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(71) Demandeur/Applicant:
NOVA CHEMICALS CORPORATION, CA

(72) Inventeurs/Inventors:
LAM, PATRICK, CA;
KER, VICTORIA, CA;
GRABOW, KAREN, CA

(74) Agent: BAAR, CLIFF

(54) Titre : COMPOSITIONS DE MELANGE DE POLYETHYLENE
(54) Title: POLYETHYLENE BLEND COMPOSITIONS

(57) Abrégé/Abstract:

A polymer blend comprising first and second polyethylene copolymers is presented which has good processability, and which when made into film shows good toughness-stiffness balance, reasonable MD tear, as well as good optical properties and seal properties.

POLYETHYLENE BLEND COMPOSITIONS

ABSTRACT OF THE DISCLOSURE

A polymer blend comprising first and second polyethylene copolymers is presented which has good processability, and which when made into film shows good toughness-stiffness balance, reasonable MD tear, as well as good optical properties and seal properties.

POLYETHYLENE BLEND COMPOSITIONS

FIELD OF THE INVENTION

A polymer blend having good processability, good toughness-stiffness balance, and which shows good optical and seal properties when made into films is presented. A polymer blend comprises from 5-95 wt% of a first polyethylene copolymer having a density of from 0.916 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of from 32 to 50, a molecular weight distribution (M_w/M_n) of from 3.6 to 6.5, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, and a composition distribution breadth index $CDBI_{50}$ of from 35 to 70 wt% as determined by TREF; and which satisfies at least one of the following relationships:

(i) $\delta^{XO} \leq [\ 80 - 1.22\ (CDBI_{50})\ /\ (M_w/M_n)]$; and

(ii) $(M_w/M_n) \geq 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$.

The balance of the polymer blend comprises a second polyethylene copolymer which is different from the first polyethylene copolymer.

BACKGROUND OF THE INVENTION

The search for polyethylene products having an improved balance of physical properties and processability has led to the development of products having improved output capacity and ever improving end use properties such as enhanced film tear or dart impact properties.

U.S. Pat. Appl. No. 2011/0003099 discusses low melt flow ratio (MFR) linear polyethylene and high melt flow ratio (MFR) linear polyethylene, which are distinguished by an I_{21}/I_2 of less than 30 and an I_{21}/I_2 of greater than 30 respectively.

Resins having both a narrow molecular weight distribution and a low melt flow ratio are well known and include resins produced with metallocene catalysts and phosphinimine catalysts. Such resins include for example Exceed 1018^{TM} from

ExxonMobil and those described in U.S. Pat. No. 5,420,220 and Canadian Pat. Appl. No. 2,734,167. These resins can be made into films having a good balance of physical and optical properties, but can be difficult to process in the absence of processing aids, as indicated by, for example, a relatively low output capacity on a blown film line.

Resins having a higher melt flow ratio are more attractive to film producers because they are generally easier to process. U.S. Pat. Nos 6,255,426 and 6,476,171 and U.S. Pat. Appl. No. 2011/0003099 each describe the production and use of resins having melt flow ratios which are in excess of 30 and which have moderately broad molecular weight distributions. The resins are thought to contain significant amounts of long chain branching. The polymers disclosed in U.S. Pat. Nos. 6,255,426 and 6,476,171 are made with a bridged bis-indenyl zirconocene catalyst and have a composition distribution breadth index of greater than 75%. The resins have been referred to as Enable™ polymers in the patent literature (see for example, the Example Polymers disclosed in U.S. Pat. Appl. No. 2011/0003099), and although the resins were relatively easy to process, they also maintained a good balance of strength and stiffness properties when blown into film. For example, the films had physical properties which were comparable to Exceed 1018 materials despite their better shear thinning behavior. The polymers disclosed in U.S. Pat. Appl. No. 2011/0003099, include a new "Enable" grade resin having a low melt index (I_2 = 0.3), a relatively high melt flow ratio (I_{21}/I_2 is from 46-58) and a moderately broad molecular weight distribution (e.g. M_w/M_n is 3.4). The polymers also have a single peak in the TREF profile, with a T(75)-T(25) of less than 4°C.

Manipulation of the comonomer distribution profile has also provided novel ethylene copolymer architectures in an effort to improve the balance between physical properties and polymer processability.

It is generally the case that metallocene catalysts and other so called “single site catalysts” typically incorporate comonomer more evenly than traditional Ziegler-Natta catalysts when used for catalytic ethylene copolymerization with alpha olefins. This fact is often demonstrated by measuring the composition distribution breadth index (CDBI) for corresponding ethylene copolymers. The definition of composition distribution breadth index ($CDBI_{50}$) can be found in PCT publication WO 93/03093 and in U.S. Pat. No. 5,206,075. The $CDBI_{50}$ is conveniently determined using techniques which isolate polymer fractions based on their solubility (and hence their comonomer content). For example, temperature rising elution fractionation (TREF) as described by Wild et al. J. Poly. Sci., Poly. Phys. Ed. Vol. 20, p441, 1982 can be employed. From the weight fraction versus composition distribution curve, the $CDBI_{50}$ is determined by establishing the weight percentage of a copolymer sample that has a comonomer content within 50% of the median comonomer content on each side of the median. Generally, Ziegler-Natta catalysts produce ethylene copolymers with a $CDBI_{50}$ lower than that of a single site catalyst at a similar density consistent with a heterogeneously branched copolymer. Typically, a plurality of prominent peaks is observed for such polymers in a TREF (temperature raising elution fractionation) analysis. Such peaks are consistent with the presence of heterogeneously branched material which generally includes a highly branched fraction, a medium branched fraction and a higher density fraction having little or no short chain branching. In contrast, metallocenes and other single site catalysts, will most often produce ethylene copolymers having a $CDBI_{50}$ higher than that of a Ziegler-Natta catalyst at similar density and which often contain a single prominent peak in a TREF analysis, consistent with a homogeneously branched copolymer.

Despite the forgoing, methods have been developed to access polyethylene copolymer compositions having a broadened comonomer distribution (i.e. more Ziegler-Natta like) while otherwise maintaining product characteristics typical of metallocene and single site catalyst resin, such as high dart impact strength for blown film. Such resins can be made, for example, by using a mixture of metallocene catalysts in a single reactor, using a plurality of polymerization reactors under different polymerization conditions, or by blending metallocene produced ethylene copolymers.

U.S. Patent Nos. 5,382,630, 5,382,631 and WO 93/03093 describe polyethylene blend compositions having broad or narrow molecular weight distributions, and broad or narrow comonomer distributions. For example, a blend may have a narrow molecular weight distribution, while simultaneously having a bimodal composition distribution. Alternatively a blend may have a broad molecular weight distribution while simultaneously having a unimodal composition distribution. The blends are made by melt blending two polyethylene resins with similar or different molecular weights and similar or different comonomer contents, where each resin is formed using a metallocene catalyst in a gas phase reactor.

U.S. Pat. No. 5,548,014 describes blends of metallocene catalyzed resin, where one component has a high molecular weight, while the other component has a low molecular weight. The blends are suitable in the manufacture of hot melt adhesives.

U.S. Pat. No. 7,018,710 discloses blends comprising a high molecular weight component having a high comonomer content and a low molecular weight component having a low comonomer content. The ethylene copolymer blend, which arises from the use of a metallocene catalyst in a cascade dual reactor process where each reactor is operated under different conditions (e.g. a cascade slurry phase-gas phase reactor), shows two distinct maxima in a TREF fractogram. The polymers were applied as a sealing layer in a heat sealable film.

A mixed catalyst system containing a “poor comonomer incorporator” and a “good comonomer incorporator” is disclosed in U.S. Pat. Nos 6,828,394 and 7,141,632. The poor comonomer incorporating catalyst may be a metallocene having at least one fused ring cyclopentadienyl ligand, such as an indenyl ligand, with appropriate substitution (e.g. alkyl substitution at the 1-postion). The good comonomer incorporating catalyst was selected from an array of well-known metallocenes and which were generally less sterically encumbered toward the front end of the molecule than the poor comonomer incorporator. These mixed catalyst systems produced polyethylene copolymers having a bimodal TREF distribution in which two elution peaks are well separated from one another, consistent with the presence of higher and lower density components. The mixed catalysts also produced ethylene copolymer having a broadened molecular weight distribution relative to ethylene copolymer made with either one of the single metallocene component catalysts.

A mixed catalyst system comprising three distinct metallocene catalysts is disclosed in U.S. Pat. No. 6,384,158. Ethylene copolymers having broadened molecular weight distributions were obtained when using these catalyst systems to polymerize ethylene with an alpha olefin such as 1-hexene.

U.S. Pat Appl. No. 2011/0212315 describes a linear ethylene copolymer having a bimodal or multimodal comonomer distribution profile as measured using DSC, TREF or CRYSTAF techniques. The copolymers maintain a high dart impact resistance when blown into film and are relatively easy to process as indicated by a reduced shear thinning index, relative to ethylene copolymers having a unimodal comonomer distribution profile. The exemplified ethylene copolymer compositions, which have a melt flow ratio of less than 30, are made in a single gas phase reactor by employing a mixed catalyst system comprising a metallocene catalyst and a late transition metal catalyst.

U.S. Pat. No. 7,534,847 demonstrates that use of a chromium based transition metal catalyst gives an ethylene copolymer having a bimodal comonomer distribution (as indicated by CRYSTAF) with a CDBI of less than 50 wt% (see Table 1 of U.S. Pat

No. 7,534,847). The patent teaches that the copolymers may have a molecular weight distribution of from 1 to 8, significant amounts of vinyl group unsaturation, long chain branching and specific amounts of methyl groups as measured by CRYSTAF fractionation.

U.S. Pat. No. 6,932,592 describes very low density (i.e. < 0.916 g/cm^3) ethylene copolymers produced with a bulky non-bridged bis-Cp metallocene catalyst. A preferred metallocene is bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dichloride. The examples show that in the gas phase, supported versions of this catalyst produce copolymer from ethylene and 1-hexene which has a CDBI of between 60 and 70% and a bimodal comonomer distribution as measured by temperature raising elution fractionation (TREF).

U.S. Pat. No. 6,420,507 describes a low density ethylene copolymer having a narrow molecular weight distribution (i.e. 1.5 to 3.0) and a bimodal TREF profile. The polymerization is carried out in the gas phase using a so called “constrained geometry” catalyst having an indenyl ligand.

