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(54) Title: POLYMER RESINS WITH IMPROVED ENVIRONMENTAL STRESS CRACK RESISTANCE

(57) Abstract: Resins comprising a relatively high-density, low-molecular-weight polyethylene component and a relatively low-density, high-molecular-weight ethylene copolymer component and methods of making the resins are disclosed. The rheological polydispersity of the high-density component exceeds that of either the resin or the low-density component. The resins are valuable for making films, sheets, coatings, pipes, fibers, and molded articles having a favorable balance of good stiffness and excellent environmental stress crack resistance.

POLYMER RESINS WITH IMPROVED ENVIRONMENTAL STRESS CRACK RESISTANCE

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FIELD OF THE INVENTION

The invention relates to thermoplastic polymer resins useful for making films, fibers, coatings, molded articles, and other products.

BACKGROUND OF THE INVENTION

10 Polyolefins, especially polyethylenes, are important thermoplastics with many uses. Traditionally, polyolefins have been manufactured using slurry, solution, and gas-phase polymerization processes and Ziegler-Natta catalysts. In recent years, polyolefins made using single-site catalysts, including metallocenes, have been commercialized.

15 Polyolefin customers continue to seek resins that have both high stiffness and good environmental stress crack resistance (ESCR), especially for molding and extrusion applications. Unfortunately, for resins made with similar catalyst and process technologies, at a given melt index, resins with higher stiffness usually have poorer ESCR.

20 The molecular weight distribution of a polymer resin influences its processability and physical properties. The most common measure of molecular weight distribution is M_w/M_n , the ratio of weight average to number average molecular weight, which is usually determined by gel permeation chromatography (GPC). Resin properties and processability are also influenced by long-chain branching and comonomer distribution, and this information is not 25 readily ascertained from GPC results.

25 Valuable information about polydispersity that takes into account differences in long-chain branching is available from rheological measurements on molten resins, i.e., from "rheological polydispersity." An overall polydispersity ratio (PDR) that uses complex viscosity data as a function of complex modulus 30 rather than frequency can be measured. An additional measure of rheological polydispersity is ER, which is determined from plots of storage modulus (G') versus loss modulus (G'') and is a measure of high-molecular-weight-end polydispersity. Both PDR and ER are conveniently determined as discussed in R. Shroff and H. Mavridis, *New Measures of Polydispersity from Rheological*

5 *Data on Polymer Melts, J. Appl. Polym. Sci. 57* (1995) 1605. In spite of the availability of this tool, differences in rheological polydispersity have not often been exploited. For a notable exception, however, see U.S. Pat. No. 6,713,585, in which ER measurements and their shifts upon pelletization were shown to be important for identifying and characterizing new ethylene copolymer resins.

Colin Li Pi Shan et al. studied the rheological properties of HDPE/LLDPE reactor blends having bimodal microstructures (see *Polymer* 44 (2003) 177). Some of the blends disclosed have a relatively high-molecular-weight (HMW), low-density copolymer component and a relatively low-molecular-weight (LMW), 10 high-density polyethylene homopolymer component (see Table 1). Figure 6 of the reference shows three rheology plots of G' versus G'' . From this data, it is apparent that the rheological polydispersity of the LMW component cannot be greater than that of either the HMW component or that of a blend of the two components. As is explained in Shroff and Mavridis, *supra*, at page 1621 and 15 Figure 2, "at a given level of G'' , the broader the spectrum, the higher the G' ." A "broader spectrum" is synonymous with a higher rheological polydispersity. In Li Pi Shan's Figure 6 plots, the resin component with relatively low G' values therefore has a relatively low rheological polydispersity. In the top two plots, which show a HMW low-density copolymer, a LMW high-density homopolymer, 20 and blends of the two, the LMW homopolymer has a rheological polydispersity less than that of either the HMW copolymer or a blend of the HMW and LMW components.

Commercial polyolefin resins are commonly produced in a single reactor with a Ziegler-Natta catalyst, ethylene, enough hydrogen to control molecular 25 weight, and enough comonomer to drive density down to a targeted value. The resulting resins have more of the comonomer typically incorporated into the lower molecular weight component of the resin. Dual reactor configurations are also used. Even with two parallel reactors, however, manufacturers often choose to make products of similar density and melt index in each reactor and 30 then blend them to give resins with narrow molecular weight distribution that are valuable for injection molding (see Comparative Examples 2, 4, and 6 below). Usually, these resins lack optimum ESCR.

Still needed in the industry are resins that have a desirable balance of high stiffness and good ESCR. Particularly needed is a better appreciation of

how differences in rheological polydispersity might be exploited to arrive at the improved resins. Methods for making the resins using readily available catalysts, equipment, and processes are also needed.

