

SHRINK FILMS AND METHOD FOR MAKING FILMS HAVING MAXIMUM HEAT SHRINK

This invention relates to an improved method for preparing
5 orienting polyolefin films. In particular, this invention relates to a
method for biaxially orienting polyolefin films wherein stretching or
orientation conditions are defined to maximize the unrestrained shrink
response of the film. The invention also relates to a shrink film and
to a shrink film made by the novel method wherein in each case the
10 shrink film comprises as the shrink control layer at least one
homogeneously branched ethylene interpolymer having a polymer density of
less than 0.91 g/cc.

Food items such as poultry, fresh red meat and cheese, as
well as nonfood industrial and retail goods, are packaged by various
15 heat shrink film methods. There are two main categories of heat shrink
films - hot-blown shrink film and oriented shrink film. Hot-blown
shrink film is made by a hot-blown simple bubble film process and
oriented shrink film is made by elaborate processes known as double
bubble, tape bubble, trapped bubble or tenter framing. Heat shrink film
20 can be monoaxial or biaxial oriented.

The shrink packaging method generally involves placing an
article(s) into a bag (or sleeve) fabricated from a heat shrink film,
then closing or heat sealing the bag, and thereafter exposing the bag to
sufficient heat to cause shrinking of the bag and intimate contact
25 between the bag and article. The heat can be provided by conventional
heat sources, such as heated air, infrared radiation, hot water,
combustion flames, or the like. Heat shrink wrapping of food articles
helps preserve freshness, is attractive, hygienic, and allows closer
inspection of the quality of the packaged food. Heat shrink wrapping of
30 industrial and retail goods, which is alternatively referred to in the
art and herein as industrial and retail bundling, preserves product
cleanliness and also is a convenient means of bundling and collating for
accounting purposes.

The biaxial heat-shrink response of an oriented polyolefin
35 film is obtained by initially stretching fabricated film to an extent
several times its original dimensions in both the machine and transverse
directions to orient the film. The stretching is usually accomplished
while the fabricated film is sufficiently soft or molten, although cold
drawn shrink films are also known in the art. After the fabricated film
40 is stretched and while still in a stretched condition, the stretch

orientation is frozen or set in by quick quenching of the film. Subsequent application of heat will then cause the oriented film to relax and, depending on the actual shrink temperature, the oriented film can return essentially back to its original unstretched dimensions, i.e., to shrink relative to its stretched dimension.

While the temperature at which a particular polymer is sufficiently soft or molten is a critical factor in various orientation techniques, in general, such temperatures are ill-defined in the art. Disclosures pertaining to oriented films that disclose various polymer types (which invariably have varying polymer crystallinities and melting points), simply do not define the stretching or orientation temperatures used for the reported comparisons. Nor do such disclosures disclose whether the particular orientation temperature used corresponded to an optimum temperature in regards to the reported shrink responses or other desired properties for a particular polymer. US Patent 4,863,769 to Lustig et al., WO 95/00333 to Eckstein et al., and WO 94/07954 to Garza et al., are three examples of disclosures wherein stretching or orientation temperatures are ill-defined or unspecified.

The direct effect of density or crystallinity on shrink response and other desired shrink film properties such as, for example, impact resistance, are known, for example, from WO 95/08441. That is, even where the orientation temperature is presumably constant, lower density polymer films will show a higher shrink response and improved impact resistance. However, the effect of density, crystallinity and compositional homogeneity on optimum orientation temperature is not known. In the prior art, there are only general rules of thumb or generalized teachings relating to suitable stretching conditions. For example, in commercial operations, it is often said that the temperature at which the film is suitably soft or molten is just above its respective glass transition temperature, in the case of amorphous polymers, or below its respective melting point, in the case of semi-crystalline polymers.

An example of teaching that's beyond ordinary rules of thumb (but is nevertheless fairly generalized) is provided by Golike in US Patent 4,597,920. Golike teaches orientation should be carried out at temperatures between the lower and higher melting points of a copolymer of ethylene with at least one C₈-C₁₈ α -olefin. Golike specifically teaches that the temperature differential is at least 10°C, however, Golike also specifically discloses that the full range of the temperature differential may not be practical because, depending on the

particular equipment and technique used, tearing of the polymer film may occur at the lower end of the range. At the higher limit of the range, Golike teaches the structural integrity of the polymer film begins to suffer during stretching (and ultimately fails at higher temperatures) because the polymer film then is in a soft, molten condition. See, US Patent 4,597,920, Col. 4, lines 52-68 bridging to Col. 5., lines 1-6. The orientation temperature range defined by Golike (which is based on higher and lower peak melting points) generally applies to polymer blends and heterogeneously branched ethylene/ α -olefin interpolymers, i.e. compositions having two or more DSC melting points, and does not apply at all to homogeneously branched ethylene/ α -olefin interpolymers which have only a single DSC melting point. Golike also indicates that a person of ordinary skill can determine the tear temperature of a particular polymer and discloses that for heterogeneously branched interpolymers having a density of about 0.920 g/cc, the tear temperature occurs at a temperature above the lower peak melting point. See, US Patent 4,597,920, Col. 7, Example 4. However, Golike does not teach or suggest how a person of ordinary skill in the art of shrink film can optimize the orientation process as to stretching temperature at a given stretching rate and ratio to maximize the shrink response.

Hideo et al. in EP 0359907 A2 teach the film surface temperature at the starting point of stretching should be within the range of from 20°C to about 30°C below the melting temperature of the polymer as determined in regards to the main DSC endothermic peak. While such teaching is considered applicable to homogeneously branched ethylene/ α -olefin interpolymers having a single DSC melting peak, the prescribed range is fairly general and broad. Moreover, Hideo et al. do not provide any specific teaching as to the optimum orientation temperature for a particular interpolymer respecting heat shrink response, nor any other desired film property.

An example of generalized teachings pertaining to homogeneously branched ethylene/ α -olefin interpolymers is provided in WO 95/08441. In the Examples of this disclosure, several different homogeneously branched substantially linear ethylene/ α -olefin interpolymers were studied and compared to one heterogeneously branched ethylene/ α -olefin interpolymers. Although the homogeneously branched substantially linear ethylene/ α -olefin interpolymers had densities that varied from about 0.896 to about 0.906 g/cc, all of the interpolymers (including the heterogeneously branched linear ethylene/ α -olefin interpolymer, Attane™ 4203, supplied by The Dow Chemical Company, which

had a density of 0.905 g/cc) were oriented at essentially the same orientation temperatures. Reported results in WO 95/08441 disclose three general findings -- (1) at an equivalent polymer density, substantially linear ethylene/ α -olefin interpolymers and heterogeneously branched linear ethylene/ α -olefin interpolymers have essentially equivalent shrink responses (compare Example 21 and Example 39 at pages 15-16), (2) shrink responses increase at lower densities and constant orientation temperatures, and (3) as orientation temperature increases, orientation rates increase. Furthermore, careful study of the Examples and unreported DSC melting point data for the interpolymers reported on in WO 95/08441 indicate for the Examples disclosed in WO 95/08441 that, at a given stretching rate and ratio, there is a preference for orienting multilayer film structures at orientation temperatures above the respective DSC melting point of the polymer employed as the shrink control layer.

