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(54) Titre : METHODE POUR MODIFIER DES POLYOLEFINES A L'AIDE DE DIORGANOPOLYSILOXANES
(54) Title: METHOD OF MODIFYING POLYOLEFIN WITH DIORGANOPOLYSILOXANE PROCESS AID

(57) Abrégé/Abstract:
There is disclosed a polyolefin composition which can be extruded at relatively high rates to provide extrudate having a low surface roughness (sharkskin), said composition comprising (A) 100 parts by weight of a polyolefin resin; and (B) 0.01 to 1 part by weight of a hydroxy-functional diorganopolysiloxane process aid, said diorganopolysiloxane having a number average molecular weight of at least 10,000. In particularly preferred embodiments, a hydroxy-functional diorganopolysiloxane in combination with a low density polyethylene is used as a process aid for linear low density polyethylene.

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METHOD OF MODIFYING POLYOLEFIN WITH DIORGANOPOLYSILOXANE PROCESS AID

ABSTRACT

There is disclosed a polyolefin composition which can be extruded at relatively high rates to provide extrudate having a low surface roughness (sharkskin), said composition comprising

(A) 100 parts by weight of a polyolefin resin; and

(B) 0.01 to 1 part by weight of a hydroxy-functional diorganopolysiloxane process aid, said diorganopolysiloxane having a number average molecular weight of at least 10,000.

In particularly preferred embodiments, a hydroxy-functional diorganopolysiloxane in combination with a low density polyethylene is used as a process aid for linear low density polyethylene.

METHOD OF MODIFYING POLYOLEFIN WITH DIORGANOPOLYSILOXANE PROCESS AID

The present invention relates to a method for modifying polyolefin compositions wherein a hydroxy-functional diorganopolysiloxane is added to said polyolefin. The resulting compositions have enchanced processing characteristics, particularly with respect to a surface defect phenomenon known in the art as melt fracture or "sharkskin."

When a high molecular weight thermoplastic resin is extruded through a die, smooth extrudates are only obtained up to a certain shear stress (i.e., shear rate; extruder output rate). Beyond that, surface irregularities begin to appear, such as haze and surface roughness. These defects are known as melt fracture or "sharkskin" and limit production rates in commercial applications. To counteract these phenomena, and thereby achieve higher output rates, process aids are typically added to the thermoplastic resin prior to extrusion. One of the primary functions of a process aid is to delay, suppress, or eliminate, the onset of surface defects such as haze and sharkskin, and to enable operation at higher shear stress.

Thus, certain fluoroelastomers have been found to delay the onset of melt fracture or surface defects such that higher shear rates and output can be attained while still producing acceptable extrudates. Such additives are typically employed at a level of 250 to 3,000 parts per million of the fluoroelastomer (based on the weight of the resin) and they are generally added to the thermoplastic resin prior to extrusion by dry blending of the fluoro-elastomer concentrate therewith.

Representative for the prior art of this invention are US-A 5,356,585; US-A 4,855,360 and CA-A 1,049,682.

For polyolefin resins, even the employ of the above described process aids falls short of the industry's need for ever increasing production rates. This quest for higher extrusion rates, which is driven primarily by economic considerations related to the efficient use of processing equipment and human resources, is of particular interest to producers of blown film.

We have found that, when a small quantity of a hydroxy-functional diorganopolysiloxane is added to a polyolefin, considerably higher extrusion rates are possible than with the prior art fluoroelastomers. Furthermore, our extrudates have a reduced surface roughness (sharkskin) relative to fluoroelastomer systems and a reduced degree of sharkskin relative to the unmodified linear low density polyethylene.

The present invention therefore provides a composition comprising:

(A) 100 parts by weight of a polyolefin resin; and

(B) 0.01 to 1.0 part by weight of a hydroxy-functional diorganopolysiloxane, said diorganopolysiloxane having a number average molecular weight of at least 10,000.

In preferred embodiments, a linear low density polyethylene (LLDPE) is modified with a combination of the hydroxy-functional diorganopolysiloxane and, additionally, a low density polyethylene (LDPE). In a still further preferred embodiment the hydroxy-functional diorganopolysiloxane is linear hydroxy-functional diorganopolysiloxane. These compositions exhibit a surprisingly low degree of sharkskin at relatively high extrusion speeds. Moreover, there is less "screw slip" associated with our three-component systems preferred embodiment relative to our two-component systems. As known in the art, output (e.g., length/unit time or mass/unit time) is approximately proportional to the rotational screw speed (revolutions/unit time) at low

extrusion rates. However, at higher screw speeds, there is a deviation from this proportionality, the difference being termed "screw slip."

