MULTILAYER EVOH/HDPE PACKAGING IN PROCESSING AND PERFORMANCE OF RECYCLED HDPE

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Abstract

Kuraray, EVAL Europe N.V. (EE) produces Ethylene Vinyl Alcohol copolymers (EVAL™), which are used in multilayer structures in a combination with a wide range of materials such as High Density Polyethylene (HDPE) to produce multilayer bottles to provide superior barrier properties to gases, flavours or bring functional barriers against external contaminants such as mineral oils (MOH, MOAH). Bottles are typically made by Co-Extrusion blow moulding (Co-EBM) technology and are used for beverage packaging such as dairy products and specialty milk and other packaging applications for sauces or dressings or for the packaging of medical products for which the Water Barrier of HDPE is of added value.

The objective of the study was to investigate if multilayer EVOH/HDPE rigid packaging material, which is a percentage of the post-consumer recycling stream, can be effectively sorted with the HDPE stream and decontaminated back to food grade approved for use as Post-Consumer Recycled (PCR)-HDPE into food packaging applications.

Multilayer rigid food packaging found in the post-consumer recycling stream has been represented in the design of materials guides and recycling guides as ‘may be suitable’ for recycling. The present work investigates the recyclability of EVOH barrier packaging due to the growing trends of multilayer rigid food packaging and more importantly, as recovery systems strive towards a better circular economy.

The steps taken to produce food grade rHDPE with analysis included; Audits of the HDPE fraction at Viridor MRF, testing on automated NIR sorting equipment at Tomra (Titech), compounding in a low pressure, elevated temperature, food-grade decontamination process and overall migration testing conducted by Smithers-Pira.

The evaluation showed that post-consumer HDPE (rHDPE) material containing at least 0.25% EVOH (equivalent to 5% multilayer EVOH/HDPE packaging) can be “super cleaned” to food grade quality without any significant impact on the process performance or physical properties compared to rHDPE only. The results showed that at the levels of multilayer EVOH packaging typically found in the recycled HDPE stream, the rHDPE can be processed and utilized in a full range of applications, without impact on migration characteristics or physical properties compared to rHDPE alone.

Introduction

Food packaging has seen significant changes over recent decades with demand for pre-packaged food increasing, hence the requirement for research and development in barrier and shelf life extending materials. Demand for food packaging resin is also increasing with HDPE behind PET but above PP and PS. [1][2]

Packaging must comply with food safety regulations to protect the consumer, therefore multilayer structures are essential in preserving and protecting the food. In certain cases, packaging provides a barrier to gas permeation because of the risk of microbial activity and food spoilage, in other cases, functional barrier helps keeping the food away from external contaminants. In Europe, the Plastics Regulation (EU) No 10/2011 defines layer B as a “functional barrier” if it reduces the level of migration of a substance from layer A to layer C to a level where it can meet regulatory limits. Section VII from the Food and Drug Administration (FDA) ‘Guidance for Industry: Use of Recycled Plastics in Food Packaging: Chemistry Considerations,’ defines the use of an effective barrier.[1][3]

Kuraray is a world leader in EVOH (ethylene vinyl-alcohol copolymers) production and technology. An EVAL™ layer thickness of only a few microns helps avoid spoilage by keeping oxygen and odours out, while locking flavours, aromas and modified atmosphere inside the package. This prolongs shelf life reducing the need for artificial additives to be added into food.Fewer resources can often be used for the same packaging function. Optimized portion size, light weight and extended freshness help improve the efficiency of storage, transport and display, saving costs and preserving resources. Kuraray quote that “1 mm of EVAL™ provides about the same gas barrier properties as a 10 metre thickness of LDPE.” [4]

EVOH will continue to be used in packaging for these reasons and ideally would be recycled with minimal detrimental effects in the polyolefin industry. It is well known that EVOH offers great barrier protection against oxygen, odours and gases however EVOH has also been reported to absorb significant amounts of moisture in humid conditions which is why multilayer structures are needed.[5][6]

Kuraray, EVAL Europe N.V. produces Ethylene Vinyl Alcohol copolymer (EVOH) which is used in blow moulded HDPE multilayer bottles to provide gas barrier...
properties for juice or specialised milk products. Food grade recycled HDPE (rHDPE) is produced in UK and other countries, primarily from clear (natural) coloured monolayer blow moulded white (fresh) milk bottles and is used back into the manufacture of new milk bottles at approximately 15%, providing closed loop recycling of this material in the UK. The food grade rHDPE is a commercial material currently only available from a few suppliers, but it will be available from an additional number of recyclers in the UK and other countries in the near future.

