The invention consists of a multilayer film prepared from high impact strength polyethylene (Hi polyethylene); a Ziegler Natta catalyzed polyethylene (ZN polyethylene) and a high pressure low density polyethylene (LD polyethylene) with the requirements that i) at least one skin layer consists essentially of Hi polyethylene and ii) at least one core layer comprises a blend of ZN polyethylene and said LD polyethylene. The Hi polyethylene has a density of from about 0.915 to 0.930 g/cc and a normalized impact strength of at least 300 g/mil. The amount of Hi polyethylene is from 30 to 55 weight % (based on the combined weights of the Hi + ZN + LD polyethylenes). The films of this invention are readily prepared on blown film equipment and provide an excellent balance of mechanical properties.
MULTILAYER FILM PREPARED FROM HIGH IMPACT STRENGTH POLYETHYLENE AND BLENDS OF
ZIEGER NATTA CATALYZED AND HIGH PRESSURE LOW DENSITY POLYETHYLENES

TECHNICAL FIELD

This invention relates to multilayer plastic films.

BACKGROUND ART

Polyethylene film is widely used in many packaging applications.

The type of polyethylene that was first commercially available is prepared under high pressure using a free radical initiator. This type of polyethylene is widely known as high pressure/low density polyethylene and as "LD" polyethylene. LD polyethylene is easy to process but monolayer films prepared with LD polyethylene have comparatively poor mechanical properties.

The use of Ziegler Natta catalysts enables the production of ethylene copolymers having better mechanical properties than LD polyethylene - but these copolymers are more difficult to process than LD polymers.

More recently, the use of metallocene catalysts has allowed the production of ethylene copolymers having enhanced impact strength (but, again, at the expense of poor processability in comparison to LD polyethylene).

The use of blends of polyethylenes to prepare monolayer films is well known. In particular, it is known to blend LD polyethylene with "Z/N" catalyzed polyethylene or metallocene catalyzed polyethylene to improve processability - but the mechanical properties of the blends are compromised. It is also known to improve multilayer films using these polyethylenes. In practical terms, the loss of impact strength is especially problematic when blending LD polyethylene with a metallocene catalyzed polyethylene having a density of from about 0.915 to 0.930 g/cc (because lower density metallocene polyethylenes have such high impact strengths that losses are more easily tolerated and because higher density metallocene resins have lower impact strength to begin with and hence are generally not used in film applications where impact strength is important).

DISCLOSURE OF INVENTION

The present invention provides:

a multilayer film comprising HI polyethylene having a density of from 0.915 to 0.930 g/cc and an SCBDI of from 70 to 100; Z/N polyethylene and an LD polyethylene, said film comprising

A) a skin layer consisting essentially of said HI polyethylene; and
B) a core layer comprising a blend of said Z/N polyethylene and said LD polyethylene, with the provisos that
a) the amount of said HI polyethylene is from 30 to 55 weight %, based on the combined weight of said HI polyethylene plus said ZN polyethylene plus said LD polyethylene; and
b) the amount of said LD polyethylene is from 5 to 20 weight %, based on the combined weight of said HI polyethylene plus said ZN polyethylene plus said LD polyethylene.

BEST MODE FOR CARRYING OUT THE INVENTION

A. Z/N Polyethylene

The term "Ziegler Natta catalyst" is well known to those skilled in the art and is used herein to convey its conventional meaning. Ziegler Natta catalysts comprise at least one transition metal compound of a transition metal selected from groups 3, 4, or 5 of the Periodic Table (using IUPAC nomenclature) and an organoaluminum component which is defined by the formula:

\[ \text{Al}(X')_a (\text{OR})_b (\text{R})_c \]

wherein: \( X' \) is a halide (preferably chlorine); \( \text{OR} \) is an alkoxy or aryloxy group; \( \text{R} \) is a hydrocarbyl (preferably an alkyl having from 1 to 10 carbon atoms); and \( a, b, \) or \( c \) are each 0, 1, 2, or 3 with the provisos text \( a+b+c=3 \) and \( b+c>1 \).

It is highly preferred that the transition metal compounds contain at least one of titanium or vanadium. Exemplary titanium compounds include titanium halides (especially titanium chlorides, of which TiCl_4 is preferred); titanium alkyls; titanium alkoxides (which may be prepared by reacting a titanium alkyl with an alcohol) and "mixed ligand" compounds (i.e. compounds which contain more than one of the above described halide, alkyl and alkoxy ligands). Exemplary vanadium compounds may also contain halide, alkyl or alkoxy ligands. In addition vanadium oxy trichloride ("VOCb") is known as a Ziegler Natta catalyst component and is suitable for use in the present invention.