U.S. Pat. Nos. 6,248,845, 6,528,597, 7,381,783 and U.S. Pat. Appl. No. 2008/0108768 disclose that a bulky ligand metallocene based on hafnium and a small amount of zirconium can be used to provide an ethylene/1-hexene copolymer which has a bimodal TREF profile. It is taught that the hafnium chloride precursor compounds used to synthesize the bulky metallocene catalysts are either contaminated with small amount of zirconium chloride or that zirconium chloride may be deliberately added. The amounts of zirconium chloride present range from 0.1 mol% to 5 mol%. Hence, the final hafnocene catalysts contain small amounts (i.e. 0.1 to 5 mol%) of their zirconocene analogues. Since zirconium based catalysts can have superior activity relative to their hafnium analogs it is possible that the products made have a significant contribution from the zirconocene species. If this is the case, then it is perhaps not surprising that a bimodal TREF profile results. The patent provides data for cast and blown film applications which shows that compared to Exceed type resins, the polymers are more easily extruded, with lower motor load, higher throughput and reduced head pressure. The resins give cast film with high tear values and blown film with high dart impact values.

U.S. Pat. Nos. 6,956,088, 6,936,675, 7,179,876 and 7,172,816 disclose that use of a “substantially single” bulky ligand hafnium catalyst provides an ethylene copolymer composition having a CDBI of below 55%, especially below 45% as determined by CRYSTAF. Recall, that hafnocene catalysts derived from hafnium chloride are expected to have zirconocene contaminants present in low amounts. U.S. Patent Nos. 6,936,675 and 7,179,876 further teach that the CDBI could be changed under different temperature conditions when using hafnocene catalysts. Polymerization at lower temperatures gave ethylene copolymer having a broader composition distribution breadth index (CDBI) relative to polymers obtained at higher temperatures. For example, use of the catalysts bis(n-propylcyclopentadienyl)hafnium dichloride or bis(n-propylcyclopentadienyl)hafnium difluoride in a gas phase reactor for the copolymerization of ethylene and 1-hexene at ≤ 80°C, gave copolymers having a CDBI of between 20 and 35%, compared to CDBI values of between 40 and 50% for copolymers obtained at 85°C. The polymers disclosed can, under certain draw down ratios, provide films having a machine direction tear value of greater than 500 g/mil, a dart impact resistance of greater than 500 g/mil, as well as good stiffness. The polymers also have good processability. Blends of polymers of the type just described with various differentiated polyethylenes such as for example high density polyethylene, linear low density polyethylene and very low density polyethylene are disclosed in U.S. Pat. No. 8,247,065.

U.S. Pat. No. 5,281,679 describes bis-cyclopentadienyl metallocene catalysts which have secondary or tertiary carbon substituents on a cylcopentadienyl ring. The catalysts provide polyethylene materials with broadened molecular weight during gas phase polymerization.

Cyclic bridged bulky ligand metallocene catalysts are described in U.S. Pat. Nos. 6,339,134 and 6,388,115 which give easier processing ethylene polymers.

A hafnocene catalyst is used in U.S. Pat. No. 7,875,690 to give an ethylene copolymer in a gas phase fluidized bed reactor. The copolymer has a so called "broad orthogonal composition distribution" which imparts improved physical properties and low extractables. A broad orthogonal composition distribution is one in which the comonomer is incorporated predominantly in the high molecular weight chains. The copolymers had a density of at least 0.927 g/cm^3. Polyethylene copolymers having a similarly broad orthogonal composition distribution but a lower density are disclosed in U.S. Pat. No. 8,084,560 and U.S. Pat. Appl. No. 2011/0040041A1. Again a hafnocene catalyst is employed in a gas phase reactor to give the ethylene copolymer.

U.S. Pat. No. 5,525,689 also discloses the use of a hafnium based metallocene catalyst for use in olefin polymerization. The polymers had a ratio of I_{10}/I_2 of from 8 to 50, a density of from 0.85 to 0.92 g/cm^3, a Mw/Mn of up to 4.0, and were made in the gas phase.

U.S. Pat. No. 8,114,946 discloses ethylene copolymers which have a molecular weight distribution (M_w/M_n) ranging from 3.36 to 4.29, a reversed comonomer incorporation and contain low levels of long chain branching. The melt flow ratios of the disclosed polymers are generally below about 30. A bridged cyclopentadienyl/fluorenyl metallocene catalyst having an unsaturated pendant group is used to make the ethylene copolymers. The patent application does not mention films or film properties.

U.S. Pat. No. 6,469,103 discusses ethylene copolymer compositions comprising a first and a second ethylene copolymer component. The individual components are defined using ATREF-DV analytical methods which show a bimodal or multimodal structure with respect to comonomer placement. The compositions have an I_{10}/I_2 value of greater 6.6 and a relatively narrow molecular weight distribution (i.e. M_W/M_n is less than or equal to 3.3) consistent with the presence of long chain branching. The polymers are made using a dual solution reactor system with mixed catalysts.

A process for making ethylene polymer compositions involving the use of at least two polymerization reactors is described in U.S. Pat. No. 6,319,989. The ethylene copolymers have a molecular weight distribution of greater than 4.0 and show two peaks when subjected to a crystallization analysis fractionation (CRYSTAF).

U.S. Pat. No. 6,462,161 describes the use of either a constrained geometry type catalyst or a bridged bis-Cp metallocene catalyst to produce, in a single reactor, a polyolefin composition having long chain branching and a molecular weight maximum occurring in the part of the composition having the highest comonomer content (i.e. a reversed comonomer distribution). The compositions made with a constrained geometry catalyst have multimodal TREF profiles, and relatively narrow molecular weight distributions (e.g. the exemplified resins have a M_w/M_n of from 2.19 to 3.4, see Table 1 in the examples section of U.S. Pat. No. 6,462,161). The compositions made with a bridged bis-Cp metallocene catalyst have complex TREF profiles and somewhat broader molecular weight distribution (e.g. the exemplified reins have a M_w/M_n of 3.43 or 6.0, see Table 1 in the Examples section of U.S. Pat. No. 6,462,161).

Ethylene copolymers are taught in U.S. Pat. No. 7,968,659 which have a melt index of from 1.0 to 2.5, a M_w/M_n of from 3.5 to 4.5, a melt elastic modulus G' (G''=500 Pa) of from 40 to 150 Pa and an activation energy of flow (Ea) in the range of 28 to 45 kJ/mol. Constrained geometry catalysts are used to make the polymer compositions in the gas phase.

U.S. Pat. No. 7,521,518 describes the use of a constrained geometry catalyst to give an ethylene copolymer composition having a reversed comonomer distribution as determined by various cross fractionation chromatography (CFC) parameters and a molecular weight distribution of from 2.5 to 10. Polymerization is carried out in the slurry phase. Blends of the copolymer composition are described in U.S. Pat. No. 7,166,676.

U.S. Pat. No. 5,874,513 describes that the use of a mixture of components which give rise to a supported metallocene catalyst can, in a gas phase reactor, give an ethylene copolymer with reduced comonomer distribution homogeneity. The patent defines a composition distribution parameter Cb which is representative of the distribution of comonomers within the polymer composition. The TREF analysis of the copolymer composition showed a bimodal distribution.

U.S. Pat. No. 6,441,116 discloses a film comprising an ethylene copolymer with a composition distribution curve obtained by TREF having four distinct areas including one peak defining area which is attributed to a highly branched component.

An ethylene/alpha olefin copolymer produced with a Ziegler-Natta catalyst and having greater than about 17 weight percent of a high density fraction, as determined by analytical TREF methods, and a molecular weight distribution (M_w/M_n) of less than about 3.6 is disclosed in U.S. Pat. No. 5,487,938. The high density fraction has little short chain branching, while the balance of the copolymer composition is referred to as the fraction containing short chain branching. Hence, the data is consistent with a bimodal distribution of comonomer incorporation into the ethylene copolymer.

U.S. Pat. No. 6,642,340 describes an ethylene copolymer having a specific relationship between a melt flow rate and melt tension. The polymers further comprise between 0.5 and 8 wt% of a component eluting at not lower than 100°C in a TREF analysis.

U.S. Pat. No. 6,359,072 describes a polymer blend comprising from 10 to 90 wt% of a first polyethylene having a molecular weight distribution of from 1.5 to 3 and a composition distribution breadth index (CDBI) of from 50 to 80 percent, and from 90 to 10 wt% of a second polyethylene having a molecular weight distribution of from 3.5 to 15 and a CDBI of 75 to 95 percent. When blown into films, the polymer blend has improved optical properties relative to film obtained from either the first or second polyethylene alone.

U.S. Pat. No. 5,530,065 describes a polymer blend of a metallocene catalyst polymer having a narrow molecular weight distribution and a narrow comonomer distribution, and a Ziegler-Natta catalyzed polymer having a broad molecular weight distribution and a broad comonomer distribution. The polymer blends give rise to films having good heat sealing properties. Similarly, U.S. Pat. Nos. 5,844,045, 5,869,575 and 5,677,383 disclose that blends of heterogeneously branched resin prepared with conventional Ziegler-Natta catalysts with homogeneously branched resin prepared with a constrained geometry catalyst are also suitable for preparing films.

It is well known to blend high pressure low density polyethylene (HPLDPE) with linear low density polyethylene (LLDPE) in order to improve the processability of the LLDPE polymer (for an example of a blend of this type see WO 95/25141). However, such blends typically have poor toughness and impact strength relative to the unblended LLDPE.

For a description of blends comprising a linear low density polyethylene (LLDPE) having a high MFR and high CDBI, including blends with HPLDPE, and of films comprising such blends see: WO 2011/129956, U.S. Pat. Nos. 7,951,873, 7,601,409, 7,235,607, 8,080,294 and U.S. Pat. Appl. Nos. 2006/0188678, US 2011/0165395, US 2012/0100356, 2011/0003099, 2007/0260016.

There is still potential for new blend compositions exhibiting a good balance of physical properties and good processability.

We recently developed a new polymer composition having good processability and good physical properties (co-pending CA Appl. No. 2,780,508). The polymer composition, which can be made with a phosphinimine catalyst, has a density of from 0.916 g/cm^3 to 0.930 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of from 32 to 50, a molecular weight distribution (M_w/M_n) of from 3.6 to 6.0, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, and a composition distribution breadth index $CDBI_{50}$ of from 35 to 70 wt% as determined by TREF. We now report on polymer blends comprising the new polymer composition and have found that the copolymer composition improves melt strength, shear thinning behavior and dart impact properties when blended with other linear low density polyethylenes, and brings about good stiffness-toughness balance, optical properties and seal performance when blends comprising the copolymer composition are made into films.

Use of phosphinimine catalysts for gas phase olefin polymerization is the subject matter of U.S. Patent No. 5,965,677. The phosphinimine catalyst is an organometallic compound having a phosphinimine ligand, a cyclopentadienyl type ligand and two activatable ligands, and which is supported on a suitable particulate support such as silica. The exemplified catalysts had the formula $CpTi(N=P(tBu)_3)X_2$ where X was Cl, Me or Cl and $-O-(2,6-iPr-C_6H_3)$.

