Abstract: A flexible packaging film is provided that exhibits a high level of internal stress distribution where all layers combine to dissipate and distribute stress internally to provide improved scratch and puncture resistance. The flexible packaging film is a multi-layer film that is configured to retain its integrity and distribute stress over a large area where all layers within the film laminate react in a similar manner to stress. The film comprises: an outer layer of a peelable sealant layer containing organoclay for forming a heat seal; a lower base layer including a metalized polymer with a metal applied to at least one surface of a polymer layer; a co-extruded tie layer between the outer layer and the lower base layer, the co-extruded tie layer including one or more layers of polyethylene-ene and one or more layers of ethylene acrylic acid; the ethylene acrylic acid bonded to the metal of the metalized polymer in the lower base layer; and a thickness ratio of the polyethylene to the ethylene acrylic acid from 1 to 5.
PACKAGING FILM CONFIGURED FOR STRESS DISTRIBUTION

REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 61/608,730, filed March 9, 2012, which is incorporated herein in its entirety.

FIELD

[0002] The field of this disclosure generally relates to packaging films and, more particularly, to multi-layer packaging films capable of distributing stress therewithin to provide improved puncture and scratch resistance.

BACKGROUND

[0003] Multi-layer flexible or polymer films are often used in food packaging and other applications such as agriculture, pharmaceutical, and electronic packaging to suggest but a few application. Production of multi-layer films generally necessitates some form of lamination to adhere the multiple layers together. A common approach to forming a multi-layer film, such as a 2-ply or two layer film, is through adhesive lamination, whereby two films of differing film materials are adhesively bonded through tie layers to form a final product. In this approach, the adhesive is first directly applied or deposited to a base layer, which is then brought into contact with a second layer to form a two-ply film. The adhesive is then cured or dried to bond the two layers together. Often, the cured adhesive in this structure tends to be relatively stiff or brittle in the context of a flexible film. By one approach, conventional two-ply flexible packaging films often rely on a two-component adhesive system based on an isocyanate-terminated polyester urethane adhesive that provides a strong bond between a metalized polymer and a polyolefin sealant films commonly used in packaging application. Such adhesives tend to require a lengthy cure time from 3 to 5 days at 70°F in order to form desired properties.

[0004] Packaging films often require a balance of many different properties, such as strength, ductility, puncture resistance, toughness, abrasion resistance, clarity, barrier properties, anti-microbial capabilities, and cost to name but a few. A concern with many packaging users is being able to maintain structural integrity during field use in order to minimize product loss caused by film puncture or failure. In general, desired packaging films
need to have a high degree of structural integrity during filling, shipping, and handling stages of a product cycle in order to maintain sterility, freshness, product appearance, and/or other desired product attributes. One concern is film puncture failure that results in a loss of barrier properties, package integrity, and/or pressure changes in the cavity of the package. The ability of a packaging film to achieve such characteristics depends on many factors, such as the specific layers in the film and the composition of those layers to suggest a few,

SUMMARY

[0005] In one approach, a packaging film is provided having improved puncture resistance. The film includes an outer layer including a monoweb organoclay peelable sealant for forming a heat seal, a lower base layer including a metalized polymer with a metal applied to at least one surface of a polymer layer, and a co-extruded tie layer between the outer layer and the lower base layer. The co-extruded tie layer includes one or more layers of polyethylene and one or more layers of ethylene acrylic acid. In some approaches, the ethylene acrylic acid is bonded to the metal of the metalized polymer in the lower base layer. In other approaches, the film has a certain thickness ratio of the polyethylene to the ethylene acrylic acid such that the packaging film is configured to deform and dissipate stress as a single unitary structure upon a deformation force being applied to an outer or an inner surface of the packaging film.

[0006] In other approaches, the co-extruded tie layer of the packaging film includes two layers of polyethylene and one layer of ethylene acrylic acid. The tie layer may have a total thickness of about 5 to about 30 microns (in some approaches, about 5 to 25 microns, and in other approaches, about 5 to about 20 microns) and, in the total thickness, a thickness of the ethylene acrylic acid (EAA) may be about 1 to about 40 percent of the total thickness of the tie layer (in other approaches, about 5 to about 40 percent, in yet other approaches, about 1 to about 5 percent).

