Adhesion to Foil – More than Just a One-Sided Story

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Abstract

Aluminium foil is widely accepted as being one of the best barrier materials in flexible packaging, even in the face of many new and up-and-coming high-barrier plastic layer combinations, copolymers, blends or nano-composites. Besides high thermal conductivity, which facilitates enhanced converting and sealing performance, other key criteria that distinguish "converter foil" from competing materials are its outstanding wettability and robust bonding to a wide range of lacquers, adhesives, films and coatings.

This presentation aims to provide a fundamental understanding of how adhesion to aluminium foil works from a foil maker's practical point of view.

Adhesion and adhesion failure in different aluminium-plastic laminates during converting and further packaging processing, as well as a result of interaction with packaged goods, are described using everyday cases.

The principles and rules for ensuring sufficient and robust adhesion are derived from these typical examples.

Introduction

Thin-gauge aluminium foil is used for billions of packages worldwide, ranging from aseptically filled board packs for juices, UHT milk and vegetable sauces, through paper/foil laminates for pharmaceutical or food tear-open flat pouches to lidding materials for packages filled with dry or wet food. Aluminium foil in these applications acts a very economical and effective barrier to any type of matter and light and, with its unrivalled properties such as thermal conductivity, frequently improves sealing by chilling molten thermoplastic seal seams faster or allowing inductive sealing.
In most of the aforementioned packaging systems, thermoplastic polyethylene or polypropylene are used as instantaneous adhesives between the laminated webs of paper and aluminium and as sealants to close and shape the packages by welding the seal seams. Robust adhesion between the aluminium foil layer and the polymers is an intrinsic part of package performance and has to withstand the whole process chain, including converting, packaging, transport and storage, until the packaged contents have been consumed. Despite this, however, the cost of the packaging system has to be much lower than the value of the filled goods.

Prerequisites for Converter Foil

As aluminium foil is produced by cold rolling a strip in series of rolling steps, a small amount of rolling oil remains on the foil surface. After the final rolling pass, which is effected with a double-layer of foil, this so-called “hard” foil is separated into the individual layers, then slit, cut and rewound to the customer’s required coil dimensions. This coil is subsequently annealed not only to allow the microstructure to recover and recrystallise but also to remove the rolling oil as far and as homogeneously as possible and to form a surface oxide layer which provides robust adhesion [1]. Annealing foil in a coil is an economic and cost-efficient way of removing the oil but, due to its typical geometry relating to coiling pressure distribution, permits the oil to leave the coil only via the ends. This leads to a concentration gradient during annealing and results in non-uniform wettability. The key quality factors for the safe and proper converting of thin-gauge foil have therefore to be closely controlled. Ultimately, the wettability profile across the web has to be as flat as possible and the sticking of adjacent surfaces have to be kept to a minimum to avoid wrinkles and/or web breaks.

The customers require two properties, which, in fact, are contradictory.
Firstly, the surface has to be passive enough to allow shipping and storage without any changes occurring and, secondly, has to be reactive or susceptible enough to form bonds with the coatings in question.
Delivering foil in the form of an annealed coil has the great advantage in that the surface does not interact markedly with its environment and can be safely transported, stored and subsequently converted [2].

Storing semi-finished laminates

In modern converting, it is common practice to produce semi-finished materials in large batches which are then printed or laminated with a reverse printed film.
Once uncoiled, the aluminium surface, however, can undergo changes if it is left uncovered. During storage, the surface can be hydroxylated in the presence of water and covered with omnipresent carboxylic acids also being bonded to the surface. In a relatively dry environment, such changes do not lead to a significant reduction in susceptibility and no adverse effect on adhesion [3].
Storage in a warm, humid environment can, however, reduce the number of reactive sites on the foil [3].
The coiling density in semi-finished laminate coils is usually less tight and homogeneous than in annealed foil so that interaction with the environment is more possible.

If the functional groups of a coating can compete and replace surface contaminants successfully, robust adhesion can be achieved.

Case studies of surface and adhesion changes in laminates

The first case deals with an aluminium/PE laminate which was stored at elevated temperature and in high humidity. The oxide on the aluminium foil has changed to form aluminium oxide/hydrate and hydroxide. Doubts about whether the surface is suitable for further converting are therefore justified.

