MIGRESIVES

HORIZONTAL ACTIVITIES INVOLVING SMES

COLL-CT-2006-030309

MIGRESIVES

RESEARCH PROGRAMME ON MIGRATION FROM ADHESIVES IN FOOD PACKAGING MATERIALS IN SUPPORT OF EUROPEAN LEGISLATION AND STANDARDISATION

Collective Research Programme

Final Executive Summary

Period covered: from 1.2.2009 to 30.4.2010 **Date of preparation**: 14.10.2010

Start date of project: 1.2.2007 **Duration**: 39 Month

Project coordinator name: Dr. Roland Franz/Dr. Angela Störmer

Project coordinator organisation: Fraunhofer IVV, Giggenhauser Str. 35, D-85354 Freising

Project coordinator contact: Dr. Angela Störmer, angela.stoermer@ivv.fraunhofer.de

Report prepared by: Dr. Angela Störmer **Revision** 2.0

Project Consortium:
Research Institutes: Fraunhofer IVV, DE; INRA, FR; FABES, DE; Universidad de Zaragoza, ES, CTCPA, FR; ITECH, FR; Université de Bourgogne, FR;
Industry Associations: FEICA Association of European Adhesive Manufacturers, BE, Industrieverband Klebstoffe, DE, Asociación Espanola de Fabricantes de Colas y Adhesivos, ES, Association Club "Materiaux pour Contact Alimentaire et Santé" filiere papier/carton, FR; Industrievereinigung Kunststoffverpackungen, DE; Groupement pour la codification des mesures des bouchons de liege, FR; Association Française des Industries de Colles, Adhesifs et Mastics, FR.
SMEs: Eukalin Spezial Klebstoff Fabrik GmbH, DE; Gludan A/S., DK ; Türmerleim GmbH, DE, Samtack S.L., ES, Mitol, SI ; Belbo Sugheri, IT, Pietec Corticas SA, PT.

Project website: http://www.migresives.eu

Publishable executive summary

Between February 2007 and April 2010 the MIGRESIVES project (COLL-CT-2006-030309) was carried out by 21 project partners including seven research institutes, seven industry associations and seven small and medium sized enterprises (SMEs). It was the intention of the project to develop a pragmatic, science based test concept to ensure the safety-in-use of adhesives used in food contact materials. Most food packages and food contact materials are manufactured using adhesives. The EU regulates all food contact materials as migration of their constituents into food should not contaminate the food and not endanger consumer's health. In contrary to plastics, adhesives are not yet covered by a specific regulation which lays down how to implement this overall requirement. On the other hand the demands to document and verify the safety in use of food contact materials including the adhesive layers are increasing in all stages of the production chain up to the food industry. The project outcome may also form a basis for future specific EU legislation and provide industry, especially small and medium sized enterprises, a tool to ensure that migration from adhesives is in compliance with the regulatory requirements.

The concept is built on the following pillars: (i) classification of adhesives according to chemistry and uses, (ii) test strategies based on physico-chemical behaviour of adhesives, (iii) modelling migration/exposure from adhesives, (iv) providing guidelines to integrate the risk assessment approach into the daily life of companies and (v) extensive training and education especially to SMEs and large dissemination to achieve general recognition of the concept in Europe.

Adhesives formulations are often very complex and contain numerous single components. Multiple parameters influence the migration of adhesive compounds through a packaging material into food. These are, apart from the concentration of the compound in the adhesive layer, the adhesive type, the raw material polymer, the used additives in the formulation, the substrates and their barrier properties, the application of the adhesive, the end uses of the adhesive in the packaging and the packaging itself, especially the type of food to be packed and its filling and storage conditions. For the categorisation of adhesive types used in food contact application, adhesives have been classified according to their raw material polymer, the solvent system (solvent free, water based, solvent based) and the curing type (reactive, non-reactive). This way a classification matrix was built based on industry experience from adhesive as well as packaging producers and the most important applications for these adhesive types had been collected. Based on this classification, 23 representative test systems had been defined and selected by the consortium. They can be considered to be typical for adhesives formulations, materials and structures used for food contact materials and include different application and handling conditions, like type of food, type of contact, temperature and storage conditions. The test systems included acrylics, ethylene vinylacetate and vinylacetate ethylene copolymers, polyvinylacetate, natural rubber, synthetic rubber, polyolefins, polyvinylalcohol, polyurethanes and starch. Substrates had been polyolefins, plasticized PVC, paper and board. Furthermore a range of cork stopper applications with polyurethane adhesives were investigated in the project.

Several analytical methods have been developed, by HS-SPME-GC-MS for the screening of volatile compounds present in the adhesives and by GC-FID and GC-MS for determining its concentration in the adhesive and in the migration solutions. For non-volatile compounds LC was used. For determining the non-volatile compounds UPLC-MS(Q-TOF) was used, this technology allows determining the accurate mass of the compounds detected and its fragments, which provides a list of possible candidates. For the screening of unknown compositions, a HPLC method with a charged aerosol detector (CAD) was used which allows detecting also substances without chromophores or UV absorbing structures. For the method development a set of more than 50 adhesive related substances was used and calibration curves were established for each of the substances by GC-FID and HPLC-CAD exploring the applicability and the boundaries of the methods.