SUMMARY OF THE INVENTION

5 The invention is a resin comprising a relatively high-density, low-molecular-weight polyethylene component and a relatively low-density, high-molecular-weight ethylene copolymer component. The rheological polydispersity of the high-density component exceeds that of either the resin or the low-density component. The invention includes films, sheets, coatings, pipes, 10 fibers, and molded articles made from the resins. It also includes series and parallel-reactor methods for making the resins. We surprisingly found that resins of the invention exhibit a favorable balance of good stiffness and excellent environmental stress crack resistance.

DETAILED DESCRIPTION OF THE INVENTION

15 Resins of the invention incorporate a polyethylene component that has a relatively high density and a relatively low molecular weight when these values are compared with those of the low-density, high-molecular-weight ethylene copolymer component. Preferably, the high-density component has a density (ASTM D1505) within the range of about 0.940 g/cm³ to about 0.975 g/cm³, 20 more preferably from about 0.950 g/cm³ to about 0.970 g/cm³. Preferably, the low-density component has a density within the range of about 0.910 g/cm³ to about 0.950 g/cm³, more preferably from about 0.925 g/cm³ to about 0.945 g/cm³.

25 Molecular weights of the resin components are generally inversely related to their melt indices. Thus, the high-molecular-weight component has a relatively low melt index, and the low-molecular-weight component has a relatively high melt index (ASTM D1238, 2.16 kg load). Preferably, the high-molecular-weight component has melt index less than about 100 g/10 min, more preferably less than about 20 g/10 min. Preferably, the low-molecular-weight 30 component has melt index within the range of about 1 to about 1000 g/10 min, more preferably from about 10 to about 400 g/10 min.

The high-density, low-molecular-weight component is a polyethylene. It is preferably a homopolymer of ethylene, but it can incorporate ethylene units and a minor proportion of olefin comonomer units, so long as its density remains

high relative to that of the low-density component. When the polyethylene component incorporates a comonomer, the comonomer is preferably propylene, 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, or mixtures thereof.

The low-density, high-molecular-weight component is an ethylene copolymer, i.e., it incorporates units from both ethylene and at least one olefin comonomer. Preferred comonomers are propylene, 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, and the like, and mixtures thereof.

Both components can incorporate comonomer; however, in preferred resins of the invention, the high-molecular-weight component incorporates a greater weight percentage of comonomer than the low-molecular-weight component. The combined resin preferably has a density within the range of about 0.93 to about 0.96 g/cm³, more preferably from about 0.940 to about 0.955 g/cm³. The melt index of the combined resin is preferably from about 0.02 to about 100 g/10 min., more preferably from about 0.05 to about 50 g/10 min.

In resins of the invention, the rheological polydispersity of the high-density component exceeds that of either the low-density component or the combined resin components (i.e., "the resin"). By "rheological polydispersity," we mean values of polydispersity derived from rheological measurements on molten resins. One suitable measure of polydispersity is PDR, which is an overall polydispersity ratio that uses complex viscosity data as a function of complex modulus. Another suitable measure of rheological polydispersity is ER, which is determined from plots of storage modulus (G') versus loss modulus (G'') and is a measure of high-molecular-weight-end polydispersity. Both PDR and ER are conveniently determined as discussed in R. Shroff and H. Mavridis, *New Measures of Polydispersity from Rheological Data on Polymer Melts*, *J. Appl. Polym. Sci.* 57 (1995) 1605. See also U.S. Pat. Nos. 6,171,993 and 5,534,472.

As noted above, the rheological polydispersity of the high-density component exceeds that of either the low-density component or the combined resin components. Table 1 below shows blends of a high-density, low-molecular-weight component (resin A) with a low-density, high-molecular-weight component (resin B or C). Comparing blends with the high-density component alone, notice that the PDR (4.27), and ER (1.52) values measured for resin A exceed those of each of the blends (Tables 2 and 3).

Moreover, for each of Examples 1, 3, and 5, compare the values of ER and PDR reported in Table 4 for the high-density ("A" reactor) components versus the same values for either the low-density ("B" reactor) component (Table 5) or the combined resin (Table 6). The values in Table 4 exceed the 5 corresponding values reported in either of Tables 5 or 6.

Resins of the invention have excellent environmental stress crack resistance (ESCR) as determined by ASTM D1693. Typically, the ESCR value is measured in either 10% or 100% Igepal® solution. In general, resins of the invention provide enhanced ESCR compared with that of conventional ethylene 10 copolymer resins of similar density and melt index. For example, in Table 6, last row, see Example 1 versus Comparative Example 2; Example 3 versus Comparative Example 4; and Example 5 versus Comparative Example 6.

In general, resins of the invention provide enhanced stiffness compared with conventional ethylene copolymer resins of similar melt index and ESCR. 15 See, for example, the tensile yield properties in Table 3.

