mg/kg, respectively.

Table 4.2 : Contents of diacrylates in tested packaging materials

Samples	Amount of DPGDA in paper(mg/kg)	Amount of TPGDA in paper(mg/kg)
P1	443±11	40±3
P2	4.0±0.37	52±3
P3	-	222±7

[1]Data represent average quantities ± standard deviation of 2 independent samples.

The details of the GC-MS chromatographic peaks and specific mass spectral ions for DPGDA and TPGDA are presented in Fig.4.1. It was also observed that (Figure 4.1.) sugar packagings contain antioxidant (Butylated hydroxytoluene (BHT)), unidentified acrylic derivatives and hydrocarbons.

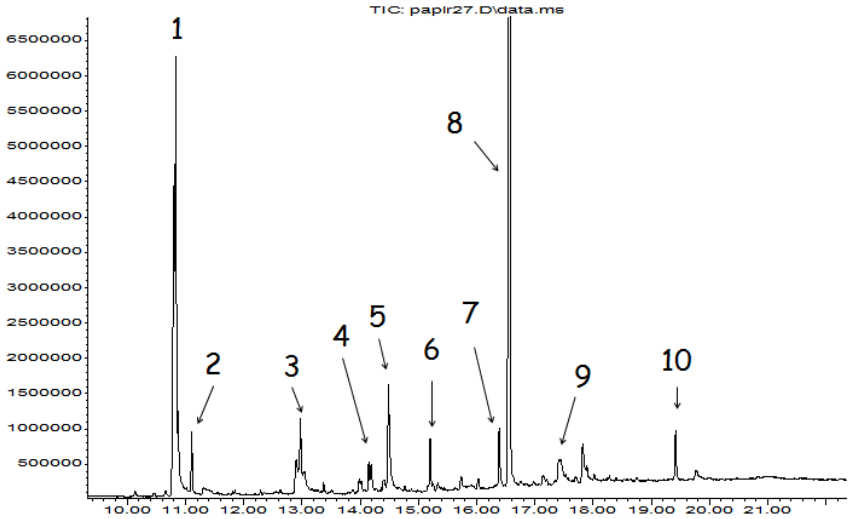


Figure 4.1 : The chromatogram of volatile substances isolated from packaging material (P1). Identified volatiles: 1) dipropylene glycol diacrylate -DPGDA, 2) BHT, 3) tripropylene glycol diacrylate - TPGDA, 4) unidentified acrylic derivative, 5) methyl 2-benzoyl benzoate, 6) unidentified acrylic derivative, 7) 2,6-dimethyl-4-nitroso phenol, 8) 2-ethylhexyl 4-(dimethylamino)benzoate, 9) 4-fluoro-6-aminopyrimidine, 10) squalene

The typical mass spectra of TPGDA and DPGDA obtained by analysis of standards are shown in Figure 4.2. It is obvious that the main ions for these compounds can be attributed to the acryloyl ion (m/z=55, [CH2=CH-C=O]+) and to theacryloyl group with attached propyloxy unit (m/z=113, [CH2=CHCO-CHCH3-O-CH2]+).

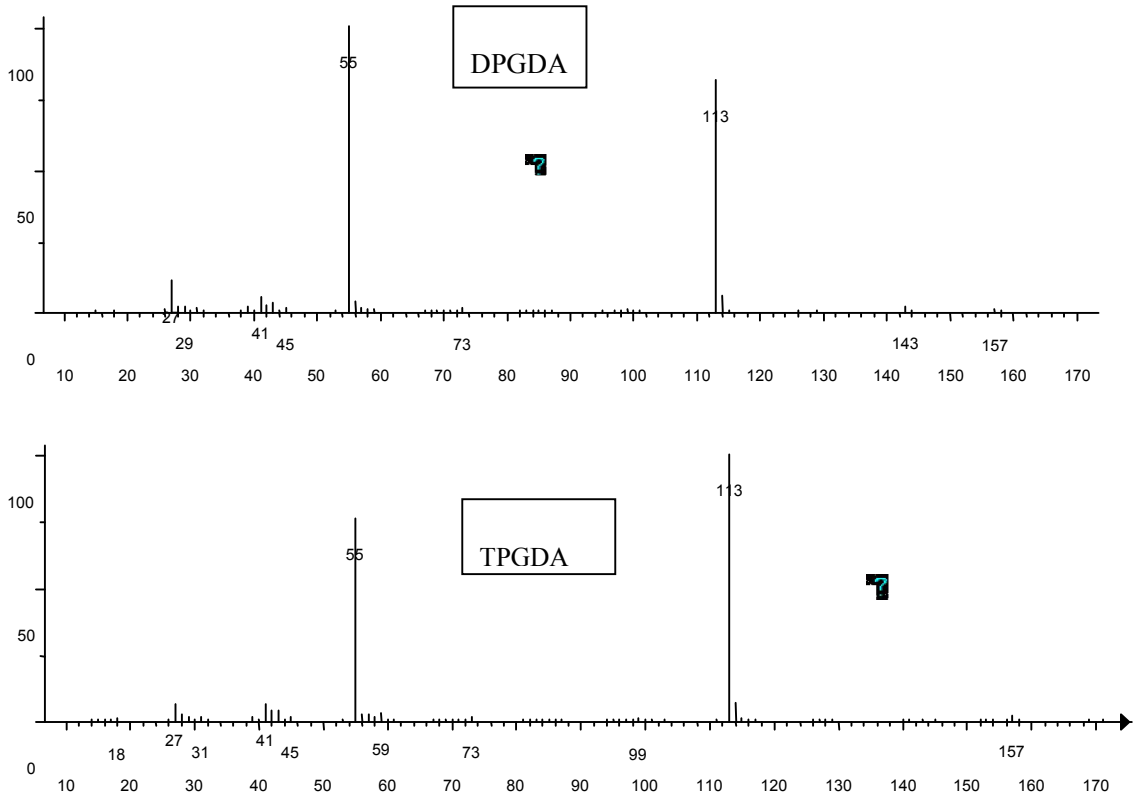


Figure 4.2 : Total mass spectrum of di(propylene glycol) diacrylate (DPGDA) and tri(propylene glycol) diacrylate (TPGDA)

4.3 Migration of Diacrylates into Different Simulants

Sample P1 was tested with regard to the level o diacrylates migration into food simulants. The results of the migration at 40 °C for 10 days into 10% ethanol solution, 3% acetic acid solution, and 50% ethanol, olive oil which are the official EU food simulants denoted A, B, D_1 and D_2 respectively. The migration into 95% ethanol as a evaporable substitute of olive oil was also tested. The results are summarized in Table 4.3. Generally, total migration (M) which refers migration of diacrylates after 10 days into food simulant, tends to increase with greater percentage of ethanol in the simulant. Migration has increased with EtOH content of food simulant among EtOH 10%, 50%, and 95%. Total migration into 95% EtOH is higher than the other simulants for both of the diacrylates. There is a significant difference between % 95 EtOH and the other simulants for both of the migrant. At the present time, no scientifically established limit values are available for assessing the migration of diacrylates from packaging to food and stimulants.

Table 4.3 : Migration of diacrylates from sugar packaging into different simulants at 40 °C for 10 days

Packaging	Substance	C[1] (mg/ dm^2)	Migration into Simulants(mg/dm^2)				
			10% EtOH	50% EtOH	95 % EtOH	3%Acetic acid	Olive oil
P1	DPGDA	0.34±0.008	0.026^{a}	0.036^{ab}	0.102^{c}	0.031^{ab}	0.052^{b}
P1	TPGDA	0.053±0.002	0.022^{a}	0.028^{a}	0.047^{b}	0.016^{a}	0.019^{a}

[1]C= concentration in the packaging sample used for migration testing

[2] Data represent average quantities ± standard deviation of 2 independent samples.Different letters for each simulants represent statistically significant differences ($p < 0.05$).

Besides, Figure 4.3 shows the percentage of migration values (relative migration) i.e. the levels of migration related to the total quantities of constituents present in tested sample. It is obvious that the relative migration of TPGDA was significanly higher for all used simulants compared with that for DPGDA. Migration of both diacrylates into 95% ethanol is quite high compare with other simulants. This is a good agreement with previous studies (Song et al., 2003; Ozaki et al.2006). In the litrature migration into 95% ethanol is 2 or 3 times higher than migration into 10% and 20% ethanol and 4% acetic acid (Song et al., 2003; Ozaki et al.2006).

The reason of higher migration into 95% ethanol is the high solubility of diacrylates in ethanol. In addition, although TPGDA and DPGDA have hydrophilic property, it is suprisingly found that migration of TPGDA and DPGDA into olive oil is similiar with 10% ethanol, 50% ethanol and 3% acetic acid.

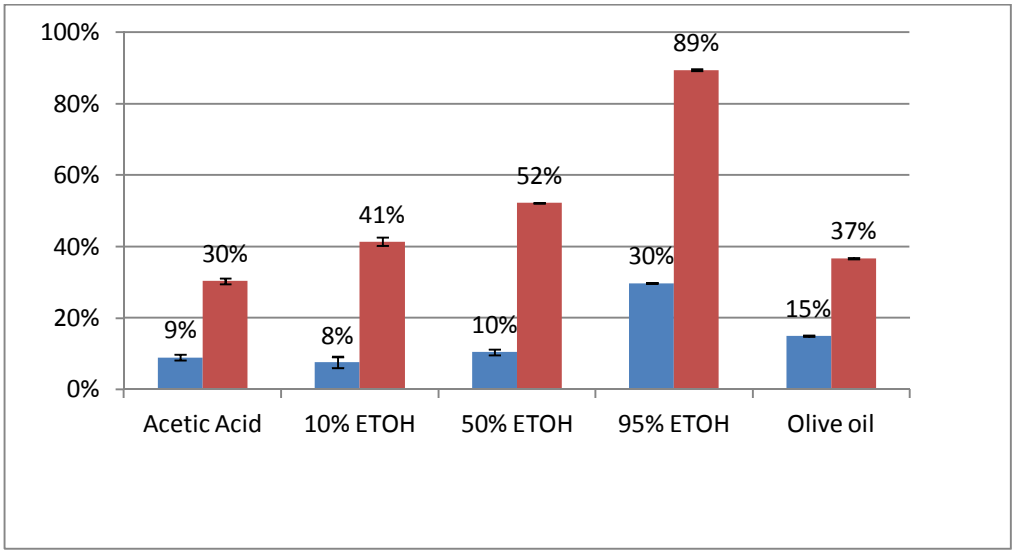


Figure 4.3 : Relative migration of diacrylates from P1 into different simulants at 40 °C for 10 days

4.4 Determination of Diacrylates in Packed Sugar

Migration of diacrylates into packaged sugar was studied in a real life situation and no migration tests were performed on the sugar. The sugar packed in the film P1 contained 0.17-0.23 mg/kg of DPGDA, the content of TPGDA was below the detection limit of used analytical method. The corresponding packagings contained 443±11mg/kg of DPGDA and 40±3 mg/kg of TPGDA. It indicates that there is no significant migration of diacrylates into packed sugar. Relative migration of DPGDA from packaging into sugar was around 1%.

Toxicological studies for diacrylates show that oral acute toxicity of TPGDA and DPGDA expressed as LD_{50} for ratis higher that 2,000 mg/kg (BASF,2006). Comparing this value with migration lavels found in this study, it is clear that there is practicaly no toxicological risk for migration of TPGDA and DPGDA into sugar. However, the presence of both solvent residuals caused unpleasant smell of crystalline sugar in stickpacks made of these packaging materials. According to the Regulation (EC) No 1935/2004 (EC 2004), food contact materials should not endanger human health and also should not cause deterioration in the organoleptic characteristics of food.