Other disclosures that set forth orientation information regarding homogeneously branched ethylene polymers yet do not specify orientation conditions relative to respective lowest stretch temperatures include EP 0 600425A1 to Babrowicz et al. and EP 0 587502 A2 to Babrowicz et al.

Accordingly, although there are general rules and general disclosure as to suitable orientation temperatures for biaxially orienting polyolefins, there is no specific information as to optimum orientation conditions as a function of polymer type and, more importantly, there is no specific information for homogeneously branched interpolymers which do not possess the "lower and higher melting peaks" required by the Golike method. Also, while there is some fragmented information regarding stretching at different orientation temperatures, there is no specific information as to the maximum shrink response at the lowest possible orientation temperature at a given stretching rate and ratio for homogeneously branched interpolymers in general, and especially no useful information for homogeneously branched interpolymers having densities less than 0.91 g/cc. Still further, although homogeneously branched ethylene interpolymers offer a variety of other useful property advantages, at equivalent densities above about 0.907 g/cc, the shrink response of multilayer film structures which contain a homogeneously branched ethylene interpolymer as the shrink control layer, is generally viewed as essentially equivalent to multilayer film structures which contain a heterogeneously branched interpolymer as the shrink control layer. See FIG. 3.

It is an object of the present invention to provide a method for defining the optimum stretching or orientation temperature to maximize the unrestrained (free) shrink response of polyolefins in general. It is a particular object of the present invention to provide a method for maximizing the shrink response of homogeneously branched ethylene interpolymers such that the maximum shrink potential of these interpolymers can be obtained for the particular stretching rate, stretching ratio and type of orientation equipment employed. Another object of the invention is to provide improved shrink film structures containing homogeneously branched ethylene interpolymers of densities less than 0.91 g/cc as the shrink control layer.

In accordance with the present invention, we have discovered that defining the lowest temperature for stretching or orienting polyolefins results in a maximized shrink response, that such optimum orientation temperature varies with polymer density and/or crystallinity, and that residual crystallinity determinations using differential scanning calorimetry (DSC) indicate homogeneously branched ethylene interpolymers have lower residual crystallinities at so-defined optimum stretching or orientation temperatures relative to heterogeneously branched ethylene interpolymers having equivalent densities. As such, while such optimum orientation conditions can be also determined by trial and error approaches, the DSC residual crystallinity methodology provides a systematic way to efficiently identify such conditions. The result of these discoveries is whereas shrink response was previously thought to strictly follow polymer density and to be independent of the polymer homogeneity, with this new method of orientation, at equivalent densities, homogeneously branched interpolymers have been found to provide utterly unexpected, dramatically superior shrink responses relative to heterogeneously branched interpolymers, especially at polymer densities less than 0.91 g/cc.

In particular, we have discovered a method of making a heat shrinkable polyolefin film comprising the steps of

- a. fabricating a polyolefin film structure in substantially unoriented form, and
- b. stretching the polyolefin film at a selected stretching rate, stretch ratio and stretching temperature, wherein the selected stretching temperature is no more than or equal to 5°C above the lowest stretch temperature for the polyolefin film structure and for the selected stretching

rate and stretching ratio and wherein the polyolefin film structure comprises at least one ethylene polymer having a polymer density less than 0.915 g/cc.

Another aspect of the present invention is a heat shrinkable film structure which comprises, as the shrink control layer, at least one homogeneously branched ethylene interpolymer having a polymer density of less than 0.91 g/cc, wherein the film structure is characterized as having a shrink response at least 10 percent greater than the shrink response of a second film structure which comprises a heterogeneously branched ethylene interpolymer as the shrink control layer and wherein the film structure and the second film structure are fabricated and stretched under essentially the same conditions and the homogeneously branched and heterogeneously branched interpolymers have essentially the same polymer density and I₂ melt index.

Still another aspect of the present invention is a heat shrink polyolefin film structure prepared by a method which comprises the steps of

(a) fabricating a polyolefin film structure in substantially unoriented form, and

(b) thereafter stretching the fabricated polyolefin film structure at a selected stretching rate, stretch ratio and stretching temperature, wherein the selected stretching temperature is below the melting point of the film and is a temperature no more than or equal to 5°C above the lowest stretch temperature for the selected stretching rate and stretching ratio, and

wherein the film structure comprises, as the shrink control layer, at least one homogeneously branched ethylene interpolymer having a polymer density of less than about 0.91 g/cc.

While the present invention allows stretching operations in general to maximize the unrestrained shrink potential of a particular polymer, the benefits of this invention are particularly useful for those common commercial instances where the orientation temperature capabilities of the stretching operation are essentially fixed. For a particular orientation temperature capability (and stretch ratio and stretching rate), this invention allows the systematic identification of the optimum interpolymer rather than haphazard selections and miscalculations which waste time and can lead to over-engineered, more costly interpolymers. Another benefit of present invention is the novel method allows direct shrink

response comparisons irrespective of polymer differences such as density; that is, the novel method is a form of comparative standardization that can facilitate the development of commercial shrink films.

5 FIG. 1 is a first heat DSC curve illustrating the residual crystallinity portion of a heterogeneously branched polymer remaining at 100°C which is a temperature below the various melting peaks of the polymer illustrated.

10 FIG. 2 is a x/y plot illustrating the shrink response of heterogeneously branched ethylene polymers and homogeneously branched ethylene polymer as a function of polymer density. The data used to generate the plot are reported in Table 2 hereinbelow. The heterogeneously branched ethylene polymer samples range in polymer densities from about 0.907 to about 0.932 g/cc while the
15 homogeneously branched ethylene polymer samples range from about 0.91 to about 0.918 g/cc.

 FIG. 3 is another x/y plot illustrating the shrink response of heterogeneously branched ethylene polymers and homogeneously branched ethylene polymer as a function of polymer
20 density. The data used to generate this plot are reported in Table 2 hereinbelow. The heterogeneously branched ethylene polymer samples range in polymer densities from about 0.907 to about 0.932 g/cc while the homogeneously branched ethylene polymer samples range from about 0.887 to about 0.918 g/cc.

25 The double bubble and trapped bubble biaxial orientation methods can be simulated on a laboratory scale using a T. M. Long stretcher which is analogous to a tenter frame device. This device can orient polyolefin films in both the monoaxial and biaxial mode at stretching ratios up to at least 5:1. The device uses films having an
30 original dimension of 2 inches x 2 inches. Biaxial stretching is usually performed by stretching in the machine direction and transverse direction of the film simultaneously, although the device can be operated to stretch sequentially.

 The residual crystallinity of polyolefin interpolymers
35 measured using a DSC partial area method can be used to characterize the nature of polyolefin film at the stretch temperature. A stretching temperature 5°C above, preferably 3°C above, more preferably 2.5°C above the lowest stretch temperature (defined herein below) is considered herein to be the optimum or near-optimum stretching or orientation
40 temperature for the particular film. Stretching temperatures higher

than 5°C above the lowest stretch temperature are not considered part of the present invention because such invariably yield lower shrink responses for a particular stretching rate, stretching ratio and shrink temperature. Stretching temperatures less than 2.5°C above the lowest stretch temperature are not preferred because they tend to yield inconsistent results, although such inconsistencies tend to depend on specific equipment and temperature control capabilities.