The above defined organoaluminum compound is an essential component of the Ziegler Natta catalyst. The mole ratio of aluminum to transition metal (for example, aluminum/(titanium + vanadium)) is preferably from 1/1 to 100/1, especially from 1.2/1 to 15/1.

As will be appreciated by those skilled in the art of ethylene polymerization, conventional Ziegler Natta catalysts may also incorporate additional components such as an electron donor - for example an amine; or a magnesium compound - for
example a magnesium alkyl such as butyl ethyl magnesium and a halide source (which is typically a chloride such as tertiary butyl chloride).

Such components, if employed, may be added to the other catalyst components prior to introduction to the reactor or may be directly added to the reactor.

The ZN polyethylene used in this invention is prepared using the above described catalyst system. The use of i) ethylene homopolymers; and ii) copolymers of ethylene with a C₄₋₈ alpha olefin is contemplated. The ZN polyethylene used in this invention has a melt index (I₂) of from 0.2 to 10 grams per 10 minutes (preferably from 0.5 to 5 grams per 10 minutes) and a density of from 0.910 to 0.965 g/cc (preferably from 0.915 to 0.960 g/cc).

B. High Impact Strength Polyethylene (HI Polyethylene)

It will be appreciated by those skilled in the art that ZN catalysts produce ethylene copolymers having a comparatively broad molecular weight distribution and a comparatively broad distribution of short chain branches in relation to ethylene copolymers prepared with a metallocene catalyst. The differences in polymer structure affect the properties of the different polyethylenes. Specifically, ethylene copolymers prepared with a metallocene catalyst typically have a higher impact strength in comparison to an ethylene copolymer having the same density and melt index but prepared with a ZN catalyst.

The HI polyethylene is preferably prepared with a metallocene catalyst. As used herein, the term metallocene catalyst means that the catalyst contains at least one cyclopentadienyl liquid. Such catalysts (and HI polyethylene prepared from them) are well known and in widespread commercial use.

The branching distribution in ethylene copolymers may be defined using the so called short chain branching distribution index (SCBDI). Polyethylene copolymers that are prepared with a metallocene catalyst generally have a narrow branching distribution (which corresponds to a to a high SCBDI value). SCBDI is defined as the weight % of the polymer that has a comonomer content with 50% of the median comonomer content of the polymer. SCBDI is determined according to the method described in United States Patent 5,089,321 (Chum et al.). The HI polymers of this invention have an SCBDI of from 70 to 100 which corresponds to a narrow branching distribution.

Very low density polyethylene (having a density of less than 0.915 g/cc) that is prepared with a metallocene catalyst typically has exceptionally high impact strength. These polymers may be blended with LD polyethylene to improve processability and the blend will still exhibit high impact strength in absolute terms. For clarity: the blend
does cause a reduction in impact strength but the real impact strength is normally still quite high (given the extremely high initial impact strength of the very low density polyethylene).

The present invention does not include the use of very low density copolymers.

Instead, the present invention utilizes only "metallocene" copolymers having a density in the range of from 0.915 to 0.930 g/cc. The preferred melt index of the HI polymers used in this invention is from 0.5 to 2.0 g/10 minutes. A blown film that is prepared from such copolymers will have a high initial impact strength - with a value of at least 300 grams for a one mil film being a typical value. However, these copolymers are comparatively difficult to extrude.

The extrusion difficulties are generally manifested in two ways: firstly, the extruder output is lowered (and/or more power is required for a given output) and secondly, the "stability" of the blown film "bubble" is compromised. The extrusion problems can be mitigated by blending the HI resin with LD resin. However, this causes a reduction in the impact strength of the final film. This problem is particularly acute with the HI polyethylenes of this invention (i.e. polyethylenes having a density of from 0.915 to 0.930 g/cc) because the initial impact strength of these resins is not as high as the initial impact strength of lower density polyethylenes.

The present invention resolves these problems (for multilayer films) in the following manner:

1) the HI resin is not blended with LD resin - instead, the LD resin is blended with the ZN resin; and
2) bubble stability is provided by extruding a layer that is a blend of Z/N resin with LD resin; with the further proviso that
3) the total amount of HI resin is less than or equal to 55 weight % (of the combined weights of HI + ZN + LD polyethylene), and
4) the total amount of LD resin is from 5 to 20 weight % (of the combined weights of HI + ZN + LD polyethylenes).