The polyolefin (A) of this invention is selected from homopolymers of olefins as well as interpolymers of one or more olefins with each other and/or up to 40 mole percent of one or more monomers which are copolymerizable with the olefins. Examples of suitable polyolefins include homopolymers of ethylene, propylene, butene-1, isobutylene, hexene, 1,4-methylpentene-1, pentene-1, octene-1, nonene-1 and decene-1. Interpolymers of two or more of the above mentioned olefins may also be employed as component (A) and they may also be copolymerized with vinyl or diene compounds or with other compounds which can be copolymerized with olefins.

Specific examples of suitable interpolymers are ethylene-based copolymers, such as ethylene-propylene copolymers, ethylene-butene-1 copolymers, ethylene-hexene-1 copolymers, ethylene-octene-1 copolymers, ethylene-butene-1 copolymers and interpolymers of ethylene with two or more of the above mentioned olefins.

Component (A) may also be a blend of two or more of the above mentioned homopolymers or interpolymers. For example, the blend can be a uniform mixture of one of the above systems with one or more of the following: polypropylene, high-pressure, low-density polyethylene, high-density polyethylene, polybutene-1 and polar monomer-containing olefin copolymers such as ethylene/acrylic acid copolymers, ethylene/methyl acrylate copolymers, ethylene/ethyl acrylate copolymers, ethylene/vinyl acetate copolymers, ethylene/acrylic acid/ethyl acrylate terpolymers and ethylene/acrylic acid/vinyl acetate terpolymers.

Particularly preferred polyolefins (A) are polyethylene (PE) polymers such as low pressure, substantially linear, ethylene homopolymers and interpolymers of ethylene with alpha-olefins having 3 to 10 carbon atoms. Such interpolymers are known as linear low density polyethylene (LLDPE) in the art. Preferably, these systems have a density of 0.85 to 0.97 g/cm^3, more preferably 0.875 to 0.930 g/cm^3, and have a weight average molecular weight (Mw) of 60,000 to 200,000.

The above interpolymers are well known in the art and further description thereof is considered unnecessary.

The diorganopolysiloxane (B) of our invention is a hydroxy-functional oil or high consistency gum having a number average molecular weight (Mn) of at least 10,000, but preferably below 1,000,000. Preferably, the Mn of component (B) is 40,000 to 400,000, more preferably 75,000 to 400,000. When Mn is below 10,000, the compositions tend to exhibit excessive screw slip. Furthermore, at the lower Mn(s) there is a marked decrease in extruder output when the compositions are extruded a second time. Such a second extrusion is often required in industrial operations. For example, errors in manufacture, such as incorrect extruder settings or inadequate amounts of key ingredients, necessitate re-extrusion of the resulting "off-spec" material. Likewise, in film blowing operations, the edge portions of a flattened bubble are trimmed and recycled to the extruder. Further, re-extrusion is employed when scrap is returned and recycled; this procedure is known as "post-consumer recycle" in the art. Similarly, when the Mn is above 1,000,000, mixing of our diorganopolysiloxane into the polyolefin becomes difficult but such a siloxane could still be employed.

Thus, to achieve a good balance with respect to sharkskin, screw slippage and extrusion efficiency of recycled material, it is preferred that component (B) is a gum having Mn in the range of 100,000 to 400,000 and, most preferably, 250,000 to 350,000.

Component (B) may be a linear or branched polymer or copolymer wherein the organic groups are independently selected from methyl or phenyl radicals. Suitable diorganopolysiloxanes include polydimethylsiloxane homopolymers, copolymers consisting of dimethylsiloxane units and methylphenylsiloxane units, copolymers consisting of dimethylsiloxane units and diphenylsiloxane units, copolymers consisting of diphenylsiloxane units and methylphenylsiloxane units, and homopolymers of methylphenylsiloxane units. Mixtures of two or more such polymers or copolymers may also be employed as component (B).

Diorganopolysiloxane (B) must contain at least 1 hydroxyl group in the molecule. The hydroxyl group or groups may be located at the ends of the molecule, they may be distributed along the chain or they may be located both at the ends as well as along the chain. Preferably, the hydroxyls reside at the molecular chain ends in the form of diorganohydroxysiloxy groups, such as dimethylhydroxysiloxy, diphenylhydroxysiloxy and methylphenylhydroxysiloxy. When the hydroxyls are located only along the chain, the terminal groups of the diorganopolysiloxane may be any non-reactive moiety, typically a triorganosiloxy species such as trimethylsiloxy.