We discovered that heterogeneously branched ethylene interpolymers possess higher residual crystallinities at their respective optimum orientation temperature relative to homogeneously branched ethylene interpolymers. Heterogeneously branched interpolymers having a density in the range of from 0.90 to 0.93 g/cc have residual crystallinities at respective optimum orientation temperatures of from 20 to 24 percent, while homogeneously branched ethylene interpolymers having a density in the range of from 0.895 to 0.91 g/cc have residual crystallinities at their respective optimum orientation temperatures of from 14 to 17 percent.

"Stretched" and "oriented" are used in the art and herein interchangeably, although orientation is actually the consequence of a film being stretched by, for example, internal air pressure pushing on the tube or by a tenter frame pulling on the edges of the film.

The term "lowest stretch temperature" as used herein means the temperature below which the film either tears and/or stretches unevenly for a given stretching rate and stretching (draw) ratio during the stretching operation or step of an orientation technique. The lowest stretch temperature is below the melting point of the film, it is a temperature at or below which the film can not be stretched uniformly (i.e., without the occurrence of banding or thick and thin spots), and it is a temperature at or below which the film tears for a particular stretching rate and stretch ratio.

Practitioners will appreciate that to maximize the orientation imparted and therefore the shrink response, the objective is to operate as close to the lowest stretch temperature as their equipment and capabilities will allow whether or not the significant stretching or orientation is accomplished in a single step or by a combination of sequential steps.

Additionally, practitioners will appreciate that the optimum or near-optimum stretching temperature for maximized shrink response at a given shrink temperature will interrelate with stretching rate and ratio. That is, while a particular stretching temperature will be

optimum or near-optimum at one combination of stretching rate and ratio, the same stretching temperature will not be optimum or near-optimum at a different combination of stretching rate and ratio.

Practitioners will also appreciate that to obtain the maximum shrink response from the orientation frozen into the film, the shrink temperature should match or exceed the stretching temperature. That is, reduced shrink temperatures do not allow full relaxation or shrinkage of the film. However, excessive shrink temperatures can diminish film integrity.

Practitioners will further appreciate that for a given combination of stretching temperature, stretching rate and stretching ratio, increases in the shrink temperature to the point of film integrity failure will yield higher shrink response performance and higher levels of shrink tension.

Stretching temperatures in the range of from 50 to about 120°C, especially from 55 to 110°C, more especially from 60 to 95°C, and most especially from 65 to 90°C are suitable in the present invention.

Shrink temperatures in the range of from 70 to 140°C, especially from 80 to 125°C, and more especially from 85 to 100°C are suitable in the present invention.

The term "residual crystallinity" is used herein to refer the crystallinity of a polymer film at a particular stretching temperature. Residual crystallinity is determined using a Perkin-Elmer DSC 7 set for a first heat at 10°C/min. of a water-quenched, compression molded film sample of the polymer. The residual crystallinity for an interpolmer at a particular temperature is determined by measuring heat of fusion between that temperature and the temperature of complete melting using a partial area technique and by dividing the heat of fusion by 292 Joules/gram. The heat of fusion is determined by computer integration of the partial area using Perkin-Elmer PC Series Software Version 3.1. An example of the residual crystallinity determination and calculation is shown in FIG. 1.

The term "shrink control layer" is used herein to refer to the film layer that provides or controls the shrink response. Such a layer is inherent to all heat shrink films. In a monolayer heat shrink film, the shrink control layer will be the film itself. In a multilayer heat shrink film, the shrink control layer is typically the core or an inside film layer and is typically the thickest film layer. See, for example, WO 95/08441.

The term "substantially unoriented form" is used herein in reference the fact that some amount of orientation is usually imparted to a film during ordinary fabrication. As such, it is meant that the fabrication step, in itself, is not used to impart the degree of orientation required for the desired or required shrink response. The present invention is thought to be generally applicable to operations where the fabrication and orientation steps are separable and occur simultaneously. However, the present invention is preferably directed to an additional and separate orientation step which is required beyond the making of tube, sock, web or layflat sheet whether or not such is soft, molten, or irradiated before substantial orientation is imparted.

The terms "homogeneous ethylene interpolymer," "homogeneously branched ethylene interpolymer" and "narrow short chain distribution" are used in the conventional sense in reference to an ethylene interpolymer in which the comonomer is randomly distributed within a given polymer molecule and wherein substantially all of the polymer molecules have the same ethylene to comonomer molar ratio. The terms refer to an ethylene interpolymer that is characterized by a relatively high short chain branching distribution index (SCBDI) or composition distribution branching index (CDBI). That is, the interpolymer has a SCBDI greater than or equal to 50 percent, preferably greater than or equal to 70 percent, more preferably greater than or equal to 90 percent and essentially lack a measurable high density (crystalline) polymer fraction.

SCBDI or CDBI is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content and represents a comparison of the monomer distribution in the interpolymer to the monomer distribution expected for a Bernoullian distribution. The SCBDI of an interpolymer can be readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, by Wild et al., Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), or in US Patent 4,798,081, or by L. D. Cady, "The Role of Comonomer Type and Distribution in LLDPE Product Performance," SPE Regional Technical Conference, Quaker Square Hilton, Akron, Ohio, October 1-2, pp. 107-119 (1985). However, the preferred TREF technique does not include purge quantities in SCBDI calculations. More preferably, the monomer distribution of the interpolymer and SCBDI are determined using ^{13}C NMR analysis in accordance with techniques described

in US Patent 5,292,845 and by J. C. Randall in Rev. Macromol. Chem. Phys., C29, pp. 201-317.

The terms "heterogeneous," "heterogeneously branched" and "broad short chain distribution" are used herein in the conventional sense in reference to a linear ethylene interpolymer having a comparatively low short chain branching distribution index. That is, the interpolymer has a relatively broad short chain branching distribution. Heterogeneously branched linear ethylene interpolymers have a SCBDI less than 50 percent and more typically less than 30 percent.

The term "homogeneously branched linear ethylene interpolymer" means that the interpolymer has a homogeneous (or narrow) short branching distribution but does not have long chain branching. That is, the ethylene interpolymer has an absence of long chain branching and a linear polymer backbone in the conventional sense of the term "linear." Such interpolymers can be made using polymerization processes (e.g., as described by Elston in USP 3,645,992) which provide uniform (narrow) short branching distribution (i.e., homogeneously branched). In his polymerization process, Elston uses soluble vanadium catalyst systems to make such polymers, however others such as Mitsui Petrochemical Corporation and Exxon Chemical Company have used so-called single site catalyst systems to make polymers having a similar homogeneous structure. Homogeneously branched linear ethylene interpolymers can be prepared in solution, slurry or gas phase processes using hafnium, zirconium and vanadium catalyst systems. Ewen et al. in U.S. Pat. No. 4,937,299 describe a method of preparation using metallocene catalysts.

The term "homogeneously branched linear ethylene interpolymer" does not refer to high pressure branched polyethylene which is known to those skilled in the art to have numerous long chain branches.

Typically, the homogeneously branched linear ethylene interpolymer is an ethylene/ α -olefin interpolymer, wherein the α -olefin is at least one C₃-C₂₀ α -olefin (e.g., 1-propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene and the like), preferably wherein at least one of the α -olefins is 1-octene. Most preferably, the ethylene/ α -olefin interpolymer is a copolymer of ethylene and a C₃-C₂₀ α -olefin, especially an ethylene/C₄-C₆ α -olefin copolymer. Commercial examples of homogeneously branched linear ethylene/ α -olefin

interpolymers are sold by Mitsui Chemical under the designation "TAFMER" and by Exxon Chemical under the designation "EXACT".