Resins of the invention can incorporate multiple components. Multi-component resins can be made by using multiple catalysts, multiple reactors, multiple process types, varied process conditions, or some combination of these. Preferably, a multi-component resin of the invention will be essentially 20 free of components having both a lower weight average molecular weight (M_w) and a lower rheological polydispersity than that of any other resin component. In other words, the resin components with relatively low M_w values are the ones with relatively high rheological polydispersities. Additionally, preferred multi-component resins of the invention will be essentially free of components having 25 both a higher density and a lower rheological polydispersity than that of any other resin component.

Resins of the invention are useful for making articles by injection molding, blow molding, rotomolding, and compression molding. The resins are also useful for making films, extrusion coatings, pipes, sheets, and fibers. Products 30 that can be made from the resins include grocery bags, trash bags, merchandise bags, pails, crates, detergent bottles, toys, coolers, corrugated pipe, housewrap, shipping envelopes, protective packaging, wire & cable applications, and many others.

The method for making the resins is not particularly critical. As will be apparent to those skilled in the art, numerous methods or combinations of methods can be employed. For example, the resins can be made by solution, slurry, or gas-phase techniques, or by a combination of these. Some suitable 5 methods will employ a single reactor; others will use multiple reactors that are operated in series or in parallel. Some methods can use a single catalyst; others will require multiple catalysts. The catalysts can be Ziegler-Natta, single-site, late transition metal, modified varieties of one or the other (e.g., an organosilane or organosiloxane-modified Ziegler-Natta catalyst), or some 10 combination of these. For examples of silane-modified Ziegler-Natta catalysts, see U.S. Pat. Nos. 6,486,270 and 6,100,351.

One convenient way to make the resins utilizes two reactors, preferably slurry stirred-tank reactors, that operate in parallel. Ethylene is polymerized, optionally with a comonomer, in a first reactor to produce a relatively high-density, low-molecular-weight polyethylene component. Additional ethylene is 15 copolymerized with a 1-olefin in a second reactor to produce a relatively low-density, high-molecular-weight ethylene copolymer component. The high and low-density components are then blended to produce a resin wherein the rheological polydispersity of the high-density component exceeds that of either 20 the low-density component or the combined resin. Preferably, catalyst, activators, ethylene, comonomers, diluent, hydrogen, and other components are fed to each of two slurry stirred-tank reactors. The resulting polymer slurries are combined and concentrated, and the polymer product is dried, compounded with other additives, and pelletized.

Another convenient method uses two reactors, preferably slurry stirred-tank reactors, that are arranged in series. Ethylene is polymerized, optionally 25 with a comonomer, in a first reactor to produce a relatively high-density, low-molecular-weight polyethylene component. The high-density component is then transferred to a second reactor where additional ethylene and 1-olefin are copolymerized in the presence of the high-density component. Polymerization in 30 the second reactor produces a relatively low-density, high-molecular-weight ethylene copolymer component. Overall, the rheological polydispersity of the high-density component exceeds that of either the low-density component or the combined resin. Preferably, catalyst is fed only to the first reactor. In this case,

the high and low-molecular-weight components are produced on the same catalyst particles and an intimate mix of the components results. Ethylene, comonomers, diluent, hydrogen, and other components such as cocatalysts can be fed to either reactor. The resulting polymer slurry is concentrated, dried, 5 compounded, and pelletized as described earlier.

In yet another method, the reactors are arranged in series, but a relatively low-density, high-molecular-weight ethylene copolymer component is produced in the first reactor, and a relatively high-density, low-molecular-weight polyethylene is produced in the second reactor. Again, the rheological 10 polydispersity of the high-density component exceeds that of either the low-density component or the combined resin. Again, an intimate product mix results if catalyst is fed only to the first reactor.

As noted earlier, resins of the invention can be made using a variety of catalysts, including Ziegler-Natta, single-site, late transition metal, modified 15 varieties of these, or combinations thereof. As those skilled in the art will appreciate, not all catalysts or combinations will be suitable for making resins having the required attributes. The catalyst/method combination must provide a resin in which the rheological polydispersity of the high-density component exceeds that of either the low-density component or the combined resin.

20 In one suitable parallel reactor approach, a Ziegler-Natta catalyst is used in the first reactor to make a high-density, low-molecular-weight component, and a single-site catalyst is used to make a low-density, high-molecular-weight component. In another suitable parallel reactor method, a Ziegler-Natta catalyst is used to make the high-density polyethylene component, and a silane-modified 25 Ziegler-Natta catalyst (or another Ziegler-Natta catalyst capable of making a resin component with narrow rheological polydispersity) is used to make the low-density copolymer component (see Examples 1, 3, and 5, below). In yet another parallel reactor method, a late transition metal catalyst (for examples, see U.S. Pat. Nos. 5,866,863, 6,063,881, and 6,693,154) is used to make the high-density polyethylene component, and a single-site catalyst is used to make the low-density ethylene copolymer component. In yet another approach, the high-density resin is made using a single-site catalyst capable of making a resin having relatively broad rheological polydispersity, and the low-density resin is 30

made using a different single-site catalyst that is capable of making a resin having relatively narrow rheological polydispersity.