We have observed that the blends and multilayer layer structure of the films of this invention allow good bubble stability for the blown film process and provide a multilayer film having a good balance of mechanical properties.

In summary, the HI polyethylenes used in this invention have

1) a density of from 0.915 to 0.930 g/cc; and
2) an SCBDI of from 70 to 100; and preferably have
3) a melt index of from 0.5 to 2.0 g/10 minutes.
A monolayer blown film that is prepared from these HI polyethylenes will typically exhibit a "normalized" impact strength of at least 300 grams. The term "normalized" is meant to convey its conventional meaning to a person skilled in the art and it reflects a correction for the thickness of the film - for example, a monolayer film having a 1.5 mil thickness would have a total (actual) impact strength 450 grams in order to have a "normalized" thickness of 300 grams/mil (i.e. 450/1.5 = 300).

C. High Pressure Low Density (LP) Polyethylene

The LD polyethylene used in this invention is a well-known item of commerce that is prepared by the polymerization of ethylene under high pressure using a free radical initiator (such as a hydroperoxide). The LD polymer used in this invention may be prepared in a tubular or autoclave reactor and has a melt index (½) of from 0.2 to 10 grams per 10 minutes (preferably from 0.3 to 3) and a density of from about 0.915 to 0.930 g/cc.

D. Film Structure

The multilayer films of this invention preferably contain 3 or 5 layers. A three layer film structure may be described as layers A-B-C, where the internal layer B (the "core" layer) is sandwiched between two external "skin" layers A and C. In many multilayer films, one (or both) of the skin layers is made from a resin which provides good seal strength and is often to as a sealant layer. The total thickness of the films of this invention is preferably from 1 to 6 mils. For films that are less than 2 mils total thickness, it is preferred that the core layer contains from 40 to 70 weight % of the total amount of polyethylene. For all films, it is preferred that the core layer is at least 0.5 mils thick.

E. Additives

The polyethylene may contain conventional additives, especially (1) primary antioxidants (such as hindered phenols, including vitamin E); (2) secondary antioxidants (especially phosphites and phosphonites); and (3) process aids (especially fluoroelastomer and/or polyethylene glycol process aid).

F. Film Extrusion Process

Blown Film Process

The extrusion-blown film process is a well known process for the preparation of multilayer plastic film. Multilayer films are prepared using multiple extruders which heat, melt and convey the molten plastics and forces them through multiple annular dies. Typical extrusion temperatures are from 330 to 500°F, especially 350 to 460°F. Thus, 3
layer films are prepared using three extruders and three dies which together form a "bubble" having three layers.

The polyethylene film is drawn from the die and formed into a tube shape and eventually passed through a pair of draw or nip rollers. Internal compressed air is then introduced from the mandrel causing the tube to increase in diameter forming a "bubble" of the desired size. Thus, the blown film is stretched in two directions, namely in the axial direction (by the use of forced air which "blows out" the diameter of the bubble) and in the lengthwise direction of the bubble (by the action of a winding element which pulls the bubble through the machinery). External air is also introduced around the bubble circumference to cool the melt as it exits the die. Film width is varied by introducing more or less internal air into the bubble thus increasing or decreasing the bubble size. Film thickness is controlled primarily by increasing or decreasing the speed of the draw roll or nip roll to control the draw-down rate. Preferred multilayer films according to this invention have a total thickness of from 1 to 4 mils.

The bubble is then collapsed into two doubled layers of film immediately after passing through the draw or nip rolls. The cooled film can then be processed further by cutting or sealing to produce a variety of consumer products. While not wishing to be bound by theory, it is generally believed by those skilled in the art of manufacturing blown films that the physical properties of the finished films are influenced by both the molecular structure of the polyethylene and by the processing conditions. For example, the processing conditions are thought to influence the degree of molecular orientation (in both the machine direction and the axial or cross direction).

A balance of "machine direction" ("MD") and "transverse direction" ("TD" - which is perpendicular to MD) molecular orientation is generally considered most desirable for key properties associated with the invention (for example, Dart Impact strength, Machine Direction and Transverse Direction tear properties).

Thus, it is recognized that these stretching forces on the "bubble" can affect the physical properties of the finished film. In particular, it is known that the "blow up ratio" (i.e. the ratio of the diameter of the blown bubble to the diameter of the annular die) can have a significant effect upon the dart impact strength and tear strength of the finished film.