In co-pending CA Pat. Appl. No. 2,734,167 we showed that suitably substituted phosphinimine catalysts gave narrow molecular weight distribution copolymers which when made into film showed a good balance of optical and physical properties.

Polymers and films made in the gas phase using various single site catalysts, including so called “phosphinimine” catalysts, were disclosed at Advances in Polyolefins II, Napa, California – October 24 – 27, 1999 (“Development of NOVA's Single Site Catalyst Technology for use in the Gas Phase Process”- I. Coulter; D. Jeremic; A. Kazakov; I. McKay).

In a disclosure made at the 2002 Canadian Society for Chemistry Conference (“Cyclopentadienyl Phosphinimine Titanium Catalysts – Structure, Activity and Product Relationships in Heterogeneous Olefin Polymerization.” R.P. Spence; I. McKay; C. Carter; L. Koch; D. Jeremic; J. Muir; A. Kazakov. NOVA Research and Technology Center, CIC, 2002), it was shown that phosphinimine catalysts bearing variously substituted cyclopentadienyl and indenyl ligands were active toward the gas phase polymerization of ethylene when in supported form.

U.S. Pat. Appl. No. 2008/0045406, discloses a supported phosphinimine catalyst comprising a C_6F_5 substituted indenyl ligand. The catalyst was activated with an ionic activator having an active proton for use in the polymerization of ethylene with 1-hexene.

U.S. Pat. Appl. No. 2006/0122054 discloses the use of a dual catalyst formulation one component of which is a phosphinimine catalyst having an n-butyl substituted indenyl ligand. The patent is directed to the formation of bimodal resins suitable for application in pipe.

SUMMARY OF THE INVENTION

Provided are polymer blends having good processability, good toughness-stiffness balance, and which show good optical and seal properties when made into films.

Provided is a polymer blend comprising a polyethylene copolymer having a density of from 0.916 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of from 32 to 50, a molecular weight distribution (M_w/M_n) of from 3.6 to 6.5, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, and a composition distribution breadth index $CDBI_{50}$ of from 35 to 70 wt% as determined by TREF and which satisfies at least one of the following relationships:

(i) $\delta^{XO} \leq [\,80 - 1.22\,(CDBI_{50}) / (M_w/M_n)]$; and

(ii) $(M_w/M_n) \geq 68\,[(I_{21}/I_2)^{-1} + 10^{-6}\,(M_n)]$.

Provided is a polymer blend comprising from 5-99 wt% based on the total weight of the polymer blend, of a first polyethylene copolymer having a density of from 0.916 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of from 32 to 50, a molecular weight distribution (M_w/M_n) of from 3.6 to 6.5, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, and a composition distribution breadth index $CDBI_{50}$ of from 35 to 70 wt% as determined by TREF and which satisfies the following relationships:

(i) $\delta^{XO} \leq [\,80 - 1.22\,(CDBI_{50}) / (M_w/M_n)]$; and

(ii) $(M_w/M_n) \geq 68\,[(I_{21}/I_2)^{-1} + 10^{-6}\,(M_n)]$.

Provided is a polymer blend comprising: a) 5-95 wt% of a first polyethylene copolymer having a density of from 0.916 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of from 32 to 50, a molecular weight distribution (M_w/M_n) of from 3.6 to 6.5, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, a composition distribution breadth index $CDBI_{50}$ of from 35 wt% to 70 wt% as determined by TREF and which satisfies the following relationships: $\delta^{XO} \leq [\,80 - 1.22\,(CDBI_{50}) / (M_w/M_n)]$ and $(M_w/M_n) \geq 68\,[(I_{21}/I_2)^{-1} + 10^{-6}\,(M_n)]$; and b) 95-5 wt% of a second polyethylene copolymer which is a linear low density polyethylene (LLDPE) different from the first polyethylene copolymer and which has a density of from 0.910 to 0.940 g/cm^3, a melt index (I_2) of 0.2 to 5.0 g/10min, and melt flow ratio (I_{21}/I_2) of less than 35.

Provided is a polymer blend comprising: a) 5-95 wt% of a first polyethylene copolymer having a density of from 0.916 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of from 32 to 50, a molecular weight distribution (M_w/M_n) of from 3.6 to 6.5, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, a composition distribution breadth index $CDBI_{50}$ of from 35 wt% to 70 wt% as determined by TREF and which satisfies the following relationships: $\delta^{XO} \leq [\,80 - 1.22\,(CDBI_{50}) / (M_w/M_n)]$; and $(M_w/M_n) \geq 68\,[(I_{21}/I_2)^{-1} + 10^{-6}\,(M_n)]$; and b) 95-5 wt% of a second polyethylene copolymer which is a linear low density polyethylene (LLDPE) having a density of from 0.910 to 0.940 g/cm^3, a melt index (I_2) of 0.2 to 5.0 g/10min, and melt flow ratio (I_{21}/I_2) of less than 32.

Provided is a polymer blend comprising: a) 5-95 wt% of a first polyethylene copolymer having a density of from 0.916 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of from 35 to 50, a molecular weight distribution (M_w/M_n) of from 3.6 to 6.5, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, a composition distribution breadth index $CDBI_{50}$ of from 35 wt% to 70 wt% as determined by TREF and which satisfies the following relationships: $\delta^{XO} \leq [\,80 - 1.22\,(CDBI_{50}) / (M_w/M_n)]$; and $(M_w/M_n) \geq 68\,[(I_{21}/I_2)^{-1} + 10^{-6}\,(M_n)]$; and b) 95-5 wt% of a second polyethylene copolymer which is a linear low density polyethylene (LLDPE) having a density of from 0.910 to 0.940 g/cm^3, a melt index (I_2) of 0.2 to 5.0 g/10min, and melt flow ratio (I_{21}/I_2) of less than 35.

Provided is a polymer blend comprising: a) 5-95 wt% of a first polyethylene copolymer having a density of from 0.916 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of at least 30, a molecular weight distribution (M_w/M_n) of from 3.0 to 6.5, a reverse comonomer distribution profile as determined by

GPC-FTIR, a multimodal TREF profile, a composition distribution breadth index $CDBI_{50}$ of from 35 wt% to 70 wt% as determined by TREF and which satisfies the following relationships: $\delta^{XO} \leq [\, 80 - 1.22\ (CDBI_{50}) / (M_w/M_n)]$; $(M_w/M_n) \geq 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$; and $\delta^{XO} \leq 96 - 2.14\ [(MFR^{0.5}) + 1 \times 10^{-4}\ (M_w - M_n)]$; and b) 95-5 wt% of a second polyethylene copolymer which is a linear low density polyethylene (LLDPE) different from the first polyethylene copolymer and having a density of from 0.910 to 0.940 g/cm^3, a melt index (I_2) of 0.2 to 5.0 g/10min, and melt flow ratio (I_{21}/I_2) of less than 35.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows a temperature rising elution fractionation (TREF) analysis and profile of a first polyethylene copolymer used according to the present invention.

Figure 2 shows a gel permeation chromatograph (GPC) with refractive index detection, of a first polyethylene copolymer used according to the present invention.

Figure 3 shows a gel permeation chromatograph with Fourier transform infra-red (GPC-FTIR) detection obtained for a first polyethylene copolymer made according to the present invention. The comonomer content, shown as the number of short chain branches per 1000 carbons (y-axis), is given relative to the copolymer molecular weight (x-axis). The upwardly sloping line (from left to right) is the short chain branching (in short chain branches per 1000 carbons atoms) determined by FTIR. As can be seen in the Figure, the number of short chain branches increases at higher molecular weights, and hence the comonomer incorporation is said to be "reversed".

Figure 4A show plots of the phase angle vs the complex modulus and the phase angle vs complex viscosity for resins 2A and 2B as determined by dynamic mechanical analysis (DMA).

Figures 4B show plots of the phase angle vs the complex modulus and the phase angle vs complex viscosity for resin 1A as determined by DMA.

Figure 5 shows a plot of the equation: $\delta^{XO} = 96 - 2.14\ [(MFR^{0.5}) + 1 \times 10^{-4}\ (M_w - Mn)]$. The value obtained from the equation $96 - 2.14\ [(MFR^{0.5}) + 1 \times 10^{-4}\ (M_w - Mn)]$ (the x-axis) is plotted against the corresponding van Gurp-Palmen crossover phase angle, δ^{XO} (the y-axis) for resin Nos. 1A-1H and resin Nos. 2A-2D.

Figure 6 shows a plot of the equation: $Mw/Mn = 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$. The values from the equation $68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$ (the y-axis) are plotted against the corresponding Mw/Mn values (the x-axis) for resins 1A-1H as well as for several commercially available resins which have a melt index I_2 of 1.5 g/10min or less and a density of between 0.916 and 0.930 g/cm^3.

Figure 7 shows a plot of the equation: $\delta^{XO} = [80 - 1.22\ (CDBI_{50}\ /\ (M_w/M_n)]$. The values of the equation $[80 - 1.22\ (CDBI_{50}\ /\ (M_w/M_n)]$ (the x-axis) are plotted against the corresponding crossover phase angle (δ^{XO}) values (the y-axis) for resins 1A-1H as well as for several commercially available resins which have a melt index I_2 of 1.5 g/10min or less and a density of between 0.916 and 0.930 g/cm^3.

Figure 8 shows a plot of the shear thinning ratio ($\eta^*_{0.1}/\ \eta^*_{10}$) against the weight fraction of the first polyethylene copolymer for blends made according to the current invention.

Figure 9 shows a graph of the melt strength (cN) for blends and blend components according to various embodiments of the present invention. The Figure also shows a plot of the improvement in melt strength (in percent) for three different blends made according to the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention provides polymer blends which have good processability and melt strength and when made into film have a relatively high dart impact strength, as well as good optical and seal properties.

The polymer blends comprise a polyethylene copolymer having a density of from 0.916 g/cm^3 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of at least 28, a molecular weight distribution (M_w/M_n) of from 3.0 to 7.0, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, and a composition distribution breadth index $CDBI_{50}$ of from 35 to 70 wt% as determined by TREF; and which satisfies at least one of the following relationships:

(i) $(M_w/M_n) \geq 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$; and

(ii) $\delta^{XO} \leq [\ 80 - 1.22\ (CDBI_{50})\ /\ (M_w/M_n)\ ]$.

As used herein, the terms "linear low density polyethylene" and "LLDPE" refer to a polyethylene homopolymer or, more preferably, a copolymer having a density of from about 0.910 g/cm^3 to about 0.945 g/cm^3. Unlike high pressure low density polyethylene (HPLDPE), the LLDPE is a linear polymer that contains a minimal amount or relatively small amount, or zero amounts of long chain branching compared to HPLDPE. HPLDPE, in contrast, is often referred to as “branched” because it has a relatively large number of long chain branches extending from the main polymer backbone.