Reaction temperatures for the polymerization reactors preferably range from about 40°C to about 300°C, more preferably from about 50°C to about 5 250°C, and most preferably from about 60°C to about 120°C. Selection of reactor temperature depends on catalyst type and concentration, the targeted melt index and density of the polymer, and many other factors. Pressures preferably range from about 2 to about 200 atmospheres, more preferably from about 3 to about 150 atmospheres, and most preferably from about 4 to about 10 30 atmospheres.

The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

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RHEOLOGICAL MEASUREMENTS AND CALCULATIONS

Rheological measurements are performed in accord with ASTM 4440-95a, which measures dynamic rheology data in the frequency sweep mode. A Rheometrics ARES rheometer is used, operating at 150-190°C, in parallel plate mode under nitrogen to minimize sample oxidation. The gap in the parallel plate geometry is typically 1.2-1.4 mm, the plate diameter is 25 mm or 50 mm, and the strain amplitude is 10-20%. Frequencies range from 0.0251 to 398.1 rad/sec.

ER is determined by the method of Shroff et al., *supra* (see also U.S. Pat. No. 5,534,472 at col. 10, lines 20-30). Thus, storage modulus (G') and loss modulus (G'') are measured. The nine lowest frequency points are used (five points per frequency decade) and a linear equation is fitted by least-squares regression to $\log G'$ versus $\log G''$. ER is then calculated from:

$$ER = (1.781 \times 10^{-3}) \times G'$$

at a value of $G''=5,000$ dyn/cm². As a skilled person will recognize, when the lowest G'' value is greater than 5,000 dyn/cm², the determination of ER involves extrapolation. The ER values calculated then will depend on the degree on nonlinearity in the $\log G'$ versus $\log G''$ plot.

The temperature, plate diameter, and frequency range are selected such that, within the resolution of the rheometer, the lowest G'' value is close to or less than 5,000 dyn/cm². The examples below use a temperature of 190°C, a plate diameter of 50 mm, a strain amplitude of 10%, and a frequency range of 0.0251 to 398.1 rad/sec.

BASE RESIN DATA and TEST METHODS

Table 1 shows properties of base resins used to make polyolefin blends. Resin A is Alathon® M6138, a relatively low-molecular-weight HDPE resin that is commercially available from Equistar Chemicals, LP. Resin B is Petrothene® GA601-030, a relatively high-molecular-weight LLDPE resin, also from Equistar, that is produced with a Ziegler-Natta catalyst. Resin C is Exceed™ 1018, a metallocene-based LLDPE resin that is commercially available from ExxonMobil.

Test methods used: Melt index and high-load melt index (MI, 2.16 kg load; and HLMI, 21.6 kg load): ASTM D1238. Density: ASTM D1505. Tensile yield: ASTM D638. ESCR: ASTM D1693. In one set of ESCR measurements, rectangular test samples are first notched and then stressed by bending. They are then immersed in a highly active surfactant (10% or 100% Igepal® solution)

at 50°C. The time (in days) for 50% of the samples to fail is reported in Table 3. The ESCR of thinner specimens is measured somewhat differently. In this case, a 50-mil sample is immersed in 10% Igepal® solution at 50°C, and the time (in hours) for the sample to fail is noted (see Table 6).

5 PDR or "polydispersity ratio" is calculated as reported by Shroff and Mavridis, *J. Appl. Polym. Sci.* **57** (1995) 1605.

η^*_{100} is the complex viscosity (in poise) measured at 100 rad/sec.

BLEND PROPERTIES

10 HDPE (Alathon® M6138) pellets are first dry blended (weight ratios are reported in the tables) with LLDPE (Petrothene® GA601-030 or Exceed™ 1018) pellets and then melt blended on a Killion single screw extruder. The extruder temperature profile for all the formulations is set at 350°F (Zone 1), 400°F (Zone 2), 420°F (Zone 3) and 425°F (Die). Extruder speed is kept at 70 rpm for all the formulations. The properties of the blends are compared with those of Resin D, 15 Petrothene® GA652-762, a commercial rotomolding resin that is available from Equistar Chemicals, LP. As Table 2 shows, all of the blends have melt indices that resemble those of the commercial resin. Table 3 compares ER, ESCR, and tensile yield (i.e., stiffness) values. The results demonstrate that although the blends have similar melt indices compared with the commercial resin, the blends 20 have higher stiffness and superior ESCR. This is true whether the LLDPE component of the blend is produced using a metallocene (Resin C) or a Ziegler-Natta catalyst (Resin B).