For PP, the recyclability characterization in the WRAP guidance states that EVOH if less than 10% of total pack weight is ‘not ideal’ (Category B) and if above 10% pack weight then it is classed as ‘detrimental’ (Category C). For HDPE milk bottle recyclability, co-extruded EVOH barriers are within category C. Category B recommends co-extruded tie-layer functional polyolefins if less than 3% total bottle weight. These constraints could have better definitions to enable manufacturers of EVOH to participate in the circular economy with growing pressures on recycling.[7][8]

Kuraray, EVAL Europe N.V. wanted to investigate in detail that multilayer natural coloured HDPE/EVOH material can be effectively recycled as a percentage of the post-consumer stream and used back into food packaging and applications. Nextek assisted with conducting this study and trials and evaluation of the recycling process with blow moulded multilayer HDPE barrier bottles. Food grade rHDPE recycling involves sorting that removes colored HDPE, although some white is often retained. The performance of EVOH was also assessed during the food grade decontamination or super cleaning stage to confirm that the presence of EVOH does not negatively impact on the process or the properties of the final food grade material.

**Market applications and percentage of EVOH in recycling streams**

An assessment was made based on available market data and material audits to establish a typical and maximum percentage of HDPE barrier packaging in the market. Market data based on the tons of sales of HDPE and EVOH into the packaging market is very limited making accurate calculation difficult. The material audit could only be conducted on a relatively small sample and this provides only a snapshot of the composition of the recycled HDPE stream.

**Volumes and applications of EVOH in the market**

It is difficult to acquire quantitative data on the volume of rigid multilayer HDPE packaging in the UK market. The segment is relatively small and so is not usually differentiated in any way, and is included in much broader and larger volume categories for rigid HDPE.

Using data from “Plastic Packaging Composition 2011” Wrap report, 498,000 tons (29%) of the UK consumer packaging market are bottles, and 158,000 tons (32%) of bottles are HDPE, which appears to have remained flat in recent years. The large majority of this volume estimated at 119,000 tons is for monolayer natural HDPE packaging used for white milk, fresh juice products, yoghurt and other refrigerated short shelf life goods. Household chemical and personal care represented another category for colored HDPE bottles. [9]

The Wrap report indicates the volume of consumer packaging HDPE bottles in the “on-the-go” category is zero (0 tons), further indicating the relatively small size of this market. Consideration should be given to the fact that in the UK a lot of packaging that is disposed of away from home, (on-the-go) is not recycled. In addition, many of the multilayer HDPE bottles have full sleeve labels, which can result in misidentification during NIR sorting, directing the bottles away from the HDPE fraction. [9]

In the European market, rigid packaging utilizes approximately 30% or 8,500 tons of EVOH. Based on a 5% by weight composition of EVOH, this represents 170,000 tons of multilayer EVOH rigid packaging. HDPE bottles made by extrusion blow molding estimated to be 30-35% of the market, based on an average 5% barrier level, this equates to 59,500 tons of HDPE multilayer rigid packaging in Europe.[9]

Further differentiation in the UK market is difficult, research does not identify or distinguish barrier HDPE as a separate category. Recovery rates of 0.42% from the audit, applied to the 158,000 tons of HDPE bottles equals to 664 tons of multilayer HDPE bottles in the UK per year. This calculation may underestimate this market volume but it is clear that the volume is relatively small as part of the overall HDPE bottle packaging market.[9]

**Experimental**

An addition rate of 10% multilayer post-industrial materials collected from various European converters with a nominal structure of HDPE/EVOH(5%)/HDPE was selected to represent a maximum peak percentage of multilayer material that might be found in the recycle stream. At these addition rates, with a HDPE/EVOH(5%)/HDPE structure, the actual EVOH content was 0.5% in the melt blend.

Biffa polymers supplied food grade rHDPE material for the melt blending trials; two compounds were prepared at Brunel University. One compound used the food grade rHDPE and a second compound using virgin HDPE, both with 10% HDPE:EVOH. Both compounds were decontaminated at Starlinger, then at W. Muller in Germany each compound was dry blended at a 1:1 ratio with virgin HDPE and extruded into a number of bottle
structures. For migration studies PIRA recommended testing using simulant D1 (50% Ethanol) at 40°C for 10 days, in accordance with EU regulation No 10/2011, testing was done in triplicate. For physical testing at ipolytech the materials were injection molded into test specimens according to ISO527-2, which were used for tensile testing; central parts of the specimens were used for Izod impact testing, and end parts were used for density determinations.