In the present invention, the term “polyethylene copolymer” is used interchangeably with the term “ethylene copolymer”, or “copolymer” and both connote a polymer consisting of polymerized ethylene units and at least one type of polymerized alpha olefin with ethylene being the majority monomer present.

The comonomers that are useful in general for making polyethylene copolymers include α-olefins, such as C_3-C_{20} alpha-olefins, preferably C_3-C_{10} alpha-olefins, and more preferably C_3-C_8 alpha-olefins. The α-olefin comonomer may be linear or branched, and two or more comonomers may be used, if desired. Examples of suitable comonomers include propylene; 1-butene; 1-pentene; 1-pentene with one or more methyl, ethyl, or propyl substituents; 1-hexene; 1-hexene with one or more methyl, ethyl, or propyl substituents; 1-heptene; 1-heptene with one or more methyl, ethyl, or propyl substituents; 1-octene; 1-octene with one or more methyl, ethyl, or propyl substituents; 1-nonene; 1-nonene with one or more methyl, ethyl, or propyl substituents; ethyl, methyl, or dimethyl-substituted 1-decene; 1-dodecene; and styrene. Specifically, but without limitation, the combinations of ethylene with a comonomer may include: ethylene propylene, ethylene butene, ethylene 1-pentene; ethylene 4-methyl-1-pentene; ethylene 1-hexene; ethylene 1-octene; ethylene decene; ethylene dodecene; ethylene 1-hexene 1-pentene; ethylene 1-hexene 4-methyl-1-pentene; ethylene 1-hexene 1-octene; ethylene 1-hexene decene; ethylene 1-hexene dodecene; ethylene 1-octene 1-pentene; ethylene 1-octene 4-methyl-1-pentene; ethylene 1-octene 1-hexene; ethylene 1-octene decene; ethylene 1-octene dodecene; combinations thereof and like permutations.

Polyethylene copolymers having more than two types of monomers, such as terpolymers, are also included within the term "copolymer" as used herein.

In embodiments of the invention, the first and second polyethylene copolymer blend components will comprise at least 75 weight% of ethylene units, or at least 80 wt% of ethylene units, or at least 85 wt% of ethylene units with the balance being an alpha-olefin unit, based on the weight of each blend component.

The term “polymer blend” is herein meant to connote a dry blend of two different polymers, in-reactor blends, including blends arising from the use of multi or mixed catalyst systems in a single reactor zone, and blends that result from the use of one or more catalysts in one or more reactors under the same or different conditions (e.g. a blend resulting from in series reactors each running under different conditions and/or with different catalysts).

In an embodiment of the invention, the polymer blend will comprise a first polyethylene copolymer and a second polyethylene copolymer, each of which are described further below.

The First Polyethylene Copolymer

The polymer blend of the present invention comprises 1-99 wt% of a first polyethylene copolymer which in an embodiment of the invention has a density of from 0.916 g/cm^3 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of at least 28, a molecular weight distribution (M_w/M_n) of from 3.0 to 7.0, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, and a composition distribution breadth index $CDBI_{50}$ of from 35 to 70 wt% as determined by TREF.

In an embodiment of the invention, the first polyethylene copolymer satisfies the following relationship: $(M_w/M_n) \geq 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$.

In an embodiment of the invention, the first polyethylene copolymer satisfies the following relationship: $\delta^{XO} \leq [\ 80 - 1.22\ (CDBI_{50})\ /\ (M_w/M_n)\ ]$, where δ^{XO} is the crossover phase angle from a van Gurp-Palmen (VGP) plot as determined by dynamic mechanical analysis (DMA) and $CDBI_{50}$ is the comonomer distribution breadth index as determined by TREF analysis.

In an embodiment of the invention, the first polyethylene copolymer satisfies both of the following relationships: $(M_w/M_n) \geq 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$ and $\delta^{XO} \leq [\ 80 - 1.22\ (CDBI_{50})\ /\ (M_w/M_n)\ ]$.

In embodiments of the invention, the first polyethylene copolymer is a copolymer of ethylene and an alpha olefin selected from 1-butene, 1-hexene and 1-octene.

In an embodiment of the invention, the first polyethylene copolymer is a copolymer of ethylene and 1-hexene.

In embodiments of the invention, the first polyethylene copolymer will have a melt index (I_2) of from 0.01 to 3.0 g/10min, or from 0.1 to 2.0 g/10min, or from 0.25 to 2.0 g/10min, or from 0.01 to 1.0 g/10min, or from 0.1 to 1.0 g/10min, or less than 1.0 g/10min, or from 0.1 to less than 1.0 g/10min, or from 0.25 to 1.0 g/10min, or from 0.25

to 0.9 g/10min, or from 0.25 to 0.80 g/10min, or from 0.2 to 0.9 g/10min, or from 0.20 to 0.85 g/10min, or from 0.25 to 0.85 g/10min.

In an embodiment of the invention, the first polyethylene copolymer has a melt index (I_2) of less than 1.0 g/10min.

In an embodiment of the invention, the first polyethylene copolymer has melt index (I_2) of from 0.25 to 0.80 g/10min.

In embodiments of the invention, the first polyethylene copolymer will have a density of from 0.916 to 0.935 g/cm^3 including narrower ranges within this range, such as for example, 0.916 to 0.932 g/cm^3, or from 0.917 to 0.932 g/cm^3, or from 0.916 to 0.930 g/cm^3, or 0.917 to 0.930 g/cm^3, or from 0.916 to 0.925 g/cm^3, or from 0.917 to 0.927 g/cm^3, or from 0.917 to 0.926 g/cm^3, or from 0.917 to 0.925 g/cm^3, or from 0.917 to 0.923 g/cm^3, or from 0.918 to 0.932 g/cm^3, or from 0.918 to 0.930 g/cm^3, or from 0.918 to 0.928 g/cm^3 (note: where applicable “g” stands for gram; “cc” stands for cubic centimeter, cm^3).

In an embodiment of the invention, the first polyethylene copolymer will have a density of from 0.916 to 0.930 g/cm^3. In an embodiment of the invention, the first polyethylene copolymer will have a density of greater than 0.916 g/cm^3 to less than 0.930 g/cm^3. In an embodiment of the invention, the first polyethylene copolymer will have a density of from 0.917 to 0.927 g/cm^3. In an embodiment of the invention, the first polyethylene copolymer will have a density of from 0.918 g/cm^3 to 0.927 g/cm^3.

The first polyethylene copolymer of the present invention may have a unimodal, broad unimodal, bimodal, or multimodal profile in a gel permeation chromatography (GPC) curve generated according to the method of ASTM D6474-99. The term “unimodal” is herein defined to mean there will be only one significant peak or maximum evident in the GPC-curve. A unimodal profile includes a broad unimodal profile. By the term “bimodal” it is meant that there will be a secondary peak or shoulder which represents a higher or lower molecular weight component (i.e. the molecular weight distribution, can be said to have two maxima in a molecular weight distribution curve). Alternatively, the term "bimodal" connotes the presence of two maxima in a molecular weight distribution curve generated according to the method of ASTM D6474-99. The term "multi-modal" denotes the presence of two or more, typically more than two, maxima in a molecular weight distribution curve generated according to the method of ASTM D6474-99.

In an embodiment of the invention, the first polyethylene copolymer will have a unimodal profile in a gel permeation chromatography (GPC) curve generated according to the method of ASTM D6474-99. The term "unimodal" is herein defined to mean there will be only one significant peak or maximum evident in the GPC-curve. A unimodal profile includes a broad unimodal distribution curve or profile.

In embodiments of the invention, the first ethylene copolymer will exhibit a weight average molecular weight (M_W) as determined by gel permeation chromatography (GPC) of from 30,000 to 250,000, including narrower ranges within this range, such as for example, from 50,000 to 200,000, or from 50,000 to 175,000, or from 75,000 to 150,000, or from 80,000 to 125,000.

In embodiments of the invention, the first ethylene copolymer will exhibit a number average molecular weight (M_n) as determined by gel permeation chromatography (GPC) of from 5,000 to 100,000 including narrower ranges within this range, such as for example from 7,500 to 100,000, or from 7,500 to 75,000, or from 7,500 to 50,000, or from 10,000 to 100,000, or from 10,000 to 75,000, or from 10,000 to 50,000.

In embodiments of the invention, the first ethylene copolymer will exhibit a Z-average molecular weight (M_Z) as determined by gel permeation chromatography (GPC) of from 50,000 to 1,000,000 including narrower ranges within this range, such as for example from 75,000 to 750,000, or from 100,000 to 500,000, or from 100,000 to 400,000, or from 125,000 to 375,000, or from 150,000 to 350,000, or from 175,000 to 325,000.

In embodiments of the invention, the first ethylene copolymer will have a molecular weight distribution (M_w/M_n) as determined by gel permeation chromatography (GPC) of from 3.0 to 7.0, including narrower ranges within this range, such as for example, from 3.5 to 7.0, or from 3.5 to 6.5, or from 3.0 to 6.5, or from 3.6 to 6.5, or from 3.6 to 6.0, or from 3.5 to 5.5, or from 3.6 to 5.5, or from 3.5 to 5.0, or from 4.0 to 6.0, or from 4.0 to 5.5.

In an embodiment of the invention, the first polyethylene copolymer has a molecular weight distribution (M_w/M_n) of from 4.0 to 5.5.

In embodiments of the invention, the first polyethylene copolymer will have a Z-average molecular weight distribution (M_z/M_w) as determined by gel permeation chromatography (GPC) of from 2.0 to 5.5, including narrower ranges within this range, such as for example, from 2.0 to 5.0, or from 2.0 to 4.5, or from 2.0 to 4.0, or from 2.0 to 2.5, or from 2.0 to 3.0.

In an embodiment of the invention, the first polyethylene copolymer has a Z-average molecular weight distribution (M_z/M_w) of from 2.0 to 4.0.