It is preferred that the diorganopolysiloxane (B) is a linear polydimethylsiloxane containing up to 50 mole percent of phenyl radicals. Most preferably, it is a

polydimethylsiloxane homopolymer having dimethylhydroxy-siloxy end groups.

Component (B) is well known in the art and such polymers and copolymers are available commercially. However, in the usual commercial preparation of these polymers, a considerable amount of low molecular weight cyclic polysiloxane species is formed. For our invention, it is preferred that these cyclics be removed (e.g., by stripping at elevated temperatures and/or reduced pressure) since they generally impart undesirable characteristics to our inventive compositions and/or our process. For example, the presence of cyclics can degrade the surface quality of the extrudate, generate foaming and/or smoke or it can increase the amount of screw slippage during extrusion.

The compositions of this invention are prepared by thoroughly dispersing from 0.01 to 1 part by weight (100 to 10,000 parts per million) of diorganopolysiloxane (B) in 100 parts by weight of a polyolefin (A). It is preferred that 0.02 to 0.5 part by weight (200 to 5,000 ppm) of component (B) is used for each 100 parts by weight of component (A). More preferably, 0.03 to 0.2 part of (B), and most preferably 0.04 to 0.2 part, per 100 parts by weight of (A) are used. When the diorganopolysiloxane is added at levels below 0.01 part per 100 parts by weight of (A), there is little improvement in the surface quality of the extrudate (i.e., sharkskin) versus the corresponding unmodified polyolefin, particularly at high rates of extrusion. Similarly, at levels higher than 1 part of (B) per 100 parts by weight of (A), the surface quality of the extrudate begins to deteriorate. Furthermore, when more than 1 part of (B) per 100 parts by weight of (A) is used, an excessive amount of siloxane is observed on the surface of the

extrudate which adversely impacts such properties as printability and sealability. Additionally, the physical properties of the final extrudate are degraded. Thus, the preferred compositional ranges result in the desired balance of good surface quality (i.e., little sharkskin), clarity, smoothness, sealability, paintability and gloss of the extruded material as well as low screw slip during processing, particularly at high extruder output rates.

The dispersion of diorganopolysiloxane (B) into polyolefin (A) may be accomplished by any of the traditional means for mixing additives into thermoplastic resin at elevated temperature. For example, the two components may be blended in a twin-screw extruder, a Banbury mixer, a two-roll mill or a single-screw extruder, either with or without a mixing head. The equipment used to mix these components is thus not critical as long as a uniform dispersion of (B) in (A) is attained. Preferably the dispersed particle size is no larger than 10 micrometers.

Compositions of the present invention may also contain up to 1 percent by weight of each of the following: fillers, cure agents, lubricants, u.v. stabilizers, antioxidants, antiblock agents, catalyst stabilizers and other process aids commonly employed in the modification of polyolefins. When more than 1 weight percent of any of these additional ingredients is used, there is interference with the process aid of our invention such that our benefits in processing and/or the character of our extruded materials are not obtained. This is particularly critical in the case of blown film production, where good surface quality is crucial.

Examples of additional ingredients include the following substances. Diatomaceous earth, octadecyl-3-(3,5-

di-5-butyl-4-hydroxyphenyl)propionate, bis(2-hydroxyethyl) tallowamine, calcium stearate, N,N-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine polymer with 2,4,6-trichloro-1,3,5-trizaine and 2,4,6-trichloro-1,3,5-trizaine and 2,4,4-trimethyl-1,2-pentanamine, dimethyl succinate polymer with 2,2,6,6-tetramethyl-1-piperridineethanol, 2,2'-thiobis(4-tert-octylphenolato)n-butylamine nickel, tris(2,4-di-tert-butylphenyl)phosphite, bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite, trisnonylphenylphosphite, polyethylene glycol, Erucamide, titanium dioxide, titanium dioxide, alumina, hydrated alumina, talc, 2-hydroxy-4-n-octyloxy-benzophenone, zinc oxide, zinc sulfide and zinc stearate.

