

Extension of fresh Asian noodles at ambient shelf-life using high barrier multi-layered, nanocomposite-fortified retortable trays

Description

1 Field of the Invention

This Invention relates to use of multi-layered, nanocomposite-fortified retortable trays to pack fresh Asian noodles. These trays have high oxygen and moisture barrier properties as well as high structural integrity properties such that after being submitted through the retorting process, the fresh Asian noodles will have an extended shelf life at ambient temperature.

2. Description of the Related Art

In general, the shelf life of retort food mainly depends on diffusion of oxygen through the package both during retorting process and during storage. The current shelf life of food in the retortable trays stored at room temperature is about 6 months, which is far shorter than that of canned food.

Retortable trays with high barrier properties are currently made from thermoforming of multi-layer materials produced by coextrusion, for example, polypropylene (PP) with ethylene vinyl alcohol (EVOH), and amorphous polyethylene terephthalate (APET) with crystallized polyethylene terephthalate (CPET).

The following are patents relating to the developments of barrier materials, retortable and barrier packages, and polymer nanocomposites:

US Patent 4,578,295 (1986): A polyester based intimate fusion blend composition comprising an admixture of a poly(ethylene terephthalate) and a copolyester of isophthalic and terephthalic acid, ethylene glycol and 1,3 bis(2-hydroxyethoxy)benzene was disclosed by Jabarin (Ohio, USA). The invented material was claimed to be suitable for producing container parison, hollow containers, sheet stock, and film due to high gas barrier properties, mechanical strength, and processability.

US Patent 4,588,648 (1986): A coextruded plastic film comprising a polypropylene layer adhered to a layer of a nylon-type polyamide was developed by Krueger and Odorzynski (Connecticut, USA). A blend of a graft copolymer of maleic anhydride onto an olefin polymer or copolymer and an ungrafted propylene-based polymer was an excellent adhesive for coextrusion of nylon and polypropylene. For coextrusion of a 5-layer film, the structure included five layers of, in sequential order in the structural layering, from outside surface to the other: polypropylene, adhesive blend, EVOH, and nylon.

US Patent 4,617,240 (1986): Krueger and Odorzynski (Connecticut, USA) developed a coextruded plastic film comprising an adhesive layer between polypropylene and nylon layers. The adhesive layer comprised a blend of polypropylene and a graft copolymer of maleic anhydride onto a polypropylene backbone. The graft copolymer was produced in a reaction carried out at a temperature of about 80 °C up to about 10 °C below the melting point of the polypropylene. Similar work was also developed by Krueger and Odorzynski (Connecticut, USA).

US Patent 4,640,852 (1987): A multiple layer sheet structure with oriented layers of nylon and EVOH was developed by Ossian (Connecticut, USA). Additional layers may or may not be included or oriented. After retorting process, the structure showed improved impact resistance over similar structures not having oriented nylon and EVOH layers. Retort processed pouches made from the developed packaging structures showed improved stress crack resistance when dropped onto a hard surface.

US Patent 4,880,706 (1989): Mazuera, G. E. Wagner (New York, USA) developed films having a core of ethylene-vinyl alcohol copolymer (EVOH) sandwiched between polyolefin, e.g. polypropylene were coextruded so that the polyolefin also encapsulated the EVOH layer on the side edges. The films which could contain adhesive layers were oriented greater in the transverse direction to give excellent oxygen and moisture barrier properties.

US Patent 4,927,677 (1990): Kesai (Kanagawa, Japan) developed composite materials for retort containers comprising a biaxially stretched film of a copolymer of vinylidene chloride and an acrylic ester and a polypropylene film formed on one or both sides of the biaxially stretched film. On the polypropylene film could be further formed a talc-blended or odorless polypropylene film directly or on another polypropylene film. Top materials for the containers comprised a biaxially stretched film of the vinylidene-acrylic ester copolymer, a sequential biaxially stretched film of nylon 6 formed on one side of the biaxially stretched film, and a heatsealable heat-resistant plastic film formed on the other side.

US Patent 5,066,443 (1991): Cloeren (Texas, USA) invented a process for coextruding a laminate containing more than one barrier layer. The process overcame the interfacial instability associated with thinning and spreading a composite stream containing a barrier layer of EVOH.

US Patent 5,069,946 (1991): Moritani and co-workers (Kurashiki, Japan) developed a gas barrier multilayered packaging materials for retort sterilization. They developed a structure that contained an outer layer of a composition comprising 55-97 wt% EVOH and 45-3 wt% resin (polyamide, polyolefin, polyester, or polycarbonate) and an inner layer comprising a hydrophobic thermoplastic resin having low moisture permeability. A gas-barrier multilayered packaging material was also developed by containing an outer layer comprising a resin layer having a moisture permeability (measured at 40°C, 90% RH) of at least 40 g/m² day, an intermediate layer of a composition comprising 55-97

wt% EVOH and 45-3 wt% resin (polyamide, polyolefin, polyester, or polycarbonate) and inner layer comprising a hydrophobic thermoplastic resin layer with a moisture permeability lower than of the outer layer.

