Summary for the final report

Systematic methodology for damage analysis of composite food packaging in the event of chemically induced delamination (Delamination of food packaging laminates)

Composite food packaging has great advantages over glass, metal or plastic materials due to its light weight, its better stackability and a smaller ecologic footprint. Furthermore, properties of composite packaging can be adapted by combining different polymers, laminating adhesives, cardboard and aluminium foil.

Not only storage and transportability are important, but also protection against ambient influences, which can be of physical or chemical nature. So, the composite food packaging must resist heat, coldness, light, shock or pressure to ensure the intactness of the barrier to the surrounding. Even more important is protection of the food against ambient chemical influences such as oxygen, water, pollutants, etc. The packaging must therefore be an intact and resistant barrier to the abovementioned impacts during transport and whole shelf life.
Damage to the packaging, possibly even to the point of complete failure, can occur not only as a result of external influences, but also as a result of certain ingredients of the packaged food itself.

The most probable damage of composite food packaging is delamination of the different composite layers. Delamination leads to a loss of function with respect to mechanical and barrier properties which might finally enable the access of oxygen, water, chemical pollutants, and bacteria or fungi.

However, not only external influences might have a negative influence of consumer's health but also internal processes. In the case of composites containing aluminium, there is a possibility of release of Al (III) compounds and a subsequent uptake into the food. Certain food ingredients may induce and enhance the formation of Al^{3+}, amongst them acids as acetic acid. The effect of aluminium on human health is still discussed and not finally understood. There are a lot of indications that aluminium is neurotoxic and may induce neurodegenerative diseases such as Alzheimer or Parkinson. Even though aluminium is taken up from (plant) food the uptake may increase by contact of food to aluminium. The precautionary principle has to be applied and the ingestion of aluminium must be as low as possible. The EFSA has set the limit of uptake at 1 mg per kg of body mass and week.

Since the broad use of composite food packaging, damages and their reasons have been under scrutiny. Focus has been on the kind, composition and arrangement of the materials, the kind of food and their aggressive components, and the mechanism of damage.
Delamination of composite beverage containers was among others observed for fruit juices, e. g. orange juice. Aroma volatiles are often among the problematic ingredients, in the case of orange juice, e. g. limonene, myrcene, and α-pinene.

The prerequisite for later damage is the migration in and the permeation through one or more of the polymeric composite layers. This causality is true for all aggressive food components. Permeation of aroma volatiles allows infiltration of laminating adhe¬sives thus reducing their adhesive strength often dramatically and leading to delamination. Such process is also found for other food ingredients such as fats and oils, especially if fatty acids are hydrolytically split off and migrate. Beyond aromas and fatty substances, other substances might migrate, e. g. acetic acid.

Even though a lot of research has already been made in this field in the last decades it still resembles a big puzzle of useful results. Therefore, we aimed in developing a systematic methodology for damage analysis of composite food packaging in the event of chemically induced delamination. Our approach included the following packages:

- Choice of foodstuffs with exemplarily problematic ingredients such as aromas, fats/ oils, or acetic acid
- Choice of food simulants for the a. m. foodstuffs
- Choice of different exemplary composite packaging such as different bags or beverage cartons
- Exposition of the a. m. different kinds of packaging with the a. m. different kinds of foodstuff and food simulants at different temperatures for a different range of time
- Characterisation of the packaging samples with peel tests
- Characterisation of migration and permeation for polymeric layers
- Characterisation of corrosion products
- Control of the integrity of polymeric cover layers on aluminium layers with respect to the formation of pores, cracks and other failures of the polymeric barrier
- Simulation of the migration process using mathematical models

In cooperation with the project-accompanying committee of industrial partners (PAC), problematic foodstuffs were selec¬ted which experience has shown to be damaging, e. g. by dela¬mi-nation. Systematic studies on damage were carried out with these foods - gherkin water, sun-flower oil, cloves, dressing and whipped cream - and their simulants - acetic acid, iso-octane, oleic acid, NaCl and eugenol. Composites matched with PAC were exposed to the influence of food at 5, 23 and 40 °C for 1, 2 and 4 weeks, respectively, and then tested.

Before any experimental investigation started, the laminar composition of the packaging was subject to some theoretical considerations such as the possible kinds of damage and the sites which the damage could appear in. Independent of individual variants in laminar composition, most of the composition packaging consist of multiple layers of different polymers, a gas barrier layer of aluminium, and, as in the case of beverages, a stabilizing cardboard layer. These layers are mostly combined using laminating adhe¬sives. Migration and permeation of food components may appear through one or all layers and laminating adhe¬sives until they reach the aluminium barrier. The aluminium layer may be damaged by corrosion if an electrolyte (aqueous components of the food with dissolved ions such as Na+ or Cl-) can come into direct contact with the aluminium surface. Besides, aggressive migrants may attack the aluminium layer, too. Among such aggressive ingredients acetic acid may have such an impact.

Reflecting all a.m. facts, we concluded that the most probable site of damage is between layers which may lead to delamination. Swelling of the laminating adhesives is expected to contribute by a decline of adhesive force. However, the exact progress is hardly to predict. A corrosively attacked aluminium layer may also give rise to delamination with the neighbouring polymeric layers.

Considering the theoretic analysis, experimental work was focussed on

- determination of adhesive forces
- localisation of delamination and other destructive processes
- experimental determination of migration and permeation
- mathematical modelling and simulation of migration
- observation of damage patterns of beverage cartons and bags containing Al-layers
- characterisation of surfaces using electrochemical impedance spectroscopy
- chemical analysis of reaction products of aluminium

The results of all project partners show that damage to the composite is possible solely by migration of substances, in the case of the selected foods and simulants by acetic acid, eugenol and oleic acid/sunflower oil. The latter migrate by hydrophobic interaction of the alkyl chain with the polyolefins. In the case of eugenol, the hydrophobic character in combination with the aromatic conformation predominates. Despite its polarity, acetic acid can migrate by forming dimers while maintaining a small molecular size.

Experiments were carried out with commercially available composite film packaging and a model system, both produced by members of the PAC. It was shown that, depending on the foodstuff used, the structure of the composite and the type of polymers, laminating adhesives and adhesion promoters play a major role. In addition to the different reduction of the adhesion force up to delamination, the separation can also occur at different contact surfaces in the composite. Acetic acid has a high damage potential on all of them.

Migration as a prerequisite for possible damage was converted into a mathematical model based on FICK's 2nd law in order to be able to simulate the time-dependent mass transport.
Experiments with bags made of PE showed a very quick permeation of acetic acid through the polymer. It was measured with filled bags that were put in a beaker with water. The increase of conductivity and decrease in pH proofed the fast permeation of acetic acid.

Foodstuffs containing vinegar can attack aluminium in a composite to form aluminium diacetate and aluminium oxide, which leads to white deposits between the aluminium layer and the PE. The extend of the formation of the two corrosion products depends on temperature and exposure time, but surprisingly also on the concentration of NaCl.

By means of electrochemical impedance spectroscopy, it was demonstrated that the PE layer remains an intact barrier to water and dissolved substances, except acetic acid, because no pores are formed in the PE that would allow direct contact of the aluminium with the food. This is true for all foodstuffs and simulants investigated.

In the future, the results will allow a targeted selection of defined composites for the safe packaging of food with aggressive components. The biggest challenge will be the packaging of food containing vinegar and fats/ oils in combination with free fatty acids.

IVLV members can download the complete final project report in German from our homepage. All you need is to register in the section "My IVLV". Non-members can request the final report from the IVLV office at office@ivlv.org.

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