METHODS OF MANUFACTURING MULTI-LAYERED POLYMER COMPOSITES WITH HIGH OXYGEN BARRIER

Technical Field of the Invention

The present invention relates to methods of manufacturing multi-layered polymer composites. In particular, the present invention relates to methods of forming multi-layered polymer composites with high oxygen barrier properties for use in food packaging.

Background of the Invention

Packaging is fundamental when it comes to protecting food products from outside influence and damage, ensuring and maintaining high standards of quality and avoiding food waste. It is estimated that one third of food produced around the world, approximately two billion tonnes, is lost before it can be consumed.

Food packaging is even more relevant now as most of the world's population live in cities, where there are few options for independently growing food. To move food product to consumers down the supply chain, food suppliers often face the problem of spoilage through insufficient product life as well as from unexpected supply chain disruption. Further, in the event that supply exceeds demand, it is not always possible to balance these periods with higher demand and low supply seasons. In this regard, seasonal food products would be able to meet demand in other non-seasonal periods if such food products can be packaged and stored for a longer duration without deterioration of quality, flavour and freshness.

In this regard, packaging is used to improve the shelf-life of food products. In particular for food products, packaging is used to reduce the rate of food oxidation. Oxidation is a reaction that takes place when oxygen has access to products containing, for example, fat or pigments. If fats oxidise, they produce “off” odours and flavours (stale, rancid odours). If pigments oxidize, they can change colour completely. For example, red meat turns grey when the myoglobin pigment oxidizes and thus makes the meat unappealing to consumers. Nutrients and minerals such as vitamins can also be oxidized and lose their nutritional value.

A material that is commonly used as an oxygen barrier material is ethylene vinyl alcohol

(EVOH). EVOH is a copolymer of ethylene and vinyl alcohol. However, EVOH is moisture sensitive and cannot be used in direct contact with foods and liquids. Additionally, EVOH is not easy to process for use as a packaging material. For example, it is known that plastic materials with an EVOH layer experience 'retort shock', in which water can migrate into the EVOH layer during the sterilisation process, render it ineffective. To overcome this, polypropylene is used in varying thicknesses between the EVOH layer and the food product to protect the EVOH layer from moisture. However, this method is limited by the thickness of the polypropylene layer. Increasing the thickness of the polyproplylene layer can have adverse effects on clarity, weight and cost of the packaging.

Accordingly, it is generally desirable to overcome or ameliorate one or more of the above mentioned difficulties, or at least to provide a useful alternative.

Summary of the Invention

According to the present invention, there is provided a method of forming a multi-layered polymer composite, including:

a) blending a first ethylene vinyl alcohol copolymer (EVOH) component and a second EVOH component to form a mixed EVOH resin;

b) extruding the mixed EVOH resin as an EVOH layer; and

c) sandwiching the EVOH layer between inner and outer support layers;

wherein the second EVOH component includes an oxygen scavenger.

Advantageously, blending at least two different EVOH components, with one including an oxygen scavenger, allows for the formation of a multi-layered polymer composite with good oxygen barrier property and good clarity. Further, the presence of an oxygen scavenger allows for a thinner EVOH layer and accordingly a multi-layered polymer composite which is more versatile and packaging friendly.

Disclosed herein is a method of forming a multi-layered polymer composite, including:

a) blending a first ethylene vinyl alcohol copolymer (EVOH) component and a second EVOH component to form a mixed EVOH resin;

b) extruding the mixed EVOH resin as an EVOH layer; and

c) sandwiching the EVOH layer between inner and outer support layers;

wherein the first EVOH and the second EVOH each comprises solely ethylene and

vinyl alcohol monomeric units; and

wherein the second EVOH component includes an oxygen scavenger molecule;

wherein the first EVOH component is subjected to a drying process under predetermined conditions;

wherein the predetermined condition for the first EVOH component is drying until a dew point <= 0 °C.

In some embodiments, wherein the first EVOH component and the second EVOH component are blended under predetermined conditions.

In some embodiments, the first EVOH component and the second EVOH component are blended by gravimetric batch blending.

