Packaging Penetration with Lamination Adhesive Components Compounds

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The paper presents the results by application of one method to study the behaviour of packaging material in contact with food products, using different type of adhesives and different types of films for the package manufacturing. The presented method is based on primary aromatic amine determination using spectrophotometer analyze. Three different types of adhesives and three types of different films were considered for testing the migration of aromatic amines. The test was made in the same conditions for each product. Results are used for selecting optimum for material and technology in packaging of food and drinks products by multi-layer lamination in flexible approach.

Key words: packaging material, adhesives, migration limit, aromatic amines, food products

The most important materials and articles intended to come into contact with food use in their composition raw materials as polypropylene, polyethylene, and adhesives made from polyurethane and printing inks for creating designs [10].

The materials used to package food should be safe from different points of view. Food is not allowed to be in contact with external contaminant like bacteria, viruses, other microorganisms, dirt, so the microstructure of the package materials must not allow this dangers to pass through and contaminate food [12].

Polypropylene has a reticulated crystalline structure that is a proper gas barrier and also a good contaminants barrier. So, the polymers of polypropylene are widely used in food packaging, conferring a good protection [1]. But some migrants could pierce the macromolecular structure of polymers and could contaminate the food stuff. Such migrants could be mainly the components of printing inks and of polyurethane adhesives.

Polyurethane adhesives are a mixture of two polymers that reacts at temperatures around 30 to 50 degrees Celsius one is a polyalcohol and the other contains isocyanate functions. These two components suffer a polymerization process, and it strengthens. So, this adhesive is used to bond the printed polymer to metalized polymer and result an alimentary package.

The components of adhesives are isocyanates that in contact with humidity from food, reacts and forms aromatic amines [9, 11].

Aromatic amines that result from moisture reactions are 2,4 -, and 2,6-, di- amine toluene [TDA], 2,2 -, 2,4 -, 2,6 – di- amine di- phenyl methane [8].

For the determination of these aromatic amines it was used a liquid chromatography method. Aromatic amines can be noticed visually when their concentration reaches high level, and that happening in the first three days after the package was produced because the lamination adhesive does not react completely and the colorimetric reaction is strong, a purple color arises, during the period between 4-14 days after reaction the aromatic amines can be determined only with spectrophotometer because the human eyes cannot detect the color changing [6].

Therefore there is a global migration and a specific migration value for the migrants of package components in food stuff.

For global migration is fixed a limit expressed in mg of components / kg of food simulant.

Maximum global limit is = 60mg/kg

Global limit is applicable only for the materials that do not have any specific migration limit.

Specific migration limit is expressed as a concentration in food or food simulants.

This limit is applicable to a group of compounds when the compounds are related by structure and toxicologically, especially isomers and compounds from the same functional group [6].

Maximum specific limit is= 0.01mg/kg

This study relates to a flexible packaging and specifically, to a laminate, the use of laminate in the packaging of food and drinks and methods of packaging articles.

It is known that for package food in wraps, and bags, are used laminates. Preferred materials for food packaging often consist of a first substrate, such as a film, which is generally thin and transparent (about 30 microns), and can be printable, and a second substrate which can be another type of material often is thinner film about 20 microns, a metal foil, a metallised film or a transparent film [1, 7].

There are general requirements imposed to materials and items, including active and intelligent materials and items, shall be manufactured in compliance with good manufacturing practice so that, under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could endanger human health or bring about an unacceptable change in the composition of the food or a deterioration in the organoleptic characteristics [6, 8].

Specifically, the use of reactive polyurethane adhesives has in some cases been found to lead to contamination of the packaged food with un-reacted isocyanates and carcinogenic aromatic amines, formed by the reaction of adhesives components with moisture from the food [6, 9].

Thus, food packaging materials may release migration compounds which result from the adhesives used in manufacturing such materials [4].

Coating weights of the adhesive used in lamination will be not higher than 1.5- 5 g/ m^2.

The method suitable for food contact packaging is the

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non contact coating with food because of the very reactive components. Thus, the film material will be a polyolefin such as LDPE (low density polyethylene), PE (polyethylene) or PP (polypropylene)[2], or such as a PET (polyethylene terephtalate), the second substrate will often be another, often thicker polyolefin such as metallised PP or PET can be used. The films used in test are usually heat sealable [3, 5].

Experimental part

Materials and method

Description of method and materials

The method uses the migration analysis of aromatic amines MDA di- amine di- phenyl methane and TDA di-amine toluene, arised only in the presence of free, un-reacted isocyanates (NCO) compounds and moisture from the food packages.