According to our method, the above described diorganopolysiloxane (B) is added to the polyolefin resin (A) and serves as a process aid therefor when the resin is extruded at elevated temperatures to form a shaped product (e.g., a cylindrical cross-section, such as a film, ribbon, bar, annulus, fiber, sheet, or the like). The resulting extrudate has an improved surface (i.e., less sharkskin) relative to a similar extrudate which does not contain diorganopolysiloxane (B). This method is particularly applicable to the production of cast films (film casting) or blown films (film blowing). It also finds utility in extrusion blow molding; injection molding; pipe, wire, or cable extrusion; fiber production; and any other high shear melt processing of polyolefin resins. All of these techniques are well known in the art. Briefly stated, blown film is typically produced by a "bubble" technique, wherein the polyolefin composition (i.e., the melt) is extruded through an annular die to form a film in the shape of a bubble. This bubble is withdrawn from the die at a rate

greater than the rate of extrusion, while a positive air pressure is maintained within the bubble. Film produced in this manner is biaxially oriented as a result of stretching in the radial and axial directions. This orientation generally imparts improved mechanical properties to the film. Cast film is generally prepared by extruding the polyolefin through a slot die followed by cooling on one or more chill rolls.

Although it is possible to obtain a relatively uniform dispersion by injecting component (B) into the screw section of an extruder while polyolefin pellets (A) are fed in through the hopper thereof, it is preferred to first thoroughly disperse component (B) in a portion of component (A) to form a masterbatch. This masterbatch (or concentrate), which preferably contains 1 to 50, more preferably 2.5 to 25, weight percent of the diorganopoly-siloxane (B), may be ground up or pelletized. The resulting particulate of (A) and (B) is then dry-blended with additional polyolefin (the matrix) and this blend is then extruded to form a preferred composition of the invention. Use of our masterbatch technique results in a more uniform dispersion of the diorganopolysiloxane in the polyolefin matrix.

The polyolefin used in the preparation of our masterbatch may be the same as, or different from, the matrix polyolefin resin. Preferably, the two are of the same general type (e.g., polyethylene in the masterbatch and the matrix). However, in highly preferred embodiments of our compositions and method wherein the polyolefin is a LLDPE, it has been found that the further addition of LDPE results in even less sharkskin as well as reduced "screw slip", relative to compositions wherein only diorgano-

polysiloxane (B) is added to LLDPE. These three-component systems result in a greater output under identical extruder conditions relative to our two-component systems of this invention.

Thus, highly preferred compositions of our invention comprise 100 parts by weight of a LLDPE, 0.01 to 1 part by weight of diorganopolysiloxane (B) and 0.01 to 10 parts by weight of a LDPE (C). Below 0.01 part of LDPE per 100 parts by weight of LLDPE, our three-component composition can not generally be distinguished over our systems comprising only components (A) and (B). Above 10 parts of LDPE per 100 parts by weight of LLDPE, the ultimate physical properties of the LLDPE are compromised. In our preferred embodiments, a favorable proportion is 0.1 to 5 parts by weight of LDPE (C) for each 100 parts by weight of LLDPE (A), while the preferred diorganopolysiloxane (B) content is as described supra.

For this invention, the LDPE may be any of the highly branched PE homopolymers having a Mn up to 4,000,000 and a density of 0.915 to 0.925 g/cm^3.

The following examples are presented to further illustrate the compositions and method of this invention. All parts and percentages in the examples are on a weight basis and all measurements were obtained at 25°C., unless indicated to the contrary.

The following materials were employed in the examples.

LLDPE1a = a linear, low density polyethylene; an octene-based copolymer of ethylene having a density of 0.917 g/cm^3 and marketed under the trade name DOWLEX™ 2047A by the Dow Chemical Co., Midland, MI (LOT 1155943).

LLDPE1b = same as LLDPE1a (LOT 1051743).

LLDPE1c = same as LLDPE1a (LOT 671043).

LLDPE2 = a linear, low density polyethylene; an octene-based copolymer of ethylene having a density of 0.923 g/cm^3 and marketed under the trade name NEO-ZEX™ 2015M by Mitsui-Sekiyu Kagaku Kogyo, Japan.

LLDPE3 = a linear, low density polyethylene; a hexene-based copolymer of ethylene having a density of 0.918 g/cm^3 and marketed under the trade name NOVACOR™ TF-0119-F by Novacor (Calgary, Alberta; Canada).

LDPE1 = a low density polyethylene having a density of 0.923 g/cm^3 and marketed as DOW™ GP-LDPE 5004IM by the Dow Chemical Co.

LDPE2 = a low density polyethylene having a density of 0.925 g/cm^3 and marketed as SUMIKATHENE™ G401 by the Sumitomo Chemical Co., Japan.

PDMS1 = a linear dimethylhydroxysiloxy-terminated polydimethylsiloxane oil having a Mn of 38,730, as determined by gel permeation chromatography (GPC).

