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Abstract

Transparent barrier films based on vacuum deposited aluminium oxide (AlO_x) layers are continuing to create large interest in the market with regards to their use as food and healthcare packaging materials. Nevertheless, their post-metalliser conversion to the final packaging material still presents challenges to current AlO_x producers and the wider converting industry. In this work, AlO_x coated PET films have been converted in long duration industrial-scale trials via topcoating, printing, lamination and finally pouch making. Throughout this process, each conversion step has been investigated for its effects on the barrier performance. It was found that the printing processes, especially, induce significant damage to the ceramic barrier layer. However, by the use of a protective topcoat prior to any conversion step, the barrier properties of the AlO_x coated film were preserved, or could even be significantly enhanced, depending on the topcoat material. Furthermore, for a barrier topcoat, remarkable stretch- and flex-durability properties were achieved in the final laminate.

Keywords	Aluminum oxide; transparent inorganic barrier layers; conversion; printing; lamination
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Corresponding Author's Institution	Manchester Metropolitan University
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The data that has been used is confidential

Dear Editors,

We would like to submit our paper entitled “Conversion of aluminium oxide coated films for food packaging applications – From a single layer material to the finished pouch”, which describes the impact of standard converting processes on the barrier properties of AlOx-based transparent packaging material. We can confirm that this paper isn’t under consideration with any other journal.

'Declarations of interest: none'

Dear Authors,

The manuscript is well written and has useful information. It can be accepted for publication is the journal after revisions are made.

Please see below:

1) line 47/48/147: PVdC (polyvinylidene chloride), EVOH, HFFS etc. should be written as polyvinylidene chloride (PVdC), please be consistent is formatting with the rest of the manuscript.

Response - corrected

2) Please define the acronym PET before first use.

Response - corrected

3) line 142: Rohm and Hass Italia Sri (Italy)... no need to be bold.

Response - corrected

Thanks

-Reviewer 2

- A well-presented summary of the effects on barrier performance of AlOx/PET films of the various film conversion properties, and then an investigation of the benefits induced by two 'protection layers'. The absence of any information on the nature of these protective layer coatings and the paucity of information on their deposition process means that it is difficult to put any 'why' on the performance improvements observed, but this report does serve to illustrate what can be achieved.
I would recommend a rewording in lines 265-270 which seems unclear in it logic - the manuscript makes reference to a critical thickness of the adhesive that depends on the thickness of barrier layer and therefore concludes that the barrier performance of the adhesive dominates that of the laminated polymer. It is not clear why a critical thickness that depends on the barrier material should be critical in dictating the relative importance of the adhesive and laminated polymer.

Response – text amended:

The thickness of the adhesive layer was between 2.5 and 3 µm (determined via light microscopy of microtome cross sections of the laminate). This means that the adhesive thickness is above the so-called critical thickness, which depends on the defect size distribution of the inorganic barrier layer and typically is less than 2.5 µm for the type of industrially produced barrier layers discussed here (Langowski, 2002). According to Langowski (Langowski, 2008), if the thickness of the polymer layer directly adjacent to the inorganic barrier layer is thicker than the critical thickness, then this layer along with the inorganic barrier layer is dictating the barrier performance of the system. For the work discussed here this means that in the final laminate, the barrier properties of the polyurethane adhesive (significantly better oxygen barrier properties compared to polypropylene) dominate over those of the material laminated on top (i.e. the CPP film), which is of importance for the above discussion on barrier enhancement due to adhesive lamination.

-Reviewer 3

- Well done investigation work. Very interesting from a practical point of view.

Conversion of aluminium oxide coated films for food packaging applications –

From a single layer material to the finished pouch

Carolin Struller [a, b], Peter Kelly [b], Nicholas Copeland [a]

Highlights

- Full industrial conversion including topcoating, printing, lamination and pouching
- Most conversion damage induced to ceramic AlO_x layer during printing process
- Successful industrial conversion of AlO_x PET via use of protective offline topcoat
- Outstanding flex and stretch durability when protective barrier topcoat is used

'Declarations of interest: none'


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Conversion of aluminium oxide coated films for food packaging applications – From a single layer material to a complete pouch

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Abstract

Transparent barrier films based on vacuum deposited aluminium oxide (AlO_x) layers are continuing to create large interest in the market with regards to their use as food and healthcare packaging materials. Nevertheless, their post-metalliser conversion to the final packaging material still presents challenges to current AlO_x producers and the wider converting industry. In this work, AlO_x coated polyethylene terephthalate (PET) films have been converted in long duration industrial-scale trials via topcoating, printing, lamination and finally pouch making. Throughout this process, each conversion step has been investigated for its effects on the barrier performance. It was found that the printing processes, especially, induce significant damage to the ceramic barrier layer. However, by the use of a protective topcoat prior to any conversion step, the barrier properties of the AlO_x coated film were preserved, or could even be significantly enhanced, depending on the topcoat material. Furthermore, for a barrier topcoat, remarkable stretch- and flex-durability properties were achieved in the final laminate.

Keywords: aluminium oxide; transparent inorganic barrier layers; conversion; printing; lamination

1 Introduction

Inorganic transparent barrier layers such as aluminium oxide (AlO_x) or silicon oxide (SiO_x) are still in demand for clear barrier packaging materials, with applications ranging from food stuffs, which have rather moderate barrier requirements, to electronic products such as displays, where ultra-high barrier levels are essential. A number of different techniques are available to deposit such inorganic layers including atomic layer deposition (ALD), plasma enhanced chemical vapour deposition (PECVD), sputtering and thermal evaporation processes (electron beam and boat evaporation) (Groner, George, McLean, & Carcia, 2006; Kelly, 1994; Schiller, Neumann, Morgner, & Schiller, 1994). Whilst sputtering and ALD are mainly of importance for high-end applications, PECVD and thermal evaporation techniques are the processes of interest with regards to the cost-sensitive food packaging market. Reactive evaporation using resistively heated boats represents an especially promising candidate with great market potential due to the relatively low associated capital investment, the use of inexpensive raw materials and the high process speeds that can be achieved, without disadvantageous effects to the barrier performance, in comparison to other deposition techniques.