Table 1. Base Resins

Resin	MI (g/10 min)	HLMI (g/10 min)	Density (g/cm ³)	HLMI /MI	ER	PDR	η^*_{100} (poise)	mp (°C)
A	3.85	120	0.962	31	1.02	4.27	7.67×10^3	133
B	0.95	27	0.919	28	0.79	3.73	1.79×10^4	124
C	1.10	18	0.920	16	0.17	2.05	2.16×10^4	119

Table 2. Polyolefin Blend Properties						
Blend (wt:wt)	MI (g/10 min)	HLMI (g/10 min)	Density (g/cm ³)	HLMI/MI	PDR	η^*_{100} (poise)
A/C (70:30)	2.35	60	0.948	25	2.93	1.23×10^4
A/C (65:35)	2.24	54	0.946	24	2.82	1.27×10^4
A/B (65:35)	2.15	70	0.946	33	4.17	1.09×10^4
D	2.07	51	0.942	25	3.04	1.29×10^4

Table 3. Polyolefin Blend Properties				
Blend (wt:wt)	ER	ESCR (75 mil), 10% Igepal (days)	ESCR (75 mil), 100% Igepal (days)	Tensile yield (psi)
A/C (70:30)	0.62	9	> 42	3730
A/C (65:35)	0.60	16	> 42	3460
A/B (65:35)	0.86	10	> 42	3250
D	0.62	2.2	> 42	3120

EXAMPLES 1, 3, and 5

5 RESIN PREPARATION: GENERAL PROCEDURE

A Ziegler-Natta catalyst slurry, prepared according to the method of U.S. Pat. No. 3,907,759, is diluted with hexane to the desired titanium concentration. The dilute catalyst slurry is fed continuously along with triethylaluminum (TEAL), hexane, 1-butene, hydrogen, and ethylene to a first reactor ("the A reactor") to 10 make a relatively low-molecular-weight, high-density polyethylene resin component as shown in Table 4. The polymerizations are performed at 81°C at the reactor pressures and vapor-space hydrogen-to-ethylene molar ratios shown in the table. The table also shows properties of the resulting resin component. A portion of the volatiles is removed from this first polymer slurry after 15 transferring the product to a flash drum.

A relatively high-molecular-weight, low-density ethylene copolymer resin component is produced at 81°C in a second reactor ("the B reactor") using more of the same catalyst slurry and reactants plus an optional silane modifier (see Table 5). After removing volatiles, this second polymer slurry is combined with 20 the first polymer slurry, and the mixture is centrifuged to remove hexane. The wet cake is dried under nitrogen and compounded with a standard stabilizer package to give the finished polymer (see Table 6).

COMPARATIVE EXAMPLES 2, 4, and 6

A similar approach is used except that the silane modifier is omitted from the B reactor, and the resins made in the A and B reactors have identical targeted melt index and density values. See Tables 4-6.

5 Examples 1 and C2 make final resins having targeted $MI_2=5$ and density=0.952 g/cm³. Examples 3 and C4 make final resins having targeted $MI_2=7$ and density=0.952 g/cm³. Examples 5 and C6 make final resins having targeted $MI_2=16$ and density=0.955 g/cm³. The examples of the invention have distinct high-density (low mol. wt.) and low-density (high mol. wt.) components,
10 while the comparative examples are "single-reactor," Ziegler-Natta polyethylenes.

Table 4. Resin Preparation -- the "A" reactor

Example	1	C2	3	C4	5	C6
[Ti]	6.0×10^{-5}	5.0×10^{-5}	7.5×10^{-5}	5.0×10^{-5}	1.0×10^{-4}	5.0×10^{-5}
Feeds ¹						
catalyst slurry	29	22	32	18	35	20
TEAL	6.2×10^{-3}	5.8×10^{-3}	7.4×10^{-3}	4.0×10^{-3}	1.0×10^{-2}	5.4×10^{-3}
hexane	174	183	170	183	167	185
1-butene	0.4	1.0	0.5	0.8	0.6	0.9
ethylene	30	30	30	30	30	30
Press. (psig)	100	120	120	120	130	130
H_2/C_2H_4 ²	1.3	0.8	1.5	1.0	2.1	1.3
Resin						
MI_2 (g/10 min)	16	4.6	25	7.6	67	16
density (g/cm ³)	0.960	0.952	0.960	0.952	0.961	0.954
ER	1.00		0.95		0.97	
PDR	3.58		3.26		2.99	

¹ Parts per hour ² Vapor space molar ratio

Table 5. Resin Preparation -- the "B" reactor

Example	1	C2	3	C4	5	C6
Feeds ¹						
catalyst slurry	15	26	15	20	25	24
TEAL	6.2×10^{-3}	5.8×10^{-3}	7.4×10^{-3}	4.0×10^{-3}	1.0×10^{-2}	5.4×10^{-3}
hexane	179	176	175	177	182	177
1-butene	3.8	0.9	4.2	0.8	2.0	0.9
ethylene	30	30	30	30	30	30
silane modifier	1.1×10^{-3}	---	1.1×10^{-3}	---	1.1×10^{-3}	---
Press. (psig)	100	120	120	120	130	130
H ₂ /C ₂ H ₄ ²	0.7	0.7	0.8	0.9	1.1	1.3
Resin						
MI ₂ (g/10 min)	2.0	5.1	2.9	7.1	7.3	20
density (g/cm ³)	0.942	0.952	0.942	0.952	0.948	0.954
ER	0.41		0.40		0.48	
PDR	2.43		2.44		2.46	