The un-reacted NCO migrate (or are carried) into the pouch where they react to form the aromatic amine.

In the following experiment were used three types of adhesives and three different types of substrates. There were made determinations for 3x3 = 9 combinations between adhesives and films.

The films in contact with food were:

-First substrate: Bio oriented polypropylene, thickness 20 microns, density of the film 900 kg/m^3. This is a film with normal sealing properties, and high coefficient of friction, good gas barrier.

-Second substrate: Bio oriented polypropylene (11 microns), co-extruded with a layer of 9 microns of PET, density of the film 910 kg/m^3. This is a film with high sealing qualities, normal coefficient of friction, and good gas barrier.

Table 1
THE ADHESIVES USED

	Film 1	Film 2	Film 3
Adhesive 1	A1F1	A1F2	A1F3
Adhesive 2	A2F1	A2F2	A2F3
Adhesive 3	A3F1	A3F2	A3F3

-Third substrate: Pearled Bi axially polypropylene 28 microns, density of the film 670 kg/m^3 this is a film with low oxygen barrier, but very strong sealing properties, low coefficient of friction.

The systems of adhesives used are (table 1):

-Adhesive 1: Liofol UR 7733- 22 + Hardener UR 6029 - 21, system viscosity = 3000 MPa*s, mixing ratio 100-70, coating weight maxim 2.8 g/m^2.

-Adhesive 2: Liofol UR 7735 + Hardener UR 6088, system viscosity = 3500 MPa*s, mixing ratio 100-40, coating weight maxim 2.8 g/m^2.

-Adhesive 3: Texacote SF 301 + Hardener Texacote CR 300, system viscosity = 3800 MPa*s, mixing ratio 100-40, coating weight maxim 2.8 g/m^2.

Sampling and Extraction

After the lamination were obtained 9 types of pouches, combining adhesives with films, indexed according to table 1.

The codes of the samples were given after this table combination.

From each reel of laminated film, first were removed 5-6 „unwinds" before cutting a sample to make up the pouches. This was in order to eliminate the accelerated curing effect due to the presence of moisture around the outside of the reel.

After that next operation was the cutting of the sample from the middle of the rewound reel to eliminate the effect of moisture ingress from the sides.

The next operation was to make up a pouch (14.14 cm x 14.14 cm = 200 cm^2 or 10 x 20 = 200 cm^2) and fill it with 100 mL test simulant (usually 3% acetic acid). 3-4 pouches are required for each laminate (1 blank + 2-3 aromatic amine determinations).

Then, it was stored at elevated temp to allow the free isocyanate to react with the test stimulant, in conditions that the entire surface of the pouch must be covered by the test simulant. The product was maintained at 70°C for 60 min and the contents of the pouch was transferred into a 125 mL glass bottle.

Derivatization

The base chemical reaction is:

Aromatic amine diazonium salt

$$R\text{-}NH_2 + 2HCl + NaNO_2 \rightarrow R\text{-}N_2^+Cl^- + NaCl + 2H_2O$$

With the next equivalence:

12.5 mL 1.0 mol HCL + 2.5 mL Sodium Nitrite

But not in the Blank

The operational steps are:

- Waiting 10 min, to allow all $-NH_2$ to react
- Adding 5 mL Ammonium Sulphamate
- Ammonium Sulphamate destroys unreacted $NaNO_2$. $NaNO_2$ affects the extinction.
- Waiting 10 min, for $NaNO_2$ to be eliminated.
- Adding 5 mL Coupling Reagent and mix thoroughly.
- N-(Napthyl)-ethylenediamine-dihydrochloride is the coupling agent. In the presence of aromatic amines a purple colour arises.
- Waiting 2 h, to allow colour to develop
- Measuring the extinction and the content of aromatic amines, expressed as μg aniline-hydrochloride ($C_6H_5NH_2$.HCl) per 100 mL test simulant, is calculated in relation to a reference curve made up with standard concentrations.

Determining of concentration supposes the use of UV spectrophotometer type Cary 50 features a unique design that uses a Xenon flash lamp as the source of UV-Vis radiation. This offers many advantages over traditional and diode array UV-Vis spectrophotometers, because the light is so intense, the Cary 50 is unaffected by room light. This allows to measure large samples with the lid off. It also means that shielding a fibre optic light probe is unnecessary.

Results and discussions

The results from UV spectrophotometer were obtained as concentration analysis report.

All these results correspond to analysis at four days after the laminating process.