Migration of diacrylates through paper packaging coated with polymer films into dry foods has not been sufficiently described, so far. Although it is generally assumed

there is low risk of migration of chemical contaminants from paper and board into dry food, some studies show that it might happen. Therefore, it is quite important to determine which kind of dry foods and possible migrants pose significant migration risk. It has been reported that migration percentage of phthalates from paper packaging into sugar was high (Aurela, 1999).

4.5 Migration of Diacrylates through Laboratory Prepared Packagings

TPGDA and DPGDA are commonly used for packaging printings and their ability to migrate through paper packaging coated with polymer films has not been sufficiently described, so far. Therefor we decided to study the course of diacrylate migration from the similar type of packaging material as used for crystallina sugar.

The papers coated with different amount of low density polyethylene (LDPE) which were obtained from one company in Czech Republic. The thickness of tested papers were 57 (Film A) and 86 µm (Film B). Film A contains 60 g/m^2 paper and 40 g/m^2 polyethylene, Film B contains 50 g/m^2 paper and 20 g/m^2 polyethylene.

The testing papers coated with LDPE containing addition of TPGDA or DPGDA were prepared by manual spraying using plastic spray as mentioned in the methods (chapter 3.3.2). The amount of additives transferred on the paper side of tested packages determined by GS-MS procedure were 4.2 $mg/dm^2 \pm$ 0.4 mg/dm^2 for TPGDA and 4,1± 0.2 mg/dm^2 for DPGDA.

The Figure 4.4 and Figure 4.5 represent the results of migration of DPGDA and TPGDA from spiked Film A into 10% ethanol at 40 °C within 24 hours storage. Migration started immediately and was negligible even after 1 hour for DPGDA and 7 hour for TPGDA. Paper packagings reached an equilibrated or maximized migration to simulants in 1 day at 40 °C. In the this case (Figure 4.4 and Figure 4.5) the migration of DPGDA and TPGDA into 10% ethanol after 24 hours is 0.063 ± 0.006 mg/dm^2 and 0.31±0.02 mg/dm^2, respectively.

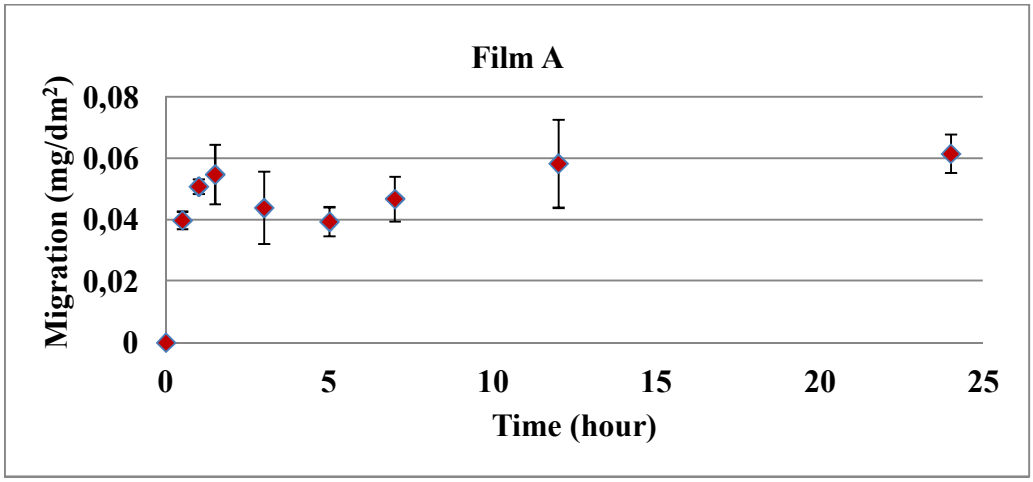


Figure 4.4 : Migration of DPGDA from the Film A into 10% ethanol at 40 °C

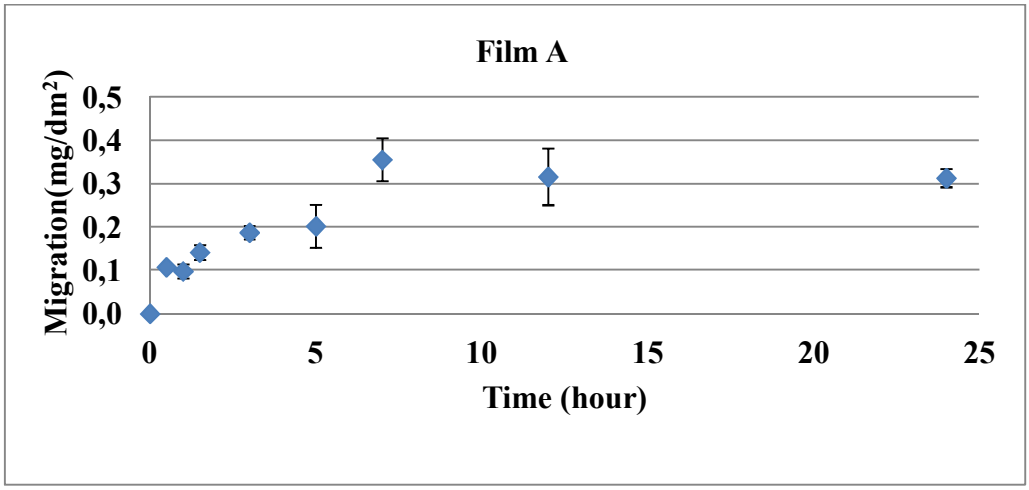


Figure 4.5 : Migration of TPGDA from the film A into 10% ethanol at 40 °C

In the second case (Figure 4.6 and Figure 4.7), the results of migration from spiked Film B into 10% ethanol at 40 °C within 24 hours storage through LDPE film are summarised for DPGDA and TPGDA. Migration started immediately and was negligible even after 1 hour for DPGDA and after 3 hours for TPGDA. The migration of DPGDA and TPGDA from spiked Film B packaging into 10% ethanol after 24 hours is 0.077 ± 0.012 mg/dm^2 and 1.69±0.16 mg/dm^2, respectively.

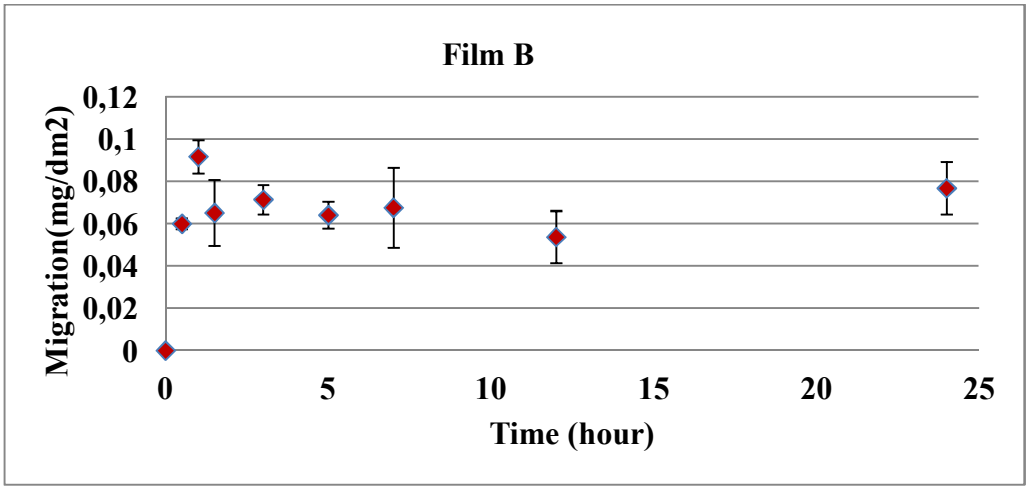


Figure 4.6 : Migration of DPGDA from the film B into 10% ethanol at 40 °C

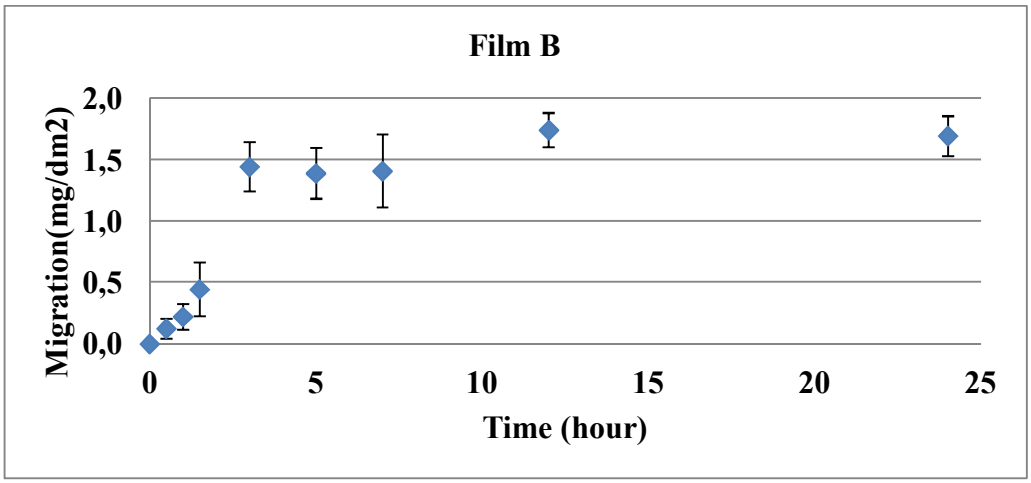


Figure 4.7 : Migration of TPGDA from the film B into 10% ethanol at 40 °C

In the third case (Figure 4.8 and Figure 4.9), the results of migration from spiked Film A into 95% ethanol at 40 °C within 24 hours storage through LDPE film are summarised for DPGDA and TPGDA. Migration was negligible after 1 hour for DPGDA and after 13 hours for TPGDA. The migration of DPGDA and TPGDA from spiked Film A packaging into 95% ethanol after 24 hours are 0.54 ± 0.1 mg/dm^2 and 1.51 ± 0.06 mg/dm^2, respectively.