Heterogeneously branched VLDPE and LLDPE are well known among practitioners of the linear polyethylene art. They are prepared using conventional Ziegler-Natta solution, slurry or gas phase polymerization processes and coordination metal catalysts as described, for example, by Anderson et al. in U.S. Pat. No. 4,076,698. These conventional Ziegler-type linear polyethylenes are not homogeneously branched, do not have any long-chain branching and have a linear polymer backbone in the conventional sense of the term "linear." Also, these polymers do not show any substantial amorphism at lower densities since they inherently possess a substantial high density (crystalline) polymer fraction. At densities less than 0.90 g/cc, these materials are more difficult to prepare than homogeneously branched ethylene polymer and are also more difficult to pelletize than their higher density counterparts. At such lower densities, heterogeneously branched VLDPE pellets are more tacky and have a greater tendency to clump together than their higher density counterparts.

The terms "ultra low density polyethylene" (ULDPE), "very low density polyethylene" (VLDPE) and "linear very low density polyethylene" (LVLDPE) have been used interchangeably in the polyethylene art to designate the polymer subset of linear low density polyethylenes having a density less than or equal to 0.915 g/cc. The term "linear low density polyethylene" (LLDPE) is then applied to those linear polyethylenes having a density above 0.915 g/cc. As used herein and in the conventional sense, these terms indicate that the polymer has a heterogeneous short chain branching distribution and linear polymer backbone. Commercial examples of heterogeneously branched VLDPE polyolefins suitable for use in the present invention include ATTANE™ ULDPE polymers supplied by the Dow Chemical Company and FLEXOMER™ VLDPE polymers supplied by Union Carbide Corporation.

Although the novel method of the present invention is useful for preparing shrink film structures comprised of heterogeneously branched ethylene polymers, and homogeneously branched ethylene polymers and these polymers are also suitable for claimed shrink film prepared by the novel method, not all of the above polymers are suitable for use in the novel film of the present invention. That is, while the method and the shrink film by the method are generally applicable to all of the above ethylene polymers, only homogeneously branched substantially linear ethylene polymers and homogeneously branched linear ethylene

polymers are suitable for all aspects of the present invention including the novel film.

The term "substantially linear ethylene/ α -olefin interpolymer" is used herein to refer to homogeneously branched ethylene/ α -olefin interpolymers that contain long chain branches as well as short chain branches attributable to homogeneous comonomer incorporation. The long chain branches are of the same structure as the backbone of the polymer and are longer than the short chain branches. The polymer backbone of substantially linear α -olefin polymers is substituted with an average of 0.01 to 3 long chain branch/1000 carbons. Preferred substantially linear polymers for use in the invention are substituted with from 0.01 long chain branch/1000 carbons to 1 long chain branch/1000 carbons, and more preferably from 0.05 long chain branch/1000 carbons to 1 long chain branches/1000 carbons.

Long chain branching is defined herein as a chain length of at least 6 carbons, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy. The long chain branch can be as long as about the same length as the length of the polymer backbone to which it is attached. Long chain branches are obviously of greater length than of short chain branches resulting from comonomer incorporation.

The presence of long chain branching can be determined in ethylene homopolymers by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and is quantified using the method described by Randall (Rev. Macromol. Chem. Phys., C29, V. 2&3, p. 285-297).

As a practical matter, current ^{13}C nuclear magnetic resonance spectroscopy cannot determine the length of a long chain branch in excess of six carbon atoms. However, there are other known techniques useful for determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers. Two such methods are gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS) and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV). The use of these techniques for long chain branch detection and the underlying theories have been well documented in the literature. See, for example, Zimm, G.H. and Stockmayer, W.H., J. Chem. Phys., 17, 1301 (1949) and Rudin, A., Modern Methods of Polymer Characterization, John Wiley & Sons, New York (1991) pp. 103-112.

A. Willem deGroot and P. Steve Chum, both of The Dow Chemical Company, at the October 4, 1994 conference of the Federation of

Analytical Chemistry and Spectroscopy Society (FACSS) in St. Louis, Missouri, presented data demonstrating that GPC-DV is a useful technique for quantifying the presence of long chain branches in substantially linear ethylene interpolymers. In particular, deGroot and Chum found that the level of long chain branches in substantially linear ethylene homopolymer samples measured using the Zimm-Stockmayer equation correlated well with the level of long chain branches measured using ^{13}C NMR.

Further, deGroot and Chum found that the presence of octene does not change the hydrodynamic volume of the polyethylene samples in solution and, as such, one can account for the molecular weight increase attributable to octene short chain branches by knowing the mole percent octene in the sample. By deconvoluting the contribution to molecular weight increase attributable to 1-octene short chain branches, deGroot and Chum showed that GPC-DV may be used to quantify the level of long chain branches in substantially linear ethylene/octene copolymers.

deGroot and Chum also showed that a plot of $\text{Log}(I_2, \text{Melt Index})$ as a function of $\text{Log}(\text{GPC Weight Average Molecular Weight})$ as determined by GPC-DV illustrates that the long chain branching aspects (but not the extent of long branching) of substantially linear ethylene polymers are comparable to that of high pressure, highly branched low density polyethylene (LDPE) and are clearly distinct from ethylene polymers produced using Ziegler-type catalysts such as titanium complexes and ordinary homogeneous catalysts such as hafnium and vanadium complexes.

The substantially linear ethylene/ α -olefin interpolymers used in the present invention are a unique class of compounds that are further defined in US Patent 5,272,236, serial number 07/776,130 filed October 15, 1991 and in US patent 5,278,272, serial number 07/939,281 filed September 2, 1992.

Substantially linear ethylene/ α -olefin interpolymers differ significantly from the class of polymers conventionally known as homogeneously branched linear ethylene/ α -olefin interpolymers described, for example, by Elston in US Patent 3,645,992, in that substantially linear ethylene interpolymers do not have a linear polymer backbone in the conventional sense of the term "linear." Substantially linear ethylene/ α -olefin interpolymers also differ significantly from the class of polymers known conventionally as heterogeneously branched traditional Ziegler polymerized linear ethylene interpolymers (for example, ultra low density polyethylene, linear low density polyethylene or high

density polyethylene made, for example, using the technique disclosed by Anderson et al. in US Patent 4,076,698 and utilized by Golike as described in US Patent 4,597,920, in that substantially linear ethylene interpolymers are homogeneously branched interpolymers. Substantially linear ethylene/ α -olefin interpolymers also differ significantly from the class known as free-radical initiated highly branched high pressure low density ethylene homopolymer and ethylene interpolymers such as, for example, ethylene-acrylic acid (EAA) copolymers and ethylene-vinyl acetate (EVA) copolymers, in that substantially linear ethylene interpolymers do not have equivalent degrees of long chain branching and are made using single site catalyst systems rather than free-radical peroxide catalysts systems.