US Patent 5,281,360 (1994): Hong and co-workers (Illinois, USA) developed polymer blends, such as aromatic condensation polymers including formable polyesters and polycarbonates with an oxygen barrier material such as aromatic or aliphatic nylon, an amorphous nylon or EVOH, which had been oriented and contained a transition metal catalyst. The developed polymer blends had improved barrier properties and oxygen absorption properties.

US Patent 5,393,832 (1995): Moulies and co-workers (Puteaux, France) invented polymer alloys that were able to facilely be shaped into gas barrier, crack-resistant packaging materials, e.g., by thermoforming. The developed polymer alloys comprised an ethylene-vinyl alcohol copolymer matrix, a polypropylene dispersed phase and a phase-compatibilizing agent (α -monoolefin graft copolymer).

US Patent 5,770,301 (1998): Murai and Miyake (Osaka, Japan) developed a film containing at least one side of a polyester or other base film covered with an inorganic layer composed of a silicon oxide or the like and a coating layer comprising a silane coupling agent and a barrier resin (e.g. vinylidene chloride-based copolymer, ethylene-vinyl alcohol copolymer) to provide a barrier composite film. The amount of the silane coupling agent was about 0.05 to 10 parts by weight relative to 100 parts by weight of the barrier resin. A heat-sealing layer was optionally formed on the surface of the barrier resin coating layer or on the other side of the base film. Such barrier composite film had excellent transparency and retained high barrier properties and adhesive properties of covering layer despite its thin covering layer.

US Patent 5,830,545 (1998): A high barrier, multilayer laminate for forming packages containing oxygen sensitive products was developed by Frisk (Pully, Switzerland). The laminate material comprised a first layer of biaxially oriented polyethylene terephthalate, a second layer of a high barrier oxide material disposed exterior to the first layer, and a third layer of an adhesive material disposed interior to the first coextruded multilayer material. The fourth coextruded multilayer material comprised from exterior to interior: i) a first layer of a polyethylene material, ii) an oxygen scavenging layer comprising a polyethylene and an oxygen scavenger material, wherein the oxygen scavenging layer was disposed interior to the first layer of the polyethylene material, and iii) a second layer of the polyethylene material disposed interior to the oxygen scavenging layer. The laminate structure comprised a first layer of biaxially oriented polyethylene terephthalate, biaxially oriented polyamide, or biaxially oriented polypropylene, a second layer of a high barrier oxide material disposed interior to the first layer, and a third layer of an adhesive material disposed interior to the second layer and joining the second layer to a fourth layer of a polyethylene material. The third layer of adhesive material contained an oxygen scavenger material.

US Patent 5,876,812 (1999): Frisk and Laurent (Pully, Switzerland) developed a high gas barrier container consisting a layer composed of a polymer material integrated with

nanoparticles of a clay mineral (0.1- 10 wt%) to enhance the barrier properties of the container. The polymer material may be polyethylene terephthalate (PET), a copolymer of polyethylene terephthalate (COPET), or its mixture. The developed nanocomposite container showed reduction of gas permeability. The nanocomposite polymer container could be produced using in situ polymerization, solution intercalation, or melt exfoliation to integrate the clay mineral with the polymer material matrix. The clay minerals included smectite, vermiculite, or halloysite, with a preference for the montmorillonite species of smectite clays.

European Patent 0,932,497 (1999): Frisk and Laurent (Switzerland) developed a transparent multilayer structure which was disclosed such as a flexible self-supporting container for a flowable food product such as fruit juice. The developed multilayer material possessed superior barrier properties (oxygen, water vapor and aromatic gases). The multilayer structure could include an outer layer having a metal oxide deposition laminated to an interior layer through use of an adhesive. The exterior layer could be composed of a polymer material incorporated with a nanoclay (0.1-10 wt%). The polymer material included polyamide, polyethylene terephthalate, copolymers of polyethylene terephthalate, and any of its mixtures.

US Patent 6,071,626 (2000): A high barrier, multilayer laminate was developed by Frisk (Pully, Switzerland). The laminate was suitable for forming packages that contained oxygen sensitive products. The laminate material had a coextruded multilayer material that included, from exterior to interior, i) an outside sealing and decorative layer, ii) a light barrier layer including an adhesive disposed interior to the outside sealing and decorative layer, iii) a barrier polymer layer disposed interior to the light barrier layer, iv) an oxygen scavenger layer including an adhesive disposed interior to the barrier polymer layer, and v) an inside sealing layer disposed interior to the oxygen scavenger layer. The further laminate included a first layer of linear low density polyethylene, a carbon black layer including an adhesive disposed interior to the first layer of linear low density polyethylene; a layer of EVOH disposed interior to the carbon black layer, an oxygen scavenger layer including an adhesive disposed interior to the EVOH layer, and a second layer of linear low density polyethylene disposed interior to the scavenger layer.