The market for transparent oxide coated films has an estimated compound annual growth rate of around 7 to 8 %, compared to only 2 to 3 % for polyvinylidene chloride (PVdC) coated films and 4 to 6 % for ethylene vinyl alcohol (EVOH) copolymer co-extruded films (Platt, 2016); both of which are polymer based transparent barrier films that can potentially be replaced by oxide coated films. Nevertheless, the market volume for these oxide based barrier films is currently a lot smaller, compared to the polymer based options of PVdC and EVOH. To date, the clear barrier flexible packaging market for AlO_x and SiO_x transparent barrier films is still dominated by Japanese material producers, such as Toppan, Toray, DNP, Mitsubishi and others with well-known film grades such as GL Film, Barrialox, IB-Film or TECHBARRIER (DNP America, 2017; Mitsubishi Chemical, 2018; Toppan USA, 2016; Toray Advanced Film Co., 2018), although Camvac's Camclear (Camvac Limited, 2018) and Amcor's AmLite (formerly Ceramis) (Amcor Limited, 2018) have also become well-established products. The Japanese producers predominantly apply electron beam evaporation or PECVD techniques for the deposition of the barrier layers (Naegli & Lohwasser, 2001), which entail substantially higher production and investment costs and more technical complexity, including potential reliability issues, compared to reactive boat evaporation. Furthermore, their products are generally topcoated with a material that not only protects the inorganic AlO_x or SiO_x barrier layer through handling and conversion, but also significantly enhances its barrier performance. This, in addition to the retortability of many of these materials, makes them very high performance products, which comes at a certain cost level and prevents real volume growth for cost-sensitive volume market applications. The reactive boat evaporation process has been developed over the last few decades and is now well-established (Günther et al., 2009; Kelly, 1993, 1994; Schiller et al., 1994; Struller, Kelly, Copeland, & Liauw, 2012). Its vast economic potential for low cost AlO_x production leads to new players continuously pushing to enter the attractive transparent barrier market and trying to obtain market share from the more advanced Japanese players. However, unlike the Japanese products, most of these 'new' products do not have a protective topcoat and their conversion is challenging with inevitable barrier deterioration.

In order to obtain a fully viable commercial AlO_x product, the successful conversion of the coated film also has to be taken into account. AlO_x coated polymer films will always need to undergo further conversion steps in order to obtain the final packaging structure. These conversion steps will include all or most of the following downstream processes; slitting, coating, printing and lamination. Since each of these steps can potentially have a detrimental impact on barrier performance, it is essential that barrier loss upon conversion is avoided or at least minimised to achieve the barrier requirements of the target application. In this study, it has been found that the printing step, especially rotogravure printing, is the most damaging conversion process with regards to the AlO_x barrier performance, which has also been identified by other researchers (Jahromi, 2016). This paper is a unique study on optimising and facilitating the conversion process of AlO_x coated films in order to meet market requirements for food packaging applications (with the aim of dry food packaging applications such as snack foods, confectionary, biscuits or cereal bars). The focus, therefore, is on developing a suitable offline topcoat solution, which is not only capable of protecting the AlO_x barrier layer through all conversion steps (including pouch making), but also offers additional barrier functionality. Once this topcoat is successfully applied using an optimised/modified platform to prevent barrier loss upon web conveying and coating application, the topcoated AlO_x polyethylene terephthalate (PET) films can be converted on standard industrial equipment, without the need for changes and without any subsequent barrier deterioration. Trials have been conducted using AlO_x coated PET film and each process step was characterised with regards to its post-processing barrier performance.

Additionally, flex-durability (Gelbo-Flex) testing as well as barrier retention upon elongation investigations were carried out.

2 Material and methods

2.1 Coating/Conversion processes and platforms

Standard low-cost commodity grade PET films (12 µm film thickness; 1250 mm width; corona treated by the film manufacturer) were chosen for this investigation (note: especially in the pre-assessment phase, PET films from a variety of film supplies were used). AlO_x coating was conducted via reactive thermal evaporation using a Bobst Manchester Ltd (Heywood, United Kingdom) K5000 vacuum metalliser with an optional AlO_x coating system. The vacuum coater has a deposition source consisting of resistively heated evaporation boats (standard intermetallic composite) onto which aluminium is continuously fed in the form of a wire. Oxygen is introduced into the aluminium vapour stream in order to produce a transparent aluminium oxide coating and an optical monitor beam and closed loop control system is used to achieve consistent optical properties of the coated film across the web width and length. The pressure during aluminium oxide deposition is of the order of 0.05 Pa. AlO_x deposition was carried out at a web speed of 600 m/min, whilst also applying optimised in-line plasma pre-treatment using a medium frequency plasma source with magnetically enhanced water cooled electrodes. To achieve enhanced convertibility of the AlO_x coated starting material, the original AlO_x process (Struller, Kelly, & Copeland, 2014) was further optimised in order to facilitate the handling of the AlO_x coated film via increasing its flexibility. Thereby, the thickness of the coating layer was reduced from an average value of 10 nm to a thickness in the range of 7 to 8 nm. For the final conversion work (including topcoating, printing and lamination), 32 km reels were AlO_x coated.

Topcoating of the produced AlO_x PET reels was performed on an AlO_x optimised Bobst CL 850D coater/laminator at Bobst Italia SpA (San Giorgio Monferrato, Italy) using a forward gravure coating system at web speeds up to 250 m/min. The two coatings chosen are water-based and were supplied by the project partner Michelman SARL (Windhof, Luxembourg). These coatings are: a protective topcoat (offering protection through conversion only) and a barrier topcoat (offering protection through conversion and additional barrier functionality). Both coatings are compliant with relevant food contact legislations.