In some embodiments, the gravimetric batch blending is performed with a spherical mixer.

In some embodiments, the mole fraction of ethylene in the EVOH layer is less than about 50 mol%.

In some embodiments, the ratio of the first EVOH component to the second EVOH component is from about 1:99 to about 40:60.

In some embodiments, the first EVOH component is subjected to a drying process under predetermined conditions.

In some embodiments, the method further includes a step (d) of disposing inner and outer regrind layers between the EVOH layer and the inner and outer support layers respectively.

Advantageously, the regrind layers can act as an intermediary layer between the EVOH layer and support layers. The regrind layers can also act as an adhesive layer between the EVOH layer and the support layers, and accordingly prevents or reduces delamination. This helps to reduce the cost of the composite. Further, the regrind layers provide additional moisture barrier to the EVOH layer and can prevent or at least reduce retort shock.

In some embodiments, the method further includes a step (e) of disposing inner and outer adhesive layers between the EVOH layer and the inner and outer support layer respectively.

In some embodiments, the inner and outer adhesive layers are disposed between the EVOH layer and the inner and outer regrind layers respectively.

In some embodiments, the method further including a step of completely enveloping the multi-layered polymer composite in an aluminium protective case under vacuum.

Brief Description of the Drawings

Embodiments of the present invention are hereafter described, by way of non-limiting example only, with reference to the accompanying drawings in which:

Figure 1 is a cross sectional view of an embodiment of a multi-layered polymer composite;

Figure 2 is a cross sectional view of another embodiment of a multi-layered polymer composite;

Figure 3 is a cross sectional view of a further embodiment of a multi-layered polymer composite;

Figure 4 is a cross sectional view of a further embodiment of a multi-layered polymer composite; and

Figure 5 is a flow chart of an example of a method of producing a multi-layered polymer composite.

Detailed Description of Embodiments of the Invention

Disclosed herein are embodiments of a multi-layered polymer composite for providing oxygen barrier properties to food packaging.

For example, a multi-layered polymer composite 100 as shown in Figure 1 includes:

a) an ethylene vinyl alcohol copolymer (EVOH) layer (102); and

b) inner and outer support layers sandwiching the EVOH layer (104 and 106).

The mole fraction of ethylene in the EVOH layer is less than about 50 mol% for retarding oxygen transmission through the composite. The EVOH layer includes an oxygen scavenger. As will be described below, the oxygen scavenger is incorporated into the EVOH layer by blending at least two EVOH resins, one of which includes the oxygen scavenger. In this regard, the EVOH layer provides the oxygen barrier properties by reducing oxygen transmission through the composite and also removes oxygen adjacent to the composite by scavenging it.

EVOH copolymers are semicrystalline. The oxygen barrier property of EVOH copolymers can be attributed to their inherent high degree of crystallinity. Oxygen permeability becomes lower as the degree of crystallinity increases. The presence of large amounts of impermeable crystalline regions in polymers with a high degree of crystallinity reduces gas permeability by creating a more irregular tortuous diffusive path for penetrant molecules and by decreasing the volume of polymer available for oxygen to pass through. This crystallinity can be controlled by the mole fraction of ethylene in EVOH, and correspondingly the mole fraction of alcohol. In this regard, the size of the hydroxyl groups on the polymer chains is small enough relative to the space available in the crystal structure such that the symmetry of the polymer is not significantly affected. Significant cohesion between adjacent polymer chains allows for polymer molecules to aggregate together into a crystalline solid, with the hydroxyl groups in EVOH copolymers providing intermolecular and intramolecular forces and hence a cohesive energy. Accordingly, both intermolecular and intramolecular hydrogen bond strength decrease with an increase in ethylene content.

To sufficiently retard oxygen transmission through the composite, the mole fraction of ethylene in the EVOH layer should be less than about 50 mol%, or less than about 48 mol%, or less than about 44 mol%, or less than about 40 mol%, or less than about 38 mol%, or less than about 35 mol%, or less than about 32 mol%, or less than about 27 mol%, or less than about 24 mol%. The mole fraction of ethylene can be from about 15 mol% to about 45 mol%, about 20 mol% to about 40 mol%, about 25 mol% to about 35 mol%, or about 25 mol% to about 32 mol%.