An Al/extrusion lamination/paper laminate which was stored for a long time (10 weeks) displays poor ink adhesion; even appropriate corona treatment could not remedy this problem. According to IR-ATR, there are compounds which look like ester wax species (similar to lanoline) on the surface. These compounds were not present on the foil surface of the newly produced material, which was checked initially after extrusion lamination.
This newly manufactured product was pressed and heated in a stack of sheets, the paper lying adjacent to the foil. After 3 days, the same compounds as those on the changed material were detected on the foil surface. After investigating the printing performance in laboratory tests, storage time limits were worked out and recommendations regarding the choice of a different paper coating made.

Another finished laminate, comprising printing/aluminium/single layer extrusion coating PE, was also stored in a coil. After a defined period of time, the inner sealant coating exhibited a drop in adhesion in certain areas; this can be attributed to the printing pattern on the adjacent surface in the coil. This surface is printed in different shades of blue and other areas where there is no print. The printing image is presumably lacquered over. In the large areas with blue printing, adhesion is poor. As expected, the adhering interface of the PE coating shows significant oxidation but, in the areas of poor adhesion, a second carboxylic absorption is attributable to carboxylic ester species, e.g. plasticiser from the blue ink.

Adhesion between Al/PE in the flat pouch filled with mixed spices was unaffected by the aroma molecules contained in the spices but adversely impacted by oleic acid from fat, which is used to coat the spice powder/grains for better pourability, passing through the polyethylene layer to the interface.
The extrusion coating used in this particular case is unsuitable for the packaged product.

Examination of affected surfaces/interfaces using IR-ATR

Studying how polymeric coatings bond to the metal surface is not simple due to the buried interface. In cases of adhesion failure, however, the interfaces become readily accessible. To study better adhering interfaces, which can hardly be peeled apart, it is useful to dissolve the aluminium foil in dilute acid (e.g. HCl) and investigate the polymeric interface. IR-ATR is the method of choice because it is fast and simple. The information depth is about 2-4µm for polymers; aluminium reflects the beam so that the information received comes from the matter on the base metal (oxide + polymer residues) [4].

Looking at oxidised PE surfaces, peeled surfaces can lead to misinterpretation because the film can be significantly elongated and species close to the surface are “diluted”. Tie layers appear thinner than they are in reality. Some of the functional groups can remain on the foil surface.

The following results were obtained by peeling the laminate layers from the aluminium foil and examining the resulting surfaces using IR-ATR:
In most cases, adhesion failure occurred between the coating and the aluminium oxide. Usually only some hydrocarbon chains or residues and hardly any functional groups from the polyolefin remain on the oxide layer. Different polymers lead to characteristically different amounts of residue on the foil. Adhesion, however, does not automatically correlate with the amount of residue on the oxide layer [x,y].

Carbonyl index –not only an issue of PE oxidation

For laminates comprising aluminium foil/ extrusion coating processed under the same conditions, significantly different adhesion strength levels were found. The coatings display the same pattern of carbonyl groups on both the outer side and the inner interface to the aluminium foil. The coatings, however, show different levels of carbonyl absorbance, ranging from strong to almost no oxidation, but the coating with the lowest adhesion displays a moderate oxidation peak.

The LDPE granulate (MI4) and the coatings were subjected to a creep and retardation test with a commonly used rotational rheometer in cone-plate geometry at 190°C. The granulate shows the highest creep deformation and almost no elasticity in the retardation phase (shear stress = 0 Pa). The coating displaying good adhesion has similar creep deformation but shows significant elastic retardation. The coating exhibiting poor adhesion has a lower creep value and recovers elastically. This indicates a certain degree of crosslinking and/or stronger entanglement due to chain transfer branching in a more stringent extrusion processing.

Nevertheless, the reason for poor adhesion is not really clear but likely results from melt processing as well. Wax is generated in every extrusion coating process but not evaporated away completely. Presumably, there are oxidised waxy species present at the interface which lead to a functionalised surface but do not contribute to adhesion because of their too short chains.

Conclusions

The surface of aluminium foil is well protected in a coil until it is unwound and converted. Uncovered foil surfaces coming into contact with other materials, such as polymers, lacquers, inks or paper, can be changed by hydroxylation or organic plaques can form during storage. This can result in reduced processability or poor adhesion. These surface changes can be offset to a certain extent by surface activation or coatings which are capable of replacing surface plaques and forming their own bonds.
A laboratory press test can help to identify and evaluate the risk of surface contamination and find suitable solutions.
Using the Carbonyl Index as an indicator of good adhesion performance can sometimes be misleading because low molecular weight species enriched on the interface can impair robust adhesion.
Where the process chain allows it, the storage of semi-finished materials should be avoided so that the risk of surface change is minimised. Otherwise, processing steps such as priming have to be considered and put in place.

A. References

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