Single site polymerization catalyst, (for example, the monocyclo-pentadienyl transition metal olefin polymerization catalysts described by Canich in US Patent 5,026,798 or by Canich in US Patent 5,055,438) or constrained geometry catalysts (for example, as described by Stevens et al. in US Patent 5,064,802) can be used to prepare substantially linear ethylene polymers, so long as the catalysts are used consistent with the methods described in US Patent 5,272,236 and in US Patent 5,278,272. Such polymerization methods are also described in PCT/US 92/08812 (filed October 15, 1992). However, the substantially linear ethylene interpolymers are preferably made by using suitable constrained geometry catalysts, especially constrained geometry catalysts as disclosed in US Application Serial Nos.: 545,403, filed July 3, 1990; 758,654, filed September 12, 1991; 758,660, filed September 12, 1991; and 720,041, filed June 24, 1991.

Suitable cocatalysts for use herein include but are not limited to, for example, polymeric or oligomeric aluminoxanes, especially methyl aluminoxane or modified methyl aluminoxane (made, for example, as described in US Patent 5,041,584, US Patent 4,544,762, US Patent 5,015,749, and/or US Patent 5,041,585) as well as inert, compatible, non-coordinating, ion forming compounds. Preferred cocatalysts are inert, non-coordinating, boron compounds.

The polymerization conditions for manufacturing the substantially linear ethylene interpolymers used in the present invention are preferably those useful in the continuous solution polymerization process, although the application of the present invention is not limited thereto. Continuous slurry and gas phase polymerization processes can also be used, provided the proper catalysts and polymerization conditions are employed. To polymerize the

substantially linear interpolymers useful in the invention, the single site and constrained geometry catalysts mentioned earlier can be used, but for substantially linear ethylene polymers the polymerization process should be operated such that the substantially linear ethylene interpolymers are formed. That is, not all polymerization conditions inherently make the substantially linear ethylene polymers, even when the same catalysts are used. For example, in one embodiment of a polymerization process useful in making substantially linear ethylene interpolymers, a continuous process is used, as opposed to a batch process.

The substantially linear ethylene interpolymer for use in the present invention is characterized as having

(a) a melt flow ratio, $I_{10}/I_2 \geq 5.63$,

(b) a molecular weight distribution, M_w/M_n , as determined by gel permeation chromatography and defined by the equation:

$$(M_w/M_n) \leq (I_{10}/I_2) - 4.63,$$

(c) a gas extrusion rheology such that the critical shear rate at onset of surface melt fracture for the substantially linear ethylene interpolymer is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture for a linear ethylene interpolymer, wherein the substantially linear ethylene interpolymer and the linear ethylene interpolymer comprise the same comonomer or comonomers, the linear ethylene interpolymer has an I_2 , M_w/M_n and density within ten percent of the substantially linear ethylene interpolymer and wherein the respective critical shear rates of the substantially linear ethylene interpolymer and the linear ethylene interpolymer are measured at the same melt temperature using a gas extrusion rheometer, and

(d) a single differential scanning calorimetry, DSC, melting peak between -30 and 150°C .

The substantially linear ethylene interpolymers used in this invention are homogeneously branched interpolymers and essentially lack a measurable "high density" fraction as measured by the TREF technique (i.e., have a narrow short chain distribution and a high SCBD index).

The substantially linear ethylene interpolymer generally do not contain a polymer fraction with a degree of branching less than or equal to 2 methyls/1000 carbons. The "high density polymer fraction" can also be described as a polymer fraction with a degree of branching less than 2 methyls/1000 carbons.

The substantially linear ethylene interpolymers for use in the novel method and the film made from the novel method of the present invention are interpolymers of ethylene with at least one C₃-C₂₀ α -olefin and/or C₄-C₁₈ diolefin. Copolymers of ethylene and an α -olefin of C₃-C₂₀ carbon atoms are especially preferred. The term "interpolymer" is used herein to indicate a copolymer, or a terpolymer, or the like, where, at least one other comonomer is polymerized with ethylene to make the interpolymer.

Suitable unsaturated comonomers useful for polymerizing with ethylene include, for example, ethylenically unsaturated monomers, conjugated or non-conjugated dienes, polyenes, etc. Examples of such comonomers include C₃-C₂₀ α -olefins as propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 1-decene, and the like. Preferred comonomers include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene, and 1-octene is especially preferred. Other suitable comonomers include styrene, halo- or alkyl-substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, 1,7-octadiene, and cycloalkenes, e.g., cyclopentene, cyclohexene and cyclooctene.

Determination of the critical shear rate and critical shear stress in regards to melt fracture as well as other rheology properties such as "rheological processing index" (PI), is performed using a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R.N. Shroff and L.V. Cancio in Polymer Engineering Science, Vol. 17, No. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on pp. 97-99. GER experiments are performed at a temperature of about 190°C, at nitrogen pressures between about 250 to about 5500 psig using about a 0.0754 mm diameter, 20:1 L/D die with an entrance angle of about 180°. For the substantially linear ethylene polymers described herein, the PI is the apparent viscosity (in kpoise) of a material measured by GER at an apparent shear stress of about 2.15×10^6 dyne/cm². The substantially linear ethylene polymer for use in the invention are ethylene interpolymers having a PI in the range of 0.01 kpoise to 50 kpoise, preferably 15 kpoise or less. The substantially linear ethylene polymers used herein have a PI less than or equal to 70 percent of the PI of a linear ethylene interpolymer (either a conventional Ziegler polymerized interpolymer or a linear homogeneously branched interpolymer as described by Elston in US Patent 3,645,992) having an I₂, M_w/M_n and

density, each within ten percent of the substantially linear ethylene interpolymers.

An apparent shear stress versus apparent shear rate plot is used to identify the melt fracture phenomena and quantify the critical shear rate and critical shear stress of ethylene polymers. According to Ramamurthy in the Journal of Rheology, 30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular film gloss to the more severe form of "sharkskin." Herein, as determined using the above-described GER, the onset of surface melt fracture (OSMF) is characterized at the beginning of losing extrudate gloss at which the surface roughness of the extrudate can only be detected by 40x magnification. The critical shear rate at the onset of surface melt fracture for the substantially linear ethylene interpolymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene interpolymers having essentially the same I_2 and M_w/M_n .

Gross melt fracture occurs at unsteady extrusion flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability and maximum abuse properties of films, coatings and profiles, surface defects should be minimal, if not absent. The critical shear stress at the onset of gross melt fracture for the substantially linear ethylene interpolymers used in the invention, that is those having a density less than 0.91 g/cc, is greater than 4×10^6 dynes/cm². The critical shear rate at the onset of surface melt fracture (OSMF) and the onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER. Preferably, in the present invention, the substantially linear ethylene interpolymers will be characterized by its critical shear rate, rather than its critical shear stress.

Substantially linear ethylene/ α -olefin interpolymers, like other homogeneously branched ethylene/ α -olefin interpolymers that consist of a single polymer component material, are characterized by a single DSC melting peak. The single melting peak is determined using a differential scanning calorimeter standardized with indium and deionized water. The method involves about 5-7 mg sample sizes, a "first heat" to

about 180°C which is held for about 4 minutes, a cool down at about 10°/min. to about -30°C which is held for about 3 minutes, and heat up at about 10°C/min. to about 150°C for the "second heat". The single melting peak is taken from the "second heat" heat flow vs. temperature curve. Total heat of fusion of the polymer is calculated from the area under the curve.