To further improve the oxygen barrier property of the multi-layered polymer composite, an oxygen scavenger is added to the EVOH layer. An oxygen scavenger is a molecule or entity that can react or combine with oxygen to reduce or remove oxygen from the

atmosphere adjacent to it, or trapped in the package. In this regard, gaseous oxygen is removed or depleted from the immediate surrounding of the composite, and thus less oxygen is available that can transmit through the composite. This is further advantageous when used in food packaging. When the composite is used to protect food in a tight seal, the space enclosed by the composite can be depleted of oxygen by action of the oxygen scavenger, thus reducing oxidation of the food.

Examples of oxygen scavenger that can be used in the EVOH layer can be selected from the group consisting of compounds containing a dioxanyl moiety, iron compounds and salts, potassium sulphite, unsaturated hydrocarbons such as dienes, ascorbic acid derivatives, sulfites, bisulfites and phenolics. These moieties can be oxidized by molecular oxygen and can thus serve as an oxygen scavenger.

The thickness of the EVOH layer can be from about 20 μm to about 140 μm, or from about 30 μm to about 130 μm, from about 40 μm to about 130 μm, from about 50 μm to about 130 μm, from about 60 μm to about 130 μm, from about 70 μm to about 130 μm, from about 80 μm to about 130 μm, from about 90 μm to about 130 μm, from about 1000 μm to about 130 μm, from about 110 μm to about 130 μm, or from about 120 μm to about 130 μm.

The EVOH layer 102 is sandwiched by an inner and outer support layer 104 and 106 respectively. The support layers 104 and 106 can be in contact with the EVOH layer 102. The support layer provides some rigidity to the composite and allows for ease of handling. Further, the support layer protects the EVOH layer from moisture. In this regard, the support layer can be a hydrophilic polymer layer.

The inner and outer support layers 104 and 106 can be selected from the group consisting of polypropylene (PP), polyethylene (PE), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC). In some embodiments, the support layer is virgin PP. Virgin plastic is the resin produced directly from the petrochemical feed-stock, such as natural gas or crude oil, which has never been used or processed before.

Multi-layered polymer composite 200 includes:

a) an ethylene vinyl alcohol copolymer (EVOH) layer (202);

b) inner and outer support layers sandwiching the EVOH layer (204 and 206); and

c) inner and outer regrind layers disposed between the EVOH layer and the inner and outer support layer respectively (208 and 210).

Similar to composite 100, the mole fraction of ethylene in the EVOH layer is less than about 50 mol%.

Regrind is a material that has undergone at least one processing method such as molding or extrusion and consists of the subsequent sprue, runners, flash, or other rejected parts that are ground or chopped and reused. Regrinds are commonly known to have poorer physical and/or chemical properties due to the mechanical processing. For example, temperature or the heat history can cause polymer degradation.

The regrind layers can be derived from the support layers. Alternatively, the regrind layers can be derived from the multi-layered composite as disclosed herein.

To further strengthen the adhesion between the layers, mulit-layered polymer composite 300 can further include inner and outer adhesive layers (312 and 314) disposed between the EVOH layer and the inner and outer support layer respectively. The inner and outer adhesive layers can be sandwiched between the EVOH layer and the inner and outer regrind layers respectively. Alternatively, the adhesive layers can be sandwiched between the inner and outer regrind layers and the inner and outer support layers respectively. The adhesive layers can be applied between the EVOH layer and the inner and outer regrind layers, and can also applied between the inner and outer regrind layers and the inner and outer support layers.

The inner and outer adhesive layer may be selected from the group consisting of acid modified polyolefin, polyurethane and nylon. For example, modified PP with beta-(3,5-di-tert-butyl-4-hydroxyphenol) propionic acid octadecanol ester can be used.