Results

Automated sorting trials

Kuraray provided 26 samples of a range of multilayer EVOH/HDPE bottles, from food & beverage, pet food and household chemical applications, with the layer of EVOH ranging from 3.8-14.5%. The bottles were sent to Tomra (Titech) to establish if their NIR detection system was able to detect the presence of EVOH or any other variation that would distinguish them from monolayer HDPE articles.

Tomra assessed the containers including labels, which can influence identification. In all but one case, the bottles were detected as HDPE, which would conventionally be sorted to a HDPE fraction in most MRFs. Sample 13 the “Veet” cosmetic bottle was identified as PP. Tomra indicated by using a modified database, six of the twenty-six bottles could be separated from “standard” HDPE. However, this would likely result in an increased number of non-barrier HDPE bottles also being identified as multilayer, and with databases designed to identify HDPE film, some multilayer bottles may be sorted to the film fraction. It should also be noted that as with other packaging, unless the full body sleeve labels are removed prior to sorting, bottles are often miss-identified and sorted according to the label material, such as PET, LDPE, etc.

These results confirm that multilayer EVOH/HDPE bottles would most typically be identified as HDPE and be sorted by NIR based automatic sorting systems, which are used in MRFs and PRFs around the world, into the HDPE stream with monolayer HDPE packaging containers. Typically, the HDPE packaging materials are further sorted based on color to isolate the higher value natural HDPE fraction. All the multilayer HDPE bottles were colored and so would be sorted in the colored “jazz” fraction.

Manual sorting bale audit at Viridor Arundel

A manual audit of the HDPE fraction at Viridor recycling facility in Arundel UK took place to determine the level of multilayer HDPE packaging that could be identified. A bale of material that had been identified by NIR sorting as HDPE was hand sorted, first selecting colored HDPE and then visually looking for articles that may be multilayer EVOH/HDPE, based on their labelling and the product type.

The following materials types were identified:

- Dairy based nutritional supplements.
- Dairy based drinkable “on the go” breakfast products.
- Dairy based high protein drink product.

A number of other dairy products, for consumption by humans and pets, personal care and household chemical and health supplements packaging was confirmed to have non-barrier structures.

Figure 1: Coloured HDPE packaging found in the post-consumer recycling stream

From the colored HDPE fraction, there were fifty-five (55) items that appeared to be potential multilayer structures, based on the application indicated by the label. These were sent to EVAL Europe N.V. laboratory for cross-section analysis, who determined that 8 of the 55 samples were indeed multilayer.
Table 1: Composition of HDPE bale from Viridor Arundel MRF.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight (kg)</th>
<th>Percentage (%)</th>
<th>Items</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td>384</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Coloured</td>
<td>96</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Resort coloured</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Possible Multilayer</td>
<td>14</td>
<td>2.9</td>
<td>55</td>
</tr>
<tr>
<td>Confirmed Multilayer</td>
<td>2</td>
<td>0.42</td>
<td>8</td>
</tr>
</tbody>
</table>

Long life dairy-based products such as drinkable yoghurt, “breakfast on the go” and health products were the majority of the multilayer barrier bottles. From this small sample from the recycled HDPE stream, it was determined that approximately 20% was colored and 0.42% was EVOH multilayer. As expected the majority of the sample (80%) of the HDPE fraction was monolayer, natural color fresh milk and juice packaging.

Typically, the HDPE materials are further sorted to extract the colored materials. Based on this audit if the multilayer was all sorted to the colored fraction, it would be 2% of the colored “jazz” fraction.

Figure 2: Dairy based protein and breakfast product in multilayer barrier packaging

Compounding Trials

Post-consumer recycled HDPE (rHDPE) that had been decontaminated and processed to pellets suitable for food grade was obtained from Biffa Polymers and 45kg was dry mixed with 5kg of granulated post-industrial bottles from multilayer extrusion blow molding using a high-speed mixer (Blend A.50). Similarly, 45kg of virgin HDPE (vHDPE) from Sabic was dry mixed with 5kg of granulate (Blend B.50). The two blends were then separately melt compounded on a twin-screw extruder to produce two batches of pellet, both containing approximately 0.5% EVOH.