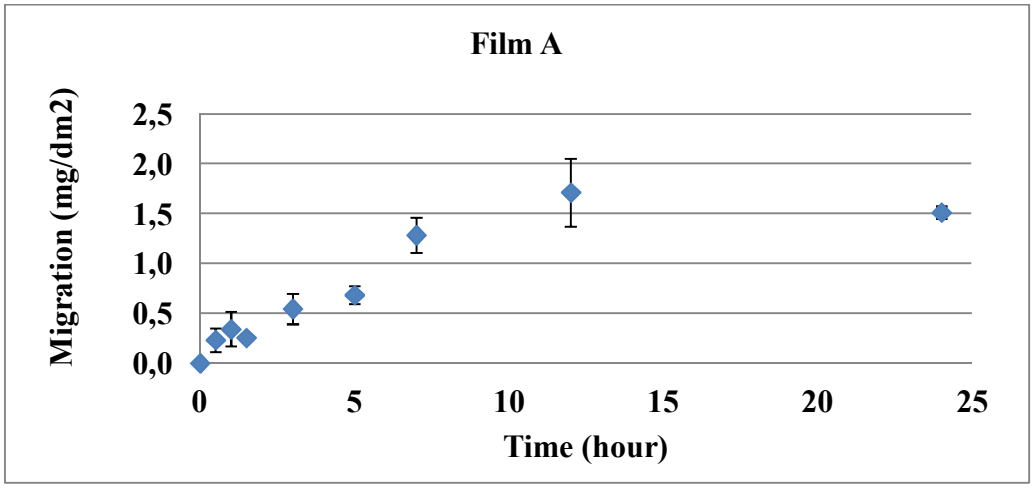


Figure 4.8 : Migration of TPGDA from the film B into 95 % ethanol at 40 °C

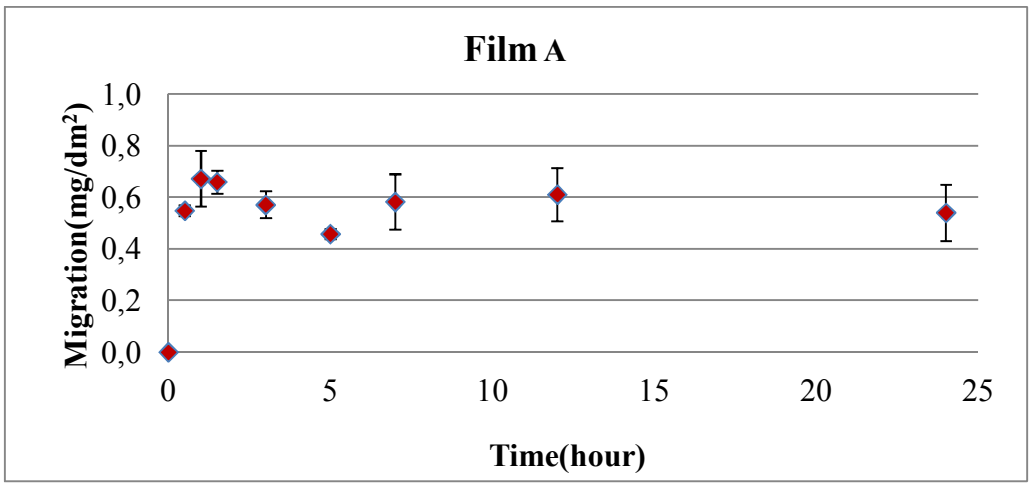


Figure 4.9 : Migration of DPGDA from the film B into 95 % ethanol at 40 °C

Additionally, in the last case (Figure 4.10 and Figure 4.11), the migration of DPGDA and TPGDA into 95% ethanol from spiked Film B are 0.54 ± 0.11 mg/dm^2 and 3.29 ± 0.30 mg/dm^2, respectively after 24 hours.

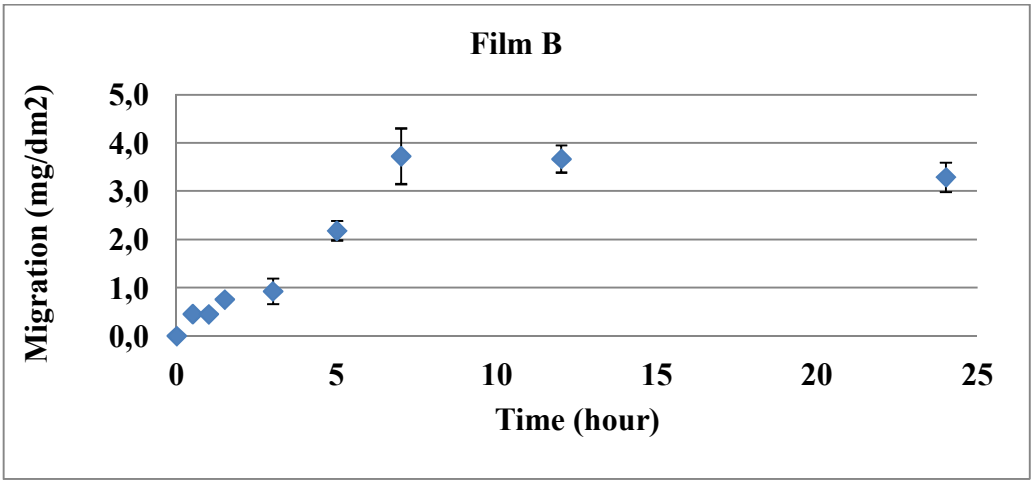


Figure 4.10 : Migration of TPGDA into 95% ethanol through Film B at 40 °C

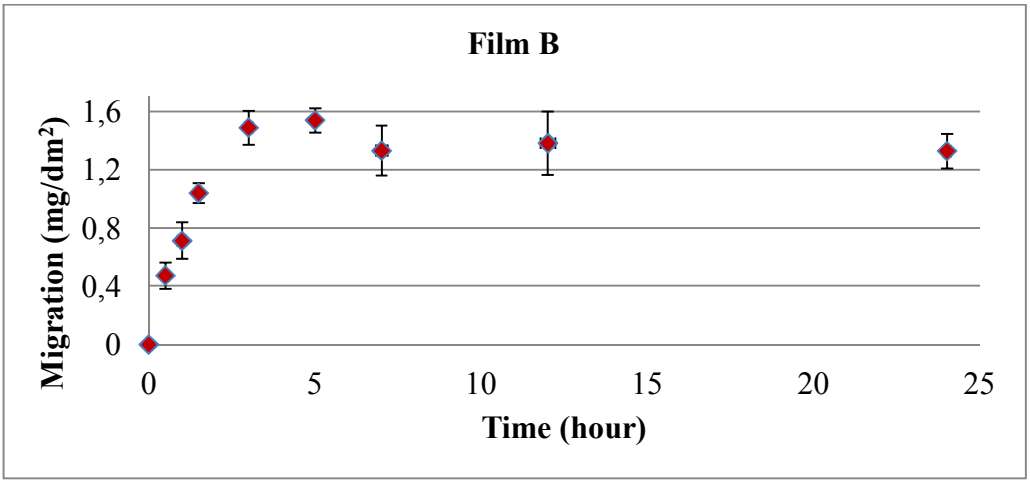


Figure 4.11 : Migration of DPGDA into 95% ethanol through Film B at 40 °C

In all cases, it is clearly seen that TPGDA showed significant migration from paper toward 95% ethanol through spiked Film B packaging. The migration of TPGDA is faster and higher for spiked Film B and migration has increased with ethanol content of food simulant. As expected the migration of both DPGDA and TPGDA into 95 % ethanol through paper packagings was higher compared with the rate of migration into 10% ethanol. Figure 4.4. and Figure 4.6. shows that DPGDA slightly migrated into 10% ethanol through both of the film and migration level was almost same during the observed time. It shows that migration of surragates may have started immediately after spiking. In addition, in the literature, it is reported that migration of non polar surragates anthracene and methyl stearate through polypropylene layer

into 95% ethanol is 2 or 3 times higher than migration into 10% ethanol (Song et al.,2003) which is in agreement with the results of this study.

On the otherhand, it was surprisingly observed that the higher levels of migration from both DPGDA and TPGDA were found for the film A compared with the film B even the LDPE layer of the film A was about twice thicker. Poorer barrier properties should have been offered by thicker coating to cause quicker rate in migration. This surprising result can be caused by the different quality of LDPE coating on both films.

Additionally, the results show that migration of TPGDA is faster and its level is higher compare with the migration of DPGDA for both paper types and simulants. It is obvious that migration of both tested substances through different thickness of paper was significantly influenced by polymer material and characteristics of migrant. There are several variables that affect the permeation and diffusion of molecules through polymers.

Several variables may influence the rate and degree of migration from paper to liquid simulants through the polyethylene layer. According to literature, paper and board materials are heterogeneous and have porous structures consisting of cellulosic fibres and air pores which provide absorbtion or desorption of migrant through the paper. Therefore, some of the paper packaging contains plastic layer which represents a functional barrier for migration of substances present in the paper or paperboard (Pocas et al., 2011). In this study it is found that LDPE coating is not an efficient barrier against diacrylates. This is in agreement with the previous study performed by Choi et al. (2002). The migration of five surrogate contaminants, anthracene, benzophenone, dimethyl phthalate, methyl stearate and pentachlorophenol, from paper and paperboard into water through a polyethylene (PE) coating layer was investigated by Choi *et al*. (2002) and the researchers indicated that PE is not a good barrier for these five surragates. Besides, migration rates through a functional barrier depend on not only the thickness of the plastic layer, and also on the solubility of the substance in the functional barrier, partitioning between paper or board and the plastic layer and on temperature (Choi, Jitsunari, Asakawa, & sun Lee, 2005; Song, Begley, Paquette, & Komolprasert, 2003)

4.6 Identification of Potentially Hazardous Substances in Fiber-Based Packagings

4.6.1 Qualitative and quantitative analyses

The main aim of this part of the study was to screen paper packaging materials commercially used in Czech Republic to obtain objective data for risk assesment of possible hazardous contaminants in paper packaging. 20 different paper food packaging materials provided from the manufacturers in Czech Republic were tested. 12 of them were printed paper board packagings used for cheeses and chocolates, 2 were raw papers without printing inks, 6 were printed paper packagings intended for flour. All packaging samples were extracted with diethylether and analyzed by GC/MS as described in chapter 3.3.3.

The results confirmed that unprinted paper board packagings generally contain much less contaminants compared with printed papers. Figure 4.12 shows some of the typical chromatograms ofanalyzed samples. The printed paper chromatograms contain a lot of peaks due to different additives, the content of which varied considerably. It was already studied that printed packagings contain phthalates (plasticizers in inks) and hydrocarbons. Besides, it was also known that both phthalates and hydrocarbons may migrate from packaging material into foods and food simulants (Aurela et al.,1999; Jickells et al., 2005, Biedermann et al., 2010).