The multi-layered polymer composite as disclosed herein can have a thickness from about 1100 μm to about 3000 μm. In other embodiments, the thickness is from about 1150 μm to about 2900 μm, from about 1200 μm to about 2800 μm, from about 1250 μm to about 2700 μm, from about 1300 μm to about 2600 μm, from about 1300 μm to about 2500 μm, from about 1300 μm to about 2000 μm, from about 1300 μm to about

1800 µm, or from about 1300 µm to about 1600 µm.

As mentioned above, the resultant multi-layered polymer composite made using the method disclosed herein has a good clarity. The multi-layered polymer composite can have a light transmittance of more than about 85%. Alternatively, the light transmittance can be more than about 86%, about 87%, about 88%, about 89%, about 90%, about 91%, about 92%, about 93%, about 94%, or about 95%. The haze of the polymer composite can also be measured. Haze is measured as the percentage of incident light scattered by more than 2.5° through the specimen. In some embodiments, the haze is less than about 15%, about 14%, about 13%, about 12%, about 11%, about 10%, about 9%, about 8%, about 7%, about 5%, about 4% or about 3%. Both the light transmittance and haze can, for example, be measured using a standardised method such as ASTM D1003 (Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics).

Embodiments of the present invention also relate to an oxygen impermeable kit, such as the kit 400 shown in Figure 4. Oxygen impermeable kit 400 includes:

a) the multi-layered polymer composite 402 as disclosed herein; and

b) an aluminium protective casing 404;

wherein the aluminium protective casing completely envelops the multi-layered polymer composite under vacuum.

The oxygen impermeable kit allows for longer term storage without degradation of the oxygen barrier function of the multi-layered composite. For example, the present embodiment is able to preserve the oxygen barrier function of the composite for at least 2 years under a temperature of about 15-25 $^{\circ}$C and humidity at about 35-65%. This reduces wastage and increases the shelf-life of the composite, allowing the composite to be manufactured and stored for some time until it is required.

The aluminium protective casing can be used with a plastic packaging formed using the multi-layered polymer composite. In this regard, the oxygen impermeable kit allows the formed plastic packaging to be stored (under vacuum conditions) at the food producer's location for some time until it is required.

The aluminium protective casing can be an aluminium bag. In other embodiments, the

aluminium protective casing is a bag with an aluminium metalized film coating of about 0.5 μm thick, a bag with an aluminium foil coating of about 6 μm thick, or a bag with an aluminium coating with a thickness between 0.5 μm and 6 μm. Depending on the requirements of the customer and the rate of usage of the multi-layered polymer composite in the aluminium protective casing, different types of protective casings can be selected. The size of the aluminium bag can also be selected to suit the usage.

Figure 5 shows an exemplary method 500 of forming a multi-layered polymer composite (514). The method may include:

a) blending 508 a first ethylene vinyl alcohol copolymer (EVOH) component 502 and a second EVOH component 504 to form a mixed EVOH resin;

b) extruding the mixed EVOH resin as an EVOH layer 102; and

c) sandwiching the EVOH layer between inner and outer support layers 104 and 106;

wherein the second EVOH component includes an oxygen scavenger.

The EVOH layer is formed from a mixture of at least two EVOH resin (502 and 504). The mixed EVOH resin can be extruded as a sheet or layer with a thickness from about 20 μm to about 140 μm (512). The support layers (510) can be co-extruded with the EVOH layer, and can be in contact with the EVOH layer. The support layers extend over two parallel surfaces of the EVOH layer to provide rigidity to the composite as well as protect the EVOH layer from moisture.

EVOH resins can be purchased from, for example, Kuraray as EVAL, Nippon Gohsei as Soarnol or Chang Chun Petrochemical as EVASIN. For example, EVAL T101B, EVAL L104B, EVAL L171B, EVAL F101B, EVAL F104B, EVAL F171B, EVAL H171B, EVAL E105B, EVAL E171B, EVAL E173B, EVAL C109B, EVAL G156B, Soarnol DC3203RB, DC3203B, BX6304B, BX6804B, BX7804B, SG1046B, BTR8002P, Soaresin RG500, Nichigo G Polymer BVE8049P, OKS-8077P, BTR8002P or a combination thereof can be used.