US Patent 6,376,591 (2002): Lan and co-workers (Illinois, USA) developed a polyamide-clay nanocomposite, products produced from the nanocomposite, and a process for preparing a polyamide-clay nanocomposite. The polyamide-clay nanocomposite comprised (a) an amorphous matrix polyamide containing (i) a residue of a dicarboxylic acid component comprising at least two diacids and (ii) a residue of a diamine component, and (b) a layered clay material, which was dispersed in the matrix polyamide.

US Patent 6,653,388 (2003): Barbee and co-workers (South Carolina, USA) developed a polymer-clay nanocomposite comprising a melt-processible matrix polymer and a mixture of at least two layered clay materials. The invention also involved articles produced from a nanocomposite and a process for preparing a nanocomposite.

European Patent 1,286,825 (2003): Robert and Chad (France) developed containers for flowable products having improved barrier and/or mechanical properties with at least one layer of the containers comprised a polymeric nanocomposite comprising a polymer and nanosize particles of a modified clay, and methods of making the containers.

US Patent 6,677,013 (2004): Curie and co-workers (Rueil Malmaison, France) developed a multilayer plastic container comprised a layer of a polypropylene and a layer of EVOH directly adjacent the layer of polypropylene with at least one of the polypropylene and EVOH layers comprised an adhesive such as maleic anhydride concentrate mixed therein to adhere the layer of polypropylene to the layer of EVOH.

US Patent 6,793,994 (2004): Tsai and Akkapeddi (New Jersey, USA) developed oxygen barrier polymer compositions exhibiting high oxygen scavenging capability suitable for extended shelflife, packaging applications. These polymer compositions comprised at least one ethylene vinyl alcohol copolymer, at least one oxidizable polydiene, and at least one metal salt catalyst. The polymer products were particularly suited for making barrier packaging articles such as monolayer or multi-layer films, sheets, tubes, pipes, thermoformed containers and coinjection/coextrusion blow molded bottles comprising PET, polyolefin or polycarbonate as structural layers.

European Patent 1,484,176 (2004): Grah and Ahlagren (USA) developed a film comprised 3 layers. The first layer comprised vinylidene chloride polymer, the second layer comprised a dispersion of tie polymer and nanoparticles, and the third layer comprised thermoplastic polymer. The second layer was between and directly adhered to both the first and third layers. The film possessed improved interlayer bond strength between the layers at the elevated temperatures during cook-in, retort, and pasteurization.

US Patent 6,841,618 (2005): Masuda (Kurashiki, Japan) developed a thermoplastic polymer composition which was obtained through dynamic vulcanization performed by mixing an ethylene-vinyl alcohol copolymer (I), a modified block copolymer (II) which comprised an aromatic vinyl polymer block and a conjugated diene polymer block and which had a functional group consisting of a carboxyl group and/or its derivative, and an amine crosslinking agent (III). The thermoplastic polymer composition was excellent in both barrier properties to gases, organic liquids and the like and flexibility.

US Patent 6,906,127 (2005): Liang and co-workers (Illinois, USA) developed nylonintercalated (concentrate nylon), layered silicates, in concentrated form, containing at least 6% to about 40% by weight layered silicate, preferably about 8% to about 30% by weight layered silicate, intercalated with a nylon that was polymerized while in contact with the clay, during ring-opening polymerization of the nylon reactants (monomers) and melt processing.

US Patent 6,964,816 (2005): Schell and co-workers (Wisconsin, USA) developed multilayer thermoformable structures for packaging film applications. The multilayer structures having at least a first layer of polyester, a second layer of a first adhesive and a third layer of a nylon blend formed into a flexible non-oriented film by coextrusion.

US Patent 20,060,165,927 (2006): Harano and co-workers (Japan) developed a retort pouch which was made from a metal laminated film having the multilayer structure of a crystalline polypropylene resin film/an adhesive resin layer including a modified polypropylene/a metal foil/an adhesive layer/an oriented nylon film/an adhesive layer/a polyester film.

US Patent 7,084,199 (2006): Chou and co-workers (Michigan, USA) developed a polypropylene nanocomposite composition having at least the following two elements. The first element was a maleated polypropylene polymer having a weight average molecular weight greater than 100,000. The second element was a cation exchanging layered silicate material dispersed in the maleated polypropylene.