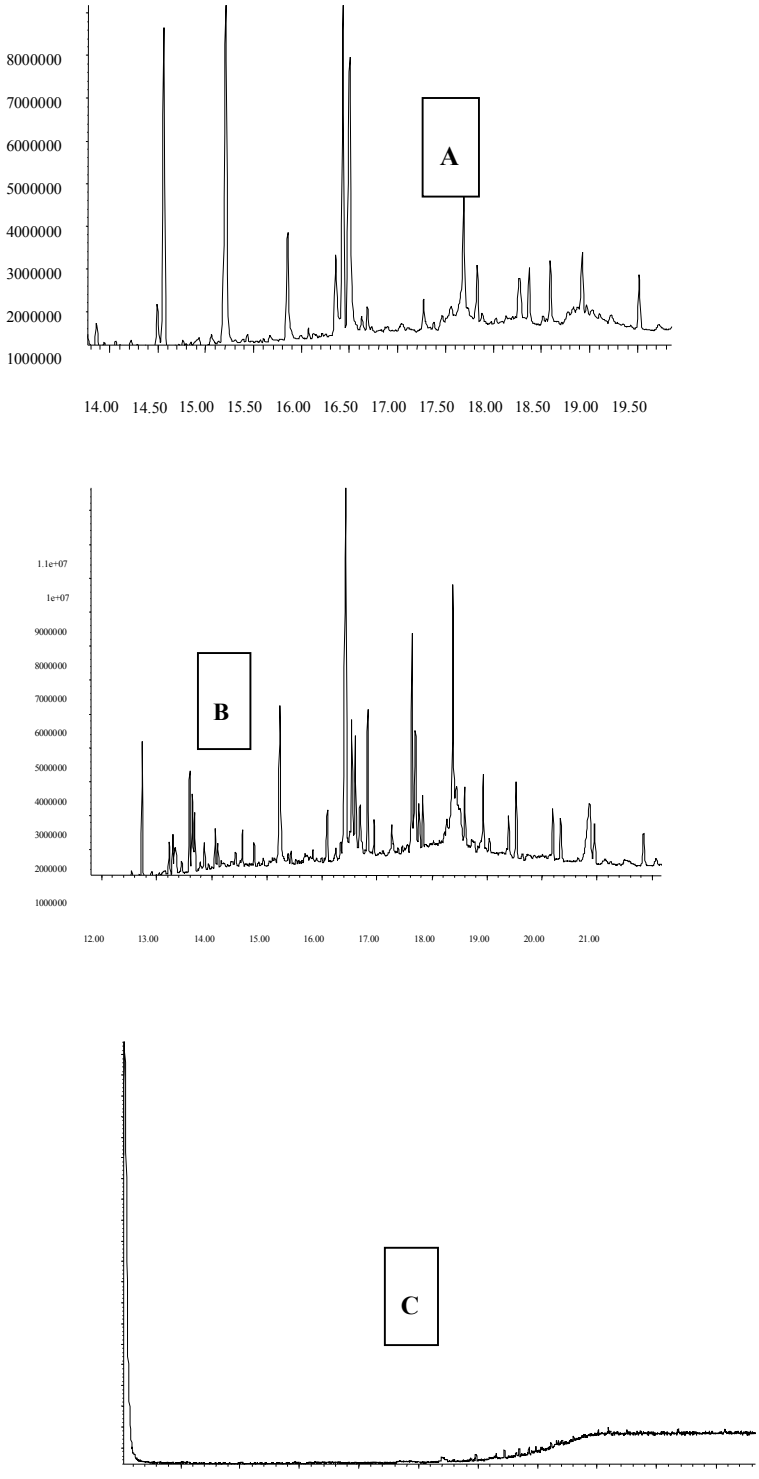


Figure 4.12 : Typical GC/MS chromatograms of the diethylether extracts of the 3 kinds of packaging sample. A) Printed paper , B) Printed Flexo paper board, C) Unprinted Paper board

Detailed information about identified substance is given on the Table 4.4. The concentrations of dibutyl phthalate (DBP), triacetin, bis(2-ethylhexyl) adipate (DEHA), tributyl acetylcitrate(ATBC), dipentyl phthalate, ethyleneglycol mono(2-ethylhexyl)ether, tri(2-Ethylhexyl)trimellitate, mono(2-ethylhexyl) phthalate tested for all samples. Triacetin, on phthalate base plasticiser, was identified in 6 sample of flour packagings at maximal level of 768.3 mg/kg. Other common substance in paper packagings is bis(2-ethylhexyl) adipate (DEHA) was identified in 5 samples of packaging materials (paper boards used for chocolate and cheese) at level up to 374.7 mg/kg. Tri(2-ethylhexyl) trimellitate was found only in paper board used for chocolate at max. level of 385 mg/kg, tributyl acetylcitrate, dipentyl phthalate in 2 sample (cheese boxes) up to 12.1 mg/kg and 9.9 mg/kg, respectively. Mono(2-ethylhexyl) phthalate was identified in cheese packagings (paper board) at maximum level of 138 mg/kg.

The identified substances included in EU positive list of monomers and/or additives for The identified substances included in EU positive list of monomers and/or additives for food contact materials are o-Phthalic Acid, diisooctyl ester, Dibutyl phthalate, 2,6-Di-tert-butyl-p-cresol (BHT), Phthalic anhydride, myristic acid, stearic acid.

It is clearly found that most of the substances are not included in the EU positive list of monomers and/or additives for food contact polymer and there is no special legislation about these substances. According to Pocaz and Hog, DIPNs, solvents, phthalates, azo-colourants, primary aromatic amines and polycyclic aromatic hydrocarbons are potential migrants for paper and board in contact with foods (2007). Considering identified substances, most common contaminants in paper packagings are plasticisers and diisopropyl naphthalenes (DIPNs) which is in a agreement with several studies executed in recent years (Aulera,2010; Tiggelman, 2012; Triantafyllou et al 2002; Zhang et al. 2008).

In this study the substances which could potentially migrate into packaged food was determined. However migration test of these substances was not executed. Therefore health risk assesment could not be done according to this study but the possible risk and danger of identified sample could be estimated.

On the other hand it must be mentioned that this study was aimed on volatile migrants which can be identified using gas chromatography. The presence of non volatile contaminants was not tested due to lack of time.

Table 4.4 : List of identified potential residuals found in analysed samples of packaging materials

No	Migrant	Cas No.	Toxicological data	Highest Content ($\mu g/dm^2$)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
1	Butyl octyl phthalate	000084-78-6	• LD50 (oral, rat) > 63 ml/kg; • TSCA listed (1)		87	3	High solvating plasticizer for PVC, PS, PVB, PVAc, Molding and dip coating in food-pkg. adhesives (1)	
2	1,2-*Butyl isobutyl phthalate*	017851-53-5			95	2		
3	Tributyl citrate	000077-94-1	• LD50(mouse): 2900 mg/kg; • TSCA listed (1)		64	1	Plasticizer for lacquers, printing inks, antifoam agent in food-pkg. adhesives (1)	

Table 4.4: List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No.	Toxicological data	Highest Content ($\mu g/dm^2$)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
4	Diisobutyl phthalate(DIBP))	000084-69-5	• LD50 oral,rat: 15g/kg, • Mildly toxic by ingestion and skin contact; • Experimental teratogen; • TSCA listed (1) • (TDI) of 0.01 mg/kg bodyweight(b.w)(2)	138 mg/kg	86	5	Plasticizer, vehicles for pigment dispersions (1)	

Table 4.4: List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No	Toxicological data	Highest Content (µg/dm^2)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
5	3,5-dichloroanilinebenzenamine	000626-43-7			91	2		
6	2,4-dichloroaniline	000554-00-7			90	1		
7	o-Phthalic Acid	000088-99-3	• Tolerable Daily Intake (TDI) 1.0 mg/kg b.w. (3)		86	1	Component of dyes, food packaging adhesives (1)	PL (SCF-L 2)
8	Diisooctylphthalate	027554-26-3	• Acceptable Daily Intake (ADI) 0.15 mg/kg b.w. (3,4)		91	1	Plasticizer, solvent (1,4)	PL SML(T) = 9 mg/kg (4)

Table 4.4 : List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No	Toxicological data	Highest Content (µg/dm2)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
9	1,2-Benzisothiazole, 3-(hexahydro-1H-azepin-1-yl)-, 1,1-dioxide	309735-29-3			91	1		
10	1,7,11-trimethyl-4-(1-methylethyl)-cyclotetradecane	001786-12-5			93	1		
11	2,6-Diisopropylnaphthalene (DIPN)	024157-81-1	Skin, eye and respiratory irritant(1)		98	5	Used for manufacture of carbonless copy paper (1)(5)	

Table 4.4 : List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No	Toxicological data	Highest Content(µg/dm^2)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
12	4,4'-Diisopropylbiphenyl(4,4 DIPN)	018970-30-4			96	1		
13	Dibutyl phthalate	000084-74-2	• LD50 (oral, rat) 2830 mg/kg, • Primary skin and eye irritant(7) • TSCA listed		94	3	Plasticizer, (1)(5)	PL SCF -L2 TDI: 0.05 mg/kg b.w.

Table 4.4: List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No	Toxicological data	Highest Content ($\mu g/dm^2$)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
14	2,6-Di-tert-butyl-p-cresol (BHT)	000128-37-0	• LD50 (oral, rat) 890 mg/kg, • Suspected carcinogen • Eye irritant • Experimental teratogen • TSCA listed (1)(6)		97	1	Antioxidant in food-contact coatings, food packaging adhesives and defoamer in food-contact paper/paperboard (1)	PL SML = 3.0 mg/kg SCF-L2 ADI: 0.05 mg/kg b.w.
15	Diethylene glycol dibenzoate	000120-55-8	• LD50 (oral, rat) 2830 mg/kg, (skin, rabbit) 20 g/kg • Primary skin and eye irritant(7) • TSCA listed		86	1	Plasticizer (1)(7)	

Table 4.4: List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No	Toxicological data	Highest Content ($\mu g/dm^2$)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
16	Eicosane	000112-95-8	• Irritating to eyes, skin, upper respiratory • TSCA list		98	3	Used in plasticizers; in closure-sealing gaskets for food containers	
17	Glycerol tricaprylate	000538-23-8			90	1		
18	Heneicosane	000629-94-7			95	1		
19	Heptadecane	000629-78-7			90	4		
20	Butyl palmitate	000111-06-8			87	3	For fiber finishing for resin-bonded filters for food contact (1)	
21	Hexacosane	000630-01-3			88	2		

Table 4.4: List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No.	Toxicological data	Highest Content ($\mu g/dm^2$)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
22	bis(2-ethylhexyl) adipate (DEHA)	000103-23-1	• LD50 (oral, rat) 9110 mg/kg • Suspected carcinogen and teratogen • Eye and skin irritant • TSCA listed (1)	374.7 mg/kg	89	5	Plasticizer (1) (8)	
23	4,5,6,7,8,8-hexachloro-1,3,3a,4,7,7a-hexahydro-4,7-methanoisobenzofuran	003369-52-6			91	1		

Table 4.4: List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No	Toxicological data	Highest Content(µg/dm^2)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
24	2-Methyl-cis-7,8-epoxynonadecane	1000130-93-3			86	1		
25	Nonadecane	000629-92-5			95	2		
26	Oleamide	000301-02-0	• TSCA listed(1)		87	5	Slip agent, antiblocking agent for extrusion of polyethylene Slip agent for printing inks; coatings (1)	
27	Octacosane	000630-02-4			99	2		

Table 4.4: List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No	Toxicological data	Highest Content(µg/dm^2)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
28	Phthalic anhydride	000085-44-9	• LD50 (oral, mouse) 1500 mg/kg; • Corrosive irritant to eyes, skin, mucous membranes • Experimental teratogen; • TSCA listed(1)		91	3	Plasticizer Curing agent Hardener for resins Polymerization control agent Retarder in food-contact rubber (1)	PL SCF-L2 TDI: 1 mg/kg b.w.
29	1-Propene-1,2,3-tricarboxylic acid, tributyl ester	007568-58-3			96	1		

Table 4.4: List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No	Toxicological data	Highest Content (µg/dm^2)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
30	Palmitic acid	000057-10-3	• LD50 (mouse) 57 mg/kg; • Acute poison • Human skin irritant • Questionable carcinogen • TSCA listed(1)		96	4	Pigment additives(EFSA), defoamer in food-contact paper coatings(1)	
31	Dehydroabietic Acid	001740-19-8 1			99	3		
32	2-Chloropropionic acid,hexadecyl ester	086711-81-1			91	2		

Table 4.4: List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No	Toxicological data	Highest Content (µg/dm^2)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
33	2,5-ditert-butylphenol	000096-76-4			87	1		
34	Phenol, 2,5-bis(1,1-dimethylethyl)	005875-45-6			91	2		
35	Vinyl palmitate	000693-38-9			88	2		
36	Stearic acid,	000057-11-4			89	5	Pigment additives(1)	PL SCF L-1 ADI:not specified.