PDMS2 = a linear polydimethylsiloxane oil having a Mn of 52,950 by GPC, wherein 1 mole percent (M%) of the terminal units are trimethylsiloxy and 99 mole percent of the terminal units are dimethylhydroxysiloxy.

PDMS3a = a linear dimethylhydroxysiloxy-terminated polydimethylsiloxane gum having a Mn of 249,800 by GPC.

PDMS3b = a linear dimethylhydroxysiloxy-terminated polydimethylsiloxane gum having a Mn of 265,100 by GPC.

PDMS5 = a linear dimethylhydroxysiloxy-terminated polydimethylsiloxane gum having a Mn of 340,200 by GPC and containing 7 weight percent dimethylcyclopolysiloxanes.

PDMS6 = a linear polydimethylsiloxane oil having a Mn of 51,240 by GPC, wherein 92 mole percent of the terminal

units are trimethylsiloxy and 8 mole percent of the terminal units are dimethylhydroxysiloxy.

PDMS7 = a linear polydimethylsiloxane gum having a Mn of 306,600 by GPC, wherein 43 mole percent of the terminal units are trimethylsiloxy and 57 mole percent of the terminal units are dimethylhydroxysiloxy.

PDMS8 = a linear polydimethylsiloxane gum having a Mn of 318,500 by GPC, wherein 80 mole percent of the terminal units are dimethylvinylsiloxy and 20 mole percent of the terminal units are dimethylhydroxysiloxy.

PDMS9 = a linear polydimethylsiloxane gum having a Mn of 340,000, wherein 51 mole percent of the terminal units are dimethylvinylsiloxy and 49 mole percent of the terminal units are dimethylhydroxysiloxy.

Masterbatches of the above siloxanes in the above polyethylenes (PE) were prepared by thoroughly mixing these components at elevated temperature. The particular components and their proportions in the masterbatches are summarized in Table 1. Masterbatches (MB) were prepared on a Haake Rheocord^{TM} 90 system twin-screw extruder (Haake - Paramus, New Jersey), equipped with a TW 100 extruder having two counter-rotating intensive-mixing screws having a 1.225 inch (3.1 cm) rear diameter, 0.775 inch (2 cm) front diameter, and a length of approximately 13 inches (33 cm). Temperatures of the four zones of the extruder were set at 170°C., 185°C., 185°C. and 185°C., respectively. In each case, the masterbatch composition was extruded through a strand die and chopped into pellets upon cooling.

Table 1

Process Aid	Silicone	% Silicone	PE	% PE
Masterbatch 1	PDMS1	6	LLDPE1a	94
Masterbatch 2	PDMS2	6	LLDPE1a	94
Masterbatch 3	PDMS3a	5	LLDPE1a	95
Masterbatch 4	PDMS3b	25	LDPE1	75
Masterbatch 5	PDMS5	5	LLDPE1a	95
Masterbatch 6	PDMS6	5	LLDPE1a	95
Masterbatch 7	PDMS7	50	LDPE2	50
Masterbatch 8	PDMS8	5	LDPE1	95
Masterbatch 9	PDMS8	5	LLDPE1a	95
Masterbatch 10	PDMS9	5	LLDPE2	95

Each of the above masterbatches (MB) was employed as a process aid for polyethylene by thoroughly dispersing it in a LLDPE1a matrix (with the exceptions of Examples 4 and 6 which employed LLDPE1b and LLDPE1c, respectively, as the matrix). The amount of masterbatch used was calculated to give a total silicone concentration of 440 parts per million (ppm) by weight in the mixture. These compositions are summarized in Table 2. In a typical mixing procedure (Example 7), 8 grams of Masterbatch 7 pellets were added to 20 pounds (9,072 g) of LLDPE1a pellets and the combination was shaken to yield a pre-mix containing 440 ppm of PDMS7. This pre-mix was extruded at various extruder speeds (revolutions per minute = RPM). The extruder used was a Davis-Standard^{TM} DS-20 single-screw extruder, equipped with a ribbon die (0.04 inch x 1.0 inch = 1.02 mm x 25.4 mm), 2-inch (50.8 mm) diameter screw (3:1 compression ratio) and 24/1 length/diameter ratio. The ribbon die was fabricated from P-20 alloy steel. Zones 1, 2 and 3 of the extruder were set at 340°F. (171°C.), 365°F. (185°C.) and 365°F. (185°C.), respectively, whereas the flange and die

temperatures were set at 350°F. (177°C.) for extruding LLDPE1a, LLDPE1b and LLDPE1c. During the extrusion, extruder amperage (i.e., power consumption), pressure near the die and extrudate output (in feet/minute) were recorded as a function of extruder speed (revolutions per minute = RPM) (Run 1).