In an embodiment of the invention, the first ethylene copolymer will have a flat comonomer incorporation profile as measured using Gel-Permeation Chromatography with Fourier Transform Infra-Red detection (GPC-FTIR). In an embodiment of the invention, the first ethylene copolymer will have a negative (i.e. “normal”) comonomer incorporation profile as measured using GPC-FTIR. In an embodiment of the invention, the first ethylene copolymer will have an inverse (i.e. “reverse”) or partially inverse comonomer incorporation profile as measured using GPC-FTIR. If the comonomer incorporation decreases with molecular weight, as measured using GPC-FTIR, the distribution is described as “normal” or “negative”. If the comonomer incorporation is approximately constant with molecular weight, as measured using GPC-FTIR, the comonomer distribution is described as “flat” or “uniform”. The terms “reverse comonomer distribution” and “partially reverse comonomer distribution” mean that in the GPC-FTIR data obtained for the copolymer, there is one or more higher molecular weight components having a higher comonomer incorporation than in one or more lower molecular weight segments. The term “reverse(d) comonomer distribution” is used herein to mean, that across the molecular weight range of the ethylene copolymer, comonomer contents for the various polymer fractions are not substantially uniform and the higher molecular weight fractions thereof have proportionally higher comonomer contents (i.e. if the comonomer incorporation rises with molecular weight, the distribution is described as “reverse” or “reversed”). Where the comonomer incorporation rises with increasing molecular weight and then declines slightly or where the comonomer incorporation initially declines with molecular weight and then rises at still higher molecular weight, the comonomer distribution is still considered “reverse”, but may also be described as “partially reverse”.

In an embodiment of the invention the first polyethylene copolymer will has a reversed comonomer incorporation profile as measured using GPC-FTIR.

In an embodiment of the invention, the ethylene copolymer will have a comonomer incorporation profile as determined by GPC-FTIR which satisfies the following condition:

SCB/1000 at MW of 200,000 – SCB/1000 at MW of 50,000 is a positive number or greater than 1.0;

where SCB/1000 is the comonomer content determined as the number of short chain branches per thousand carbons and MW is the corresponding molecular weight (i.e. the absolute molecular weight) on a GPC or GPC-FTIR chromatograph.

In an embodiment of the invention, the ethylene copolymer will have a comonomer incorporation profile as determined by GPC-FTIR which satisfies the following condition:

SCB/1000 at MW of 200,000 – SCB/1000 at MW of 50,000 > 2.0;

where SCB/1000 is the comonomer content determined as the number of short chain branches per thousand carbons and MW is the corresponding molecular weight (i.e. the absolute molecular weight) on a GPC or GPC-FTIR chromatograph.

In an embodiment of the invention, the first polyethylene copolymer will have a comonomer incorporation profile as determined by GPC-FTIR which satisfies the following condition:

SCB/1000 at MW of 200,000 – SCB/1000 at MW of 50,000 > 5.0;

where SCB/1000 is the comonomer content determined as the number of short chain branches per thousand carbons and MW is the corresponding molecular weight (i.e. the absolute molecular weight) on a GPC or GPC-FTIR chromatograph.

In an embodiment of the invention, the first polyethylene copolymer will have a comonomer incorporation profile as determined by GPC-FTIR which satisfies the following condition:

SCB/1000 at MW of 200,000 – SCB/1000 at MW of 50,000 > 6.0;

where SCB/1000 is the comonomer content determined as the number of short chain branches per thousand carbons and MW is the corresponding molecular weight (i.e. the absolute molecular weight) on a GPC or GPC-FTIR chromatograph.

In an embodiment of the invention, the first polyethylene copolymer will have a comonomer incorporation profile as determined by GPC-FTIR which satisfies the following condition:

SCB/1000 at MW of 200,000 – SCB/1000 at MW of 50,000 > 7.0;

where SCB/1000 is the comonomer content determined as the number of short chain branches per thousand carbons and MW is the corresponding molecular weight (i.e. the absolute molecular weight) on a GPC or GPC-FTIR chromatograph.

In embodiments of the invention, the first polyethylene copolymer will have a melt flow ratio (the MFR = I_{21}/I_2) of from 28 to 60, or from 30 to 60. In further embodiments of the invention, the copolymer will have an I_{21}/I_2 of at least 28, or at least 30, or from 30 to 55, or from 30 to 50, or from 30 to 45, or from 32 to 50 or from 35 to 55, or from 36 to 50, or from 36 to 48, or from 36 to 46.

In an embodiment of the invention, the first polyethylene copolymer has a melt flow ratio (I_{21}/I_2) of from 32 to 50. In an embodiment of the invention, the first polyethylene copolymer has a melt flow ratio (I_{21}/I_2) of from 35 to 50. In an embodiment of the invention, the first polyethylene copolymer has a melt flow ratio (I_{21}/I_2) of from 36 to 50.

In embodiments of the invention, the first polyethylene copolymer will have a composition distribution breadth index $CDBI_{50}$, as determined by temperature elution fractionation (TREF), of from 35% to 75% by weight, or from 35 to 70 wt%, or from 40% to 75% by weight. In embodiments of the invention, the first polyethylene copolymer will have a $CDBI_{50}$ of from 40% to 70%, or 45% to 70%, or from 45% to 65%, or from 45 to 60%, or from 45% to 69%, or from 50% to 69%, or from 50% to 70%, or from 50% to 66%, or from 50% to 65%, or from 50% to 60%, or from 55% to 70%, or from 55 to 65%, or from 60% to 70%, or from 60% to 65% (by weight).

In an embodiment of the invention, the first polyethylene copolymer has a $CDBI_{50}$ of from 35 wt% to 70 wt%. In an embodiment of the invention, the first polyethylene copolymer has a $CDBI_{50}$ of from 45 wt% to 69 wt%.

The composition distribution of the polyethylene copolymer may also be characterized by the T(75)−T(25) value, where the T(25) is the temperatures at which

25 wt% of the eluted copolymer is obtained, and T(75) is the temperature at which 75 wt% of the eluted copolymer is obtained in a TREF experiment as described in the Examples section.

In an embodiment of the present invention, the first polyethylene copolymer will have a T(75)−T(25) of from 10 to 30°C as determined by TREF. In an embodiment of the present invention, the first polyethylene copolymer will have a T(75)−T(25) of from 10 to 25°C as determined by TREF. In an embodiment of the present invention, the first polyethylene copolymer will have a T(75)−T(25) of from 10 to 22.5°C as determined by TREF. In an embodiment of the present invention, the first polyethylene copolymer will have a T(75)−T(25) of from 12.5 to 25°C as determined by TREF. In an embodiment of the present invention, the first polyethylene copolymer will have a T(75)−T(25) of from 12.5 to 22.5°C as determined by TREF. In an embodiment of the present invention, the first polyethylene copolymer will have a T(75)−T(25) of from 12.5 to 20.0°C as determined by TREF. In an embodiment of the present invention, the first polyethylene copolymer will have a T(75)−T(25) of from 10.0 to 20°C as determined by TREF.

In embodiments of the invention, the first polyethylene copolymer will have a CY *a*-parameter (also called the Carreau-Yasuda shear exponent) of from 0.01 to 0.4, or from 0.05 to 0.4, or from 0.05 to 0.3, or from 0.01 to 0.3, or from 0.01 to 0.25, or from 0.05 to 0.25.

In embodiments of the invention, the first polyethylene copolymer will have a normalized shear thinning index, SHI @0.1 rad/s (i.e. the $\eta^*_{0.1}/\eta_0$) of from 0.001 to 0.90, or from 0.001 to 0.8, or from 0.001 to 0.5, or less than 0.9, or less than 0.8, or less than 0.5, or less than 0.35.

In an embodiment of the invention, the first polyethylene copolymer will have a TREF profile, as measured by temperature rising elution fractionation, which is multimodal, comprising at least two elution intensity maxima or peaks.

In an embodiment of the invention, the first polyethylene copolymer will have an amount of copolymer eluting at a temperature at or below 40°C, of less than 5 wt% as determined by temperature rising elution fractionation (TREF).

In an embodiment of the invention, the first polyethylene copolymer will have an amount of copolymer eluting at a temperature of from 90°C to 105°C, of from 5 to 45 wt% as determined by temperature rising elution fractionation (TREF). In an embodiment of the invention, the first polyethylene copolymer will have an amount of copolymer eluting at a temperature of from 90°C to 105°C, of from 5 to 40 wt% as determined by temperature rising elution fractionation (TREF). In an embodiment of the invention, the first polyethylene copolymer will have an amount of copolymer eluting at a temperature of from 90°C to 105°C, of from 5 to 35 wt% as determined by temperature rising elution fractionation (TREF). In an embodiment of the invention, from 5 to 30 wt% of the first polyethylene copolymer will be represented within a temperature range of from 90°C to 105°C in a TREF profile. In an embodiment of the invention, from 10 to 30 wt% of the first polyethylene copolymer will be represented within a temperature range of from 90°C to 105°C in a TREF profile. In an embodiment of the invention, from 5 to 25 wt% of the first polyethylene copolymer will be represented within a temperature range of from 90°C to 105°C in a TREF profile. In an embodiment of the invention, from 10 to 25 wt% of the first polyethylene copolymer will be represented within a temperature range of from 90°C to 105°C in a TREF profile. In another embodiment of the invention, from 12 to 25 wt% of the first polyethylene copolymer will be represented at a temperature range of from 90°C to 105°C in a TREF profile. In another embodiment of the invention, from 10 to 22.5 wt% of the first polyethylene copolymer will be represented at a temperature range of from 90°C to 105°C in a TREF profile.

In embodiments of the invention, less than 1 wt%, or less than 0.5 wt%, or less than 0.05 wt%, or 0 wt% of the first polyethylene copolymer will elute at a temperature of above 100°C in a TREF analysis.

In an embodiment of the invention, the first polyethylene copolymer will have a TREF profile, as measured by temperature rising elution fractionation, comprising: i) a multimodal TREF profile comprising at least two elution intensity maxima (or peaks); ii) less than 5 wt% of the copolymer represented at a temperature at or below 40 °C; and iii) from 5 to 40 wt% of the copolymer represented at a temperature of from 90°C to 105°C.

In an embodiment of the invention, the first polyethylene copolymer has a trimodal TREF profile comprising three elution intensity maxima (or peaks).

In an embodiment of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or "med" for short) and T(high), where T(low) is from 60°C to 82°C, T(med) is from 75°C to 90°C but higher than T(low), and T(high) is from 90°C to 100°C but higher than T(low). In an embodiment of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or "med" for short) and T(high), where T(low) is from 62°C to 82°C, T(med) is from 76°C to 89°C but higher than T(low), and T(high) is from 90°C to 100°C. In an embodiment of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three intensity peaks occurring at elution temperatures T(low), T(med) and T(high);

wherein T(low) occurs at from 64°C to 82°C, T(med) occurs at from 78°C to 89°C but is higher than T(low), and T(high) occurs at from 90°C to 100°C. In an embodiment of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three intensity peaks occurring at elution temperatures T(low), T(med) and T(high); wherein T(low) occurs at from 64°C to 82°C, T(med) occurs at from 78°C to 87°C but is higher than T(low), and T(high) occurs at from 90°C to 96°C.