US Patent 7,138,452 (2006): Kim and co-workers (Republic of Korea) developed a nanocomposite blend composition having superior barrier properties, and more particularly to a nanocomposite blend composition comprising a polyolefin resin; one or more nanocomposites having barrier properties, selected from an ethylene-vinyl alcohol (EVOH)/intercalated clay nanocomposite, a polyamide/intercalated clay nanocomposite, an ionomer/intercalated clay nanocomposite, and a polyvinyl alcohol (PVA)/intercalated clay nanocomposite; and a compatibilizer. This nanocomposite blend composition had (i) superior mechanical strength, (ii) superior barrier properties to oxygen, organic solvent, and moisture, (iii) superior chemical barrier properties. This nanocomposite blend was applicable to single/multi-layer blow molding and film processing.

3. Summary of the Invention

The Invention involves packing fresh Asian noodles in multi-layered, nanocomposite-fortified retortable trays that have high oxygen and moisture barrier properties, so as to extend the ambient shelf life of these fresh noodles.

The fresh Asian noodles can be broadly divided into 2 categories: wheat-based (yellow) noodles and rice-based (white) noodles.

4. Detailed description of the Invention

Currently, fresh Asian noodles such as the wheat-based (yellow) noodles and rice-based (white) noodles have a shelf life of only 3 days. Thus, noodle manufacturers have to produce and deliver their fresh noodles to their customers daily. As a result, these noodle manufacturers incur heavy logistics cost. Moreover, these manufacturers are unable to export their products thereby limiting their growth potential.

As described in section 2 above, food packed using commercially available retortable trays has a shelf life of only 6 months. High oxygen and moisture barrier materials,

though available, are too expensive to be used in the production of retortable food tray for low-value items such as fresh noodles.

This Invention relates to using a new multi-layered, nanocomposite-fortified retortable tray that have high oxygen and moisture barrier properties, as well as strong mechanical properties that enable such trays to withstand the retorting process. By packing fresh noodles in such trays and subsequently treating these packages using the retorting process, the ambient shelf life of packaged fresh noodles can be extended potentially beyond 6 months.

The multi-layered, nanocomposite-fortified retortable trays are developed from individual layers of neat polymers and polymer nanocomposites produced via a melt mixing masterbatch process with the use of suitable compatibilizers. The nanocomposite layer is based on homogeneously dispersed nanomaterials including nanoclay and silicon dioxide into a polymer using an extrusion process.

The presence of nanocomposites is expected to improve barrier (oxygen and moisture), mechanical (tensile), and thermal (glass-transition and melting temperatures) properties, while the presence of other active compounds will act to enhance the functionality of the retortable trays. Layers of the polymers and nanocomposites will be combined together using a food grade adhesive to form a multi-layer sheet and then thermoformed to produce a tray.

Four types of polymers, in combination and/or individually, are used. They include polypropylene (PP), nylon 6 (Ny), polyethylene terephthalate (PET), and ethylene vinyl alcohol (EVOH). These are commodity polymers usually used for packaging applications. The multi-layers are then formed into trays via a thermoforming process. The trays are sealed with an oxygen and moisture impermeable film.

Addition of a small quantity of a nanocomposite barrier such as nanoclay or silicon dioxide into a low-cost matrix material can lead to a low-cost product with greatly improved oxygen and moisture barrier properties, strength, and heat resistance. Because of the large surface area of nanoparticles, it takes only a small quantity of nanomaterials to obtain a high concentration of constrained areas within the polymer. The increase in barrier properties are a result of the disruption of oxygen and water diffusion paths by the presence of nanomaterials. The presence of nanomaterials can also improve the structural integrity of trays when the trays are exposed to retorting conditions of temperatures of 105°C–135°C and pressures of 30–40 psig, under high humidity, as well as during handling at the manufacturing stage or at storage.

The description of the invention set forth herein is illustrative, and is not intended to limit the scope of the invention as set forth in the above claims.

Claims

What are claimed are:

1. Asia's first multi-layered nanocomposite-fortified packaging for fresh Asian noodles comprising:
 - a. a multi-layered tray developed from combining nanocomposite-fortified polymers and polymer layers, such as polypropylene (PP), nylon 6 (Ny), polyethylene terephthate (PET), and ethylene vinyl alcohol (EVOH), to form a high oxygen and water barrier material; and
 - b. thermoforming the multi-layered nanocomposite-fortified polymer into trays; and
 - c. sealed using an oxygen and moisture impermeable film.
2. The multi-layered nanocomposite-fortified tray recited in claim 1 has strong mechanical properties with high structural integrity that is able to withstand the retorting process.
3. The multi-layered nanocomposite-fortified tray recited in claim 1 enables its contents, i.e. the fresh Asian noodles, to have an extended shelf life, after being treated with the retorting process.
4. The multi-layered nanocomposite-fortified tray recited in claim 1 has high oxygen and moisture barrier properties.