The mixed EVOH resin can be formed by blending at least two EVOH resins, wherein one of the EVOH resin includes an oxygen scavenger. The oxygen scavenger can be present as an entity separate from the EVOH polymer. In this regard, the oxygen scavenger can be a molecule, a compound, a complex or a macromolecule. Alternatively, the oxygen scavenger can be covalently bonded to a polymer. For

example, the oxygen scavenger can be incorporated into a polymer as a monomeric unit such that it forms part of the polymer backbone, or can be incorporated as a side chain attached to the polymer. The skilled person would understand and know of commonly used techniques to incorporate the oxygen scavenger into the EVOH resin. For example, melt mixing can be used.

Examples of oxygen scavengers and EVOH resins with oxygen scavengers are O2Block, ShelfPlus O2, Oxbar, MonOxbar, DiamondClear, Soarnol NC7003, EVAL AP931B, OS1000, Zero2, Amosorb 3000, CPTX312, Tri-SO2RB and Ageless.

Advantageously, mixing at least two EVOH components, with one including an oxygen scavenger, allows for the formation of a multi-layered polymer composite with both a good oxygen barrier property and good clarity. Further, the presence of an oxygen scavenger allows for a thinner EVOH layer and accordingly a multi-layered polymer composite which is more versatile and packaging friendly.

Step (a) can include blending a first EVOH component (502) and a second EVOH component (504) under predetermined conditions to form a mixed EVOH resin for extruding as an EVOH layer. The predetermined conditions can be using gravimetric batch blending with spherical mixer controlled by PLC at room temperature.

The first component can be EVOH with a mole fraction of ethylene of less than about 50 mol%. The second component can be EVOH with a mole fraction of ethylene of at least 24 mol% and an oxygen scavenger.

The ratio of the first component to the second component is from about 0:100 to about 40:60, or from about 1:99 to about 40:60. In a preferred embodiment, the ratio is about 40:60.

Because EVOH resin can be added in at least two components, each of the components can be separately processed without adversely impacting the other before blending (508). In this regard, the first EVOH component can be subjected to a drying process under predetermined conditions (506). The drying process further removed excess moisture from the resin and 'activates' the OH groups. The drying process may not be required for the second component if, for example, it has an oxygen scavenger. In this

case, the oxygen scavenger may react adversely with the heat such that it loses its function. By selectively and separately processing the resin components, the processibility of the composite is improved by allowing for better reproducibility and consistency in the manufacturing of the composite; i.e. regardless of environmental conditions.

For example, the predetermined condition for the first EVOH component can be drying at 80 °C for at least 4 hours or until dew point <= 0 °C.

The rate and extent to which crystallization of the EVOH layer occurs is also controlled by the physical conditions (temperature, time, strain), quenching rate, orientation and/or aging under which crystallization occurs. EVOH has an extremely rapid crystallization rate compared to other thermoplastic polymers which can cause difficulties in controlling the degree of crystallinity during cooling of the polymer from the molten state. Further, when at least two components are used and well blended, the components may phase separate when a slow extrusion is performed.

The extrusion of the EVOH layer can be optimised by using a screw extrusion process (512). The EVOH component(s) is gradually melted by the mechanical energy generated by turning screws and by heaters arranged along the extrusion barrel, after which the molten EVOH is forced into a die. In this regard, by controlling the rate of extrusion and the length of the screw, the EVOH layer can be extruded without phase separation of the components and with good control of the crystallisation. Further, extrusion through a layer control feed block can maintain the layer profile as desired and prevent separation of layers.

The method can further include a step (d) of disposing inner and outer regrind layers between the EVOH layer and the inner and outer support layers 208 and 210 respectively.

The regrind layer (516) is can be positioned such that it is in contact with the EVOH layer as well as the support layer. The regrind layer can also be subjected to a further drying process (518), for removing moisture. The adhesive property of the regrind layer can also be improved. By processing the regrind layer as mentioned above, a good clarity can be obtained for the final multi-layer polymer composite and without defects.