For substantially linear ethylene interpolymers having a density of 0.875 g/cc to 0.91 g/cc, the single melting peak may show, depending on equipment sensitivity, a "shoulder" or a "hump" on the low melting side that constitutes less than 12 percent, typically, less than 9 percent, and more typically less than 6 percent of the total heat of fusion of the polymer. Such an artifact is observable for other homogeneously branched polymers such as Exact™ resins and is discerned on the basis of the slope of the single melting peak varying monotonically through the melting region of the artifact. Such an artifact occurs within 34°C, typically within 27°C, and more typically within 20°C of the melting point of the single melting peak. The heat of fusion attributable to an artifact can be separately determined by specific integration of its associated area under the heat flow vs. temperature curve.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968) to derive the following equation:

$$M_{\text{polyethylene}} = a * (M_{\text{polystyrene}})^b.$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, M_w , and number average molecular weight, M_n , is calculated in the usual manner according to the following formula:

$$M_j = (\sum w_i (M_i^j))^{\frac{1}{j}}; \text{ where } w_i \text{ is the weight fraction of the molecules with molecular weight } M_i \text{ eluting from the GPC column in fraction } i \text{ and } j = 1 \text{ when calculating } M_w \text{ and } j = -1 \text{ when calculating } M_n.$$

For the homogeneously branched ethylene interpolymers used in the present invention, the M_w/M_n is preferably less than 3, more preferably less than 2.5, and especially from 1.5 to about 2.5 and most especially from 1.8 to 2.3.

Substantially linear ethylene interpolymers are known to

have excellent processability, despite having a relatively narrow molecular weight distribution. Surprisingly, unlike homogeneously and heterogeneously branched linear ethylene polymers, the melt flow ratio (I_{10}/I_2) of substantially linear ethylene interpolymers can be varied essentially independently of the molecular weight distribution, M_w/M_n . Accordingly, the preferred ethylene α -olefin interpolymer for use in the present invention is a substantially linear ethylene interpolymer.

Homogeneously branched substantially linear ethylene interpolymers are available from The Dow Chemical Company as Affinity™ polyolefin plastomers, and as Engage™ polyolefin elastomers. Homogeneously branched substantially linear ethylene polymers can be prepared by the continuous solution, slurry, or gas phase polymerization of ethylene and one or more optional α -olefin comonomers in the presence of a constrained geometry catalyst, such as is disclosed in European Patent Application 416,815-A.

The density of the polyolefin polymer (as measured in accordance with ASTM D-792) for use in the presently claimed method is generally greater than 0.85 g/cc, especially from 0.86 g/cc to 0.93 g/cc, more preferably, from about 0.88 g/cc to 0.92 g/cc and most preferably, from 0.88 to 0.91. When used as the shrink control polymer layer of the shrink film, the preferred polymer density of the polyolefin polymer is less than 0.915 g/cc. The density of the homogeneously branched ethylene polymer for use in all aspects of the present invention is less than 0.91 g/cc, generally in the range of 0.85 to 0.91 g/cc, preferably less than 0.907 g/cc, more preferably less than or equal to 0.905 g/cc, most preferably less than or equal to 0.902 g/cc, and especially in the range of 0.880 to 0.90 g/cc.

The molecular weight of polyolefin polymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg (formerly known as "Condition E" and also known as I_2). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The melt index for the polyolefin polymers useful herein is generally from 0.01 g/10 min. to 20 g/10 min., preferably from 0.01 g/10 min. to 10 g/10 min., and especially from 0.1 g/10 min. to 2 g/10 min.

Other measurements useful in characterizing the molecular weight of substantially linear ethylene interpolymers and homopolymers involve melt index determinations with higher weights, such as, for

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common example, ASTM D-1238, Condition 190°C/10 kg (formerly known as "Condition N" and also known as I₁₀). The ratio of a higher weight melt index determination to a lower weight determination is known as a melt flow ratio, and for measured I₁₀ and the I₂ melt index values the melt flow ratio is conveniently designated as I₁₀/I₂. For the substantially linear ethylene polymers used to prepare the films of the present invention, the melt flow ratio indicates the degree of long chain branching, i.e., the higher the I₁₀/I₂ melt flow ratio, the more long chain branching in the polymer. The I₁₀/I₂ ratio of the substantially linear ethylene polymers is preferably at least 7, and especially at least 9.

Additives such as antioxidants (e.g., hindered phenolics (such as Irganox® 1010 or Irganox® 1076), phosphites (e.g., Irgafos® 168), cling additives (e.g., PIB), PEPQ™ (a trademark of Sandoz Chemical, the primary ingredient of which is believed to be a biphenylphosphonite), pigments, colorants, fillers, and the like can also be included in the polyolefin polymers, to the extent that they do not interfere with the method and the enhanced shrink response discovered by Applicants. The fabricated film may also contain additives to enhance its antiblocking and coefficient of friction characteristics including, but not limited to, untreated and treated silicon dioxide, talc, calcium carbonate, and clay, as well as primary and secondary fatty acid amides, silicone coatings, etc. Other additives to enhance the film's anti-fogging characteristics may also be added, as described, for example, in US Patent 4,486,552 (Niemann). Still other additives, such as quaternary ammonium compounds alone or in combination with EAA or other functional polymers, may also be added to enhance the film's antistatic characteristics and allow packaging of electronically sensitive goods.

Film structures of the present invention can be made using conventional simple bubble or cast extrusion techniques, however, preferred film structures are prepared using more elaborate techniques such as "tenter framing" or the "double bubble," "tape bubble" or "trapped bubble" process. The double bubble technique is described by Pakle in US Patent 3,456,044.

The presently claimed method for preparing shrink film structures and the novel film structures of the present invention are more fully described in the following examples, but are not limited to the examples shown. The homogeneously branched substantially linear



ethylene polymers used in the following examples were prepared according to procedures and techniques described in the Examples of U.S. Patent 5,272,236 and 5,278,272. The homogeneously branched linear ethylene interpolymer used in the following Examples was made by the Exxon Chemical Company.

Examples

In an experiment to determine the comparative shrink response of ethylene interpolymers, a homogeneously branched substantially linear ethylene interpolymer and a heterogeneously branched linear ethylene interpolymer were evaluated. Example 1 utilized a substantially linear ethylene/1-octene copolymer having a density of 0.90 g/cc, a melt index (I_2) of 0.8 g/10 minutes, a molecular weight distribution (M_w/M_n) of 2.2, and a melt flow ratio (I_{10}/I_2) of 8.5. Example 2 utilized the polymer of Example 1 which had been irradiated at 5.0 Mrad. Comparative Run 3 utilized a heterogeneously branched ULDPE ethylene/1-octene copolymer having a density of 0.905 g/cc, a melt index (I_2) of 0.8, a molecular weight distribution (M_w/M_n) of 3.5 and a melt flow ratio (I_{10}/I_2) of 8. Comparative Run 4 utilized the polymer of Comparative Run 3 which had been irradiated at 5.0 Mrad. Irradiation was performed on pellets of the respective interpolymers by exposure to electron beam radiation at E Beam Services, Inc. (Canterbury, NJ). The DSC melting point for the non-irradiated interpolymers was determined, all four samples were prepared into sheeting (18.5 ± 1.5 mil thick) ($0.47 \text{ mm} \pm 0.04 \text{ mm}$) and subsequently biaxially stretched using a T.M. Long laboratory stretching frame. The stretching temperature utilized was a temperature below the DSC melting point of the copolymer but 5°C above the temperature at which tearing of the sheet occurs during stretching. These stretched sheets were tested for unrestrained (free) shrink at 95°C in accordance with procedures in ASTM D-2732 by cutting four inch by four inch ($10.2 \text{ cm} \times 10.2 \text{ cm}$) samples from each of the stretched sheets and carefully placing them flat into the bottom of silicone-coated metal pans. The metal pans had sides 1 inch (2.5 cm) high and were well-coated with 200 centipoise silicone oil. The pans containing the film samples were then placed into a forced-air convection oven at 95°C for ten minutes. After ten minutes, the pans were removed from the oven and allowed to cool to an ambient temperature. After cooling, the film samples were removed and the dimensions in both the machine and transverse directions were measured. The Vicat softening point was measured in accordance with ASTM