Table 4.4: List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No	Toxicological data	Highest Content (µg/dm^2)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
37	Tricosane	000638-67-5			98	5		
38	Tri(2-ethylhexyl) trimellitate	3319-31-1		385 mg/kg	91	1	Plasticiser(9)	PL
39	Tri-n-butyl acetyl citrate	000077-90-7	• LD50 (intraperitoneal , mouse) > 4 g/kg; • TSCA listed	12.1 mg/kg		2	Plasticizer (1)	PL
40	Tridecane	000629-50-5			94	3		

Table 4.4: List of identified potential residuals found in analysed samples of packaging materials (continuing)

No	Migrant	Cas No	Toxicological data	Highest Content ($\mu g/dm^2$)	Quality	Number of occurance	Origin/function	Included in EU positive list for polymers
41	Myristic acid	000544-63-8	• LD50 (oral, rat) > 10 g/kg, • Eye and human skin irritant • TSCA listed(1)			2	Defoamer in food-contact paper coatings (1)	PL SCF L-1 ADI:Not specified
42	Triacetin	000102-76-1	• LD50 (oral, rat) 3000 mg/kg, • Eye irritant • TSCA listed	768.3 mg/kg		6	Plasticizer	SCF L1 ADI: not specified

References: (1) Ash and Ash, 1999 ,(2) Anon., 2012,(3) Anon., 2010 , (4) Dupáková *et al*. 2009, (5) Zhang *et al*. 2008,(6) Anon., 2004, (7) EPA 2001,(8) Petersen and Naamansen 1998, (9) Ito et al. 2008 (PL = included in EU positive list of Directive 2002/72/EC, SCF-L = Scientific Committee of Food list as defined e.g.in EFSA 2008, TSCA = Toxic Substances Control Act)

5. CONCLUSION

The following conclusions can be formulated on the base of the results described in this study;

- The residuals of DPGDA and TPGDA originated from acrylic printing inks can penetrate through the packaging material based on laminate of paper and polyethylene and they can cause unacceptable sensory failure of the product packaged in such film. In this study the DPGDA in concentration about 0.2 mg/kg caused the senzory failure of crystalline sugar.
- The migration of diacrylates from the samples of commercially producedfilms tested in this study did not pose any healthy risk for potential consummer.
- The migration of DPGDA and TPGDA from the packaging materials based on laminate of paper and polyethylene into food simulants is quite fast, i.e. polyethylene layer is notefficient barrier against diacrylate migration.
- The highest level of diacrylates migration was found in the case of 95% ethanol. There were much lower differences in migration extent into other tested simulants, i.e. 10% ethanol, 50% ethanol, 3% acetic acid and olive oil. In all cases the level of TPGDA migration was higher compared with that of DPGDA.
- The course of migration was affected by packaging material parameters, in this study the diacrylate transport through the film with thicker layerof polyethy\lene was significantly easier compared with the sample covered with thiner polyethylene coating.
- The analysis of 20 samples of paper based packaging materials proved the presence of many substances with potential to migrate into food. Most of identified contaminants originated from printings and many of them are not aproved for food contact in EU polymer legislation.

Possible recommendations:

The study confirmed the importance of creation of harmonised EU legislation which enable to control the quality of paper based packaging materials intended for food contact as well as the grade of printinginks used for food package.

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APPENDIXES

APPENDIX A: Calibration Curves

APPENDIX B: GC-MS Chromatograms

APPENDIX C: Picture of Paper Packagings Used for Screening

APPENDIX D: Results of Migration Tests for Laboratory Prepared Packagings Samples