The extrudate from Run 1 was then granulated and re-extruded as a function of extruder speed at the above noted conditions (Run 2). Extruder amperage, pressure, and extrudate output were again recorded at each speed.

Samples of extruded ribbon were obtained at various extruder speeds for evaluation of surface roughness. At an extruder speed of 20 RPM, a 20 foot-long ribbon sample was taken and cut into 20 1-foot (0.305 m) sections. Surface roughness measurements were performed on each 1-foot (0.305 m) section and an averaged surface roughness was determined. This process was repeated at a speed of 40 RPM. The average surface roughness values R_a (in nanometers) are reported in Table 2.

Surface roughness was determined with a Mitutoyo™ Surftest 402 surface roughness tester. Briefly, this test comprised dragging a diamond-tipped stylus, coupled to a variable reluctance transducer, over the top surface of the extruded sample (in the longitudinal or extrusion direction). Each stroke was 3 mm long and the mean height of the irregularities was obtained.

For comparison purposes, unmodified PE controls using only virgin LLDPE1a, LLDPE1b and LLDPE1c were evaluated for surface roughness and these results are also shown in Table 2 (Controls 1-3, respectively).

Table 2

Example/Masterbatch	PDMS Endgroup	PDMS Mn	Masterbatch PE Type	Surface Roughness (nm) 20 RPM	40 RPM
Control 1 = LLDPE1a	-----	-----	-----	15,814	16,317
Control 2 = LLDPE1b	-----	-----	-----	15,979	19,962
Control 3 = LLDPE1c	-----	-----	-----	16,866	19,202
Example 1/MB 1	OH (100 M%)	38730	LLDPE1a	27.9	508
Example 2/MB 2	OH (99 M%)/Me_3 (1 M%)	52950	LLDPE1a	33.0	864
Example 3/MB 3	OH (100 M%)	249800	LLDPE1a	38.1	2,139
Example 4/MB 4	OH (100 M%)	265100	LDPE1	12.7*	51*
Example 5/MB 5	OH (100 M%)	340200	LLDPE1a	63.5	2,090
Example 6/MB 6	OH (8 M%)/Me_3 (92 M%)	51240	LLDPE1a	10,602**	17,750**
Example 7/MB 7	OH (57 M%)/Me_3 (43 M%)	306600	LDPE2	5,743	10,064
Example 8/MB 8	OH (20 M%)/Me_2Vi (80 M%)	318500	LDPE1	1,107	13,767
Example 9/MB 9	OH (20 M%)/Me_2Vi (80 M%)	318500	LLDPE1a	4,023	14,077
Example 10/MB 10	OH (49 M%)/Me_2Vi (51 M%)	340000	LLDPE2	2,715	9,629

* Evaluated in LLDPE1b instead of LLDPE1a matrix.

** Evaluated in LLDPE1c instead of LLDPE1a matrix.

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As an added comparison, LDPE1 was used by itself as the process aid in LLDPE1a at a level of 1,321 ppm. The corresponding surface roughness values at 20 and 40 RPM were 577.3 and 619.6 microinches (14,663 and 15,738 nm), respectively.

Although it is apparent that all of the siloxane-containing compositions showed some reduction in surface roughness relative to pure LLDPE controls, several points may be gleaned from the above data.

First, when the polydimethylsiloxane Mn is relatively constant (i.e., 39,000 to 53,000) there is a dramatic reduction of surface roughness for extrusions wherein the siloxane component has hydroxyl end groups (Example 1) versus the case wherein the siloxanes have trimethylsiloxy end groups (Example 6). This is also seen for Mn in the range 320,000 to 340,000 from the comparison of Example 5 with Example 10 and Example 9.

Second, when the end groups on the siloxane component are essentially all dimethylhydroxysiloxy, the surface roughness is inversely related to Mn (Examples 1, 2, 3 and 5 wherein Mn is 39,000, 53,000, 250,000 and 340,000, respectively).