[0007] The metalized polymer of the outer layer may include a metal applied to or deposited on a polyester film or material. In addition, the co-extruded tie layer may be extrusion laminated between the outer layer and the base layer. As discussed further herein, it is unexpectedly been discovered that use of extrusion lamination combined with the particular composition of the tie layer, outer layer, and base layer provides an improvement in stress distribution over other forms of adhesive applications and films. In some approaches, the
polyethylene is a low density polyethylene having a density from about 0.9 to about 0.93 g/cc, and the ethylene acrylic acid includes about 3 to about 20 percent of the acrylic acid.

[0008] In some approaches, the outer layer includes a first layer having about 3 to about 35 percent of an inorganic filler (in other approaches, about 3 to about 15 percent), about 5 to about 25 percent of maleic anhydride grafted linear low density polyethylene (in some approaches, about 10 to about 20 percent), and about 50 to about 95 percent ethylene vinyl acetate (in some approaches, about 65 to about 95 percent) having about 4 to about 12 percent vinyl acetate content (in some approaches, about 5 to about 7 percent). The inorganic filler may be micro- or nano-sized organically modified montmorillonite. In some approaches, the inorganic filler may be blends of organically modified clay and other inorganic fillers. The outer layer may also include a second layer of neat polyethylene where the second layer of neat polyethylene is bonded to the polyethylene in the tie layer.

[0009] In another approach, a method of extrusion laminating a packaging film having improved puncture resistance is provided. The method includes first providing an outer layer of a monoweb organoclay sealant for forming a heat seal to a nip of an extrusion lamination die. At the same time or substantially simultaneously, providing a lower base layer including a metalized polymer with a metal applied to at least one surface of a polymer layer to the nip of the extrusion lamination die. Next, co-extruding at the nip between the outer layer and the lower base layer a tie layer including one or more layers of polyethylene and one or more layers of ethylene acrylic acid. The ethylene acrylic acid is extruded to be bonded to the metal of the metalized polymer in the lower base layer. During extrusion, a thickness ratio of the polyethylene to the ethylene acrylic acid forms about 1:1 to about 5:1 such that the packaging film is configured to deform as a single unitary structure upon a deformation stress applied to an outer surface of the packaging film. The method may optionally include any of the additional features as described above with the packaging film.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0010] FIG. 1 is a cross-sectional view of an exemplary film;

[0011] FIG. 2 is a schematic of an extrusion lamination process;

[0012] FIG. 3 is another cross-sectional view of an exemplary film;
FIG. 4 is an image of an isolated scratch path in an exemplary film;

FIG. 5 is a schematic of a sectioning procedure for film cross-sectional imaging;

FIGS. 6-12 are microscopy analysis slides; and

FIGS. 13-20 are further microscopy analysis slides.

DETAILED DESCRIPTION

A flexible packaging film is provided that exhibits a high level of internal stress distribution where all layers of the film combine to dissipate and distribute stress internally to provide improved scratch and puncture resistance. The packaging film has a construction effective to distribute stress independent of whether a stress or force (such as a scratch or puncture) is imparted on the inside or outside of the film. The flexible packaging film is a multi-layer film that is configured to retain its integrity and distribute stress, whether impacted from an inside or outside of the package, over a large area where all layers within the film laminate react in a similar manner to stress. In one aspect, the flexible packaging film is a two-ply laminate film where one layer or one side is a polyolefin sealant mono-web suitable for forming a peelable heat seal or other peelable heat bond. The other layer or base layer forming the other side may be a metalized polymer layer or, in some approaches, a biaxially oriented polypropylene. A tie layer bonds the sealant layer to the base layer or metalized polymer layer. In this approach, the flexible packaging film employs a coextruded polyolefin and polyolefin acrylic acid extrusion lamination adhesive as the tie layer to bond the outer sealant layer to the metalized polymer layer. In another aspect, the polyolefin and EAA tie layer provides a softer internal structure that is effective to not only provide a strong bond between the two outer layers, but also permits the film to deform as a single unitary structure such that the web is capable of absorbing a high level of internal stress distribution to increase the puncture resistance of the film.