APPENDIX A: Calibration Curves

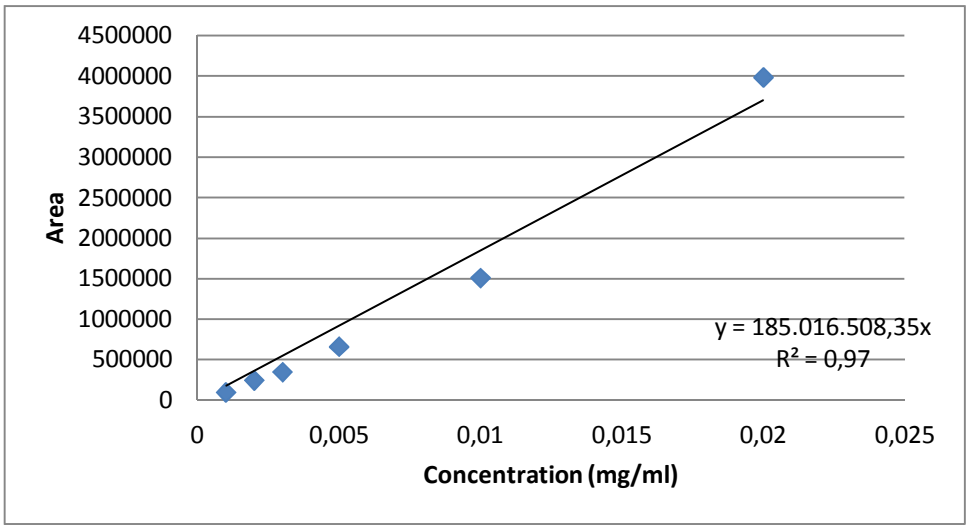


Figure A.1: Calibration Curve for DPGDA

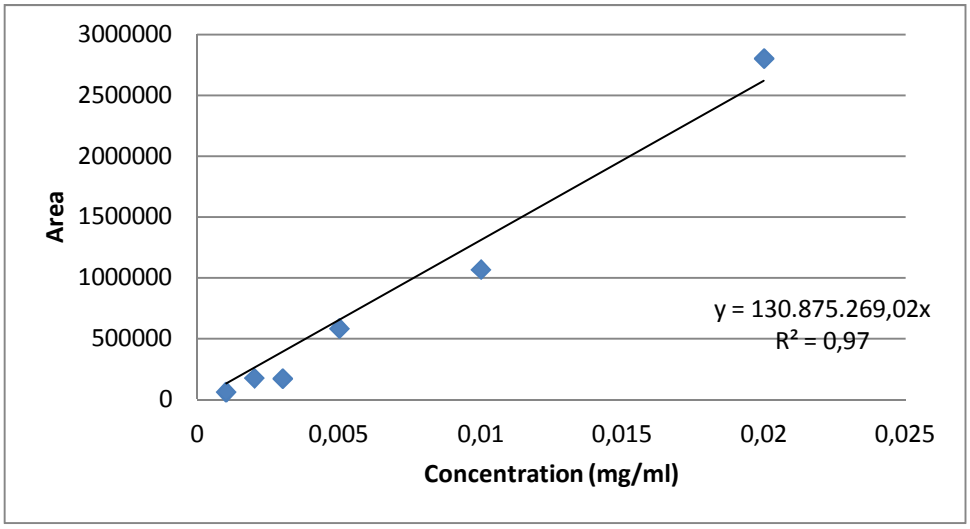


Figure A.2: Calibration Curve for DPGDA

APPENDIX B : GC-MS Chromatograms

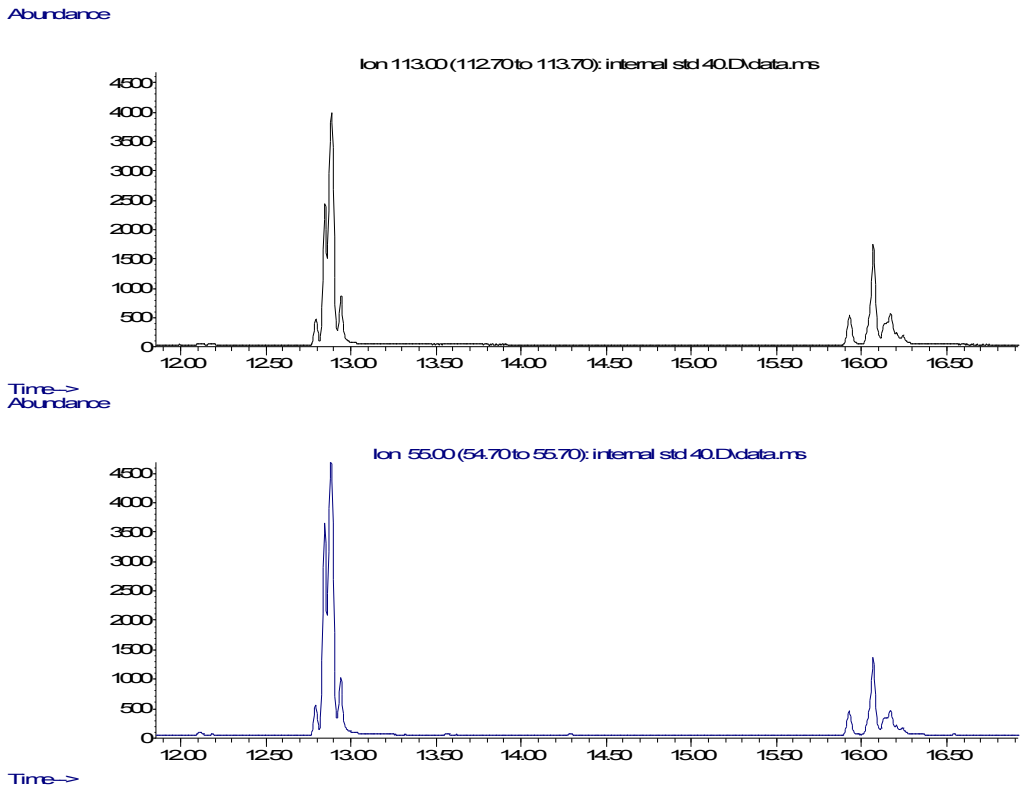


Figure B.1: GC-MS chromatograms of DPGDA and TPGDA standarts

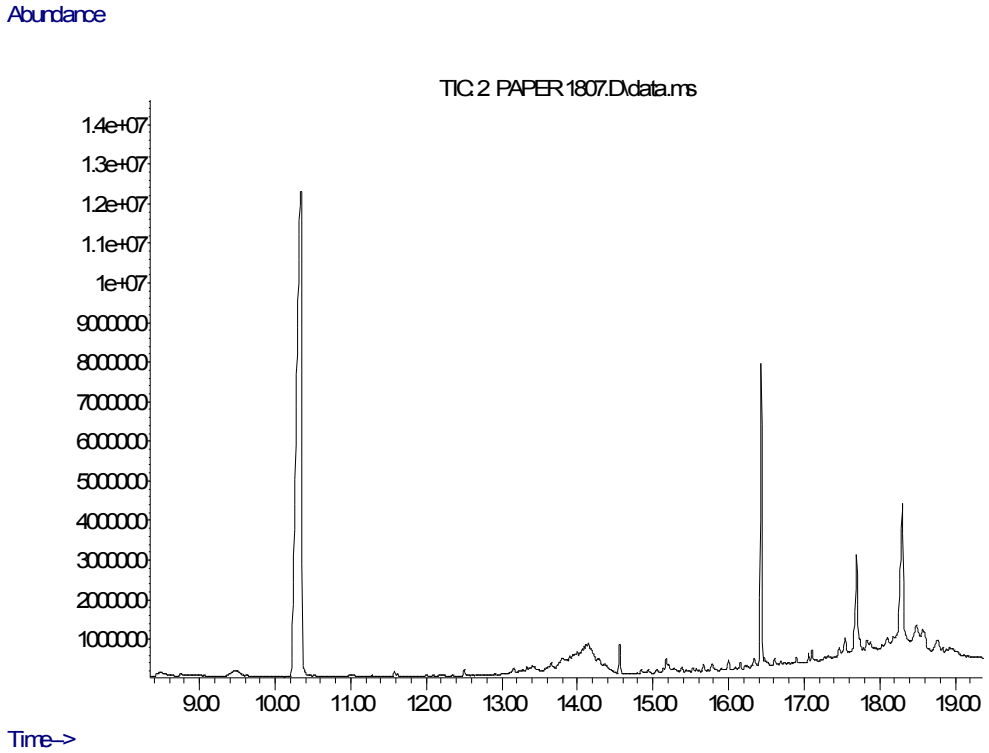


Figure B.2: GC-MS chromatograms of extract of paper used for flour

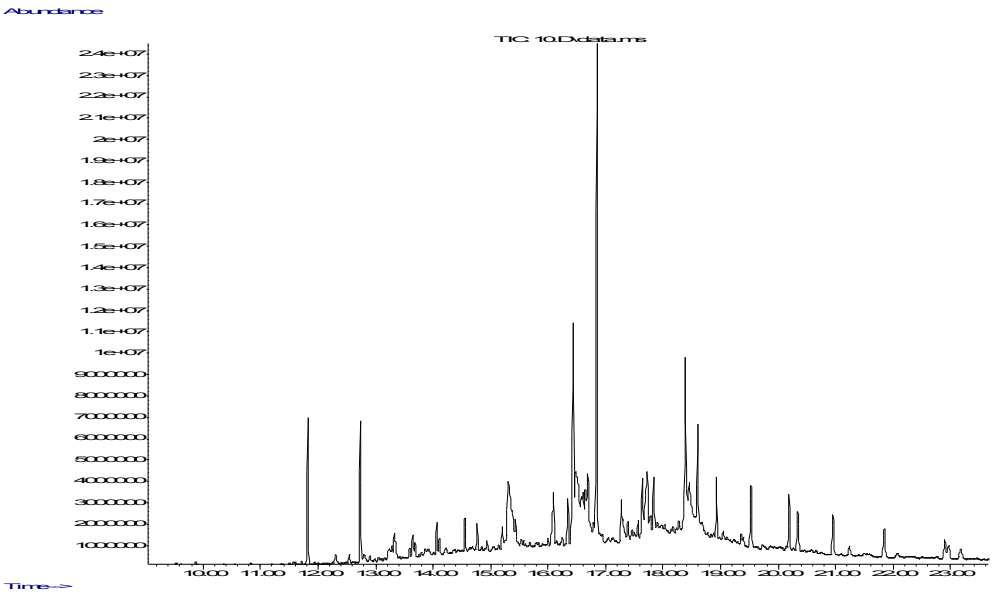


Figure B.3: GC-MS chromatograms of extract of flexo printed paper board packaging used for cheese

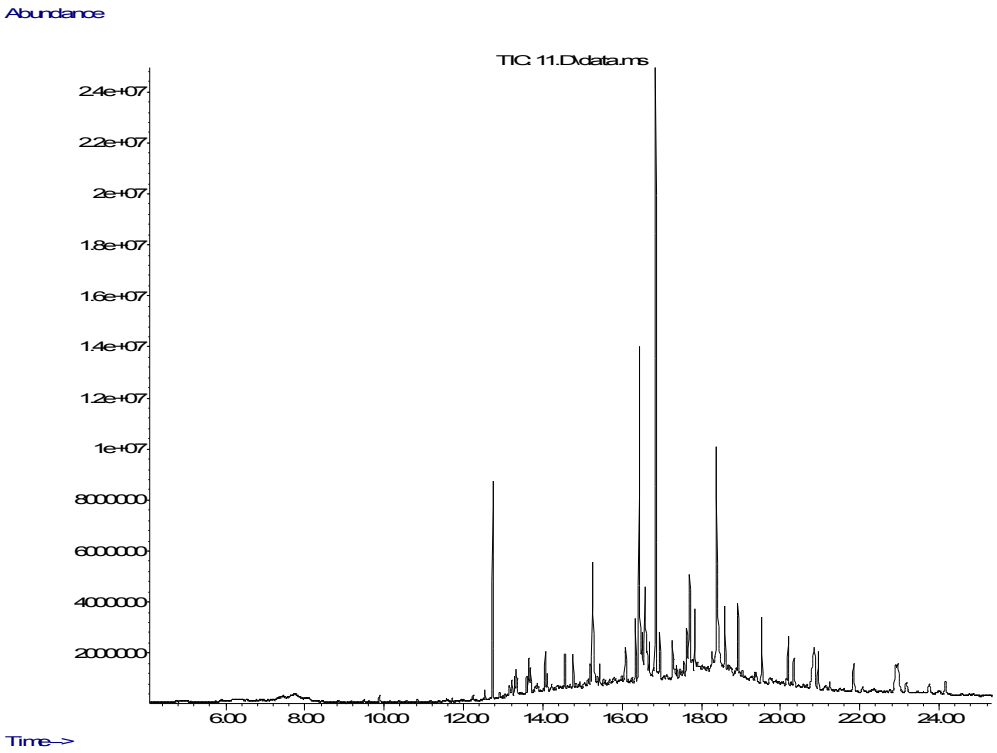


Figure B.4: GC-MS chromatograms of extract of flexo printed paper board packaging used for cheese(3).

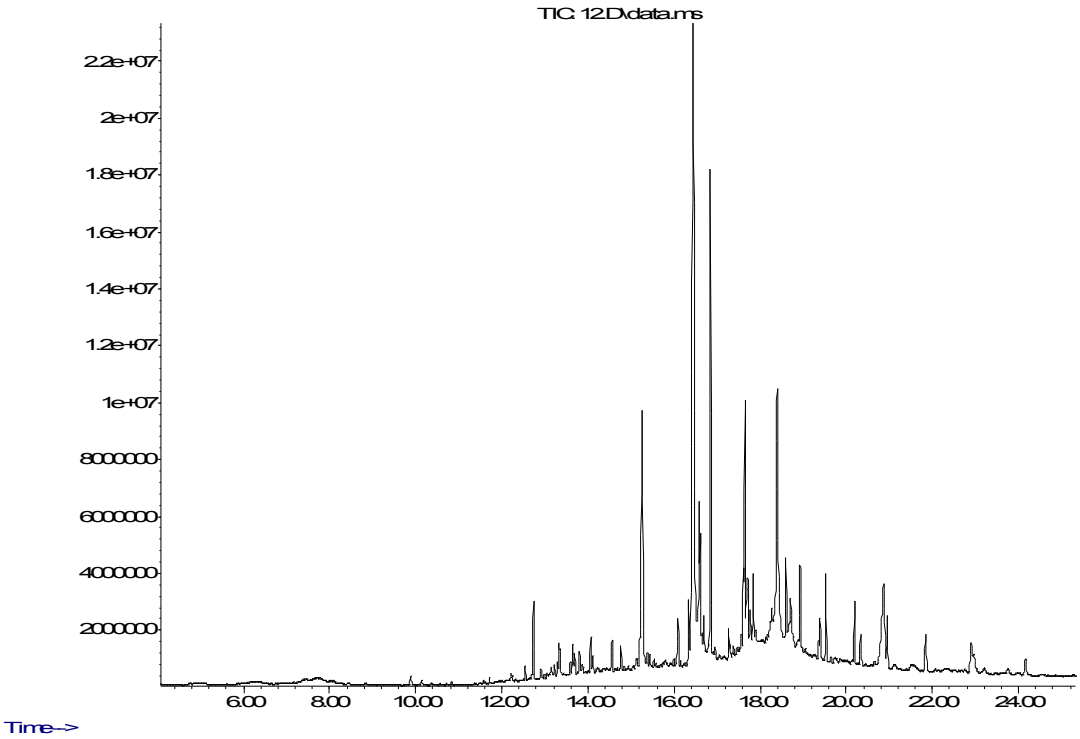


Figure B.5: GC-MS chromatograms of extract of flexo printed paper board packaging used for cheese(3).

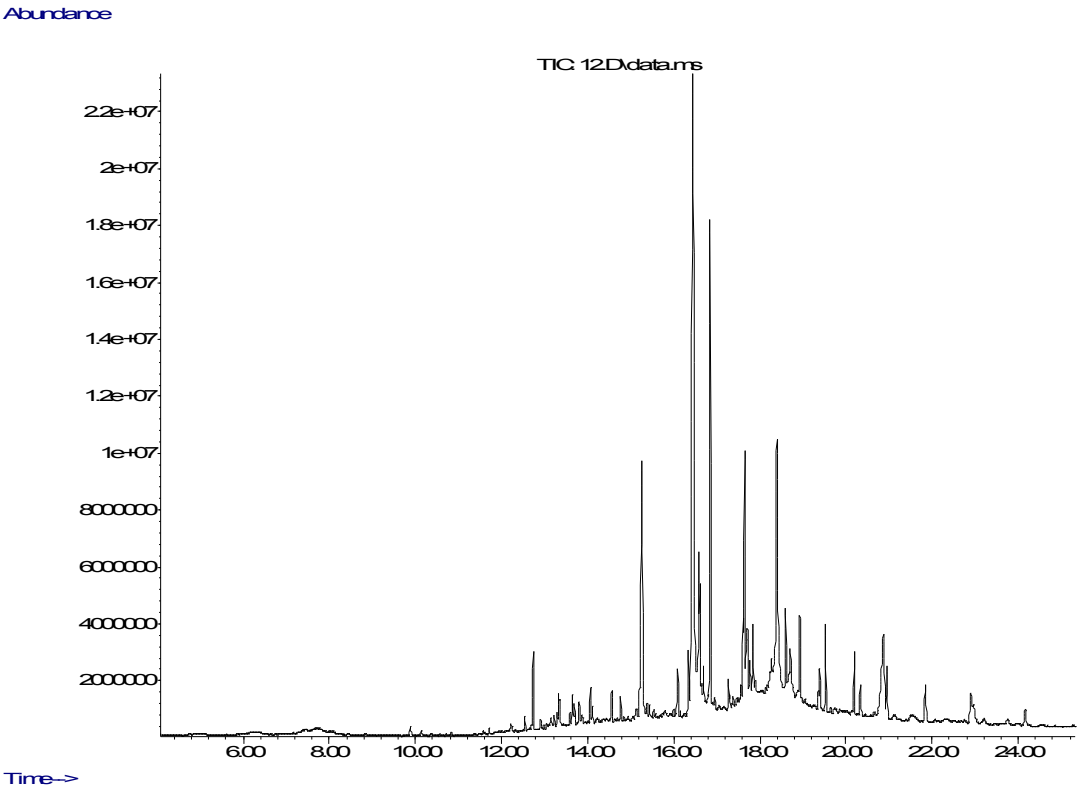


Figure B.6: GC-MS chromatograms of extract of flexo printed paper board packaging used for chocolate (5).