Third, although modification of LLDPE1a with only LDPE1 had little effect on surface roughness relative to the controls of pure LLDPE1, the inclusion of both a hydroxy-terminated siloxane gum (440 ppm) and LDPE1 (1,320 ppm) in the LLDPE1a matrix (Example 4) resulted in a dramatically reduced roughness, particularly at 40 RPM, versus the composition wherein an essentially identical siloxane was dispersed in a LLDPE1a matrix (Example 3). This benefit of incorporating the LDPE was observed, albeit in less

dramatic fashion, in the compositions wherein only a fraction of the siloxane end groups were hydroxyl. Thus, Example 9 containing only 440 ppm of PMDS8 had an average roughness of 158.4 microinches (4,023 nm) at 20 RPM while Example 8 containing 440 ppm of PMDS8 and 8,360 ppm of LDPE1 had a roughness of only 43.6 microinches (1,107 nm) at the same speed.

The above procedures were repeated using LLDPE3 as the matrix PE wherein 440 ppm of siloxane was introduced (Examples 11 and 12). In this case, the extruder settings for Run 1 and Run 2 were: zones 1, 2 and 3 = 370°F. (188°C.), 390°F. (199°C.) and 400°F. (204°C.), respectively; flange and die temperatures = 400°F. (204°C.). Table 3 summarizes these compositions and roughness results.

Table 3

Example/Masterbatch	PDMS Endgroup	MB PE Type	Averaged Surface Roughness (nm) 20 RPM	40 RPM
Control 4 = LLDPE3	-----	-----	2,781	17,386
Example 11/MB 4	OH (100 M%)	LDPE1	43	1,763
Example 12/MB 7	OH (57 M%)/ Me_3 (43 M%)	LDPE2	671	6,368

It is again seen that LDPE, in combination with the hydroxy-terminated polydimethylsiloxane gum imparted the lowest roughness values for the LLDPE3 matrix.

The effect of siloxane (PDMS3b) content on surface roughness was evaluated using Masterbatch 4 in LLDPE1c matrix. These compositions were processed at the same

conditions as were Examples 1-10, supra, the results are presented in Table 4.

Table 4

Example	Siloxane Concentration (ppm PDMS3b)	Averaged Surface Roughness (nm) 20 RPM	40 RPM
Control 3 (LLDPE1c)	0	16,866	19,202
Example 13	55	15,494	18,034
Example 14	110	10,871	14,503
Example 15	220	4,978	10,439
Example 16	440	330	3,734
Example 17	880	36	122
Example 18	1760	180	81
Example 19	3520	1,524	358
Example 20	10014	5,791	2,388

The results from Run 1 of previous examples were compared with the results from Run 2 (i.e., material extruded a second time). The maximum extrusion speed (i.e., the speed at which the maximum rated amperage of the extruder was attained) was determined for each case; these data are summarized in Table 5. In this table, the last column indicates the relative drop in maximum extrusion speed between Run 1 and Run 2 (e.g., for Example 3, the % drop = 100 x (60 - 55)/60 = 8 %).

Table 5

Process Aid	Maximum Extrusion Speed (RPM) Run 1	Run 2	% Drop in Extrusion Speed (%)
Control 1 = LLDPE1a	55	55	0
Control 2 = LLDPE1b	55	55	0
Example 1	100	55	45
Example 2	75	55	27
Example 3	60	55	8
Example 4	70*	65*	7
Example 5	60	55	8

* Evaluated using LLDPE1b instead of LLDPE1a matrix.

From Table 5 it can be seen that compositions employing low Mn polydimethylsiloxane oil (Examples 1 and 2) show a considerable decrease of maximum possible extrusion rate between Runs 1 and 2 relative to systems which employ higher Mn gums (Examples 3 and 5). This limits the practical utility of compositions containing low Mn siloxane oil relative to gum since a diminished reprocessing capability is associated with the former systems.

The extruder output rate (in feet per minute) of Example 4 (Run 2) was compared with the corresponding rate of Example 3 (Run 2) as a function or extruder speed (in RPM). The results are shown in Table 6.

Table 6

Extruder Speed (RPM)	Output Rate (m/Minute) Example 3	Example 4
10	3.05	2.74
15	3.66	4.27
20	4.88	5.18
25	6.40	5.18
30	7.92	7.92
35	9.14	9.45
40	10.67	10.67
45	11.28	11.28
50	12.19	14.02
55	12.19	15.24
60	*	16.46
65	*	18.29

* Beyond maximum extruder power capability.

From Table 6 it can be seen that the addition of LDPE1 to LLDPE1a matrix (Example 4) containing 440 ppm of a hydroxy-terminated polydimethylsiloxane gum of approximately equal molecular weight (Example 3) resulted in significantly improved output rate at the higher extruder speeds. This difference between the output rate and the extruder speed is attributable to greater screw slippage. This table also shows that the extruder capacity (i.e., maximum amperage) was exceeded below a speed of 60 RPM in the case of Example 3, whereas a speed of at least 65 RPM was possible when extruding the composition of Example 4.