The compounding trial was conducted by Nextek at Brunel University, and attended by Kuraray. Blend A.50 had a green/grey color, consistent with using recycled HDPE; Blend B.50 was natural white, consistent with virgin HDPE.

![Blends A and B](image1.png)

Decontamination of the blended material

The pelletised HDPE blends were sent to Starlinger for decontamination on a pilot scale Viscotec unit in the Starlinger laboratory. Both blends were processed under high vacuum for 2 hours at 125°C to remove volatiles. This ensures that the 0.5% EVOH blended materials experience the same thermal process typically used for monolayer rHDPE to provide a material suitable for food grade applications.

The thermally processed Blend A.50 (rHDPE) and Blend B.50 (vHDPE) material were then sent to Germany for extrusion (Co-extrusion) blow molding trials to produce monolayer and multilayer bottles.

Co-extrusion Blow Molding (Co-EBM) Trial.

The EVOH/HDPE blends were made into a number of bottle structures at W. Muller facilities in Germany. Bottles from selected trials were subsequently used by Pira for
migration studies to compare the performance of the EVOH/rHDPE blend with EVOH/vHDPE materials.

A range of bottle structures were made with Blend A.25 and Blend B.25 compounds, both of which were obtained from Blend A.50 and Blend B.50, dry mixed with virgin HDPE 1:1 prior to extrusion, to have a final EVOH concentration of 0.25%. Different bottle structures and trial conditions are summarized in Table 2, the order of which was modified from the original trial plan, to optimise the sequence of material changes. Extruder and machine settings were set to standard conditions, to produce the 350 ml ketchup bottle.

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Layer Outside</th>
<th>Layer 2</th>
<th>Layer 3</th>
<th>Layer 4</th>
<th>Layer 5</th>
<th>Layer 6</th>
<th>Inside</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>vHDPE</td>
<td>vHDPE</td>
<td>Blend A.25</td>
<td>Blend A.25</td>
<td>Blend A.25</td>
<td>vHDPE</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Blend B.25</td>
<td>Blend B.25</td>
<td>Tie</td>
<td>EVOH</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Blend A.25</td>
<td>Blend B.25</td>
<td>Tie</td>
<td>EVOH</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>vHDPE</td>
<td>vHDPE</td>
<td>Tie</td>
<td>EVOH</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>vHDPE</td>
<td>vHDPE</td>
<td>Tie</td>
<td>EVOH</td>
<td>Tie</td>
<td>vHDPE</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>vHDPE(white)</td>
<td>Blend A.25</td>
<td>Tie</td>
<td>EVOH</td>
<td>Tie</td>
<td>vHDPE</td>
<td></td>
</tr>
</tbody>
</table>

Virgin HDPE used was Sabic™ 5823, Tie layer was Admer™ NF0408E and EVOH was EVAL™ F101B, in addition to Blend A.50 and Blend B.50, which were dry mixed with the Sabic 5823 at 1:1 to give a final EVOH concentration of 0.25% in Blend A.25 and Blend B.25, used to produce the bottles.

Standard process conditions were used during the trial for Blend A.25, Blend B.25 and vHDPE materials. Good quality bottles were formed using all the materials and structure variations.

Migration testing

Bottles from trials #2, #3, #4 and #9 were sent to PIRA to conduct overall migrations studies. The test was carried out by filling the bottles with the simulant and the average migration level of three samples tested is reported. In all test samples, the overall migration was well below the specified limit of 10.0mg/dm³.

<table>
<thead>
<tr>
<th>Trial Sample</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall Migration (mg/dm³)</td>
<td>0.0</td>
<td>0.5</td>
<td>0.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Migration results show that under these test conditions, neither the rHDPE Blend A.25 nor the vHDPE Blend B.25 materials had high levels of migration. These results indicate that the presence of 0.25% EVOH in the recycled HDPE material does not contribute to overall migration. In addition, when used external to EVOH barrier layer, or external to a virgin HDPE layer or as a monolayer structure that is in direct contact with the product, migration levels are well below maximum allowable limits.
Physical Testing

Samples of the dry mixed Blend A.25 and Blend B.25 prepared at W. Muller for extrusion blow molding were sent to the independent testing facility ipolytech for evaluation of physical properties.