To the figures, FIG. 1 shows one exemplary film structure 10 of the present disclosure. In this approach, film 10 includes an outer sealant layer 12, which may be a polyolefin film, capable of forming peelable heat seals and other peelable heat-type bonds. Layer 14 in this approach may be an intermediate or tie layer of one or more coextruded polyolefin layers and one or more ethylene acrylic acid (EAA) layers. Lower or base layer 16 in
one approach may be a metalized polyethylene terephthalate (PET) generally having a metalized layer 17a and a PET layer 17b. Lower or base layer 16 may also be biaxially oriented polypropylene. The metalized layer 17a is on an inner surface of the layer 16 generally adjacent the tie layer 14.

[0019] The film 10 is, by one approach, formed using an extrusion lamination process where the tie layer 14 is extruded between the outer layer 12 and the base layer 16 in an extrusion laminator 18, such as that shown in FIG. 2. By one approach, the extrusion laminator 18 deposits melted or molten adhesive or a melt flow of adhesive from one or more extrusion dies 19 into a nip 21 or to an area between the layers 12 and 16 in a continuous process. The resultant laminate 20 formed at the nip is squeezed and/or contacted with a pressure roll 22 and then cooled via a chill roll 24 to form the packaging film 10. The film can be formed at speeds from about 200 to about 1000 ft/min, but other speeds may be used as needed for a particular application.

[0020] FIG. 3 shows another approach of an exemplary film structure 100 where the polyolefin sealant layer 12 is a multi-layer monoweb and the tie layer 14 is a three layer co-extruded film combined together with the metalized PET 16. Each of these layers will be discussed in detail.

[0021] The multi-layer monoweb 12. Starting from top to bottom, the multi-layer monoweb 12 includes an outer sealant layer 102 combined with a polyethylene base layer 104, which can be one or more layers of a high density polyethylene (HDPE), a low density polyethylene (LDPE), a linear low density polyethylene (LLDPE), or a blended polyethylene of low density polyethylene and linear low density polyethylene (by one approach a 50/50 weight percent blend). Layer 104 can also include more than one polyethylene layer that may be a combination of various layers of HDPE, LDPE, LLDPE or blends thereof.

[0022] The outer sealant layer 102 may be a sealant layer filled with an inorganic filler particle. Examples of which are described in US 7,871,696; US 7,871,697; US 2011/0211778; and US 2012/0168340, which are each incorporated herein by reference in their entirety. The inorganic filler particle used in layer 102 may be an organoclay or an organically modified clay such as micro- or nano-sized fillers of clay, calcium carbonate, montmorillonite, microcrystalline silica, dolomite, talc, mica, oxides (silicon oxides, aluminum oxides, titanium oxides, and the
like) and other additives, and/or combinations thereof. In some approaches, the inorganic filler particle may be blends of organically modified clay and other inorganic fillers, such as calcium carbonate, talc, and other micron-sized inorganic particles, and the like. In some approaches, the sealant layer may include about 5 to about 15 percent by weight of organically modified clay and about 5 to about 20 percent of a first additional inorganic filler, and optionally, about 5 to about 20 percent of a second additional inorganic filler, where the organically modified clay, the first additional inorganic filler, and the second additional inorganic filler are different from each other in average size, type, kind, or quality. In another approach, the outer sealant layer 102 may include about 20 to about 30 percent of an organoclay master-batch (such as that described in US 2011/0211778), about 5 to about 25 percent of maleic anhydride grafted linear low density polyethylene carrier, and about 65 to about 90 of ethylene vinyl acetate having from about 5 to about 7 percent vinyl acetate content. In some cases, the layer 102 may also include a slip agent, such as about 1000 ppm or less of fatty add amides. In one approach, layer 102 may include about 3 to about 15 percent of the inorganic filler particles.

Layer 104 may be a polyethylene based single layer or polyethylene based multilayer film, which can be coextruded by blown process with the outer sealant layer 102. The choices of polyethylene layer are linear low density polyethylene, low density polyethylene and high density polyethylene, or any combination of their blends. The low density layers may have a density of about 0.93 g/cc or less, and in some cases, a density of about 0.9 g/cc about 0.93 g/cc. The high density polyethylene layers may have a density of about 0.95 g/cc or greater, and in some cases, a density of about 0.95 to about 0.99 g/cc. Layer 104 may be a 50/50 weight percent blend of low density polyethylene and linear low density polyethylene.

The various internal layers of outer layer 12 may be assembled through a blown film line to form a monoweb or a single web of film having all the various internal layers bonded together. Other methods of forming layer 12 may also be used as needed for a particular application.