The rotogravure printing was also conducted at Bobst Italia using a standard Bobst RS 4003MP 8 colour rotogravure printing press at web speeds of up to 400 m/min. For the final conversion work (using a topcoat prior to printing), a solvent-based high performance commercially available ink system was used, which was supplied by the project partner Flint Group Italia SpA (Cinisello Balsamo, Italy).

Flexo printing was carried out on a standard Bobst 20SIX 8 colour CI (central impression) flexo printing press at Bobst Bielefeld GmbH (Bielefeld, Germany). For the final conversion work, printing was conducted at web speeds of 200 m/min using the flexo version of the solvent-based high performance ink system used in the gravure printing trials, supplied by Flint Group Germany GmbH (Willstätt, Germany). Printing (flexo and gravure) was conducted as ‘reverse’ printing with the white colour printed last, since the printed material itself will be on the outside of the packaging structure with the ink embedded within the laminate (i.e. one looks through the PET film at the print or, in areas of no print, at the packaged food stuffs).

Lamination was again carried out at Bobst Italia SpA using a solvent-based adhesive on a Bobst CL 850D coater/laminator. A commercially available high performance, two component polyurethane adhesive (supplied by the project partner Dow/**Rohm and Haas Italia Srl (Mozzate, Italy**) was used and applied via a flexo trolley coating application system at a speed of 150 m/min. For the lamination in the pre-assessment stage, a 40 µm thick corona treated cast polypropylene (CPP) sealant film was used; whilst for the full conversion work a 32 µm corona treated linear low-density polyethylene (LLDPE) sealant film was applied as secondary material.

All further conversion steps (slitting, pouch making via HFFS (horizontal form fill & seal) and pouch filling) were arranged and managed by collaborator Printpack Inc. (Atlanta, GA, United States) using their facilities, contacts and customer base.

2.2 Analytical methods

Barrier properties in terms of oxygen and water vapour transmission rates (OTR/WVTR) were analysed in accordance with ASTM F 1927 and ASTM F 1249/ISO 15106-3 using a Mocon Oxtran 2/20 and Systech Illinois 8001 for oxygen permeation and a Mocon Permatran-W 3/33 and Systech Illinois 7001 for water vapour permeation. Test conditions were 23 °C and 50 % relative humidity (RH) for OTR measurements and 37.8 °C and a gradient of 90 % RH for WVTR measurements. Barrier properties were typically measured at several points across the 1250 mm web width and average values are given.

A Zeiss Supra 40VP field emission gun scanning electron microscope (FEG SEM) was used to acquire SEM images. All samples were examined using a low acceleration voltage to avoid the need for coating with a conductive layer (which could potentially mask important surface detail). Cross-sections were cut on a Leica RM2125 microtome prior to SEM analysis.

The flex durability or Gelbo-Flex (ASTM F392) of the laminated AlO_x coated films was investigated using a Gelbo-Flex tester model 5000 manufactured by United States Testing Co., Inc. For this investigation 1, 5 and 20 flexing cycles were performed and the barrier performance was determined successively.

For the evaluation of the barrier retention on elongation behaviour, the films were stretched to a pre-defined strain (between 0.5 and 5 %, stretching in the machine direction) by a tensile testing unit (Hounsfield H10KS with QMat 5.52 software) and subsequently the barrier properties were measured (test for stretch durability/resistance (Felts, 1993), however samples are analysed in the relaxed state).

3 Results and discussion

3.1 Printing and lamination pre-assessment

3.1.1 Flexographic and gravure printing

During the initial assessment, printing conversion processes were analysed for their impact on the barrier performance of AlO_x coated PET film (i.e. when the non-protective topcoat is present). Therefore, trials were conducted using standard ‘non-optimised’ conversion equipment at Bobst Italia and Bobst Bielefeld. During each interaction, several trials were conducted on the printing presses, in order to investigate the variability that can be obtained during direct printing onto the sensitive AlO_x PET material. Additionally, trials were conducted on different machines of the same model, i.e. the RS 4003MP as well as the 20SIX presses were investigated on two different occasions, whereby the machines were of the same model, but not ‘physically’ the same machines. This was also part of the pre-assessment to show the range of barrier deterioration that can occur on the same machine type. No special care was taken in regards to the sensitiveness of the AlO_x PET film, but the web was printed using parameters and run conditions typical for 12 µm uncoated PET film. Additionally, trials were also carried out at a customer site in China. The latter was conducted in order to acquire true field data of a trial that has not been executed under the supervision and control of the authors/team at Bobst as well as using non-Bobst and older equipment (Chinese supplied 7 colour gravure printing press; make, model and age of machinery unknown to the authors; solvent based inks used from Chinese supplier).

For each of the assessments, 4 km long rolls of AlO_x coated PET film were produced and used to carry out the conversion trials and the results are summarised in Table 1. Barrier numbers before conversion are given as a range which is typical for the PET films coated in this work. For the post printing barrier performance, a large spread of data was obtained in the different assessments of the same machine types as well as the various trials run on the same machine. Due to this variability of transmission rates, the post printing ranges obtained are given for OTR and WVTR, rather than an average value. As can be seen, after printing (gravure and flexo) the barrier is deteriorated in all cases, although to a larger degree for the gravure printing. This is due to the longer web path and larger amount of web handling involved in the gravure process (printing units inline), versus CI flexo printing (printing units arranged around central impression drum). The fact that web handling can have a detrimental impact on the barrier performance of ceramic inorganic barrier layers, such as AlO_x coatings deposited onto a polymer web, has also been shown by a group of researchers (Lahtinen, Lahti, Johansson, Seppänen, & Cameron, 2014) who investigated the effect of post deposition film handling on atomic layer deposited aluminium oxide coatings on biaxially oriented polypropylene film. Also, the barrier data obtained from a gravure printing field trial at a customer site falls within the spread of post-printing data obtained on the Bobst gravure platform. Furthermore, Jahromi (Jahromi, 2016), has reported comparable barrier values for printed unprotected AlO_x PET (OTR 6 to 12 $cm^3/(m^2\ d)$ and WVTR 2 to 7 $g/(m^2\ d)$), although these samples were flexo printed, which in our case has been found to be significantly less destructive than gravure printing.