¹ Parts per hour ² Vapor space molar ratio

Table 6. Combined Resin Properties

Example	1	C2	3	C4	5	C6
MI ₂ (g/10 min)	4.9	5.2	7.2	7.5	15	17
density (g/cm ³)	0.952	0.953	0.951	0.952	0.955	0.956
ER	0.65	0.94	0.64	0.90	0.88	0.94
PDR	3.07	3.66	2.99	3.40	3.28	3.27
ESCR (50 mil), 10% Igepal (h)	7.0	5.0	5.1	3.5	2.0	0.55

Resin performance needs to be compared using resins of like melt index and density. Thus, when we compare the ESCR results from Example 1 and 5 Comparative Example 2, we see the advantage of using a two-component resin that has a relatively high-density, low-molecular-weight component (from the "A" reactor) and a relatively low-density, high-molecular-weight component (from the "B" reactor) versus the commercially available one-component resin (5 MI, 0.952 g/cm³) of Comparative Example 2. The 10% ESCR value improves from 5.0 to 10 7.0 hours. Similar ESCR improvements are observed when comparing other two-component resins of the invention (Examples 3 and 5) with commercial injection molding resins of like melt index and density (C4, C6).

Note that analysis of the resin of Example 1 shows rheological polydispersity measures (ER, PDR) of the high-density component in excess of that of either the low-density component or the combined resin. For example, the ER of the high-density component is 1.00, which exceeds the ER of both the 5 low-density component (0.41) and the ER of the combined resin (0.65).

CALCULATING RESIN RHEOLOGY: SERIES REACTORS

When resins of the invention are produced using two parallel reactors (as shown in Examples 1, 3, and 5), each resin component is easily sampled and measured prior to combining them to determine the rheological polydispersities 10 of the high and low-density components. Of course, the rheological polydispersity of the combined resin is thereafter also easily measured.

The situation is more complicated when a resin of the invention is produced using two reactors that are configured in series. In this case, the second resin is made, at least in part, on catalyst particles used to make the first 15 resin. (In this context, "first resin" is the first resin component made in the series process, whether it be the high- or low-density component.) While the rheological polydispersity of the first resin made is easily determined after sampling, the second resin is not available as a separate and independent product; rather, the final resin is an intimate reactor mix of the first and second 20 components. If the second resin is not available separately for testing, how then do we characterize its rheological polydispersity? As we show below, the rheology of the second resin can be *calculated* from a theoretical subtraction of the rheology of the first resin from the rheology of the "total" or "final" resin.

Blending rules for the calculation of the linear viscoelastic rheology of 25 blends are known in the literature (see, e.g., J.P. Montfort et al., *Polymer* 19 (1978) 277). The blending rule used in the present work is:

$$(G^*(\omega))^{1/\alpha} = \varphi_A \cdot (G_A^*(\omega))^{1/\alpha} + \varphi_B \cdot (G_B^*(\omega))^{1/\alpha} \quad (1)$$

30 where φ is the volume fraction, A and B subscripts denote the blend components A and B, respectively and $G^*(\omega)$ is the complex modulus at frequency ω . The exponent α is related to the zero-shear-viscosity versus molecular weight relationship (see W.W. Graessley in *Physical Properties of*

Polymers, J.E. Mark et al., eds., 2nd ed. (1993) ACS, Washington, DC) and is fixed at a value of $\alpha=3.4$.

5 The complex modulus, $G^*(\omega)$, is a complex number related to the storage (G') and loss (G'') modulus, through:

$$G^*(\omega) = G'(\omega) + i \cdot G''(\omega) \quad (2)$$

and i is the imaginary unit number ($i^2=-1$). Alternatively, eq.(2) can be written as:

10 $G^*(\omega) = |G^*(\omega)| \cdot e^{i \cdot \delta(\omega)} \quad (3)$

where

$$|G^*(\omega)| = [G'(\omega)^2 + G''(\omega)^2]^{1/2} \quad (4a)$$

$$\delta(\omega) = \tan^{-1} \left(\frac{G''(\omega)}{G'(\omega)} \right) \quad (4b)$$