In an embodiment of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or “med” for short) and T(high), where T(low) is from 64°C to 82°C, T(med) is from 75°C to 90°C but is higher than T(low), and T(high) is from 90°C to 100°C but is higher than T(med). In an embodiment of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or “med” for short) and T(high), where T(low) is from 65°C to 75°C, T(med) is from 76°C to 89°C, and T(high) is from 90°C to 100°C.

In an embodiment of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or “med” for short) and T(high), where T(low) is from 65°C to 75°C, T(med) is from 76°C to 87°C, and T(high) is from 90°C to 100°C.

In an embodiment of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or “med” for short) and T(high), where T(low) is from 65°C to 75°C, T(med) is from 75°C to 85°C but is higher than T(med), and T(high) is from 90°C to 100°C.

In an embodiment of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or "med" for short) and T(high), where the intensity of the peaks at T(low) and T(high) are greater than the intensity of the peak at T(med).

In embodiments of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or "med" for short) and T(high), where T(med)−T(low) is from 3°C to 25°C, or from 5°C to 20°C; or from 5°C to 15°C, or from 7°C to 15°C.

In embodiments of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or "med" for short) and T(high), where T(high)−T(med) is from 3°C to 20°C, or from 3°C to 17°C, or from 3°C to 15°C, or from 5°C to 20°C, or from 5°C to 17°C, or from 5°C to 15°C, or from 7°C to 17°C, or from 7°C to 15°C or from 10°C to 17°C, or from 10°C to 15°C.

In embodiments of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or "med" for short) and T(high), where T(high)−T(low) is from 15°C to 35°C, or from 15°C to 30°C, or from 17°C to 30°C, or from 15°C to 27°C, or from 17°C to 27°C, or from 20°C to 30°C or from 20°C to 27°C.

In an embodiment of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or "med" for short) and T(high), where the intensity of the peaks at T(low) and T(high) are greater than the intensity of the peak at T(med); and where T(med)−T(low) is from 3°C to 25°C; where T(high)−T(med) is from 3°C to 20°C; and where T(high)−T(low) is from 15°C to 35°C.

In an embodiment of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three elution intensity maxima (or peaks) occurring at elution temperatures T(low), T(medium or “med” for short) and T(high), where the intensity of the peaks at T(low) and T(high) are greater than the intensity of the peak at T(med); and where T(med)−T(low) is from 3°C to 15°C; where T(high)−T(med) is from 5°C to 15°C; and where T(high)−T(low) is from 15°C to 30°C.

In embodiments of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three intensity peaks occurring at elution temperatures T(low), T(med) and T(high), where T(low) is from 64°C to 82°C, T(med) is from 76°C to 89°C but is higher than T(low), and T(high) is from 90°C to 100°C and where the intensity of the peak at T(low) and T(high) is greater than the intensity of the peak at T(med); and where T(med)−T(low) is from 3°C to 25°C, or from 5°C to 20°C; or from 5°C to 15 °C, or from 7°C to 15°C.

In embodiments of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three intensity peaks occurring at elution temperatures T(low), T(med) and T(high), where T(low) is from 64°C to 75°C, T(med) is from 76°C to 86°C, and T(high) is from 90°C to 100°C and where the intensity of the peak at T(low) and T(high) is greater than the intensity of the peak at T(med); and where T(med)−T(low) is from 3°C to 25°C, or from 5°C to 20°C; or from 5°C to 15 °C, or from 7°C to 15°C.

In embodiments of the invention, the first polyethylene copolymer has a multimodal TREF profile defined by three intensity peaks occurring at elution temperatures T(low), T(med) and T(high), where T(low) is from 64°C to 82°C, T(med) is from 76°C to 89°C but is higher than T(low), and T(high) is from 90°C to 100°C and where the intensity of the peak at T(low) and T(high) is greater than the intensity of the peak at T(med); and where T(high)−T(med) is from is from 3°C to 20°C, or from 3°C to

17°C, or from 3°C to 15°C, or from 5°C to 20°C, or from 5°C to 17°C, or from 5°C to 15°C, or from 7°C to 17°C, or from 7°C to 15°C or from 10°C to 17°C, or from 10°C to 15°C.

In embodiments of the invention, the first ethylene copolymer has a multimodal TREF profile defined by three intensity peaks occurring at elution temperatures T(low), T(med) and T(high), where T(low) is from 64°C to 75°C, T(med) is from 76°C to 86°C, and T(high) is from 90°C to 100°C and where the intensity of the peak at T(low) and T(high) is greater than the intensity of the peak at T(med); and where T(high)−T(med) is from 3°C to 20°C, or from 3°C to 17°C, or from 3°C to 15°C, or from 5°C to 20°C, or from 5°C to 17°C, or from 5°C to 15°C, or from 7°C to 17°C, or from 7°C to 15°C or from 10°C to 17°C, or from 10°C to 15°C.

In embodiments of the invention, the first ethylene copolymer has a multimodal TREF profile defined by three intensity peaks occurring at elution temperatures T(low), T(med) and T(high), where T(low) is from 64°C to 82°C, T(med) is from 76°C to 89°C but is higher than T(low), and T(high) is from 90°C to 100°C and where the intensity of the peak at T(low) and T(high) is greater than the intensity of the peak at T(med); and where T(high)−T(low) is from 15°C to 35°C, or from 15°C to 30°C, or from 17°C to 30°C, or from 15°C to 27°C, or from 17°C to 27°C, or from 20°C to 30°C or from 20°C to 27°C.

In embodiments of the invention, the first ethylene copolymer has a multimodal TREF profile defined by three intensity peaks occurring at elution temperatures T(low), T(med) and T(high), where T(low) is from 65°C to 75°C, T(med) is from 76°C to 86°C, and T(high) is from 90°C to 100°C and where the intensity of the peak at T(low) and T(high) is greater than the intensity of the peak at T(med); and where T(high)−T(low) is from 15°C to 35°C, or from 15°C to 30°C, or from 17°C to 30°C, or from 15°C to 27°C, or from 17°C to 27°C, or from 20°C to 30°C or from 20°C to 27°C.

In an embodiment of the invention, the first polyethylene copolymer has two melting peaks as measured by differential scanning calorimetery (DSC).

In an embodiment of the invention, the first polyethylene copolymer will satisfy the condition:

$$(\mathrm{CDBI}_{50} - 3) \leq [15 / (a + 0.12)];$$

where the CDBI_{50} is the composition distribution breadth index in wt%, determined by TREF analysis and "*a*" is the is the Carreau-Yasuda shear exponent determined by dynamic mechanical analysis (DMA).

In embodiments of the invention, the first polyethylene copolymer will have a hexane extractables level of ≤ 3.0 wt%, or ≤ 2.0 wt%, or ≤ 1.5 wt% or ≤ 1.0 wt%. In an embodiment of the invention, the first polyethylene copolymer has a hexane extractables level of from 0.2 to 3.0 wt%, or from 0.2 to 2.5 wt%, or from 0.2 to 2.0 wt%.

In an embodiment of the invention, the first polyethylene copolymer will have a processability enhancement index (χ) of at least 1.0, where the processability enhancement index (χ) is defined by:

$$\chi = 96 - 2.14\,[(\mathrm{MFR}^{0.5}) + 1 \times 10^{-4}\,(M_w - M_n)] / \delta^{XO}$$

where δ^{XO} is the crossover phase angle from a van Gurp-Palmen (VGP) plot as determined by dynamic mechanical analysis (DMA), MFR is the melt flow ratio I_{21}/I_2, M_w is the weight average molecular weight and M_n is the number average molecular weight determined by gel permeation chromatography (GPC).

In an embodiment of the invention, the first polyethylene copolymer will have processability enhancement index (χ) of greater than 1.0 and less than 1.50.

In an embodiment of the invention, the first polyethylene copolymer will have processability enhancement index (χ) of greater than 1.0 and less than 1.30.

In an embodiment of the invention, the first polyethylene copolymer will have processability enhancement index (χ) of greater than 1.0 and less than 1.20.

In an embodiment of the invention, the first polyethylene copolymer will satisfy the condition:

$$\delta^{XO} \leq 96 - 2.14\ [(MFR^{0.5}) + 1 \times 10^{-4}\ (M_w - M_n)]$$

where δ^{XO} is the crossover phase angle at a frequency of 1.0 rad/s in a VGP plot as determined by dynamical mechanical analysis (DMA), MFR is the melt flow ratio I_{21}/I_2, M_w is the weight average molecular weight and M_n is the number average molecular weight determined by gel permeation chromatography (GPC).

<u>The Second Polyethylene Copolymer</u>

The polymer blend of the present invention may comprise from 99 to 1 wt% of second polyethylene copolymer. Preferably, the second polyethylene copolymer is a linear low density polyethylene (LLDPE). The second polyethylene copolymer is preferably a different polymer than the first polyethylene copolymer. The second polyethylene copolymer can be distinguished from the first polyethylene copolymer by differing in at least one property or characteristic. For example, the second polyethylene copolymer can be distinguished from the first polyethylene copolymer by not satisfying at least one of the following relationships: $(M_w/M_n) \geq 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$; or $\delta^{XO} \leq [\ 80 - 1.22\ (CDBI_{50})\ /\ (M_w/M_n)\ ]$. Alternatively, the second polyethylene copolymer can be distinguished from the first polyethylene copolymer by having a lower melt flow ratio (I_{21}/I_2) than the first polyethylene copolymer.

The second polyethylene copolymer can have a density of from about 0.910 g/cm^3 to about 0.940 g/cm^3. For example, the second polyethylene copolymer can have a density ranging from a low of about 0.910 g/cm^3, about 0.912 g/cm^3, or about 0.915 g/cm^3, or about 0.916 g/cm^3, or about 0.917 g/cm^3 to a high of about 0.927 g/cm^3, or about 0.930 g/cm^3, or about 0.935 g/cm^3, or about 0.940 g/cm^3. The second polyethylene copolymer can have a density of from 0.912 to 0.940 gcm^3, or from 0.915 g/cm^3 to 0.935 g/cm^3, or from 0.915 to 0.930 g/cm^3, or from 0.916 to 0.930 g/cm^3, or from 0.915 to 0.925 g/cm^3, or from 0.916 to 0.924 g/cm^3, or from 0.917 to 0.923 g/cm^3, or from 0.918 to about 0.922 g/cm^3.

The second polyethylene copolymer can have a molecular weight distribution (Mw/Mn) of from about 1.5 to about 6.0. For example, the second polyethylene copolymer can have a molecular weight distribution (Mw/Mn) ranging from a low of about 1.5, about 1.7, about 2.0, about 2.5, about 3.0, about 3.5, about 3.7, or about 4.0 to a high of about 5, about 5.25, about 5.5, or about 6.0. The second polyethylene copolymer can have a molecular weight distribution (Mw/Mn) of from 1.7 to 5.0, or from 1.5 to 4.0, or from 1.8 to 3.5, or from 2.0 to 3.0. Alternatively, the second polyethylene copolymer can have a molecular weight distribution (Mw/Mn) of from 3.6 to 5.4, or from 3.8 to 5.1, or from 3.9 to about 4.9.

