OPTIMIZATION OF LAMINATION PROCES.THE PENETRATION OF FOOD PACKAGINGS BY THE LAMINATION ADEZIVES COMPONENTS

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REZUMAT: Lucrarea prezintă o metodă pentru studiul comportamentului materialului de ambalare în contact cu produsele alimentare, folosind diferite tipuri de adezivi si de folii pentru ambalaje. Metoda se bazează pe determinarea primara a aminelor aromatice cu ajutorul analizei spectrofotometrice.

Cuvinte cheie: ambalaje, adezivi, spectrofotometru

ABSTRACT: The paper presents one method for study the behaviour of packaging material in contact with food products, using different type of adhesives and different type of films for the package. The method is based on primary aromatic amine determination using spectrophotometer analyze.

Keywords: packaging, adhesives, spectrophotometer

1. LEGISLATION, STANDARDS

This study is in conformity with the UE regulation no. 10 from 14 January 2011 of the European Committee for the materials and articles intended to come into contact with food.

The European Committee, regarding the treaty for the functioning of European Union, and considering the regulation (CE) no. 1935/2004 of European Parliament and of Council from 27 October 2004 regarding materials and objects intended to come in contact with alimentary products, and after the consulting of European Authority for the Food Safety, took the decision to pass this regulation no.10/2011.

Regulation (CE) no. 1935/2004 establishes the general principles for the elimination of differences between the legislations of UE states, regarding objects and materials intended to enter in direct contact with food and presents a detailed procedure of authorization for this objects and materials.

This regulation repeals the Directive 2002/72/CE regarding objects and materials intended to enter in direct contact with food. Directive 2002/72/CE was repealed because it regards only to the materials and objects made from plastics and to the plastic fittings.

And due to the newest technologies appeared *multilayer multi material*, fact that involves the extension of scope for the Directive 2002/72/CE [UE Directive 2002]

Regulation no. 10/2011, establishes new values for the global migration, and for the specific migration of package components in food stuff. For global migration we have a limit that is expressed in mg of components / kg of food simulant,

Maximum global limit is = 60mg/kg

Global limit is applicable only for the materials that don't 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 toxicological, especially isomers and compounds from the same functional group.

Maximum specific limit is= 0,01mg/kg[UE Directive 2011].

2. ACTUAL STAGE

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

It is known to package food in wraps, pouches, it is 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, often is thinner film about 20 microns, an metal foil, a metallised film or a transparent film[Andrew J. 1979]. Polyurethane dispersions are specially suited for indirect food contact.

Recently, the laminating industry has begun to investigate into solvent free two components reactive adhesives. Although some of these are not hot melt adhesives.

Also the food industry has begun to use similar laminates, as food packaging materials. Such laminates are produces using reactive, generally polyurethane based laminating adhesives [Koji 1996].

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.

There are general requirements impose: "materials and articles, including active and intelligent materials and articles, 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 bring about a deterioration in the organoleptic characteristics therefore"[Mamoru 1984].

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.

Thus, food packaging materials may release migration compounds which results from the adhesives used in manufacturing such materials.

Coating weights of the adhesive used in lamination will not pass the interval 1,5- 5 g/ m^2[Nidal 1998].

The method suitable for food contact packaging is non contact coating with food because of very reactive components. Thus, the film material will be a polyolefin such as LDPE, PE or PP, or such as a PET, 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 [Tsutomu 1979]

3. METHOD

Description of method and materials

The method uses the migration analysis of aromatic amines (e.g. MDA and TDA) arise only in the presence of *free*, *un-reacted* NCO and moisture from the food packages.

The un-reacted NCO migrates (or is carried) into the pouch where it reacts to form the aromatic amine[Andrew F. 1994]

In the following experiment we will use three types of adhesives and three different types of substrates. I will make determinations for 3x 3 = 9 of combinations between adhesives and films.

The films that will be in contact with food are:

First substrate: Bio oriented polypropylene, thickness of 20 microns, density of the film 0,900 g/cm^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 0,910 g/cm^3. This is a film with high sealing qualities, normal coefficient of friction, and good gas barrier.

Third substrate: Pearled Bi axially polypropylene 28 microns, density of the film 0,670 g/cm^3 this is a film with low oxygen barrier, but very strong sealing properties, low coefficient of friction.

The systems of adhesives used are:

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 we obtained 9 types of pouches, combining adhesives with films after the table 1.

Table 1. *Combinations between films and adhesives.*

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

We will name the samples after this table combination.

From each reel of laminated film, first time remove of 5-6 „unwinds" before cutting a sample to make up the pouches. This is to eliminate the accelerated curing effect due to the presence of

moisture around the outside of the reel [T. Wellner 2008]

After that next operation will be 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 is to make up a pouch (14,14 cm x 14,14 cm = 200 cm² or 10 x 20 = 200 cm²) 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).

The next operation is to make up a pouch (14,14 cm x 14,14 cm = 200 cm² or 10 x 20 = 200 cm²) 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).

- Store at elevated temp to allow the free isocyanate to react with the test simulant.
- The entire surface of the pouch must be covered by the test simulant.
- Maintaining at 70°C for 60 min
- Transfer the contents of the pouch into a 125 ml glass bottle[Harry 1992].