In order to investigate the nature and origin of the damage to the AlO_x layer, further analysis was conducted. In principle, the damage to the AlO_x layer (and hence barrier deterioration) could be caused by either chemical, thermal or mechanical stress to the film. However, AlO_x as a ceramic material should be chemically inert and also temperature resistant, which was investigated and proven via laboratory assessment trials. Therefore, mechanical damage to the AlO_x layer appeared to be the most likely cause of the barrier deterioration. In this case, damage to the AlO_x coating could be due to stretching the film and hence cracking of the AlO_x layer or mechanically scratching/scuffing the brittle AlO_x due to contact with rollers (driven or idler) or the gravure printing head in the web handling mechanism. With regards to the stretch durability of AlO_x coated PET film, the authors have previously shown (Struller et al., 2012) that OTR can withstand up to 3 % elongation, whilst water vapour barrier is retained up to 1 % elongation before deterioration. Based on the web tensions used during the printing process, this is very unlikely to be the cause of the barrier decline seen after printing and, hence, samples of the printing trials were analysed via scanning electron microscopy in order to discover any visible kind of mechanical damage in the AlO_x layer. An example SEM micrograph revealing the damaged AlO_x layer is show in Figure 1. The image on the left side is at lower magnification in order to show the location of the damage on a larger scale. Obviously, damage to the AlO_x coating can only be detected in the unprinted area, since it will be covered up by the ink in the printed areas. On the right hand side, a higher magnification image of the scratch marked in the low magnification image can be seen. It is clearly noticeable that the AlO_x layer is damaged. Scratches like this were found to cover all post-printing samples (exhibiting barrier deterioration) that were investigated and their typical orientation was the machine direction (i.e. movement direction of the film during processing). Consequently, it can be concluded that the barrier loss induced during printing is caused by mechanical damage of the AlO_x coating during web handling on the printing press.

3.1.2 Lamination

In addition to assessment of the two printing processes, the lamination process was also investigated for non-protected AlO_x coated PET film using a standard ‘non-optimised’ laminator. A range of lamination trials was conducted, whereby the adhesive was applied directly onto the AlO_x layer and a CPP film was used as the secondary web. Unlike the printing assessment, the post-lamination barrier performance was comparable to pre-lamination properties and, hence, average values and associated standard deviations are given in Table 1 for the AlO_x PET as well as the laminated structure (note, the average given has been obtained from several lamination trials). Overall, no significant barrier deterioration is seen when non-protected AlO_x PET film is laminated via direct application of the adhesive onto the ceramic barrier layer using standard industrial equipment. Nevertheless, an oxygen barrier improvement effect is frequently observed by lamination of vacuum coated (i.e.

metallised) films when using polyurethane based adhesives, based on the good oxygen barrier properties of the adhesive itself (Mueller, Schoenweitz, & Langowski, 2012). It should be noted here that the aluminium layer of a metallised film is less prone to damage during conversion due to its ductility, compared to an AlO_x layer which is ceramic and hence brittle. Langowski (Langowski, 2008) states that for a multilayer system with an inorganic barrier layer embedded between two polymer layers 'when the two polymer layers have the same or very similar permeation coefficients, the permeability (i.e. transmission rate) is halved compared to a system comprising a single polymer layer and the inorganic layer'. As no degree of barrier improvement was seen when laminating the AlO_x coated PET film, it may well be that damage of the AlO_x layer took place during the conversion process of lamination. However, as we obtain a post-lamination barrier level comparable to the pre-lamination level, it is assumed that the barrier performance loss is recovered due to the barrier properties of the adhesive, as well as by a possible infiltration of the adhesive into the defects/damage in the AlO_x layer (Miesbauer, Schmidt, & Langowski, 2008). The thickness of the adhesive layer was between 2.5 and 3 µm (determined via light microscopy of microtome cross sections of the laminate). This means that the adhesive thickness is above the so-called critical thickness, which depends on the defect size distribution of the inorganic barrier layer and typically is less than 2.5 µm for the type of industrially produced barrier layers discussed here (Langowski, 2002). According to Langowski (Langowski, 2008), if the thickness of the polymer layer directly adjacent to the inorganic barrier layer is thicker than the critical thickness, then this layer along with the inorganic barrier layer dictates the barrier performance of the system. For the work discussed here this means that in the final laminate, the barrier properties of the polyurethane adhesive (significantly better oxygen barrier properties compared to polypropylene) dominate over those of the material laminated on top (i.e. the CPP film), which is of importance for the above discussion on barrier enhancement due to adhesive lamination.

Another important conversion step with the potential to damage is the slitting process. This has been found not to impair AlO_x barrier performance when conducted in a controlled manner on standard slitting equipment and has been discussed by the authors in more detail elsewhere (Struller et al., 2015).