Further details are provided in the following examples.

**EXAMPLES**

Polyethylenes
The HI polyethylene has a melt index, $I_2$, of 0.65 grams/10 minutes; a density of 0.916 g/cc; and a SCBDI of greater than 70. It is an ethylene-octene copolymer sold under the trademark SURPASS® FPS 016 by NOVA Chemicals. A normalized impact strength of 7.11/g/mil is reported on the MatWeb internet website and may be regarded as a typical value for a blown film having a thickness of 1 mil that is prepared from this HI polyethylene.

The LD polyethylene is an ethylene homopolymer having a melt index of 2.3 and a density of 0.919 and is sold under the trademark NOVAPOL® LF 0219 A.

The ZN polyethylene is an ethylene-butene copolymer having a melt index of 0.8 g/10 minutes and a density of 0.921 g/cc sold under the tradename NOVAPOL PF-Y821-CP by NOVA Chemicals. The normalized impact strength of a film prepared from this polyethylene is reported on MatWeb internet website as 94 grams/mil and this value may be regarded as typical.

Test Methods

Impact strength is measured according to ASTM D1709/A ($F_{50}$ standard) and is reported in grams/mil.

Machine Direction (MD) Tear and Transverse Direction (TD) Tear is measured according to ASTM D1922 and is reported in grams/mil.

Machine Direction (MD) Modulus and Transverse Direction (TD) Modulus is measured according to ASTM D882 and is reported in mega Pascals (MPa).

Density is measured according to ASTM D792 and is reported in grams/cubic centimeter (g/cc).

Melt index, $I_2$, is measured according to ASTM D1238 (using a 2.16 kg weight at a temperature of 190°C).

Example 1 The films were made on a three layer coextrusion film line manufactured by Brampton Engineering. Three layer films having a total thickness of 3 mils were prepared using a blow up ratio (BUR) of 2.5/1.

The A-B-C structures of these three layer films are described in more detail in Table 1. For clarity: the inventive film 4 has an A/B/C layer ratio of 20/60/20 (meaning that each of the skin layers A and C contained 20 weight % of the total amount of polyethylene and the core layer B contained 60 weight %). Each of the skin layers (A and C), was made with HI polyethylene, and the core layer was made with a blend of 90% ZN + 10% LD.
Example 2  Five layer films were prepared on a blown film line that was fed with 5 extruders. The A/B/C/D/E structures are defined in Table 2. The films had a thickness of 3.5 mils and were prepared using a BUR of 2.5/1.

Example 3 (Comparative)  A series of comparative three layer films were prepared in which the skin layers were prepared with the above described HI resin and the core layer was prepared with a blend of the HI resin with a homopolymer Z/N resin having a density of 0.958 g/cc and a melt index of 1 (sold under the trademark SCLAIR® 19C). The layer ratio of the A/B/C structures were 20/60/20 (as per example 1) and films having a thickness of 3 mils were prepared at a BUR of 1.7/1. These films were comparative as they are difficult to process - but the physical properties of the films are very good. Four different films were studied in which the core layer composition was varied for a blend of 72% HI + 28% ZN to a blend of 25% HI + 75% ZN. As expected, the stiffness of the resin increased as the amount of high density ZN resin in the core layer increased. In addition, the hot tack of the films (as determined by ASTM F1921-28) remained surprisingly high. These films would be especially suitable for the preparation of heavy duty sacks.

### TABLE 1
Three Layer Films

<table>
<thead>
<tr>
<th>Layer Ratio</th>
<th>Film Structures</th>
<th>Impact Strength</th>
<th>MD Tear</th>
<th>TD Tear</th>
<th>MD Modulus</th>
<th>TD Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - C</td>
<td>HI</td>
<td>&gt;600</td>
<td>332</td>
<td>391</td>
<td>139</td>
<td>148</td>
</tr>
<tr>
<td>20/60/20</td>
<td>HI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 - C</td>
<td>HI</td>
<td>287</td>
<td>349</td>
<td>389</td>
<td>177</td>
<td>164</td>
</tr>
<tr>
<td>20/60/20</td>
<td>ZN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 - C</td>
<td>85% HI + 15% LD</td>
<td>188</td>
<td>269</td>
<td>376</td>
<td>162</td>
<td>182</td>
</tr>
<tr>
<td>85% ZN + 15% LD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20/60/20</td>
<td>HI</td>
<td>279</td>
<td>302</td>
<td>420</td>
<td>175</td>
<td>192</td>
</tr>
<tr>
<td>90% ZN + 10% LD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Comparative Structure 1** contains all the three layers of HI polyethylene. This film has excellent impact strength but is difficult to extrude.
- **Comparative Structure 2** contains ZN in the core. This film has a desirable balance of properties but is also difficult to extrude.
- **Comparative Structure 3** contains LD blended in skins to improve melt strength. This structure shows lower impact strength but the presence of the LD resin improves extrusion.
Inventive Structure 4 contains LD blended with ZN in the core which improves melt strength. This film has higher impact and tear strength than the film in structure 3. The use of LD resin allows this film to be more easily extruded than structures 1 and 2.