Applying these methods the adhesives and the finished applications have been screened on their composition including non-intentionally added substances. Using the test systems systematic migration and partitioning studies were performed in order to derive parameters for the prediction of migration. Additional experiments to derive partition coefficients were carried out by fortification of adhesives as well as of paper samples. Furthermore using fluorescence recovery after photobleaching (FRAP) technique, intrinsic diffusion coefficients of fluorescent test substances were determined directly in the adhesive layers.

The data from migration kinetic and concentration profile experiments were evaluated by mathematical modelling using Migratest Exp software. From the experiments more than 1200 migration and diffusion and partition coefficients have been derived at different temperatures in a range of 20 to 70 °C and in different material s by fitting the modelled curve to the experimental data. Partition and diffusion coefficients are the main parameters for the prediction of migration via mathematical modelling. From these data a general estimation of the diffusion coefficients in acrylic, vinylic and rubber adhesives as well as in plastics, paper and board could be derived. Partition coefficients were obtained for 39 substances in 224 conditions. These can be directly used for the migration prediction. For additional substances, reference partition coefficients were proposed for the groups of polar, medium polar and non-polar substances.

For validation purposes and in order to check and broaden the applicability of the modelling approach to additional adhesive formulations from the types under investigation, 45 glued packaging samples from the market had been analysed on their composition and subjected to migration testing on Tenax® (MPPO) at the condition 10 days / 40 °C for all laminates with measurable amounts of migrants. These data were used for comparison with modelling results.. Twenty nine different adhesives were used in the manufacture of the laminates: 9 polyurethanes (PU), 6 acrylics (AC), 2 hotmelts (HM), 1 starch, 5 based on vinyl acetate ethylene (VAE), 4 based on polyvinyl acetate (PVAc), 1 based on polyvinyl alcohol (PVOH) and 1 mixture of vinylic adhesive and starch. The substrates used were cardboard, coated cardboard, corrugated paper, polypropylene, polyethylene, polyamide, polyethylene terephthalate, metallized PET, aluminum and ethylene vinyl alcohol copolymer. Migration from these laminates has been modelled using the reference diffusion parameters and the reference partitioning coefficients as well as the experimentally determined concentrations in the material. The calculated values have been compared then to the experimentally derived ones. In the two rubber samples higher migration was found onto Tenax than possible from the measured concentration in the material. These were excluded from evaluation. Overall 142 data were included into the statistical evaluation: 38 VAE, 42 PVA, 4 PVOH, 9 acrylics, 41 hotmelt and 8 polyurethanes. Most of the calculated data met or overestimated the measured values. The ratio between modeled values and measured migration onto Tenax (10 days / 40 °C) was in 92 % of all cases higher t han one. Taking the analytical tolerance of the measurements into account from migration and initial content determination as well as layer thickness data, the ratios 0.8 to 1.2 can be considered as that range in which modeling reflects directly the measurement. Twelve modelings (8 %) were in this range, 1 VAE, 7 PVA, 1 PVOH, 1 acrylic, 2 hotmelts, 1 polyurethane. Seven values were below 0.8 (5 %), 4 VAE, 1 acrylic and 2 hotmelt. This means that 95 % of all simulations met or overestimated the measured migration, 87 % had a ratio higher than 1.2 between modeled and measured value. These results from the market samples show that the modeling approach including extrapolation to other substances gives reliable results.

The food regulatory evaluation is based on the amount of migration into food. The migration value can be derived by theoretical considerations, analytical measurements or a combination of both. These tools are embedded into a testing concept and a decision tree. The decision tree shall help to find a suitable testing procedure for the specific application. As theoretical calculations are in general less time and working effort consuming than analytical tests, the decision tree was construed such that it checks the possibilities for such estimates and the necessary input data. Experimental migration tests are always an alternative which can be chosen at each level of the decision tree.

A freeware multilayer modelling software was developed further within the project. The link to download this 'Safe Food Packaging Portal version 3' (SFPP3) is available on the MIGRESIVES website (www.migresives.eu). The use of the tools and the application of the decision tree are described and explained in a guideline document.

The feasibility of a complementary approach using the bioassays developed within the 'Biosafepaper' EU project (QLK1-CT-2001-00930) was investigated. Six laminates (PVOH, PVAC, four Acrylics) and the corresponding paper and adhesives were tested using the following toxicity endpoints: cytotoxicity (RNA synthesis inhibition assay), genotoxicity (comet assay) on HepG2 human cell line and mutagenicity on bacteria (Ames test). Feasibility of the bioassays applied to adhesives extracts was successful in regards to realistic exposure and risk assessment. Laminates extracts were neither genotoxic, nor mutagenic. Some were cytotoxic in the test. The observed cytotoxic effect was never due to the adhesive alone, in one case it could be assigned to the paper, in others only the laminate showed the cytotoxic effect which could not be explained by the analytical data.

Training lessons have been worked out in order improve understanding and awareness of the food regulatory requirements, diffusion and migration processes, use of the Migresives tools and the software. The trainings have been run successfully in Germany, France and Spain. Additionally experts from further European countries have been trained to enable them to give trainings in their countries. The lessons are made available for future use.

More information: www.migresives.eu

Contact: Dr. Angela Stoermer
Fraunhofer Institut Verfahrenstechnik und Verpackung
angela.stoermer@ivv.fraunhofer.de