3.2 Topcoat development

After the initial assessment of conversion processes and their impact on the barrier performance of AlO_x coated films, the approach taken in this research work was to apply a topcoat prior to any damaging conversion (such as printing). This topcoat serves the purpose of protecting the AlO_x layer during conversion, thus avoiding damage/barrier deterioration and enabling the use of standard industrial equipment for downstream processing of AlO_x coated films. In this manner, any conversion after topcoating can be decoupled. A topcoat can be applied in two ways, either inline in the vacuum chamber or offline via an atmospheric pressure 'wet' coating process. The former can, for example, be achieved by the use of an acrylate-based topcoat, flash evaporated (Affinito, Eufinger, Gross, Graff, & Martin, 1997; Affinito et al., 1996; Shipman, 2016) or flexo printed in vacuum (Ferrari, 2016), or also via a melamine based topcoat (Jahromi, 2011). Acrylate coatings have been widely investigated, including by the authors of this paper (Struller, Kelly, Copeland, et al., 2014). Nevertheless, the guarantee of fully cured acrylate layers without any residual monomer (as would be required for food safety reasons) has been the main hurdle and, despite recent advances, acrylate topcoated films have not yet found a place in the market for food packaging materials, but are predominantly used for industrial applications. Melamine based topcoats on the other hand, also suffer from low market acceptance; here, though, mainly based on the negative connotation associated with melamine. Hence, in this work, the focus lies on investigating offline applied wet topcoats, which do not exhibit any of the above drawbacks.

The initial work started here with material screening trials, in order to find a suitable coating material (polymer) and assess the material properties required. These investigations were conducted on a laboratory-scale as well as pilot-scale prior to moving onto industrial-scale, and won't be discussed in further detail here. An effective laboratory-scale conversion simulation technique was developed in order to subject the topcoated AlO_x PET samples (from laboratory, pilot and industrial coating work) to the levels of damage and stress that they would generally endure during conversion processes such as gravure printing. Once this proprietary technique was refined to match the effects of conversion, this method could then be used to examine and test topcoated samples for the protective properties of the applied topcoat without the need of having to conduct actual printing trials. When the step was taken to move onto industrial-scale, the right coating application technique had to be selected (a forward gravure coating system) and adjusted and the web handling system also had to be adapted in order to optimise the platform for the coating of the AlO_x PET material. This is in order to avoid any damage of the sensitive AlO_x layer on the offline coater due to the web handling before the coating head as well as during the coating application process. Nevertheless, these platform and coating technique optimisations are of confidential nature to Bobst and can't be discussed in further detail.

Results of some of the initial investigations conducted are summarised in Table 2. As can be seen, after the conversion simulation test on unprotected AlO_x PET, OTR and WVTR are drastically increased with the OTR rising from a value of around 1 $cm^3/(m^2\ d)$ to more than 10 $cm^3/(m^2\ d)$ and WVTR from values of less than 1 $g/(m^2\ d)$ to an average value of 5.62 $g/(m^2\ d)$. These values fall within the range of results obtained during print tests (refer to Table 1) of non-topcoated AlO_x PET, which confirms the suitability of the conversion simulation test developed.

Also displayed in Table 2 are the barrier performances obtained before and after conversion simulation tests for the two topcoats, which were selected for the conversion/pouch making trials (see next section). As can be seen, the protective topcoat only offers a small OTR improvement (from OTR values > 1 $cm^3/(m^2\ d)$ to values consistently < 1 $cm^3/(m^2\ d)$), whilst the barrier topcoat increases the oxygen barrier properties remarkably. Furthermore, the barrier topcoat also offers some water barrier improvement, from a typical value of around 0.7 $g/(m^2\ d)$ to values around 0.4 $g/(m^2\ d)$. The barrier improvement obtained by applying the topcoat can be attributed to two aspects; a potential pore-filling effect (Affinito & Hilliard, 2004) (something the authors have previously reported for acrylate topcoats (Struller, Kelly, Copeland, et al., 2014)) and the effect of the permeability/barrier properties of the topcoat material itself (in comparison to the PET substrate), which is now adjacent to the inorganic barrier layer (Langowski, 2008). With regards to the conversion simulation test, it can be seen that the barrier is unchanged or only marginally increased after conducting this test. The latter is the case for the barrier topcoat (refer to oxygen barrier) and indicates that the coat weight needs to be slightly increased. As will be shown later, the results obtained here are very reproducible and are consistently achieved in the subsequent long duration industrial trials.

3.3 Conversion trials

After the initial investigations presented in the previous section, as well as successful short-run industrial topcoating trials, the next step was to conduct long-duration conversion trials, whereby the full downstream conversion chain was investigated, from topcoating, via printing, lamination and slitting to the final packaging structure (such as pouch/bag or lid) including the filling of this packaging material with actual food stuffs. Being able to directly print onto the topcoated AlO_x PET material and hence achieve a two-ply laminate structure instead of a three-ply structure helps to fulfil the demand for cost reduction and down gauging. Appropriate inks were selected based on printability and ink adhesion studies carried out by the ink manufacturer. Furthermore, compatibility tests were conducted with the inks selected in order to avoid any negative effects on the barrier performance due to a potential incompatibility between topcoats and inks. Two topcoats were used in the conversion work:

- Protective topcoat: offering protection through conversion only
- Barrier topcoat: offering protection and additional barrier functionality

The final laminate structure produced during the conversion trials is shown in an SEM image (microtome cross section) in Figure 2. The picture clearly shows the individual layers added in each conversion step: AlO_x, topcoat, inks & adhesive, apart from the LLDPE sealant web which would be on top of the adhesive. For the printing process, one can also distinguish between the different coloured inks, based on the larger pigments (titanium dioxide) in the white ink. Finally, even the thin AlO_x layer can be made out as a lighter coloured line. This is thought to be caused by electrons backscattered from the aluminium (higher atomic number of aluminium compared to atoms in the surrounding PET film and polymer topcoat) in the AlO_x barrier layer.

The oxygen and water barrier was assessed after each individual conversion process step and results are summarised in Table 3 for the gravure printing and in Table 4 for flexo printing (note: not in all cases, the full conversion of the produced material was assessed). These results are very much in agreement with the barrier performance obtained during the topcoat development stages (see Table 2). If one compares the barrier properties measured after each individual conversion step, it is clear that no oxygen or water vapour barrier deterioration took place through the conversion exercise. This is the case for both the protective and the barrier topcoat. Some fluctuations in the barrier data are noticeable, which are, however, put down to typical fluctuations within the large film reels converted and the samples being taken at different positions (lengthwise). Although not all conversion steps have been conducted for the flexo printing, it is clear that also in this case, no further barrier deterioration can be expected, especially since flexo printing has been found to be less aggressive and damaging compared to gravure printing.