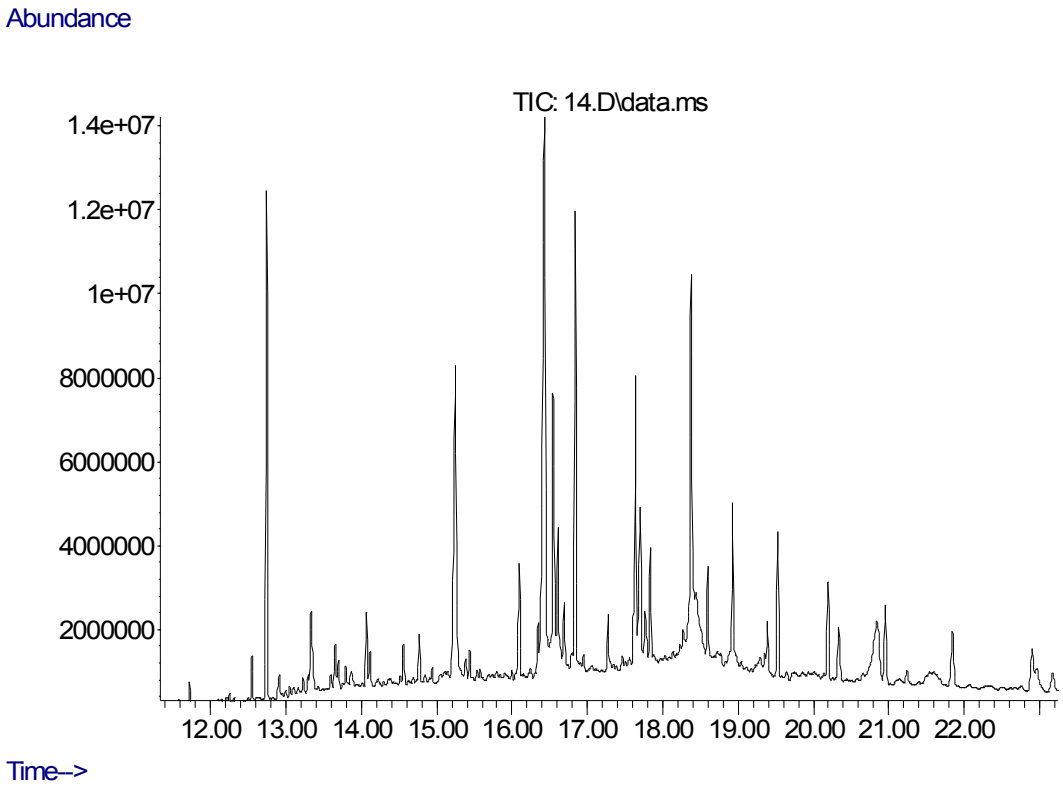


Figure B.7: GC-MS chromatograms of extract of flexo printed paper board packaging used for chocolate (6).

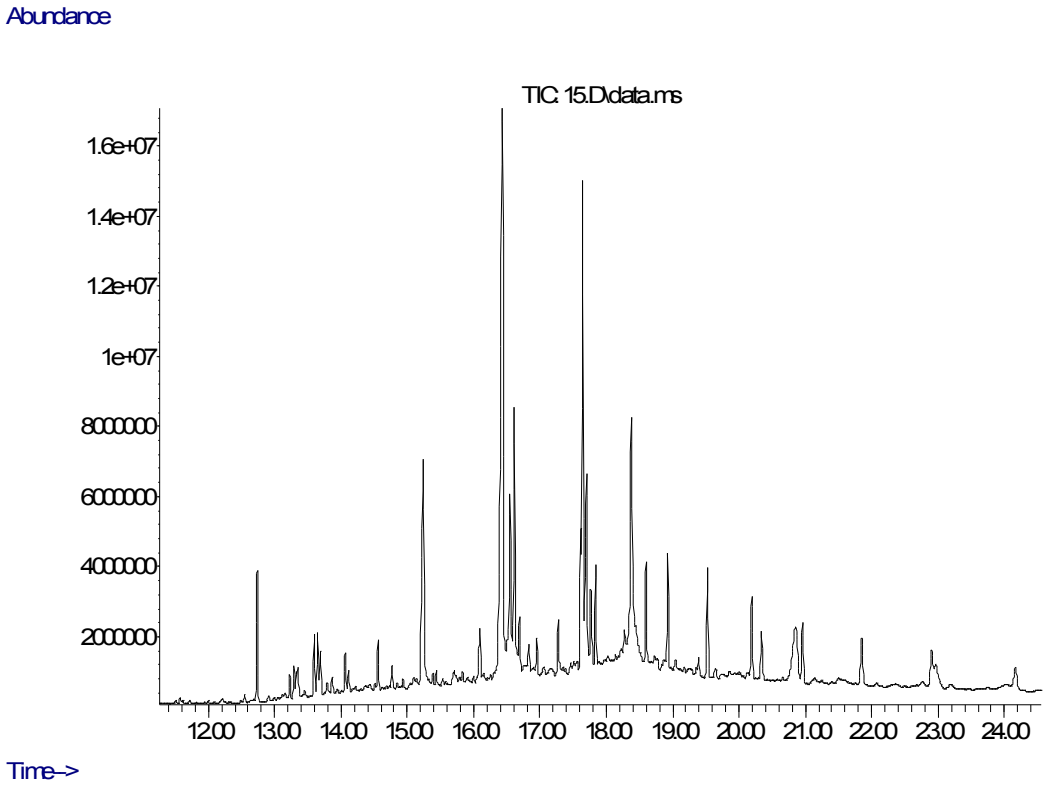


Figure B.8: GC-MS chromatograms of extract of flexo printed paper board packaging used for chocolate (6).

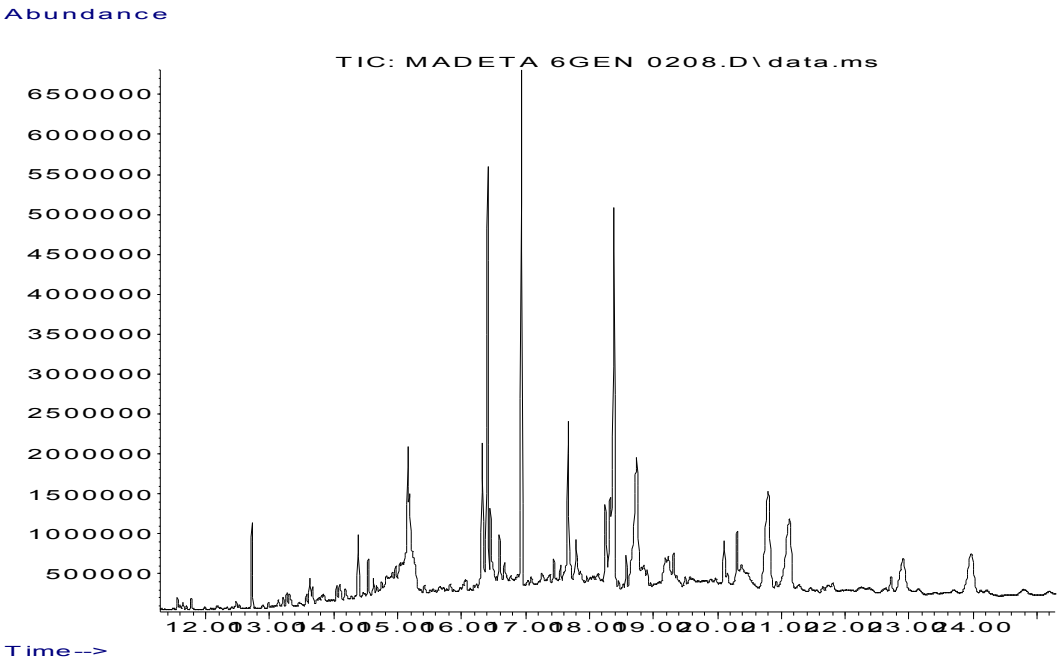


Figure B.9: GC-MS chromatograms of extract of flexo printed paper board packaging used for chocolate(8).

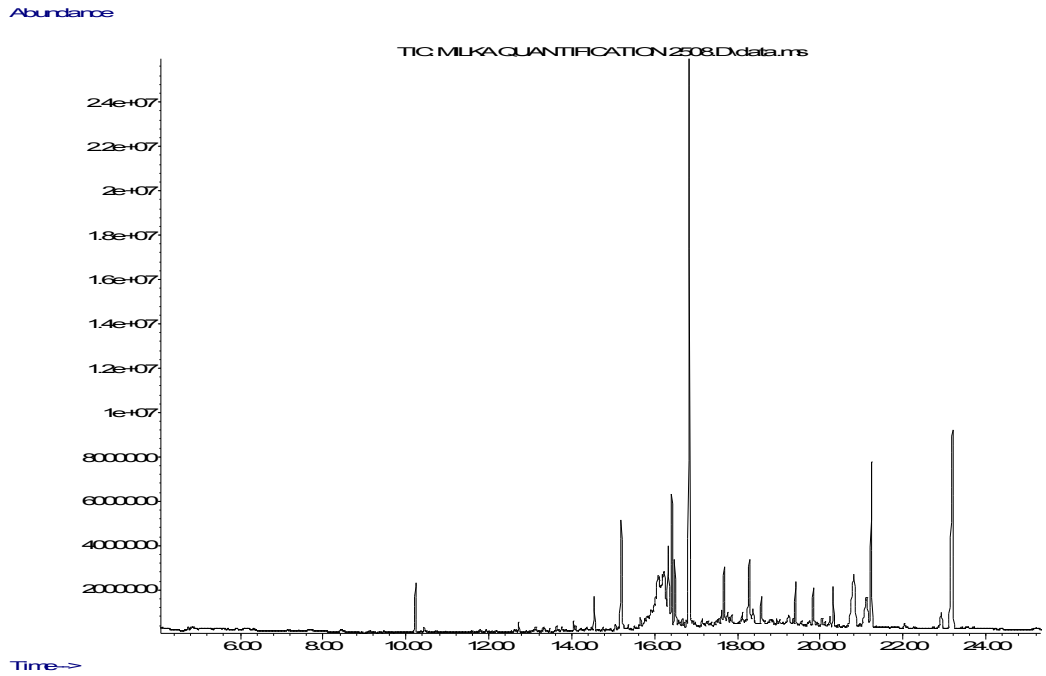


Figure B.10: GC-MS chromatograms of extract of flexo printed paper board packaging used for chocolate(8)

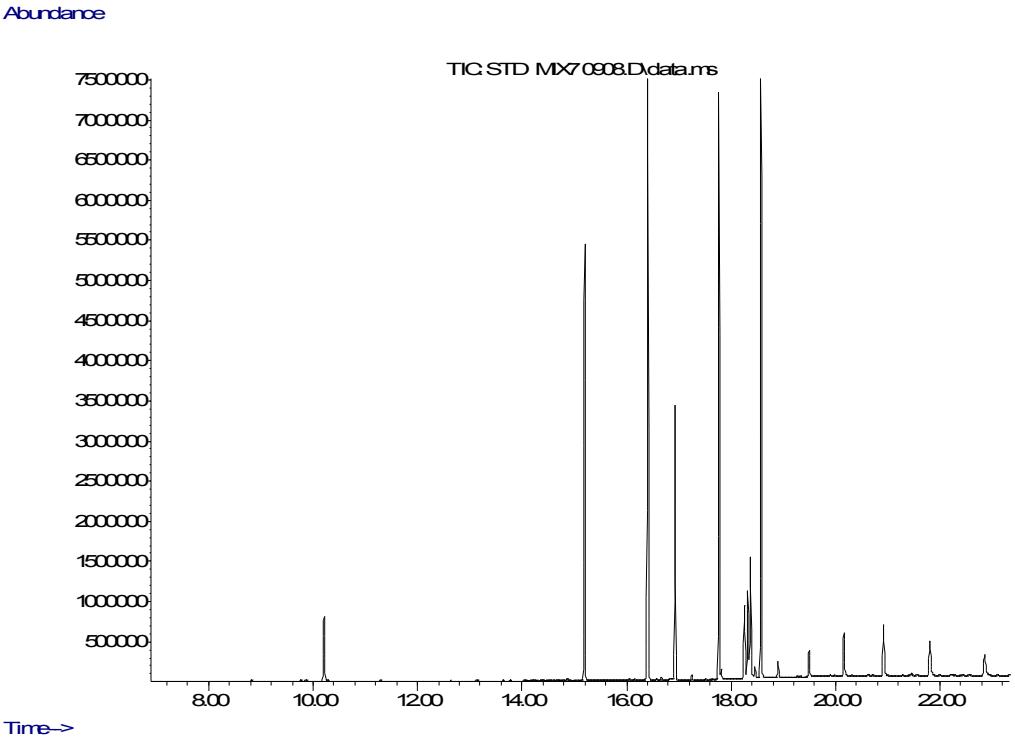


Figure B.11: HPLC chromatograms of standarts (dibutyl phthalate (DBP), triacetin, , bis(2-ethylhexyl)adipate(DEHA), tributyl acetylcitrate(ATBC), dipentyl phthalate,ethyleneglycolmono(2-ethylhexyl)ether,tri(2-Ethylhexyl) trimellitate,1,2-Benzenedicarboxylicacid,mono(2-thylhexyl)