Tie Layer. The tie layer 14 may be a co-extruded melt including two or more co-extruded layers. In the approach of FIG. 3, there are three exemplary co-extruded layers in tie layer 14. First, layer 120 is adjacent and bonded to one of the polyethylene layers 104 of outer sealant layer 12. Layer 120 may be a low density polyethylene layer. Next, intermediate layer
122 is also a low density polyethylene layer. Lastly, layer 124 is an ethylene acrylic acid, which is adjacent and bonded to the metalized layer 17a of the inner base layer 16. In some approaches, the acrylic acid content of layer 124 may be about 3 to about 20 weight percent, in other cases about 5 to about 15 weight percent, and in yet other cases, about 8 to about 12 percent. The EAA, in some approaches, may have a density of about 0.9 to about 0.95 g/cc. In some approaches, it is believed that the soft EAA layer may help in forming a visco-elastic layer that aids in stress distribution. In some approaches, the tie layer 14 may have an elongation at break of about 500 to about 600 percent, which (without being limited by theory) may aid in stress distribution.

[0026] In some approaches, the tie layer 14 may have a total thickness of about 5 to about 30 microns thick, in other approaches, about 5 to about 25 microns thick, and in yet other approaches, about 5 to about 20 microns thick. In other approaches, the tie layer 14 may also have a total thickness that is about 1 to about 40 percent of the EAA (in some approaches, about 1 to about 5 percent, and in yet other approaches about 5 to about 40 percent) and about 60 to about 99 percent of one or more layers of LDPE (in some approaches, about 95 to about 99 percent LDPE). In yet another approaches, the tie layer 14 may also have a thickness ratio of EAA to total LDPE of about 0.01 to about 0.05, in other approaches, about 0.2 to about 1.0. In other instances, the tie layer 14 may have a thickness ratio of total LDPE to EAA of about 70 to about 19 and in other approaches about 1:1 to about 7:1. The ratios and thicknesses may vary depending on the particular application and packaging use of the film.

[0027] While not wishing to be limited by theory, it is believed that the co-extruded LDPE and EAA melt tie layer 14 aids in forming an overall film structure that is capable of distributing stresses internally to the film 10 or film 100 and allowing the all layers of the film structures to deform as a single unitary structure, which results in a dramatic increase in puncture resistance thereof. It is believed that the entire film structure (that is, layers 12, 14, and 16) may be contributing to stress redistribution and not just the outer layers. To this end, it is believed that the EAA and LDPE tie layer, because it is a relatively flexible and ductile layer that strongly bonds to the layers 12 and 16, may allow the film as a whole to absorb and distribute stresses. Again, while not wishing to be limited by theory, the internal stress distribution may be related to selected viscoelastic properties of the tie layer. That is, the tie layer as a whole (that is all layers 120, 122, and 124) may be a composite visco-elastic layer or
exhibit viscous and elastic tendencies at the same time at ambient temperatures (about 70 to about 75°F) enabling it to effectively absorb and distribute externally applied stresses over a large surface area to dramatically reduce punctures. While not wishing to be limited by theory, the improvement of puncture resistance of the films herein may be due to the coextruded EAA and LDPE layers being selected in the above specified ratios and processed in such a manner that they maintain a softer more extensible mechanical behavior than adjacent laminated films (PET, Metalized PET, Oriented PET, Oriented PP and sealant polyolefins). This extensibility may provide a discontinuity in the propagation of any fracture (puncture) originated on the adjacent films of the lamination (PET etc). The properties of the EAA in combination with the LDPE in the tie layer may also contribute to the puncture resistance.

[0028] The Base Layer. In one approach, the base layer is a metalized polymer layer 16 which, by one approach, has an upper metalized layer 17a applied to an upper surface of a polyethylene terephthalate (PET) layer 17b. The metalized layer may be a thin deposit of aluminum, tin or other metal oxides and may be about 0.1 micron to about 10 microns thick. The PET layer 17b may be about 0.25 mils to about 2.0 mils thick. The metalized layer 17a is adjacent to and bonded to a lower layers of the tie layer and in particular the EAA layer of the tie layer. In other approaches, the base layer 16 may be a biaxially oriented polypropylene.

[0029] Advantages and embodiments of the film structures and tie layer compositions described herein are further illustrated by the following examples; however, the particular conditions, processing schemes, materials, and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit the construction of the film and methods of assembly thereof. All percentages and parts listed within this disclosure are by weight unless otherwise indicated.