3.4 Gelbo-Flex testing and barrier retention on elongation

Laminated samples of the conversion trials with gravure printing have been further investigated for their flex-durability (Gelbo-Flex). During this test, the laminate is repeatedly twisted and crushed, which serves the purpose of simulating the strain that the laminated material may be subjected during further conversion (i.e. folding and forming into packaging structures) and whilst handled in typical transport, storage and retail environments as finished packages of food products. Results of this investigation are shown in Figure 3. As can be seen, the laminate with the barrier topcoat reveals very good barrier performance. The OTR is predominantly unaffected, even after 20 Gelbo-Flex cycles, whilst WVTR is slightly increased after 20 cycles from values around 0.4 g/(m^2 d) for the unflexed laminate to values around 0.7 g/(m^2 d). This flex-durability performance is comparable to or even outperforms data published by some of the large and more established transparent barrier film producers (DNP America, 2017; Toppan USA, 2016). In the case of the protective topcoat, the effect of the Gelbo-Flex test is more pronounced. OTR increases from 0.77 cm^3/(m^2 d) for the unflexed sample to an average of 3.87 cm^3/(m^2 d) after 20 cycles, whilst WVTR rises from 0.68 g/(m^2 d) to 1.44 g/(m^2 d). This performance is, however, still remarkable in regards to the destructiveness of this test. Finally, it should also be noted here that, as stated previously (Struller, Kelly, Copeland, & Read, 2013), the specific effects of the Gelbo-Flex test are influenced by many factors, such as the type/chemistry of the inorganic barrier layer (Chiba, Mikami, Sakamoto, & Tsuchiya, 2006) and its thickness, the deposition process (Komada, Oboshi, & Ichimura, 2000), the substrate used and the characteristics of the lamination process (Abedin & Jopko, 2013) (type of adhesive, secondary material, duplex/triplex laminate etc.).

The laminates were additionally tested for their barrier retention on elongation behaviour, whereby the samples were subjected to uniaxial deformation in the machine direction. This test has been previously used in our research in order to assess how the AlO_x coated film can withstand downstream processing in terms of web tension (Struller et al., 2012). In the case of conducting this test with laminates, the objective is similar, as also the laminate is further converted to a packaging structure (pouch) via HFFS. On these types of machinery, the laminate may be subjected to stretching due to high web tensions and it is important to exclude any barrier deterioration based on this process step.

The barrier results from this test, presented in Figure 4, indicate that oxygen barrier remains unchanged for both topcoats up to 2 % elongation. After this, the OTR rises for the barrier topcoat to an average value of only 0.65 cm³/(m² d) at 5 % elongation. As observed for the flex-tests, this again shows the durability of the barrier topcoat laminate when subjected to different forms of tensile stress and strain. In the case of the protective topcoat. However, the increase in OTR for 3 % elongation onwards is drastic. When investigating the water barrier retention for both topcoats, it was found that water barrier properties are maintained up to 1.5 % elongation. For elongation values of 2 % and onwards, the WVTR increases; although, the barrier topcoat performs significantly better than the protective topcoat. Looking back at the barrier performance obtained for the structure with the barrier topcoat post pouch-making (see Table 3), one can see that neither OTR nor WVTR is deteriorated after this conversion step, hence indicating that no stretching beyond 1.5 % elongation occurs due to the web tensions on the pouch making equipment.

4 Summary and Conclusions

It has been shown with the work presented here that AlO_x coated PET films can be converted without barrier deterioration using standard equipment once a protective offline topcoat has been applied. Extensive research has been conducted in assessing the various conversion processes for their impact on the conversion of AlO_x coated PET film as well as developing and characterising optimised topcoats. Two different topcoat variations have been established and investigated, with one topcoat giving protection through conversion only, and the other topcoat offering additional and significant barrier enhancement. Long duration conversion trials, including printing (flexo and gravure), lamination, slitting and pouch making/filling were successfully carried out with both topcoats. Furthermore, tests on flex-durability and barrier retention on elongation also showed that the barrier topcoat laminate especially has remarkably good properties when subjected to this kind of repetitive or uniaxial strain.

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Table and figure headings

Table 1 – Barrier performance – Assessment of printing and lamination processes for ‘unprotected’ AlO_x PET

Table 2 – Barrier performance – Effect of conversion simulation test

Table 3 – Barrier performance through conversion – Gravure printing

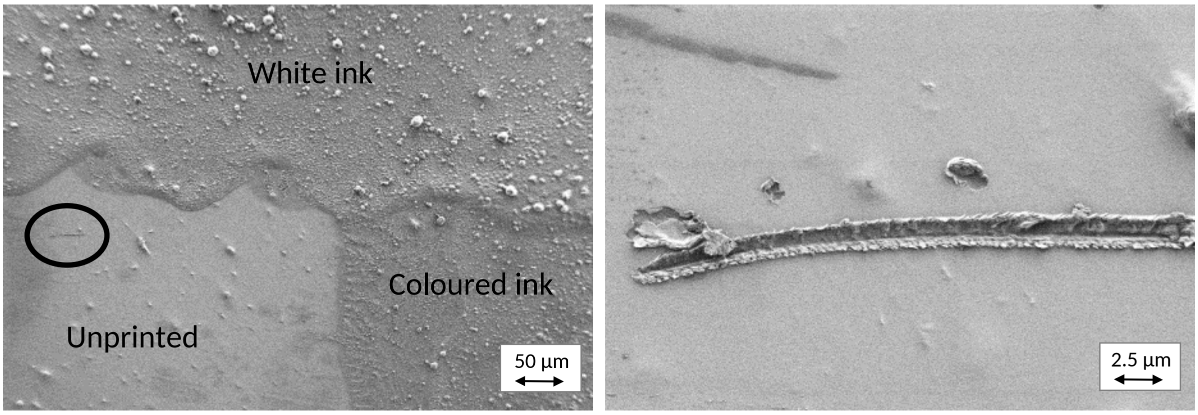
Table 4 – Barrier performance through conversion – Flexo printing