D1525. Table 1 summarizes the shrink response data as well as provides the stretch ratio information for each sample:

Table 1

Sample	Stretching Temperature* (C)	Stretch Ratio	Free Shrink (%) MD	Free Shrink (%) TD
Inventive Example 1	88	3 x 3	> 35	> 35
Inventive Example 2	88	4 x 4	> 35	> 35
Comparative Run 3	97	4 x 4	< 25	< 25
Comparative Run 4	97	4 x 4	< 25	< 25

*Stretching temperature at $\pm 1^\circ\text{C}$

The data in Table 1 show that the sheets fabricated from the homogeneously branched substantially linear ethylene interpolymer exhibited superior shrink response performance (at least 14 percent greater) over comparable sheets fabricated from the conventional heterogeneously branched linear ethylene interpolymer. The superior shrink response is exhibited even when the amount of biaxial stretching is significantly lower for the Inventive Examples relative to the comparative examples (i.e., 3 x 3 versus 4 x 4). The Inventive Examples even show superior free shrink performance regardless of whether the comparative examples were irradiated or nonirradiated prior to orientation (stretching). The stretching temperature for the homogeneously branched substantially linear ethylene interpolymer was 7°C below its single DSC melting point. Conversely, the stretching temperature for the heterogeneously branched linear ethylene interpolymer was 25°C below its highest DSC melting peak, 21°C below its intermediate melting peak and 2°C above its lowest melting peak. The stretching temperature for the homogeneously branched substantially linear ethylene polymer is considered the optimum or near-optimum stretching temperature for the polymer and for the particular stretch ratio and stretching rate. That is, the shrink response is the maximum obtainable for the sample at a 95°C shrink temperature wherein a higher stretching temperature would yield a reduced shrink response.

In another evaluation, rather than utilizing the method disclosed by Golike where ethylene polymer compositions are arbitrarily biaxially oriented at a temperature within 10°C of the highest melting polymer compound (as per polymer blends) or compositional fraction (as per a heterogeneously branched ethylene interpolymer), the percent residual crystallinity as a function of temperature was determined for a series of ethylene polymers. The series included heterogeneously branched linear low density polyethylenes (LLDPEs) supplied by The Dow Chemical Company under the trademark "DOWLEX;" heterogeneously branched ultra or very low density polyethylenes (ULDPEs or VLDPEs) supplied by The Dow Chemical Company under the trademark "ATTANE" and by Union Carbide under the trademark "FLEXOMER;" homogeneously branched substantially linear ethylene interpolymers supplied by The Dow Chemical Company under the trademarks "AFFINITY" and "ENGAGE;" homogeneously branched linear ethylene interpolymers supplied by Exxon Chemical Corporation under the trademark "EXACT" and Mitsui Chemical Company under the trademark "TAFMER;" and ethylene vinyl acetate (EVA) copolymers supplied by Dupont Chemical Company under the trademark "ELVAX" and Nova Polymers under the trademark "NOVAPOL."

The polymer samples were made into 30 mil sheets on a standard cast film extrusion line by cast extrusion and quick quenching with a chill roll. The melt temperature of the cast extrusion at the die was set at 480°F (249°C) and the chill roll temperature was set at 75°F (24°C). DSC first heat at 10°C/min. was determined on tap water-quenched, compression molded thin films of each polymer sample (unextruded) to simulate the quenching encountered by the extrusion cast sheets. The temperature that corresponded to 22.5 weight percent absolute residual crystallinity was determined for each polymer sample.

The evaluation proceeded by initially setting the stretching temperature in the T.M. Long stretcher such that 22.5 weight percent residual crystallinity was maintained for each polymer sample. The so-defined stretching temperature was substantially less than the temperature of the lowest melting peak of the sample. If a given sample sheet could not oriented (i.e., tore during stretching and/or stretched unevenly), the stretching temperature was raised for subsequent sample sheets of the same polymer sample in 3°C intervals until or such that a corresponding sample sheet could be consistently and uniformly oriented at a stretching ratio of 4.5 x 4.5 and a stretching rate 5 inches/second (12.7 cm/second). The first interval of a higher temperature where the polymer sample could be consistently and uniformly oriented was taken as

the optimum stretching temperature for the particular polymer sample, stretch ratio and stretching rate and, as such, provides the highest residual crystallinity that the particular polymer sample sheet could be oriented.

5 Tafmer™ A4090 could not be uniformly stretched apparently due its relatively high melt index. Similarly, Tafmer™ P0480 was not oriented due to its very low density. The optimum orientation
10 temperatures for all of the polymer samples evaluated as well as the DSC melting points, the residual crystallinity at the optimum stretching temperature for tap water quenched film samples and the Vicat softening
15 temperatures for the various polymer samples are reported in Table 2. With the exception of Example 9, all the stretching temperatures reported in Table 2 were 3°C above the respective lowest stretch temperature for each polymer sample. The stretching temperature
15 reported in Table 2 for Example 9 is more than 3°C above its lowest stretch temperature.

 For the stretching step, initial sample dimensions of 2" x 2" (5.1 cm x 5.1 cm) were used. A stretching (draw) ratio of 4.5 x 4.5 and a stretching rate of 5 inches/ second (12.7 cm/s) were used. The
20 samples were preheated to the identified optimum or near-optimum stretching temperature in the T. M. Long stretcher for 3 minutes. The hot air was deflected so as not to impinge on the sample directly to avoid hot spots on the sheets. Sheets were stretched at the highest possible level of residual crystallinity (i.e., at their respective
25 optimum or near-optimum stretching temperatures) to maximize the shrink response potential of the sheets for the above stretching ratio and stretching rate.

 The hot-water shrinkage at 90°C for the biaxially oriented sheets are also shown in Table 2. Shrinkage values were obtained by
30 measuring the unrestrained shrink in a water bath kept at 90°C. The samples were cut into 12 cm x 1.27 cm pieces. The samples were marked 10 cm. from one end for identification. Each sample was completely immersed in the water bath for five seconds and then removed. Film shrinkage was obtained from the calculation using ASTM method D 2732-83.
35 The average of four samples was calculated and the data are also reported in Table 2. Since the samples were equi-biaxially oriented (i.e., 4.5 x 4.5), the shrinkage in the machine and transverse directions were equivalent as expected. Also, the shrink response at 90°C for the various heterogeneously branched and homogeneously branched

ethylene interpolymers as a function of polymer density are shown in FIG. 2 and FIG. 3.