**TABLE 2**

**Five Layer Films**

<table>
<thead>
<tr>
<th>Layer Ratio</th>
<th>Five Layer C-ex Film Structures</th>
<th>Impact Strength</th>
<th>MD Tear</th>
<th>TD Tear</th>
<th>MD Modulus</th>
<th>TD Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 26/19/10/18/27</td>
<td>100% HI 80% ZN + 20% LD 100% HI 80% ZN + 20% LD 100% HI</td>
<td>212</td>
<td>417</td>
<td>580</td>
<td>267</td>
<td>284</td>
</tr>
<tr>
<td>B 26/19/10/18/27</td>
<td>95% HI + 5% LD 95% ZN + 5% LD 100% PEB 95% ZN + 5% LD</td>
<td>168</td>
<td>370</td>
<td>558</td>
<td>278</td>
<td>306</td>
</tr>
<tr>
<td>Comparative</td>
<td>95% HI + 5% LD</td>
<td></td>
<td></td>
<td></td>
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</table>

- **Inventive Structure A** contains HI skins. The sub-skin layers of ZN contain LDPE blended in them to improve melt strength. This film exhibits good impact and is easily extruded.

- **Structure B** contains LDPE in skin and sub-skin layers. This structure shows lower dart and tear properties than structure B. The "PEB" in the middle layer is a polyethylene homopolymer sold under the trademark SURPASS HPs 167 and in wide use as a barrier resin. This structure would be suitable for use as a "barrier film" (for packaging dry goods such as crackers or breakfast cereal).

**INDUSTRIAL APPLICABILITY**

The present films are suitable for a wide variety of packaging applications.
CLAIMS

1. A multilayer film comprising HI polyethylene having a density of from 0.915 to 0.930 g/cc and an SCBDI of from 70 to 100; Z/N polyethylene and an LD polyethylene, said film comprising
   A) a skin layer consisting essentially of said HI polyethylene; and
   B) a core layer comprising a blend of said Z/N polyethylene and said LD polyethylene, with the provisions that
      a) the amount of said HI polyethylene is from 30 to 55 weight %, based on the combined weight of said HI polyethylene plus said Z/N polyethylene plus said LD polyethylene; and
      b) the amount of said LD polyethylene is from 5 to 20 weight %, based on the combined weight of said HI polyethylene plus said Z/N polyethylene plus said LD polyethylene.

2. The multilayer film of claim 1 wherein said HI polyethylene has a melt index, I2, of from 0.5 to 2.0 g/10 minutes.

3. The multilayer film of claim 1 wherein said Z/N polyethylene has a density of from 0.915 to 0.960 g/cc and a melt index, I2, of from 0.5 to 5 g/10 minutes.

4. The multilayer film of claim 3 wherein said LD polyethylene has a melt index, I2, of from 0.3 to 5 g/10 minutes.
### A. CLASSIFICATION OF SUBJECT MATTER

IPC: **B32B 27/08** (2006.01), **B32B 27/32** (2006.01)

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

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**B32B 27/08** (2006.01), **B32B 27/32** (2006.01)

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

Electronic database(s) consulted during the international search (name of databases) and, where practicable, search terms used

EPOQUE (Epodoc) - keywords: polyethylene, metallocene, high impact.

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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**Date of the actual completion of the international search**

25 March 2014 (25-03-2014)

**Date of mailing of the international search report**

02 May 2014 (02-05-2014)

**Name and mailing address of the ISA/CA**

Canadian Intellectual Property Office

Place du Portage 1, C114 - 1st Floor, Box PCT

50 Victoria Street

Gatineau, Quebec K1A 0C9

Facsimile No.: 001-8 19-953-2476

**Authorized officer**

Amanda Livingston (819) 953-1614
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