Figure 1: SEM images showing damage to AlO_x layer after gravure printing (note: machine direction is horizontal)

Figure 2: SEM cross-sectional image of final laminate structure

Figure 3: Barrier performance of printed and laminated AlO_x PET material after Gelbo-Flex testing

Figure 4: Barrier retention on elongation behaviour for printed and laminated AlO_x PET material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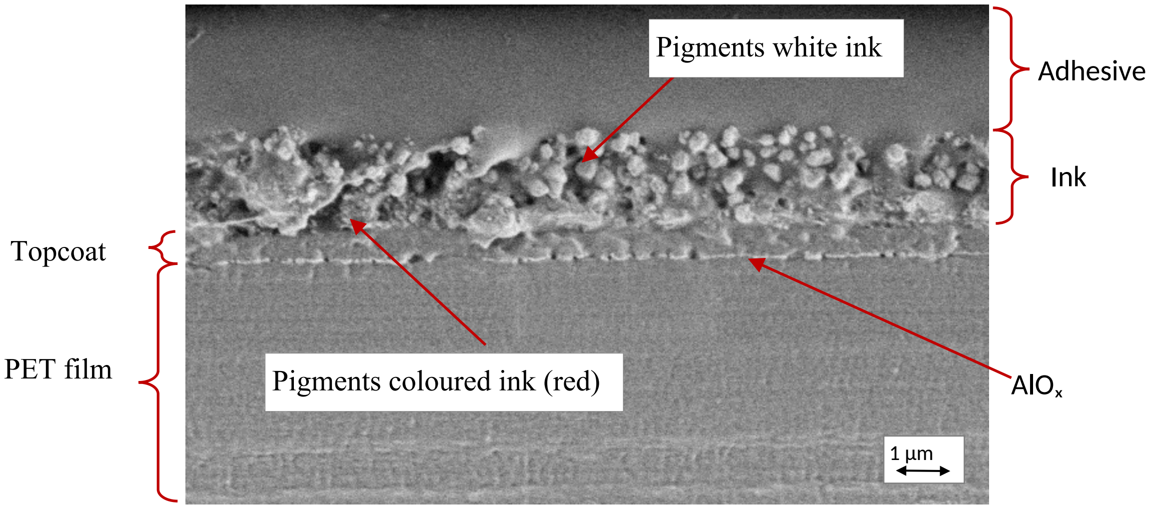
Unprinted
Coloured ink
50 µm
2.5 µm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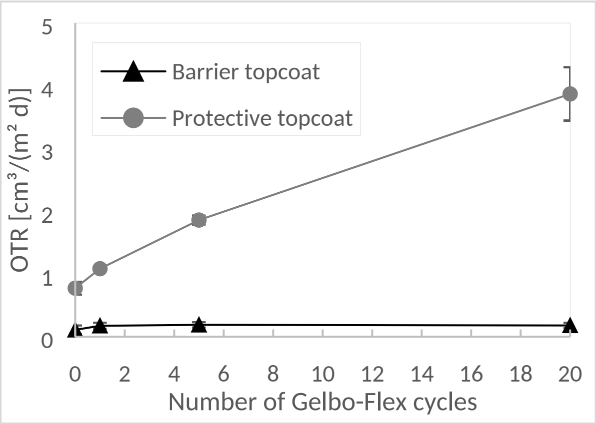
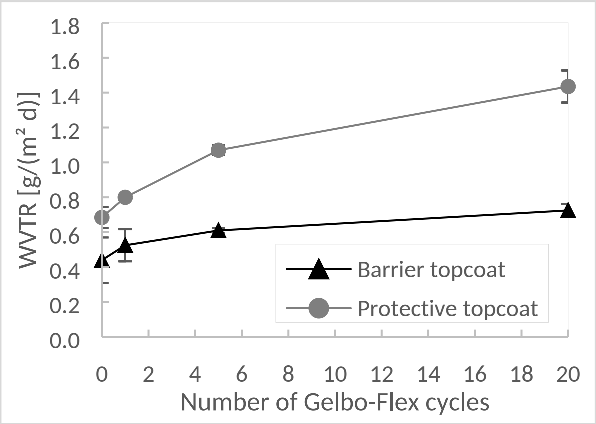
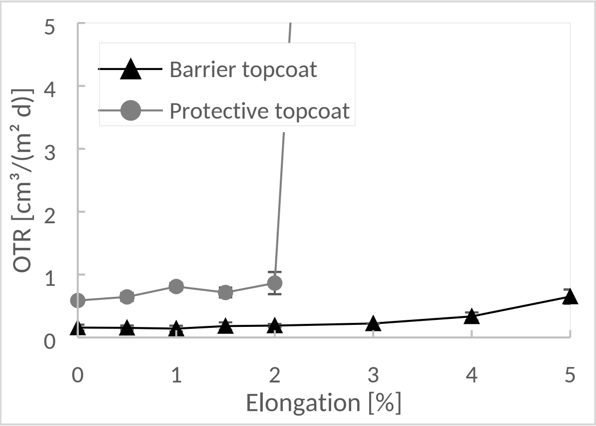
Adhesive
Ink
Topcoat
PET film
Pigments coloured ink (red)
AlOx
1 µm