The second polyethylene copolymer can have a melt index (I_2) of from 0.1 g/10min to 20 g/10min. The second polyethylene copolymer can have a melt index (I_2) ranging from 0.75 g/10min to 15 g/10 min, or from 0.85 g/10min to 10 g/10 min, or from 0.9 g/10 min to 8 g/10 min. For example, the second polyethylene copolymer can have a melt index (I_2) ranging from a low of about 0.20 g/10min, 0.25 g/10min, about 0.5 g/10 min, about 0.75 g/10 min, about 1 g/10 min, or about 2 g/10 min to a high of about 3 g/10 min, about 4 g/10 min, or about 5 g/10 min.

The second polyethylene copolymer can have a melt index (I_2) of from about 0.75 g/10 min to about 6 g/10 min, about 1 g/10 min to about 8 g/10 min, about 0.8 g/10 min to about 6 g/10 min, or about 1 g/10 min to about 4.5 g/10 min, or from 0.20 g/10min to 5.0 g/10 min, or from 0.30 g/10min to 5.0 g/10 min, or from 0.40 g/10min to 5.0 g/10 min, or from 0.50 g/10min to 5.0 g/10 min.

The second polyethylene copolymer can have a melt flow ratio (I_{21}/I_2) of less than about 36, or less than 35, or less than 32, or less than 30. For example the second polyethylene copolymer can have a melt flow ratio (I_{21}/I_2) of from 10 to 36, or from 10 to 35, or from 10 to 32, or from 10 to 30, or from 12 to 35 or from 12 to 32, or from 12 to 30, or from 14 to 27, or from 14 to 25, or from 14 to 22, or from 15 to 20.

The second polyethylene copolymer can have a $CBDI_{50}$ of ≥50 weight percent or a $CBDI_{50}$ of ≤ 50 weight percent as determined by TREF analysis.

In embodiments of the invention, the second polyethylene copolymer will have a composition distribution breadth index $CDBI_{50}$, as determined by temperature elution fractionation (TREF), of from 25% to 95% by weight, or from 35 to 90% by weight, or from 40% to 85% by weight, or from 40% to 80% by weight.

Catalysts and Process

The first and second polyethylene copolymers can be made using any appropriate catalyst, including for example so called single site catalysts, or a traditional Ziegler-Natta catalysts or chromium based catalysts. Processes such as solution phase polymerization, gas phase polymerization or slurry phase polymerization can be employed to make the first and second polyethylene copolymers.

Illustrative Ziegler-Natta catalyst compounds are disclosed in Ziegler Catalysts 363-386 (G. Fink, R. Mulhaupt and H.H. Brintzinger, eds., Springer-Verlag 1995); European Patent Nos. EP 103120; EP 102503; EP 231102; EP 703246; U.S. Patent Nos. 4,115,639; 4,077,904; 4,302,565; 4,302,566; 4,482,687; 4,564,605; 4,721,763; 4,879,359; 4,960,741 ; 5,518,973; 5,525,678; 5,288,933; 5,290,745; 5,093,415; and 6,562,905; and U.S. Patent Application Publication No. 2008/0194780. Examples of such catalysts include those comprising Group 4, 5 or 6 transition metal oxides, alkoxides and halides, or oxides, alkoxides and halide compounds of titanium, zirconium or vanadium; optionally in combination with a magnesium compound, internal and/or external electron donors (alcohols, ethers, siloxanes, etc.), aluminum or boron alkyl and alkyl halides, and inorganic oxide supports.

Illustrative examples of chromium based polymerization catalysts include Phillips polymerization catalysts, chromium oxide catalysts, silyl chromate catalysts, and chromocene catalysts, examples of which are described in for example U.S. Pat. Nos. 4,077,904, 4,115,639, 2,825,721, 3,023,203, 3,622,251, 4,011,382, 3,704,287, 4,100,105 and US Pat. App. No. US20120302707 and the references therein.

Single site catalysts include for example phosphinimine catalysts (which have at least one phosphinimine ligand), metallocene catalysts (which have two cyclopentadienyl type ligands), and constrained geometry catalysts (which have an amido type ligand and a cyclopentadienyl type ligand).

Some non-limiting examples of phosphinimine catalysts can be found in U.S. Pat. Nos. 6,342,463; 6,235,672; 6,372,864; 6,984,695; 6,063,879; 6,777,509 and 6,277,931 all of which are incorporated by reference herein.

Some non-limiting examples of metallocene catalysts, which may or may not be useful, can be found in U.S. Pat. Nos 4,808,561; 4,701,432; 4,937,301; 5,324,800; 5,633,394; 4,935,397; 6,002,033 and 6,489,413, which are incorporated herein by reference.

Some non-limiting examples of constrained geometry catalysts, which may or may not be useful, can be found in U.S. Pat. Nos 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,703,187 and 6,034,021, all of which are incorporated by reference herein in their entirety.

In some embodiments, an activator may be used with the catalyst compound. As used herein, the term "activator" refers to any compound or combination of compounds, supported or unsupported, which can activate a catalyst compound or component, such as by creating a cationic species of the catalyst component.

Illustrative activators include, but are not limited to, aluminoxane (e.g., methylaluminoxane "MAO"), modified aluminoxane (e.g., modified methylaluminoxane "MMAO" and/or tetraisobutyldialuminoxane "TIBAO"), alkylaluminum compounds, ionizing activators (neutral or ionic) such as tri(n-butyl)ammonium tetrakis(pentafluorophenyl)boron and combinations thereof.

The catalyst compositions can include a support material or carrier. As used herein, the terms "support" and "carrier" are used interchangeably and are any support material, including a porous support material, for example, talc, inorganic oxides, and inorganic chlorides. The catalyst component(s) and/or activator(s) can be deposited on, contacted with, vaporized with, bonded to, or incorporated within, adsorbed or absorbed in, or on, one or more supports or carriers. Other support materials can include resinous support materials such as polystyrene, functionalized or crosslinked organic supports, such as polystyrene divinyl benzene polyolefins or polymeric compounds, zeolites, clays, or any other organic or inorganic support material and the like, or mixtures thereof. Suitable catalyst supports are discussed and described in, for example, Hlatky, Chem. Rev. (2000), 100, 1347 1376 and Fink et al, Chem. Rev. (2000), 100, 1377 1390, U.S. Patent Nos. 4,701,432; 4,808,561; 4,912,075; 4,925,821; 4,937,217; 5,008,228; 5,238,892; 5,240,894; 5,332,706; 5,346,925; 5,422,325; 5,466,649; 5,466,766; 5,468,702; 5,529,965; 5,554,704; 5,629,253; 5,639,835; 5,625,015; 5,643,847; 5,665,665; 5,698,487; 5,714,424; 5,723,400; 5,723,402; 5,731,261; 5,759,940; 5,767,032; 5,770,664; and 5,972,510; and PCT Publication Nos. WO 95/32995; WO 95/14044; WO 96/06187; WO 97/02297; WO 99/47598; WO 99/48605; and WO 99/50311.

In the present invention, the first polyethylene copolymer is preferably made with a polymerization catalyst system comprising a phosphinimine catalyst.

In an embodiment of the invention, the first polyethylene copolymer is made using a catalyst system comprising a phosphinimine catalyst, a support, and a catalyst activator.

In an embodiment of the invention, the first polyethylene copolymer is made in the gas phase using a catalyst system comprising a phosphinimine catalyst, a support, and a catalyst activator.

In an embodiment of the invention, the first polyethylene copolymer is made in a single gas phase reactor using a catalyst system comprising a phosphinimine catalyst, a support, and a catalyst activator.

Preferably, the phosphinimine catalyst is based on metals from group 4, which includes titanium, hafnium and zirconium. The most preferred phosphinimine catalysts are group 4 metal complexes in their highest oxidation state.

The phosphinimine catalysts described herein, usually require activation by one or more cocatalytic or activator species in order to provide polymer from olefins.

A phosphinimine catalyst is a compound (typically an organometallic compound) based on a group 3, 4 or 5 metal and which is characterized as having at least one phosphinimine ligand. Any compounds/complexes having a phosphinimine ligand and which display catalytic activity for ethylene (co)polymerization may be called "phosphinimine catalysts".

In an embodiment of the invention, a phosphinimine catalyst is defined by the formula: $(L)_n(PI)_mMX_p$ where M is a transition metal selected from Ti, Hf, Zr; PI is a phosphinimine ligand; L is a cyclopentadienyl type ligand; X is an activatable ligand; m is 1 or 2; n is 0 or 1; and p is determined by the valency of the metal M. Preferably m is 1, n is 1 and p is 2.

In an embodiment of the invention, a phosphinimine catalyst is defined by the formula: $(L)(PI)MX_2$ where M is a transition metal selected from Ti, Hf, Zr; PI is a phosphinimine ligand; L is a cyclopentadienyl type ligand; and X is an activatable ligand.

In a preferred embodiment of the invention, the phosphinimine catalyst will have a phosphinimine ligand which is not bridged to, or does not make a bridge with another ligand within the metal coordination sphere of the phosphinimine catalyst, such as for example a cyclopentadienyl type ligand.

In a preferred embodiment of the invention, the phosphinimine catalyst will have a cyclopentadienyl type ligand which is not bridged to, or does not make a bridge with another ligand within the metal coordination sphere of the phosphinimine catalyst, such as for example a phosphinimine ligand.

The phosphinimine ligand is defined by the formula: $R^1{}_3P=N-$ wherein each R^1 is independently selected from the group consisting of a hydrogen atom; a halogen atom; a C_{1-20} hydrocarbyl radical which is unsubstituted or further substituted by one or more halogen atom; a C_{1-20} alkyl radical; a C_{1-8} alkoxy radical; a C_{6-10} aryl or aryloxy radical; an amido radical; a silyl radical; and a germanyl radical; P is phosphorus and N is nitrogen (and bonds to the metal M).

In an embodiment of the invention, the phosphinimine ligand is chosen so that each R^1 is a hydrocarbyl radical. In a particular embodiment of the invention, the phosphinimine ligand is tri-(tertiarybutyl)phosphinimine (i.e. where each R^1 is a tertiary butyl group).