EXAMPLES

[0030] EXAMPLE 1

[0031] A three layer extruder was used to laminate a 48 gauge metalized PET to an organoclay sealant web using an extrusion laminator similar to that shown in FIG. 2. The organoclay sealant web include inner layers of LDPE, LLDPE, HDPE (in this order and identified as the PE side of the sealant web), and an outer organoclay sealant layer of
organically modified montmorillonite, maleic anhydride grafted linear low density-polyethylene carrier, and ethylene vinyl acetate as described herein.

[0032] The extrusion laminator co-extruded three layers, which are identified herein as layers A, B, and C. Layer B was EAA and extruded adjacent to and bonded with the metalized layer of the PET. Layers A and C were LDPE and between the EAA and the polyethylene side of the organoclay sealant web. Layer C is adjacent to and bonded with the PE side of the organoclay sealant web.

[0033] The extrusion was conducted at about 250 ft/minute with a nip distance of about 9.5 inches from the exit of the die to the nip point. The extrusion temperature was set at about 610°F, and the chill roll temperature was about 60°F. The total thickness of the 3 co-extruded layers (i.e., layers A-C) in this trial was about 0.7 mils.

[0034] The bonds of the LDPE (Layer C) to the polyethylene of the sealant web as about 1498 g/in, and the bonds of the EAA (Layer B) to the metalized PET was about 351 g/in.

[0035] The sealant monoweb was also heat sealed to itself at about 350°F for about 1 second at about 70 psi. This resulted in a peel force of this heat seal of about 935 g/in as tested by an Instron peel test at about 12 inches per minute.

[0036] The resultant film was formed into a bag package using a Vertical Form Fill Seal machine having end heat seals and a longitudinal or fin heat seal along a side thereof. Approximately 3060 packages were prepared from the film described above. The packs were studied for failures after 2 weeks of room temperature storage (about 70 to about 75°F) and after transportation. In the context of this evaluation, transport involved loading the samples on a truck and transporting in the truck. Afterwards, the samples were kept for two more weeks and then inspected for punctures. Results are set forth in Table 1 below. Out of 3060 packages using film of the present disclosure, only 4 puncture failures were observed after two week of storage and only 1 addition puncture was observed after transport for a total of 5 punctures. The film only experienced 0.16% total puncture failures.
Table 1: Puncture results for extrusion lamination film

<table>
<thead>
<tr>
<th>Total Packs</th>
<th>Number of Punctures After 2 Weeks Storage</th>
<th>Number of Punctures After Transport</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Failure mode</td>
<td>Failure mode</td>
</tr>
<tr>
<td></td>
<td>UA (puncture from outside to inside)</td>
<td>UI (puncture from inside to outside)</td>
</tr>
<tr>
<td>3060</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

COMPARISON EXAMPLE 1

A similar analysis was completed on two different lots of a comparison packaging film using an isocyanate-terminated polyester urethane two-component adhesive that was assembled using a direct gravure coating process instead of the adhesive lamination discussed herein and in Example 1. The same metalized PET and organoclay sealant web from Example 1 was used in this comparison study. Packages were prepared in the same manner and evaluated in the same manner as Example 1 except they used a different adhesive applied through a gravure coating process instead of the extrusion lamination of Example 1. In a first study, 3156 of the comparative packages were evaluated. In a second study, 3610 of the comparative packages were evaluated. Results are set forth in Tables 2A and 2B below.

Table 2A: Comparative Packaging Film

<table>
<thead>
<tr>
<th>Lot</th>
<th>Total Packs</th>
<th>Number of Puncture After 2 Weeks Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Failure mode</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UI</td>
</tr>
<tr>
<td>1</td>
<td>3156</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>3610</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>
In this study, the comparative packages exhibited a total of 20 failures or about 0.3% total puncture failures, which is almost double that of Example 1.