15

Substituting into eq.(1) and carrying out the complex algebra leads to:

$$|G^*(\omega)| = \left\{ \left[\varphi_A \cdot |G_A^*|^{1/\alpha} \cdot \cos(\delta_A/\alpha) + \varphi_B \cdot |G_B^*|^{1/\alpha} \cdot \cos(\delta_B/\alpha) \right]^2 + \left[\varphi_A \cdot |G_A^*|^{1/\alpha} \cdot \sin(\delta_A/\alpha) + \varphi_B \cdot |G_B^*|^{1/\alpha} \cdot \sin(\delta_B/\alpha) \right]^2 \right\}^{\alpha/2} \quad (5a)$$

$$\delta(\omega) = \alpha \cdot \tan^{-1} \left(\frac{\varphi_A \cdot |G_A^*|^{1/\alpha} \cdot \sin(\delta_A/\alpha) + \varphi_B \cdot |G_B^*|^{1/\alpha} \cdot \sin(\delta_B/\alpha)}{\varphi_A \cdot |G_A^*|^{1/\alpha} \cdot \cos(\delta_A/\alpha) + \varphi_B \cdot |G_B^*|^{1/\alpha} \cdot \cos(\delta_B/\alpha)} \right) \quad (5b)$$

20

The storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, of the blend are then calculated from eq.(6) below:

$$G'(\omega) = |G^*(\omega)| \cdot \cos(\delta) \quad (6a)$$

$$G''(\omega) = |G^*(\omega)| \cdot \sin(\delta) \quad (6b)$$

25

In the event that the rheology of one of the components, for example, component B, needs to be calculated from the known rheology of the blend and the rheology of component A, eq.(1) can be rearranged to give:

$$5 \quad (G_B^*(\omega))^{1/\alpha} = \frac{-\varphi_A}{\varphi_B} \cdot (G_A^*(\omega))^{1/\alpha} + \frac{1}{\varphi_B} \cdot (G^*(\omega))^{1/\alpha} \quad (7)$$

or

$$(G_B^*(\omega))^{1/\alpha} = \psi_A \cdot (G_A^*(\omega))^{1/\alpha} + \psi \cdot (G^*(\omega))^{1/\alpha} \quad (8)$$

$$\text{with: } \psi_A = \frac{-\varphi_A}{\varphi_B} \quad \text{and} \quad \psi = \frac{1}{\varphi_B} \quad (9)$$

10 The derivations for the storage modulus, $G_B'(\omega)$, and loss modulus, $G_B''(\omega)$, follow similarly as eqs.(5-6):

$$|G_B^*(\omega)| = \left\{ \left[\psi_A \cdot |G_A^*|^{1/\alpha} \cdot \cos(\delta_A/\alpha) + \psi \cdot |G^*|^{1/\alpha} \cdot \cos(\delta/\alpha) \right]^2 + \left[\psi_A \cdot |G_A^*|^{1/\alpha} \cdot \sin(\delta_A/\alpha) + \psi \cdot |G^*|^{1/\alpha} \cdot \sin(\delta/\alpha) \right]^2 \right\}^{\alpha/2} \quad (10a)$$

$$\delta_B(\omega) = \alpha \cdot \tan^{-1} \left(\frac{\psi_A \cdot |G_A^*|^{1/\alpha} \cdot \sin(\delta_A/\alpha) + \psi \cdot |G^*|^{1/\alpha} \cdot \sin(\delta/\alpha)}{\psi_A \cdot |G_A^*|^{1/\alpha} \cdot \cos(\delta_A/\alpha) + \psi \cdot |G^*|^{1/\alpha} \cdot \cos(\delta/\alpha)} \right) \quad (10b)$$

15

$$G_B'(\omega) = |G_B^*(\omega)| \cdot \cos(\delta_B) \quad (11a)$$

$$G_B''(\omega) = |G_B^*(\omega)| \cdot \sin(\delta_B) \quad (11b)$$

20 Thus, it is apparent that the rheological polydispersity of all components of even a resin produced using two reactors configured in series can be estimated from the above calculations.

25 The preceding examples are meant only as illustrations. The following claims define the invention.

We claim:

1. A resin comprising a relatively high-density, low-molecular-weight polyethylene component and a relatively low-density, high-molecular-weight ethylene copolymer component, wherein the rheological polydispersity of the 5 high-density component exceeds that of the resin.
2. The resin of claim 1 having enhanced environmental stress crack resistance compared with that of a conventional ethylene copolymer resin of similar density and melt index.
3. The resin of claim 1 having enhanced stiffness compared with that of 10 a conventional ethylene copolymer resin of similar melt index and environmental stress crack resistance.
4. The resin of claim 1 wherein the high-molecular-weight component incorporates a greater wt.% of comonomer than the low-molecular-weight component.
- 15 5. The resin of claim 1 having a density within the range of 0.93 to 0.96 g/cm³.
6. A multi-component resin of claim 1 that is essentially free of components having both a lower weight average molecular weight and a lower rheological polydispersity than that of any other resin component.
- 20 7. A multi-component resin of claim 1 that is essentially free of components having both a higher density and a lower rheological polydispersity than that of any other resin component.
8. An injection molded, blow molded, compression molded, or rotomolded article made from the resin of claim 1.
- 25 9. A film, extrusion coating, pipe, sheet, or fiber made from the resin of claim 1.
10. A method comprising:
 - (a) in a first reactor, polymerizing ethylene to produce a high-density component;
 - 30 (b) in a second reactor, polymerizing ethylene and a 1-olefin to produce a low-density component; and
 - (c) blending the high- and low-density components to produce a resin of claim 1.