OTR [cm³/(m² d)]
0
1
2
3
4
5
0
2
4
6
8
10
12
14
16
18
20
Number of Gelbo-Flex cycles
Barrier topcoat
Protective topcoat


WVTR [g/(m² d)]
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
0
2
4
6
8
10
12
14
16
18
20
Number of Gelbo-Flex cycles
Barrier topcoat
Protective topcoat


5
4
3
2
1
0
OTR [cm³/(m² d)]
Barrier topcoat
Protective topcoat
0
1
2
3
4
5
Elongation [%]

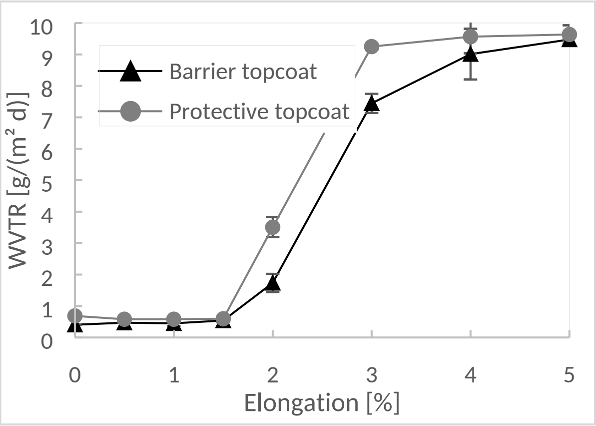

10
9
8
7
6
5
4
3
2
1
0
WVTR [g/(m² d)]
Barrier topcoat
Protective topcoat
0
1
2
3
4
5
Elongation [%]

Table 1 – Barrier performance – Assessment of printing and lamination processes for 'unprotected' AlO_x PET

Structure	**Description**	**OTR**	**WVTR**
		cm³/(m² d)	**g/(m² d)**
PET 12 µm		≈ 120	40 – 50
PET/AlO_x	Before printing	1.0 – 1.5	0.5 – 1.0
PET/AlO_x/ink	Bobst Italia, gravure press RS 4003MP 250 m/min	2.5 – 18	1 – 12
PET/AlO_x	Before printing	1.0 – 1.5	0.5 – 1.0
PET/AlO_x/ink	Chinese customer, gravure press 200 m/min	15 – 20	8 – 10
PET/AlO_x	Before printing	1.0 – 1.5	0.5 – 1.0
PET/AlO_x/ink	Bobst Bielefeld, CI flexo press 20SIX 250 and 400 m/min	1.5 – 8	1 – 3.5
PET/AlO_x	Before lamination	1.29 ± 0.21	0.82 ± 0.11
PET/AlO_x/ad*/CPP	Bobst Italia, laminator CL 850D 150 m/min	1.34 ± 0.23	0.85 ± 0.10

*ad = adhesive layer

Table 2 – Barrier performance – Effect of conversion simulation test

Structure	**Description**	**OTR**	**WVTR**
		$cm^3/(m^2\ d)$	**$g/(m^2\ d)$**
PET/AlO_x	-	1.07 ± 0.10	0.66 ± 0.05
PET/AlO_x	After conversion simulation test	13.47 ± 2.32	5.62 ± 2.12
PET/AlO_x/protective topcoat	-	0.73 ± 0.12	0.58 ± 0.02
PET/AlO_x/protective topcoat	After conversion simulation test	0.66 ± 0.11	0.74 ± 0.03
PET/AlO_x/barrier topcoat	-	0.15 ± 0.06	0.36 ± 0.01
PET/AlO_x/barrier topcoat	After conversion simulation test	0.27 ± 0.08	0.44 ± 0.04

Table 3 – Barrier performance through conversion – Gravure printing

Conversion process	**Structure**	**OTR**	**WVTR**
		$cm^3/(m^2\ d)$	**$g/(m^2\ d)$**
-	PET 12 μm	≈ 120	40 – 50
AlO_x coating	PET/AlO_x	1.0 – 1.5	< 1.0
Protective topcoat			
Topcoating	PET/AlO_x/topcoat	0.65 ± 0.09	0.56 ± 0.10
Printing	PET/AlO_x/topcoat/ink	0.78 ± 0.10	0.70 ± 0.05
Lamination	PET/AlO_x/topcoat/ink/ad/P	0.77 ± 0.10	0.69 ± 0.06
Slitting	PET/AlO_x/topcoat/ink/ad/P	0.59 ± 0.02	0.69 ± 0.01
Barrier topcoat			
Topcoating	PET/AlO_x/topcoat	0.09 ± 0.04	0.42 ± 0.03
Printing	PET/AlO_x/topcoat/ink	0.12 ± 0.08	0.45 ± 0.06
Lamination	PET/AlO_x/topcoat/ink/ad/P	0.11 ± 0.07	0.44 ± 0.13
Slitting	PET/AlO_x/topcoat/ink/ad/P	0.11 ± 0.09	0.41 ± 0.01
Pouch making	PET/AlO_x/topcoat/ink/ad/P	0.11 ± 0.09	0.44 ± 0.01

Table 4 – Barrier performance through conversion – Flexo printing

Conversion process	**Structure**	**OTR** **cm³/(m² d)**	**WVTR** **g/(m² d)**
-	PET 12 µm	≈ 120	40 – 50
AlO_x coating	PET/AlO_x	1.0 – 1.5	< 1.0
Protective topcoat			
Topcoating	PET/AlO_x/topcoat	0.67 ± 0.01	0.64 ± 0.01
Printing	PET/AlO_x/topcoat/ink	0.72 ± 0.06	0.67 ± 0.17
Barrier topcoat			
AlO_x coating	PET/AlO_x	1.0 – 1.5	< 1.0
Topcoating	PET/AlO_x/topcoat	0.12 ± 0.03	0.39 ± 0.05
Printing	PET/AlO_x/topcoat/ink	0.12 ± 0.03	0.39 ± 0.03