The orientation (stretching) temperatures shown in Table 2 represent the low end of the orientation window for each sample. The high end of an orientation window is usually just below the higher melting peak of the polymer. Thus, it can be concluded from Table 2 that heterogeneously branched ethylene interpolymers have a much broader orientation window than homogeneously branched ethylene interpolymers (i.e., Affinity, Engage and Exact resins).

Golike in US Patent 4,597,920 teaches orientation should be carried out between the lower and higher melting points of a heterogeneously branched copolymer or polymer blend. The DSC melting information for Dowlex™ LLDPE 2045, Attane™ ULDPE 4201, Attane™ ULDPE 4203 and Affinity™ substantially linear interpolymer PL 1880 are also provided Table 2. Table 2 indicates, contrary to the teachings of Golike, that the heterogeneously branched Dowlex™ and Attane™ polymers can be oriented for a maximized shrink response at stretching temperatures below their respective lower melting peaks. As set forth above, the homogeneously branched Affinity™ polymer sample has a single DSC melting point and, as such, Golike's teachings are not specifically applicable to such polymers. However, it is noted that the homogeneously branched Affinity™ polymer sample can also be oriented for a maximized shrink response at a stretching temperature below its respective lower melting peak.

Moreover, Table 2 indicates heterogeneously branched LLDPE and ULDPE polymers having a density in the range from 0.907 g/cc to 0.937 g/cc can be oriented at a maximum residual crystallinity of from 20 weight percent to 24 weight percent and that the maximum residual crystallinity for optimum or near-optimum orientation of these polymers is predominately influenced by polymer crystallinity or crystalline polymer fractions. Table 2 also indicates homogeneously branched ethylene interpolymers in the density range from 0.899 g/cc to 0.918 g/cc can be oriented at a maximum residual crystallinity of from 14 weight percent to 17 weight percent. These maximum residual crystallinity differences indicate that, at least as to shrink response, heterogeneously branched ethylene interpolymers differ completely from homogeneously branched ethylene interpolymers.

Additionally, whereas FIG. 2 indicates that at polymer densities greater than 0.91 g/cc, heterogeneously branched polymers show

a higher shrink response than homogeneously branched polymers at an equivalent density, FIG. 3 indicates that at densities less than 0.91 g/cc for interpolymers stretched in accordance with the present invention, homogeneously branched ethylene polymers show greater than or equal to 10 percent greater, especially 15 percent greater, more especially 20 percent greater and most especially 25 percent greater shrink response than heterogeneously branched ethylene polymers having equivalent densities in that range and fabricated (including orientation) at essentially the same conditions. Such is particularly true where the interpolymer densities are less than 0.907 g/cc, more especially equal to or less than 0.905 g/cc, more especially less than or equal to 0.902 g/cc and most especially equal to or less than 0.90 g/cc.

The shrink response of the homogeneously branched ethylene polymers as shown in FIG. 3 is especially surprising since reasonable extrapolation of the data shown in FIG. 2 as well as the data disclosed in WO Publication 95/08441 suggest the shrink response of homogeneously branched ethylene polymers are expected to be inferior to or, at best, essentially equivalent to heterogeneously branched ethylene polymers at densities less than 0.91 g/cc.

Table 2

[illegible]

NA denotes not applicable; ND denotes not determined



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We claim:

1. A method of making a heat shrinkable polyolefin film comprising the steps of

- 5 a. fabricating a polyolefin film structure in substantially unoriented form, and
- 10 b. stretching the polyolefin film at a selected stretching rate, stretch ratio and stretching temperature, wherein the selected stretching temperature is no more than 5°C above the lowest stretch temperature for the polyolefin film structure and for the selected stretching rate and stretching ratio and wherein the polyolefin film structure comprises at least one ethylene polymer having a polymer density less than 0.915 g/cc.

15 2. The method of Claim 1 wherein the ethylene polymer is a substantially linear ethylene polymer which is characterized as having:

- 20 i. a short chain branching distribution index (SCBDI) greater than about 50 percent,
- ii. a single differential scanning calorimetry, DSC, melting peak between -30° and 150°C,
- iii. a melt flow ratio, I_{10}/I_2 , ≥ 5.63 ,
- 25 iv. a molecular weight distribution, M_w/M_n , defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and
- 30 v. a gas extrusion rheology critical shear rate wherein the critical shear rate at the onset of surface melt fracture for the substantially linear ethylene polymer is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture for a linear ethylene polymer, wherein the linear ethylene polymer is characterized as having an I_2 , M_w/M_n and density
- 35 within ten percent of the substantially linear ethylene polymer, and wherein the critical shear rates of the substantially linear ethylene polymer





and the linear ethylene polymer are measured at the same melt temperature using a gas extrusion rheometer.

5 3. The method of Claim 1 wherein the film structure is a monolayer film structure.

 4. The method of Claim 1 wherein the film structure is a multilayer film structure.

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 5. The method of Claim 4 wherein the multilayer film structure is prepared by a coextrusion technique.

 6. The method of Claim 4 wherein the multilayer film structure is prepared by a lamination technique.

15

 7. The method of Claim 4 wherein at least one layer of the multilayer film structure comprises a polymer mixture and the mixture includes at least one homogeneously branched ethylene interpolymer.

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 8. The method of Claim 7 wherein the polymer mixture includes at least one homogeneously branched substantially linear ethylene interpolymer and at least one heterogeneously branched ethylene polymer.

 9. The method of Claim 4 wherein the multilayer film structure comprises a barrier film layer.

25

 10. The method of Claim 1, wherein the ethylene polymer is a copolymer of ethylene and at least one C₃-C₂₀ α -olefin.

30

 11. The method of Claim 1, wherein the ethylene polymer is a copolymer of ethylene and 1-octene.

 12. The method of Claim 2, wherein the substantially linear ethylene polymer has from 0.01 to 3 long chain branches/1000 carbons along the polymer backbone.

35

 13. The method of Claim 1, wherein the stretching temperature is in the range of from 50°C to 125°C.

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14. A heat shrinkable film structure which comprises, as the shrink control layer, at least one homogeneously branched ethylene interpolymer having a polymer density of less than 0.91 g/cc, wherein the film structure is characterized as having a shrink response at least 5 10 percent greater than the shrink response of a second film structure which comprises a heterogeneously branched ethylene interpolymer as the shrink control layer and wherein the film structure and the second film structure are fabricated and stretched under essentially the same conditions and the homogeneously branched and heterogeneously branched 10 interpolymers have essentially the same polymer density and I₂ melt index.

15. A heat shrinkable polyolefin film structure prepared by a method which comprises the steps of

15 (a) fabricating a polyolefin film structure in substantially unoriented form, and

(b) thereafter stretching the fabricated polyolefin film structure at a selected stretching rate, stretch ratio and stretching temperature, wherein the selected stretching temperature is 20 below the melting point of the film and is a temperature no more than 5°C above the lowest stretch temperature for the selected stretching rate and stretching ratio, and

wherein the film structure comprises, as the shrink control layer, at 25 least one ethylene polymer having a polymer density of less than 0.915 g/cc.