EXAMPLE 2

Scratch and puncture testing was also performed using standardized linearly increasing load scratch test per ASTM D7027-15/ISO 1952:008 on the film of Example 1 and comparative films similar to that of Comparison Example 1. In general, the testing used a pneumatic fixture to secure the subject film to a backing material by drawing about an 86 kPa vacuum beneath the sample, which allows ambient air pressure to secure the film uniformly over its entire surface. The backing material was poly methyl methacrylate. Scratch length was set to about 100 mm (see, e.g., FIG. 4), with a scratch speed of about 1mm/sec using about a 1 mm diameter spherical stainless steel tip. Films were tested on their entire surface in both the machine direction (MD) and transverse direction (TD) film orientation. The linear load range for the scratch test was set at about 1 to about 20 N. The final load was selected to generate a puncture between approximately about 50 to about 75% of the total scratch length. The results are set forth below. An exemplary isolated scratch path is shown in the image of FIG. 4.

The extrusion laminated films prepared with the tie layer adhesives using co-extruded LDPE and EAA of Example 1 displays the highest loads to generate puncture. These extrusion laminated films exhibit superior mechanical integrity between the metalized PET layers and the sealant layer, which is better able to distribute the scratch-induced stresses through its structure. Turning to FIGS. 7 and 14 for a moment, these figures compares the load required to induce a puncture in the inventive film I (from Example 1 and identified as Film 883 sti-ong bonding) and two comparison films CI and C2. Film C1 is an extrusion laminated film
made similar to inventive film 1 (from Example 1), but included 3 layers of co-extruded LDPE that were co-extruded at a temperature of about 520°F (C1 is also identified as Film 883 weak bonding). Thus, comparison film C1 was extrusion laminated but did not include the EAA layer. Film C2 is the adhesive coated film of Comparison Example 1 (C2 is also identified as Film 883 (adhesive). Results are shown in Table 1 below and graphically in FIGS 7 and 14.

Table 1: Average Force (N) to first puncture

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tie Layer</th>
<th>Application Method</th>
<th>Average Force to First Puncture, N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Transverse Direction (TD)</td>
</tr>
<tr>
<td>I1</td>
<td>LDPE, LDPE, EAA</td>
<td>Extrusion Lamination</td>
<td>12.5</td>
</tr>
<tr>
<td>C1</td>
<td>LDPE, LDPE, LDPE</td>
<td>Extrusion Lamination</td>
<td>7.9</td>
</tr>
<tr>
<td>C2</td>
<td>isocyanate-terminated polyester urethane</td>
<td>Adhesive lamination</td>
<td>8.3</td>
</tr>
</tbody>
</table>

FIGS. 8 to 12 show micrographs of cross-sectional views of the samples I1 and C1 above at various locations along the scratch length. The general procedure for sectioning the film is generally shown in FIG. 5. Discussion of the cross-sectional analysis is provided further in the examples below.

EXAMPLE 3

The films of Example 2 were also evaluated by cross-sectioning the scratches and viewed by microscopy to visually compare how the overall film structure absorbs and distributes the stresses imparted by the scratch testing (See Fig. 5). First, the inventive film I (identified as Film 883 Strong bonding) was compared to the comparison film C1 (identified as Film 883 Weak bonding). Both of these films were assembled by extrusion lamination as described above. The inventive film I was co-extruded layers of LDPE and EAA as set-forth in Example 1. The comparison film C1 was co-extruded layers of LDPE as set forth in Example 2 above. A summary of the microscopy analysis is set-forth in FIGS, 6-12.
EXAMPLE 4

Secondly, the inventive film I (still identified as Film 883 Strong bonding) was compared to the adhesive coated film C2 (identified as Film 883 adhesive laminated or Film 883 AdLam) of Example 1 and Comparison Example 1, respectively. A summary of the microscopy analysis is set-forth in FIGS. 13-19.

As apparent from FIGS. 6-19, the inventive films herein demonstrate superior layer integrity during the scratch testing. There is no visible delamination between the sealant layers or between the sealant layers and the PET layer. The comparison films C1 and C2 shows failure of the adhesive layer, which may contribute to the lower loads required for puncture. The analysis of this microscopy study compares to the damages found in the actual field testing summarized in Example 1 and Comparison Example 1.

EXAMPLE 5

An study was performed that directly compared the performance of a same film and same base layer using different bonding methods as produced by adhesive lamination versus extrusion lamination. The images of FIG. 20 provide a cross-sectional comparison at an early point of the scratch compared to a late portion of the scratch. In the images of FIG. 20, the film identified as "Film 3 Adh Lam" is a comparison adhesive lamination film and shows substantial delamination of the layers in the late stick-slip location. The film identified as "Film 4 Ext Lam" is an inventive extrusion lamination film that shows the films ability to deform as a whole that adequately dissipate stresses from the scratch.