The method can further include a step (e) of disposing inner and outer adhesive layers (520) between the EVOH layer and the inner and outer support layer respectively. As mentioned above, the adhesive layers act to prevent delamination of the composite layers. Accordingly, adhesive layer is in contact with the adjacent layers. The inner and outer adhesive layers can be disposed between the EVOH layer and the inner and outer regrind layers respectively. Alternatively, the inner and outer adhesive layers can be disposed between the inner and outer support layers and the inner and outer regrind layers respectively.

The method can further include a step (f) of completely enveloping the multi-layered polymer composite 514 after co-extrusion 512 in an aluminium protective case (522) to form an oxygen impermeable kit 528. When enveloped in this way, the multi-layered polymer composite can be subjected to a vacuum and can be maintained in this state for a prolonged period of time. This allows for long term storage at the manufacturers' end. Alternatively, the packaging product 526 can be formed using the multi-layer polymer composite 514, following which it is completely enveloped in the aluminium protective case 524 to form an oxygen impermeable kit 530. This allows for long term storage at the customer's end.

Many modifications will be apparent to those skilled in the art without departing from the scope of the present invention.

In this specification and the claims that follow, unless stated otherwise, the word "comprise" and its variations, such as "comprises" and "comprising", imply the inclusion of a stated integer, step, or group of integers or steps, but not the exclusion of any other integer or step or group of integers or steps.

References in this specification to any prior publication, information derived from any said prior publication, or any known matter are not and should not be taken as an acknowledgement, admission or suggestion that said prior publication, or any information derived from this prior publication or known matter forms part of the common general knowledge in the field of endeavour to which the specification relates.

Claims Defining the Invention

1. A method of forming a multi-layered polymer composite, including:

a) blending a first ethylene vinyl alcohol copolymer (EVOH) component and a second EVOH component to form a mixed EVOH resin;

b) extruding the mixed EVOH resin as an EVOH layer; and

c) sandwiching the EVOH layer between inner and outer support layers;

wherein the first EVOH and the second EVOH each comprises solely ethylene and vinyl alcohol monomeric units; and

wherein the second EVOH component includes an oxygen scavenger small molecule;

wherein the first EVOH component is subjected to a drying process under predetermined conditions;

wherein the predetermined condition for the first EVOH component is drying until a dew point <= 0 °C.

2. The method of claim 1, wherein the first EVOH component and the second EVOH component are blended under predetermined conditions.

3. The method of claim 1 or 2, wherein the first EVOH component and the second EVOH component are blended by gravimetric batch blending.

4. The method of claim 3, wherein the gravimetric batch blending is performed with a spherical mixer.

5. The method according to any one of claims 1 to 4, wherein the mole fraction of ethylene in the EVOH layer is less than 50 mol%.

6. The method according to any one of claims 1 to 5, wherein the ratio of the first EVOH component to the second EVOH component is from 1:99 to 40:60.

7. The method according to any one of claims 1 to 6, further including a step (d) of disposing inner and outer regrind layers between the EVOH layer and the inner and outer support layers respectively.

8. The method according to any one of claims 1 to 7, further including a step (e) of disposing inner and outer adhesive layers between the EVOH layer and the inner and outer support layer respectively.

9. The method of claim 8, wherein the inner and outer adhesive layers are disposed between the EVOH layer and the inner and outer regrind layers respectively.

10. The method according to any of claims 1 to 9, further including a step of completely enveloping the multi-layered polymer composite in an aluminium protective case under vacuum.

11. The method according to any one of claims 1 to 10, wherein the oxygen scavenger molecule is selected from a group consisting of a compound containing a dioxanyl moiety, iron compound and salt, potassium sulphite, unsaturated hydrocarbon such as diene, ascorbic acid derivative, sulfite, bisulfite and phenolic.

12. The method according to any one of claims 1 to 11, wherein the predetermined condition for the first EVOH component is drying at 80 $^{\circ}$C for at least 4 hours.