11. The method of claim 10 wherein the high-density component is produced using a Ziegler-Natta catalyst and the low-density component is produced using a silane-modified Ziegler-Natta catalyst.

12. A method comprising:

5 (a) in a first reactor, polymerizing ethylene to produce a high-density component;

(b) transferring the high-density component to a second reactor; and

(c) in the second reactor, copolymerizing additional ethylene and a 1-olefin to produce a resin of claim 1.

10 13. A method comprising:

(a) in a first reactor, polymerizing ethylene and a 1-olefin to produce a low-density component;

(b) transferring the low-density component to a second reactor; and

(c) in the second reactor, polymerizing additional ethylene to produce a

15 resin of claim 1.

14. A resin comprising a relatively high-density, low-molecular-weight polyethylene component and a relatively low-density, high-molecular-weight ethylene copolymer component, wherein the rheological polydispersity of the high-density component exceeds that of the low-density component.

20 15. The resin of claim 14 having enhanced environmental stress crack resistance compared with that of a conventional ethylene copolymer resin of similar density and melt index.

25 16. The resin of claim 14 having enhanced stiffness compared with that of a conventional ethylene copolymer resin of similar melt index and environmental stress crack resistance.

17. The resin of claim 14 having a density within the range of 0.93 to 0.96 g/cm³.

30 18. A multi-component resin of claim 14 that is essentially free of components having both a lower weight average molecular weight and a lower rheological polydispersity than that of any other resin component.

19. A multi-component resin of claim 14 that is essentially free of components having both a higher density and a lower rheological polydispersity than that of any other resin component.

20. An injection molded, blow molded, compression molded, or rotomolded article made from the resin of claim 14.

21. A film, extrusion coating, pipe, sheet, or fiber made from the resin of claim 14.

5 22. A method comprising:

(a) in a first reactor, polymerizing ethylene to produce a high-density component;

(b) in a second reactor, polymerizing ethylene and a 1-olefin to produce a low-density component; and

10 (c) blending the high- and low-density components to produce a resin of claim 14.

23. The method of claim 22 wherein the high-density component is produced using a Ziegler-Natta catalyst and the low-density component is produced using a silane-modified Ziegler-Natta catalyst.

15 24. A method comprising:

(a) in a first reactor, polymerizing ethylene to produce a high-density component;

(b) transferring the high-density component to a second reactor; and

(c) in the second reactor, copolymerizing additional ethylene and a 1-

20 olefin to produce a resin of claim 14.

25 25. A method comprising:

(a) in a first reactor, polymerizing ethylene and a 1-olefin to produce a low-density component;

(b) transferring the low-density component to a second reactor; and

25 (c) in the second reactor, polymerizing additional ethylene to produce a resin of claim 14.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/014403

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F10/02 C08F110/02 C08F220/02 C08L23/04 C08L23/06

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C08L

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/093363 A (SOLVAY POLYOLEFINS EUROPE-BELGIUM ; GOLDBERG, ANNE; SIBERDT, FABIAN) 13 November 2003 (2003-11-13) the whole document -----	1-25
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

23 August 2005

05/09/2005

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Schmitz, V

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/014403

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category	Relevant to claim No.
X	EP 0 989 141 A (FINA RESEARCH S.A) 29 March 2000 (2000-03-29) paragraph '0010!; claims; examples
X	EP 1 083 183 A (FINA RESEARCH S.A) 14 March 2001 (2001-03-14) paragraph '0039!; examples
X	US 2002/065368 A1 (DEBRAS GUY ET AL) 30 May 2002 (2002-05-30) paragraph '0017! - paragraph '0038!; examples
X	EP 0 517 222 A (HOECHST AKTIENGESELLSCHAFT) 9 December 1992 (1992-12-09) claims; examples
X	SHAN ET AL.: "HDPE/LLDPE reactor blends with bimodal microstructures" POLYMER, vol. 44, no. 1, January 2003 (2003-01), pages 177-185, XP002341752 cited in the application the whole document

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: -

Present claims 1-9 and 14-21 relate to a product defined by reference to a desirable characteristics or properties and/or unclear parameters. Examples for those properties are eg. the comparissions of the rheological polydispersity in claim 1, of the enhanced environmental stress crack resistance in claim 2 and of the enhanced stiffness in claim 3. Therefore these claims are searched incompletely.

The claims cover all products having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such product. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the product by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the product comprising a hight density, low molecular weight polyethylene component and a low density, high molecular weight polyethylene copolymer component as described in the examples based and is based on the clear parts of the description. The methods disclosed in claims 10, 12, 13, 22, 24 and 25 were searched completely.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2005/014403

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US2005/014403

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2005/014403

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