Comparative Film 3 Adh Lam was a film produced using adhesive lamination and a two-component isocyanate-terminated polyester urethane that was applied as a low viscosity adhesive by a system of rotogravure cylinders directly onto the metalized layer of the base film layer. Then, the inner layer or sealant layer was pressed onto the wet adhesive layer to create a temporary bond that eventually formed a strong bond after several days of heat curing and storage at elevated temperatures (above room temp).

Inventive Film 4 Ext Lam was a film produced using the same base layer and same sealant layer as Film 4 Adh Lam, but made using an extrusion lamination process that coextruded molten polymers as 2 layers of LPDE and 1 layer of EAA between the two films.
The formed laminate was then cooled and pressed together to form the resultant film. No curing of heating of the laminate was needed to achieve the resultant product.

[0057] It will be understood that various changes in the details, materials, and arrangements of the process, compositions, and components thereof, which have been herein described and illustrated in order to explain the nature of the films and methods of formation thereof may be made by those skilled in the art within the principle and scope of the embodied method as expressed in the appended claims.
What is claimed is:

1. A packaging film having improved puncture resistance, the film comprising:
   - an outer layer of a monoweb organoclay containing a peelable sealant layer for forming a heat seal;
   - a lower base layer including a metalized polymer with a metal applied to at least one surface of a polymer layer;
   - a co-extruded tie layer between the outer layer and the lower base layer, the co-extruded tie layer including one or more layers of polyethylene and one or more layers of ethylene acrylic acid;
   - the ethylene acrylic acid bonded to the metal of the metalized polymer in the lower base layer; and
   - a thickness ratio of the polyethylene to the ethylene acrylic acid from about 1 to about 5 such that the packaging film is configured to deform as a single unitary structure upon a deformation stress applied to an outer surface of the packaging film.

2. The packaging film of claim 1, wherein the co-extruded tie layer includes two layers of polyethylene and one layer of ethylene acrylic acid.

3. The packaging film of any of the proceeding claims, wherein the tie layer has a total thickness of about 5 to about 30 microns and a thickness of the ethylene acrylic acid is about 1 to about 5 percent of the total thickness of the tie layer.

4. The packaging film of any of the proceeding claims, wherein the metalized polymer includes a metal applied to a polyester.

5. The packaging film of any of the proceeding claims, wherein the co-extruded tie layer is extrusion laminated between the outer layer and die base layer.
6. The packaging film of any of the proceeding claims, wherein the polyethylene is a low density polyethylene having a density from about 0.9 to about 0.93 g/cc.

7. The packaging film of any of the proceeding claims, wherein the outer layer includes a first layer having about 3 to about 40 percent of an inorganic filler, about 5 to about 25 percent of maleic anhydride grafted linear low density polyethylene, and about 50 about 95 percent ethylene vinyl acetate having about 4 to about 12 percent vinyl acetate content.

8. The packaging film of claim 7, wherein the inorganic filler is micro- or nanosized organically modified montmorillorute.

9. The packaging film of claim 7, wherein the outer layer includes a second layer of polyethylene and the second layer of polyethylene is bonded to the polyethylene in the tie layer.

10. The packaging film of any of the proceeding claims, wherein the ethylene acrylic acid includes about 3 to about 20 percent of acrylic acid.

11. A method of extrusion laminating a packaging film having improved puncture resistance, the method comprising:

   providing an outer layer of a monoweb organoclay sealant for forming a heat seal to a nip of an extrusion lamination die;

   providing a lower base layer including a metalized polymer with a metal applied to at least one surface of a polymer layer to the nip of the extrusion lamination die;

   a co-extruded at the nip between the outer layer and the lower base layer a tie layer including one or more layers of polyethylene and one or more layers of ethylene acrylic acid;

   wherein the ethylene acrylic acid is extruded to be bonded to the metal of the metalized polymer in the lower base layer; and

   wherein a thickness ratio of the polyethylene to the ethylene acrylic acid from about 19 to about 70 such that the packaging film is configured to deform as a single unitary structure upon a deformation stress applied to an outer surface of the packaging film.
12. The method of claim 12, wherein the co-extruded tie layer includes two layers of polyethylene and one layer of ethylene acrylic acid.