Table 4: Physical test results on HDPE:EVOH blends using in moulding trials.

<table>
<thead>
<tr>
<th>Test</th>
<th>HDPE (Ref)</th>
<th>rHDPE Blend A.25</th>
<th>Blend B.25</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.956</td>
<td>0.956</td>
<td>0.956</td>
<td>ISO1183</td>
</tr>
<tr>
<td>Izod Impact (kJ/m²)</td>
<td>31.2</td>
<td>29.1</td>
<td>39.1</td>
<td>ISO 180:2000</td>
</tr>
<tr>
<td>E-Modulus (Mpa)</td>
<td>1245</td>
<td>1324</td>
<td>1280.3</td>
<td>ISO527-2:2012</td>
</tr>
<tr>
<td>Strain at Break (%)</td>
<td>407</td>
<td>427</td>
<td>263.7</td>
<td>ISO527-2:2012</td>
</tr>
<tr>
<td>Yield Stress (MPa)</td>
<td>23.5</td>
<td>23.2</td>
<td>23.2</td>
<td>ISO527-2:2012</td>
</tr>
<tr>
<td>Yield Strain (MPa)</td>
<td>10.2</td>
<td>10.4</td>
<td>10.6</td>
<td>ISO527-2:2012</td>
</tr>
</tbody>
</table>

Results show only small variations in properties of the rHDPE and vHDPE blended compounds, consistent with a slight reduction in performance typically observed between recycled and virgin HDPE materials.

Conclusions

These results indicate that there are no reasons that multilayer HDPE/EVOH structures could not be included in the recycling of HDPE packaging and that levels as high as 5% will have no significant impact on properties or performance of the recycled HDPE resins. Trial results show that at levels of 0.25% EVOH in recycled HDPE and virgin HDPE, the extrusion blow molding processing performance, overall migration for direct food contact and physical properties were all unaffected, compared to rHDPE alone. An audit of a bale of post-consumer HDPE bottles identified that only 0.42% was multilayer, the percentage increases to 2% multilayer of the colored HDPE fraction, into which most multilayer bottles would be sorted. Commercially only natural rHDPE is recycled back to food grade, and used primarily in the manufacture of new natural milk bottles. It is most likely that the current formats of multilayer bottles would be sorted into the colored fraction, which is not currently processed to food grade material. At measured levels of approximately 2%, the multilayer bottles would have no impact on the reprocessing of these colored materials. The multilayer EVOH bottle format is not specified in recycling surveys and published data. One Wrap survey indicated that there was no discernible quantity of HDPE recovered in the “on-the-go” bottle packaging market segment. However, products designed for out of home consumption such as drinkable yoghurt and breakfast products were the most common multilayer bottles found in the audit. It should be noted that in the UK, most public bins are not sorted or recycled, so packaging disposed of “away from home” and kerbside collection systems, is unlikely to be recovered for recycling. The compounding and blow molding trial utilized natural rHDPE, so that any effects from the presence of the post-industrial HDPE/EVOH blended material could be more easily seen if it occurred. In practice, multilayer HDPE bottles are all colored and would most often be sorted into the colored (jazz) fraction. Some MRFs leave white HDPE containers in the natural HDPE fraction to boost yields, and at low levels, this has a minimal impact on color or quality of the natural rHDPE. Tomra trials confirmed that bottles would be sorted as HDPE, or according to the label material, which can happen with bottles that have full body sleeves. Some multilayer products may be able to be differentiated by NIR sorting if a modified database was used. The test material with 0.25% EVOH was converted to bottles under standard conditions, indicating processing characteristics were unaffected. A few black specks were identified; however, these were not considered inherent to the test material and on occasion even appeared to be present in the virgin HDPE layer, indicating they may be from the bottle making process. Overall migration testing showed very low migration levels below 0.5mg/dm³ for all structures, including 100% monolayer blend material in direct contact with the simulant, compared to the specified limit of 10mg/dm³. With this low overall migration result, no discernible difference could be seen with different bottle structures. With a virgin HDPE inner layer or with an EVOH functional layer between the blend material and the simulant, migration results were not reduced further. Other than a slight reduction of physical properties that would be expected between virgin and recycled HDPE, testing showed good tensile and impact strength.

References

2. Rigid Food Packaging, BCC research Food and Beverage Report, FOD039C, July 2014.


7. RECOUP Plastics Packaging, Recyclability by Design, 2016, Pages 25-34.