As a further comparison, several commercially available process aids were evaluated in LLDPE1a matrix at a level of 440 ppm according to the procedures of Examples 1-10. The following materials were used:

KYNAR™ 460 = a poly(vinylidene fluoride) and a product of Atochem (Philadelphia, PA).

VITON™ FREE FLOW TA = a copolymer of vinylidene fluoride and hexafluoropropylene having carboxyl end groups and Mn of 90,000. It is a product of E.I. duPont (Wilmington, DE).

EPOLENE™ N-34 = a polyethylene wax having Mn of 2,200 and a product of Eastman Chemicals (Kingsport, TN).

DYNAMAR™ FX5920 = a blend of polyethylene oxide and a copolymer of vinylidene fluoride and hexafluoropropylene and a product of 3M (St. Paul, MN).

HUNTSMAN™ A27527 = a process aid polyethylene additive concentrate and a product of Polycom Huntsman (Washington, PA).

UNION CARBIDE™ PA-1 = a polyoxyethylene-grafted polydimethylsiloxane and a product of Union Carbide (Danbury, CT). Results of roughness tests on the above extrudates appear in Table 7.

Table 7

Process Aid (440 ppm in LLDPE1a)	Averaged Surface Roughness (nm) 20 RPM	40 RPM
KYNAR™ 460	363	7,196
VITON™ FREE FLOW TA	142	4,018
EPOLENE™ N-34	1,748	8,852
DYNAMAR™ FX5920	76	6,530
HUNTSMAN™ A27527	205	6,701
UNION CARBIDE™ PA-1	457	6,101

It can be seen that the reduction of the surface roughness imparted by these process aids is generally less than that attained by the present invention, as illustrated by the examples above which employ the same matrix

polyethylene. This is particularly true at higher extruder speeds.

A comparison composition, which incorporated a filler and a silicone "plasticizer," was prepared as follows. A uniform mixture was first prepared, said mixture consisting of 61 parts of PDMS3a, 4 parts of a hydroxyl-terminated polydimethylsiloxane having a Mn of 850 and 35 parts of a fumed silica having a nominal surface area of 250 m^2 per gram. This mixture was then dispersed in LLDPE1c matrix, as described above, such that the polydimethyl-siloxane gum content in the combination was 403 ppm. When this modified polyethylene was extruded (Run 2; zone 1 = 171°C., zones 2-3 and die = 177°C.), the average surface roughness was 574 microinches (1,458 nm) at 20 RPM and 799 microinches (20,295 nm) at 40 RPM.

Claims:

1. A method of extruding a polyolefin resin in which a process aid is added to the resin to facilitate processing of the resin, characterized in that said process aid comprises from 0.02 to 0.5 part by weight of a hydroxy-functional diorganopolysiloxane, wherein the hydroxyl groups reside at ends of the molecular chain in the form of diorgano-hydroxyalloxy groups, having a number average molecular weight of at least 10,000 per 100 parts by weight of said polyolefin resin.

2. A method of extruding a polyolefin resin according to claim 1 in which said process aid comprises a uniform blend of said hydroxy-functional diorganopolysiloxane and from 0.01 to 10 parts by weight of a low density polyethylene wherein said polyolefin resin is linear, low density polyethylene resin present in an amount of 100 parts by weight.

3. The method according to claim 1 or 2 wherein said diorganopolysiloxane is a linear hydroxy-terminated polydimethylsiloxane and said polyolefin is a linear low density polyethylene.

4. The method according to claim 1 wherein said diorganopolysiloxane is a linear hydroxy-terminated polydimethylsiloxane and said polyolefin is a polymer or copolymer of ethylene.

5. The method according to claim 1 wherein said polyolefin is a polyethylene resin.

6. The method according to claim 3 wherein the number average molecular weight of said polydimethylsiloxane is 100,000 to 400,000.

7. The method according to claim 6 wherein the number average molecular weight of said polydimethylsiloxane is 250,000 to 350,000 and from 0.04 to 0.2 part by weight of said polydimethylsiloxane is used for each 100 parts by weight of said polyethylene.

8. The method according to claims 1 or 2 wherein the resulting extrudate is further subjected to a film blowing step.

9. The method according to claims 1 or 2 wherein the resulting extrudate is further subjected to a film casting step.