13. The method of any of claims 11-12, wherein the tie layer has a total thickness of about 5 to about 20 microns and a thickness of the ethylene acrylic acid is about 1 to about 5 percent of the total thickness of the tie layer.

14. The method of any of claims 11-13, wherein the metalized polymer includes a metal applied to a polyester.

15. The method of any of claims 11-14, wherein the co-extruded tie layer is extrusion laminated between the outer layer and the base layer.

16. The method of any of claims 11-15, wherein the polyethylene is a low density polyethylene having a density from about 0.9 to about 0.93 g/cc.

17. The method of any of claims 11-16, wherein the outer layer includes a first layer having about 3 to about 40 percent of an inorganic filler, about 5 to about 25 percent of maleic anhydride grafted linear low density polyethylene, and about 50 to about 95 percent ethylene vinyl acetate having about 4 to about 12 percent vinyl acetate content.

18. The method of claim 17, wherein the inorganic filler is micro- or nano-sized organically modified montmorillonite.

19. The method of claim 17, wherein the outer layer includes a second layer of polyethylene and the second layer of polyethylene is bonded to the polyethylene in the tie layer.

20. The method of any of claims 11-19, wherein the ethylene acrylic acid includes about 3 to about 20 percent of acrylic acid.
21. The packaging film of any one of the proceeding claims, wherein the organo clay sealant contains organoclay and other inorganic fillers.
Sectioning Procedure for Film Cross-Sectional Imaging

Figure 5

Cross section of the scratch path

Road

*not to scale
Scratch Length: 100mm
Rate: 1mm/s
Load: 1-20N
Orient. MD
Surface: Outside
Backing: PMMA
Tip: 1mm SS spherical tip

Imaged samples were tested under the following conditions:

- Film 883 weak bonding
- Film 883 strong bonding
- Films

Figure 6: Scratch test condition for extrusion laminated films
Figure 7: Scratch test Results on Extrusion Laminated Films

First Puncture (N)

TD: Film 883 weak bonding (extrusion lamination)

MD: Film 883 strong bonding (extrusion lamination)
Figure 8: Film Structure for Extrusion Laminated Films with Strong and Weak Bonding.
Figure 9: Smooth Deformation of Extrusion laminated Films

Red Arrow shows where the cross section image was taken.

Film 883
Strong Bonding

Film 883
Weak Bonding

Smooth Deformation
Figure 10: Early Stick Slip of Extrusion Laminated Films
Scratch Length: 100mm
Rate: 1 mm/s
Load: 1 - 20N
Orientation: MD
Surface: Outside
Backing: PMMA
Tip: 1mm SS spherical tip

Imaged samples were tested under the following conditions:

- Film 883 (Adhesive Laminate)
- Film 883 Strong Bonding (Extrusion Laminate)
- Films Lamination

Figure 13: Comparing Films From Extrusion Lamination and Adhesive
Figure 2a: Scratch Test Results on Films From Extrusion Lamination and Adhesive Lamination
Figure 15: Film Structure for Extrusion Laminated Film with Strong and Adhesive Laminated Film
Figure 16: Smooth Deformation of Extrusion Laminated Film and Adhesive Laminated Film

Red Arrow Shows Where the Cross Section Image was Taken

Film 883 Strong

(Extrusion Laminated)

Film 883

(Adhesive Laminated)
Figure 17: Early Stick Slip of Extrusion Laminated Film and Adhesive Laminated Film

Red Arrow shows where the cross section image was taken.
Figure 18: Mid Stick Slip of Extrusion Laminate Film and Adhesive Laminate Film

Red arrow shows where the cross section image was taken.
Figure 19: Late Stick Slip of Extrusion Lamintated Film and Film 883 Strong (Adhesive Lamintated). Red arrow shows where the cross section image was taken
Puncture Test Method Developed
Comparing Adhesive Vs. Extrusion Lamination

Fig. 20

Film L1
Film L2
Film L3
Film L4

Cross-sectional views A, B, C.

A: Early stick-slip
B: Late stick-slip

100um
## INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. B32B27/30 B32B27/32 B65D75/12 B65D75/58

ADD.

According to International Patent Classification (IPC) into both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

B32B B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search 16 May 2013

Date of mailing of the international search report 07/06/2013

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Authorized officer Okunowski, Joachim

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### INTERNATIONAL SEARCH REPORT

**Information on patent family members**

**International application No:** PCT/US2013/029804

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