The result is considered as corresponding to the migration limits if it will not release primary aromatic amines (expressed as aniline), in a detectable quantity (DL=0.01 mg/kg or 0.01 mg/L of food stimulant, analytical tolerance included). All the results are presented in table 1 and will be analyzed in section conclusions.

The risk of migration of aromatic amines in food by laminating adhesive plastic material is very important. For adhesives that rely on isocyanates aromatic and apply layers, adhesives reaction with moisture in food producing unwanted primary aromatic amines such as 2.4 - and 2.6 – di-amino toluene (TDA) and 2.2 - 2.4- and 2.6 – di phenyl methane (MDA).

Sample	Sample description	Concentration, F [mg/kg]	Readings
A1F1	A1(Liofol 7733 -22/6029-21) F1(Bio oriented polypropylene)	0.00385	0.0015
A1F2	A1(Liofol 7733 -22/6029-21) F2 (Bio oriented polypropylene 11 microns + 9 microns of PET)	0.00375	0.0013
A1F3	A1(Liofol 7733 -22/6029-21) F3 (Pearled Bi axially polypropylene)	0.00534	0.0048
A2F1	A2(1 Liofol 7735/6088) F1(Bio oriented polypropylene)	0.00409	0.0020
A2F2	A2(1 Liofol 7735/6088) F2 (Bio oriented polypropylene 11 microns + 9 microns of PET)	0.00298	0.0004
A2F3	A2(1 Liofol 7735/6088) F3 (Pearled Bi axially polypropylene)	0.00454	0.0030
A3F1	A3(Texacote SF 301/ CR 300) F1(Bio oriented polypropylene)	0.00553	0.0052
A3F2	A3(Texacote SF 301/ CR 300) F2 (Bio oriented polypropylene 11 microns + 9 microns of PET)	0.00484	0.0037
A3F3	A3(Texacote SF 301/ CR 300) F3 (Pearled Bi axially polypropylene)	0.00834	0.0114

Table 2
MEASUREMENTS, TYPE OF ADHESIVES AND FILMS

This is the reason we should evaluate lots of factors, as it was done in this experiment; we evaluated three different types of adhesives and three types of different films. Combining the raw materials were obtained 9 types of final products that were tested for the migration of aromatic amines (table 2). The test was made in same conditions for each product.

After the evaluation were obtained different results in conformity with the raw materials used. The conclusion is that the films with low density allows the migration more than the films with high density, even though the thickness is higher, it is the case of Pearled Bi axially polypropylene. The film made from a layer of PP and a layer of PET has the lowest transfer of isocyanates because the sudden changes of layers and the crystalline structure of PET. BOPP had a normal migration according to its structure.

The adhesives had also theirs specific influence on the results. We concluded that a very concentrated adhesive gives good bond strength but also the migration is higher, the case of Texacote SF 301/ CR 300. If you want a fast curing adhesive for the products that must enter in production faster you risk to exceed the migration limits.

Liofol 7735/6088 – is the perfect system for lamination, good curing time and bond strength, also the migration is acceptable comparing with the concentration of raw materials.

Liofol 7733 -22/6029-21 – has a lower curing time the reactivity is a lower one, but has a small migration, this system is recommended for laminations that do not require immediate use in production.

The most important fact is that the specific limit for the aromatic amines expressed as aniline chlorhidrate of 0.01 mg/kg, was not exceeded by any product, so it is safe to use the products in food industry 4 days after lamination.

Conclusions

It is well known that packaged food in wraps, pouches, use laminates and preferred materials for food packaging often consist of a first substrate, such as a film, which is generally thin and transparent, and can be printable, and a second substrate which can be another, often is a thinner film about 20 microns, a metal foil, a metallised film or a transparent film.

In the past, such film to film and film to foil laminations were often produced using volatile organic solvent based laminating adhesives, but environmental and regulatory restrictions from the last years imposed to the industry to use water based adhesives and specially polyurethane dispersions and acrylic emulsions.

Film to film laminates using solvent free reacting laminating adhesives, even including two component polyurethane laminating adhesives, may lead to problems specifically in food. In some cases, solvent free reactive laminating adhesives may retain relatively high levels of monomer, unless they are very carefully cured. Such careful curing requires time and energy expenditure. Whereas in many applications of laminated materials, such monomer contamination does not present a problem, this is not true in the food industry, since the monomers may migrate into the food which is not acceptable.

Specifically, the use of reactive polyurethane adhesives has in some cases been found to lead to contamination of the packaged food with un-reacted isocyanates and carcinogenic aromatic amines, formed by the reaction of adhesives components with moisture from the food.

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