Derivitisation

The base chemical reaction is:

$$\underset{\text{aromatic amine}}{R{-}NH_2} + 2\,HCL + NaNO_2 \longrightarrow \underset{\text{diazonium salt}}{R{-}N_2^+\ Cl^-} + NaCl + 2\,H_2O$$

With the next equivalence:

12,5 ml 1,0 mol HCL + 2,5 ml Sodium Nitrite

But not in the Blank

- 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 hours, 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 application 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. Another advantage of the Xenon lamp based is, because the light is so intense, the Cary 50 is unaffected by room light. This allows permit to measure large samples with the lid off. It also means that shielding a fibre optic light probe is unnecessary[H.M.Pinheiro 2004]

3. RESULTS AND DISCUTIONS

Concentration Analysis Report

```
Report time                    12.04.2011 15:49:51
Method                         C:\Varian\Cary Winuv\curbe de
                               etalonare\3 adhezives 3 films.MCN
Batch name                     C:\Varian\Cary Winuv\curbe de etalonare\
                               3 adhezives 3 films ziua 4.BCN
Application                    Concentration 3.00(303)
Operator                       eng. Damacus Gabriel

Instrument Settings
Instrument                     Cary 50
Instrument version no.         3,00
Wavelength (nm)                550,0
Ordinate Mode                  Abs
Ave Time (sec)                 0,1000
Replicates                     1
Standard/Sample averaging      OFF
Method Weight                  1,0000
Weight units                   mg
Method Volume                  1,000
Volume units                   l
Factor =                       = (Method Wt * Sample Vol)/(Sample Wt * Method Vol)
Fit type                       Linear
Min R2                         0,95000
Concentration units            mg/l

Comments: The testing was executed 4 days after the lamination process.

Zero Report

     Read             Abs             nm
_____________________________________________
     Zero              (0,1011)          550,0
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Calibration
Collection time                28.10.2008 14:32:00

      Standard       Concentration     Readings
                         mg/l
_________________________ ____________________
Std 1                      0,00125       0,0007
Std 2                      0,00250       0,0034
Std 3                      0,00375       0,0062
Std 4                      0,00500       0,0090
Std 5                      0,01000       0,0201
Std 6                      0,01500       0,0312
Std 7                      0,02000       0,0423
Std 8                      0,02500       0,0534
Std 9                      0,03000       0,0645
Std 10                     0,04000       0,0867

Calibration eqn                Abs = 2,21989*Conc -0,00206
Correlation Coefficient        0,95052
Calibration time               28.10.2008 12:53:05

Analysis

       Sample      Concentration    Weight   Volume  Factor     Readings
                    mg/l (mg/kg)       mg       l
_____________________ ____________________________________________________
      A1F1 /1        0,00385       1,0000    1,000  1,0000      0,0065
      A1F2 /2        0,00375       1,0000    1,000  1,0000      0,0063
      A1F3 /3        0,00534       1,0000    1,000  1,0000      0,0098
      A2F1 /4        0,00409       1,0000    1,000  1,0000      0,0070
      A2F2 /5        0,00298       1,0000    1,000  1,0000      0,0054
      A2F3 /6        0,00454       1,0000    1,000  1,0000      0,0080
      A3F1 /7        0,00553       1,0000    1,000  1,0000      0,0102
      A3F2 /8        0,00484       1,0000    1,000  1,0000      0,0087
      A3F3 /9        0,00834       1,0000    1,000  1,0000      0,0164

Results Flags Legend
U = Un-calibrated               O = Overage
N = Not used in calibration    R = Repeat reading


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```

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

The result is considered as corresponding to the migration limit according to UE regulation no. 10 from 14 January 2011 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 noted in table 2 and will be analyzed in section 5, conclusions.

Table 2 – *Measurements, type of adhesives and films*

Sample	Sample description	Concentration, F[mg/kg]	Readings
A1F1	A1(Liofol 7733 -22/6029-21) F1(Bio oriented polypropylene)	0,00385	0,0065
A1F2	A1(Liofol 7733 -22/6029-21) F2 (Bio oriented polypropylene 11 microns + 9 microns of PET)	0,00375	0,0063
A1F3	A1(Liofol 7733 -22/6029-21) F3 (Pearled Bi axially polypropylene)	0,00534	0,0098
A2F1	A2(l Liofol 7735/6088) F1(Bio oriented polypropylene)	0,00409	0,0070
A2F2	A2(l Liofol 7735/6088) F2 (Bio oriented polypropylene 11 microns + 9 microns of PET)	0,00298	0,0054
A2F3	A2(l Liofol 7735/6088) F3 (Pearled Bi axially polypropylene)	0,00454	0,0080
A3F1	A3(Texacote SF 301/ CR 300F1(Bio oriented polypropylene)	0,00553	0,0102
A3F2	A3(Texacote SF 301/ CR 300) F2 (Bio oriented polypropylene 11 microns + 9 microns of PET)	0,00484	0,0087
A3F3	A3(Texacote SF 301/ CR 300) F3 (Pearled Bi axially polypropylene)	0,00834	0,0164

5. 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-amino-di-fennel-methane (MDA) and can be carcinogenic or cancer causing.

That's why we should evaluate lots of factors, like I did in this experiment; I evaluated three different types of adhesives and three types of different films. Combining the raw materials I obtained 9 types of final products that were tested for the migration of aromatic amines. The test was made in same conditions for each product.

After the evaluation I obtained different results in conformity with the raw materials used. So, we can conclude 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 change of layers and the crystalline structure of PET. BOPP had a normal migration after its structure.

The adhesives had also theirs specific influence on the results, I 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 overage the migrations limit.

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 don't requires 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 after 4 days after lamination.

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