APPENDIX C: Picture of Paper Packagings Used for Screening

Figure C.1: Picture of flour packaging bags (1)

Figure C.2: Picture of flexo printed paper board packaging used for cheese (2)

Figure C.3: Picture of flexo printed paper board packaging used for cheese (3)

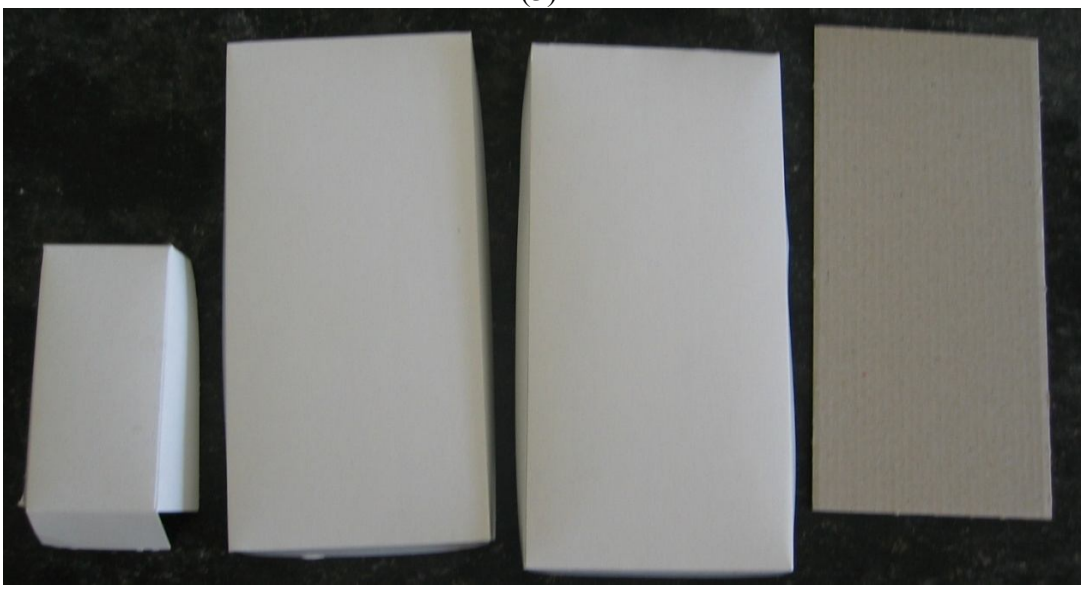


Figure C.4: Picture of unprinted paper board packaging used for cheese (4)

APPENDIX D: Results of Migration Tests for Laboratory Prepared Packagings Samples

Table D.1 : Results DPGDA migration into 95% ethanol through Film A

Migration of DPGDA Through Film A					
Hour	**Migration into %95 ETOH(mg/dm^2)**	**Migration into %95 ETOH(mg/dm^2)**	**Average**	**Standart Deviation**	**% migration**
0	0,000	0,000	0,000	0,000	0%
0,5	0,533	0,563	0,548	0,021	12%
1	0,595	0,748	0,672	0,108	15%
1,5	0,628	0,691	0,660	0,045	15%
3	0,608	0,535	0,571	0,052	13%
5	0,444	0,472	0,458	0,019	10%
7	0,658	0,506	0,582	0,108	13%
12	0,538	0,684	0,611	0,103	14%
24	0,618	0,463	0,540	0,109	12%

Table D.2 : Results DPGDA migration into 95% ethanol through Film B

Migration of DPGDA Through Film B					
Hour	**Migration into %95 ETOH(mg/dm^2)**	**Migration into %95 ETOH(mg/dm^2)**	**Average mg/dm^2**	**Standart Deviation**	**% migration**
0	0,000	0,000	0,000	0,000	0%
0,5	0,410	0,536	0,473	0,090	11%
1	0,624	0,801	0,712	0,125	16%
1,5	0,991	1,088	1,039	0,068	23%
3	1,571	1,406	1,489	0,117	33%
5	1,479	1,598	1,539	0,084	34%
7	1,451	1,209	1,330	0,171	30%
12	1,537	1,227	1,382	0,219	31%
24	1,412	1,243	1,328	0,119	30%

Table D.3: Results TPGDA migration into 95% ethanol through Film A

Migration of TPGDA Through Film A					
Hour	**Migration into %95 ETOH(mg/dm^2)**	**Migration into %95 ETOH(mg/dm^2)**	**Average mg/dm^2**	**Standart Deviation**	**% migration**
0	0,000	0,000	0,000	0	0%
0,5	0,148	0,316	0,232	0,118585	5%
1	0,463	0,219	0,341	0,172764	8%
1,5	0,269	0,239	0,254	0,021049	6%
3	0,436	0,653	0,545	0,153326	12%
5	0,746	0,621	0,683	0,08836	15%
7	1,407	1,161	1,284	0,174117	29%
15	1,953	1,470	1,712	0,341618	38%
24	1,554	1,466	1,510	0,062476	34%

Table D.4 : Results TPGDA migration into 95% ethanol through Film B

Migration of TPGDA Through Film B					
Hour	**Migration into %95 ETOH(mg/dm^2)**	**Migration into %95 ETOH(mg/dm^2)**	**Average mg/dm^2**	**Standart Deviation**	**% migration**
0	0,0000	0,0000	0,0000	0	0%
0,5	0,4286	0,4856	0,4571	0,040324	10%
1	0,4060	0,5003	0,4531	0,066648	10%
1,5	0,7951	0,7208	0,7579	0,05254	17%
3	1,1150	0,7402	0,9276	0,265061	21%
5	2,0417	2,3259	2,1838	0,200978	49%
7	4,1376	3,3208	3,7292	0,577539	83%
15	3,4735	3,8732	3,6733	0,282615	82%
24	3,5109	3,0805	3,2957	0,304349	73%

Table D.5 : Results DPGDA migration into 10% ethanol through Film A

Migration of DPGDA Through Film A					
Hour	**Migration into %10 ETOH(mg/dm^2)**	**Migration into %10 ETOH(mg/dm^2)**	**Average mg/dm^2**	**Standart Deviation**	**% migration**
0	0,0000	0,0000	0,0000	0,0000	0%
0,5	0,0378	0,0418	0,0398	0,0029	1%
1	0,0492	0,0525	0,0509	0,0024	1%
1,5	0,0479	0,0616	0,0547	0,0097	1%
3	0,0355	0,0523	0,0439	0,0118	1%
5	0,0360	0,0427	0,0394	0,0048	1%
7	0,0519	0,0417	0,0468	0,0073	1%
15	0,0685	0,0481	0,0583	0,0144	1%
24	0,0660	0,0571	0,0615	0,0063	1%

Table D.6 : Results DPGDA migration into 10% ethanol through Film B

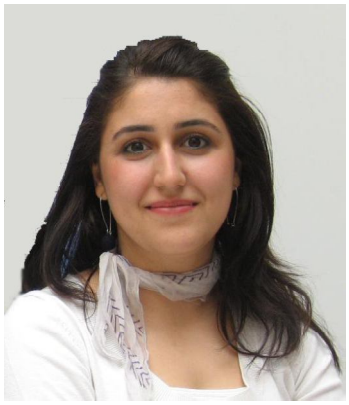
Migration of DPGDA Through Film B					
Hour	**Migration into %10 ETOH(mg/dm^2)**	**Migration into %10 ETOH(mg/dm^2)**	**Average mg/dm^2**	**Standart Deviation**	**% migration**
0	0,000	0,000	0,000	0,000	0%
0,5	0,062	0,058	0,060	0,003	1%
1	0,097	0,086	0,092	0,008	2%
1,5	0,054	0,076	0,065	0,016	1%
3	0,067	0,076	0,071	0,007	2%
5	0,060	0,069	0,064	0,006	1%
7	0,054	0,081	0,068	0,019	2%
15	0,045	0,062	0,054	0,012	1%
24	0,068	0,086	0,077	0,012	2%

Table D.7 : Results TPGDA migration into 10% ethanol through Film A

Migration of TPGDA Through Film A					
Hour	**Migration into %10 ETOH(mg/dm^2)**	**Migration into %10 ETOH(mg/dm^2)**	**Average mg/dm^2**	**Standart Deviation**	**% migration**
0	0,000	0,000	0,000	0,000	0%
0,5	0,105	0,109	0,107	0,002	2%
1	0,086	0,110	0,098	0,017	2%
1,5	0,154	0,129	0,141	0,017	3%
3	0,176	0,198	0,187	0,016	4%
5	0,237	0,167	0,202	0,050	4%
7	0,320	0,390	0,355	0,049	8%
15	0,362	0,270	0,316	0,065	7%
24	0,327	0,298	0,313	0,021	7%

Table D.8 : Results TPGDA migration into 10% ethanol through Film B

Migration of TPGDA Through Film B					
Hour	**Migration into %10 ETOH(mg/dm^2)**	**Migration into %10 ETOH(mg/dm^2)**	**Average mg/dm^2**	**Standart Deviation**	**% migration**
0	0,000	0,000	0,000	0,000	0%
0,5	0,183	0,066	0,125	0,082	3%
1	0,296	0,146	0,221	0,106	5%
1,5	0,290	0,599	0,444	0,219	10%
3	1,301	1,585	1,443	0,201	32%
5	1,243	1,535	1,389	0,206	31%
7	1,618	1,198	1,408	0,297	31%
15	1,643	1,840	1,742	0,140	39%
24	1,579	1,808	1,694	0,162	38%



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  May 2011 – February 2012 (Project Assistant)

PUBLICATIONS/PRESENTATIONS

Yavuz H.T., Votavová L., Čížková H., Dobiáš J., Ozcelik B., 2012 Migration of dipropyleneandtripropylene glycol diacrylatesfrom packaging materials into food simulants. *Chemical Reaction in Food VII (CRF)*,14-16 November 2012, Prague, Czech Republic (Poster Presentation).

Serpen, A.; Pelvan, E.; Alasalvar, C.; Mogol, B.; **Yavuz, H.T**.; Gökmen, V.; Özcan, N.; Ozcelik, B.2012. Nutritional and Functional Characteristics of Seven Grades of Black Tea Grown in Turkey, Journal of Agricultural and Food