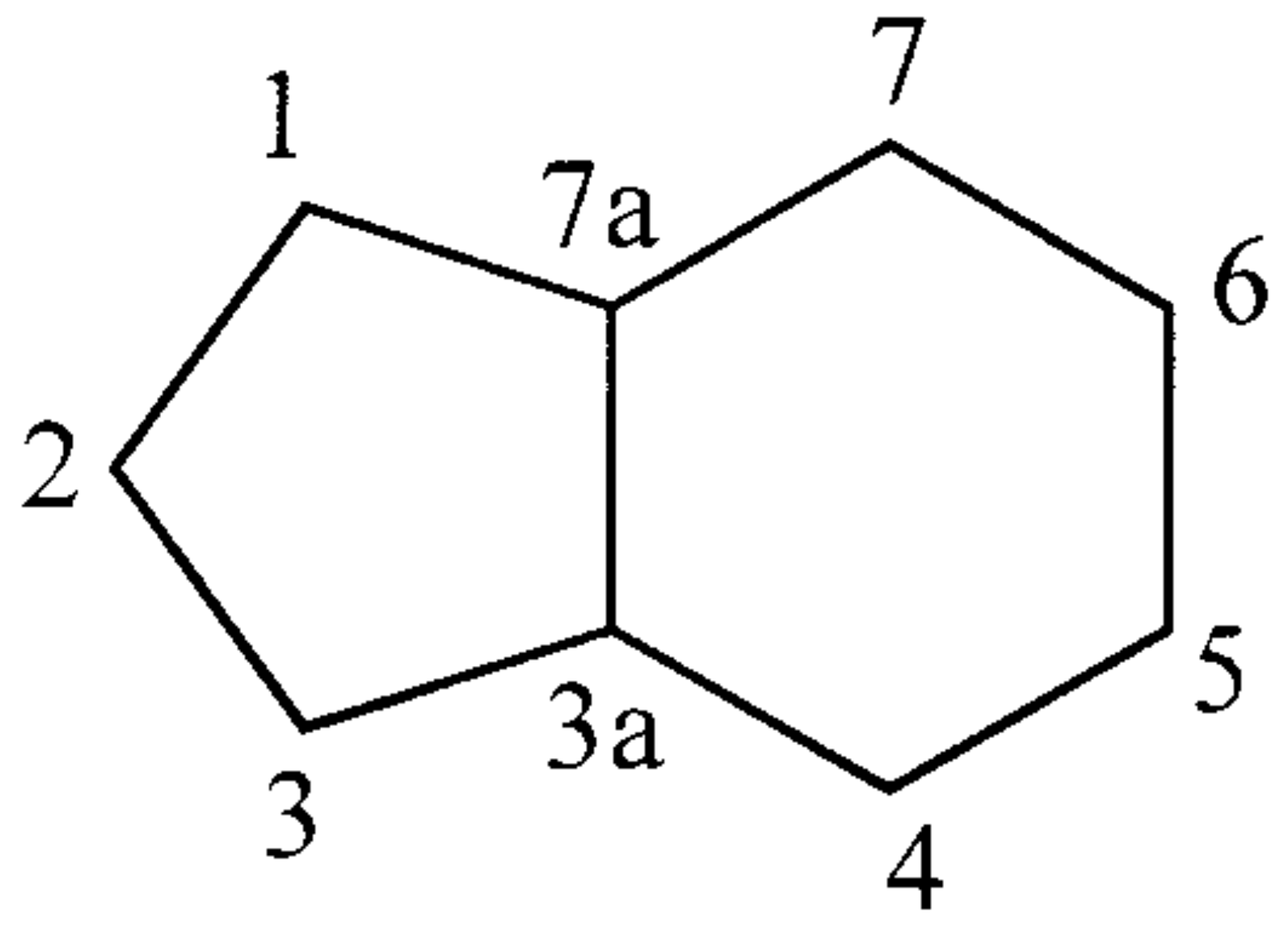
As used herein, the term “cyclopentadienyl-type” ligand is meant to include ligands which contain at least one five carbon ring which is bonded to the metal via eta-5 (or in some cases eta-3) bonding. Thus, the term "cyclopentadienyl-type" includes, for example, unsubstituted cyclopentadienyl, singly or multiply substituted cyclopentadienyl, unsubstituted indenyl, singly or multiply substituted indenyl, unsubstituted fluorenyl and singly or multiply substituted fluorenyl. Hydrogenated versions of indenyl and fluorenyl ligands are also contemplated for use in the current invention, so long as the five carbon ring which bonds to the metal via eta-5 (or in some cases eta-3) bonding remains intact. An exemplary list of substituents for a cyclopentadienyl ligand, an indenyl ligand (or hydrogenated version thereof) and a fluorenyl ligand (or hydrogenated version thereof) includes the group consisting of a C_{1-20} hydrocarbyl radical (which hydrocarbyl radical may be unsubstituted or further substituted by for example a halide and/or a hydrocarbyl group; for example a suitable substituted C_{1-20} hydrocarbyl radical is a pentafluorobenzyl group such as $-CH_2C_6F_5$); a halogen atom; a C_{1-8} alkoxy radical; a C_{6-10} aryl or aryloxy radical (each of which may be further substituted by for example a halide and/or a hydrocarbyl group); an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a silyl radical of the formula $-Si(R')_3$ wherein each R′ is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals; and a germanyl radical of the formula $-Ge(R')_3$ wherein R′ is as defined directly above.

The term “perfluorinated aryl group” means that each hydrogen atom attached to a carbon atom in an aryl group has been replaced with a fluorine atom as is well understood in the art (e.g. a perfluorinated phenyl group or substituent has the formula $-C_6F_5$).

In an embodiment of the invention, the phosphinimine catalyst will have a single or multiply substituted indenyl ligand and a phosphinimine ligand which is substituted by three tertiary butyl substituents.

Unless stated otherwise, the term “indenyl” (or “Ind” for short) connotes a fully aromatic bicyclic ring structure.

An indenyl ligand (or "Ind" for short) as defined in the present invention will have framework carbon atoms with the numbering scheme provided below, so the location of a substituent can be readily identified.



In an embodiment of the invention, the phosphinimine catalyst will have a singly substituted indenyl ligand and a phosphinimine ligand which is substituted by three tertiary butyl substituents.

In an embodiment of the invention, the phosphinimine catalyst will have a singly or multiply substituted indenyl ligand where the substituent is selected from the group consisting of a substituted or unsubstituted alkyl group, a substituted or an unsubstituted aryl group, and a substituted or unsubstituted benzyl (i.e. $C_6H_5CH_2$-) group. Suitable substituents for the alkyl, aryl or benzyl group may be selected from the group consisting of alkyl groups, aryl groups, alkoxy groups, aryloxy groups, alkylaryl groups (e.g. a benzyl group), arylalkyl groups and halide groups.

In an embodiment of the invention, the phosphinimine catalyst will have a singly substituted indenyl ligand, R^2-Indenyl, where the R^2 substituent is a substituted or unsubstituted alkyl group, a substituted or an unsubstituted aryl group, or a substituted or unsubstituted benzyl group. Suitable substituents for an R^2 alkyl, R^2 aryl or R^2 benzyl group may be selected from the group consisting of alkyl groups, aryl groups, alkoxy groups, aryloxy groups, alkylaryl groups (e.g. a benzyl group), arylalkyl groups and halide groups.

In an embodiment of the invention, the phosphinimine catalyst will have an indenyl ligand having at least a 1-position substitutent (1-R^2) where the substituent R^2 is a substituted or unsubstituted alkyl group, a substituted or an unsubstituted aryl group, or a substituted or unsubstituted benzyl group. Suitable substituents for an R^2 alkyl, R^2 aryl or R^2 benzyl group may be selected from the group consisting of alkyl groups, aryl groups, alkoxy groups, aryloxy groups, alkylaryl groups (e.g. a benzyl group), arylalkyl groups and halide groups.

In an embodiment of the invention, the phosphinimine catalyst will have a singly substituted indenyl ligand, 1-R^2-Indenyl where the substituent R^2 is in the 1-position of the indenyl ligand and is a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a substituted or an unsubstituted benzyl group. Suitable substituents for an R^2 alkyl, R^2 aryl or R^2 benzyl group may be selected from the group consisting of alkyl groups, aryl groups, alkoxy groups, aryloxy groups, alkylaryl groups (e.g. a benzyl group), arylalkyl groups and halide groups.

In an embodiment of the invention, the phosphinimine catalyst will have a singly substituted indenyl ligand, 1-R^2-Indenyl, where the substituent R^2 is a (partially/fully) halide substituted alkyl group, a (partially/fully) halide substituted benzyl group, or a (partially/fully) halide substituted aryl group.

In an embodiment of the invention, the phosphinimine catalyst will have a singly substituted indenyl ligand, 1-R^2-Indenyl, where the substituent R^2 is a (partially/fully) halide substituted benzyl group.

When present on an indenyl ligand, a benzyl group can be partially or fully substituted by halide atoms, preferably fluoride atoms. The aryl group of the benzyl group may be a perfluorinated aryl group, a 2,6 (i.e. ortho) fluoro substituted phenyl group, 2,4,6 (i.e. ortho/para) fluoro substituted phenyl group or a 2,3,5,6 (i.e. ortho/meta) fluoro substituted phenyl group respectively. The benzyl group is, in an embodiment of the invention, located at the 1 position of the indenyl ligand.

In an embodiment of the invention, the phosphinimine catalyst will have a singly substituted indenyl ligand, 1-R^2-Indenyl, where the substituent R^2 is a pentafluorobenzyl ($C_6F_5CH_2$-) group.

In an embodiment of the invention, the phosphinimine catalyst has the formula: (1-R^2-(Ind))M(N=P(t-Bu)$_3$)X_2 where R^2 is a substituted or unsubstituted alkyl group, a substituted or an unsubstituted aryl group, or a substituted or unsubstituted benzyl group, wherein substituents for the alkyl, aryl or benzyl group are selected from the group consisting of alkyl, aryl, alkoxy, aryloxy, alkylaryl, arylalkyl and halide substituents; M is Ti, Zr or Hf; and X is an activatable ligand.

In an embodiment of the invention, the phosphinimine catalyst has the formula: (1-R^2-(Ind))M(N=P(t-Bu)$_3$)X_2 where R^2 is an alkyl group, an aryl group or a benzyl group and wherein each of the alkyl group, the aryl group, and the benzyl group may be unsubstituted or substituted by at least one fluoride atom; M is Ti, Zr or Hf; and X is an activatable ligand.

In an embodiment of the invention, the phosphinimine catalyst has the formula: (1-R^2-(Ind))M(N=P(t-Bu)$_3$)X_2 where R^2 is an alkyl group, an aryl group or a benzyl group and wherein each of the alkyl group, the aryl group, and the benzyl group may be unsubstituted or substituted by at least one halide atom; M is Ti, Zr or Hf; and X is an activatable ligand.

In an embodiment of the invention, the phosphinimine catalyst has the formula: (1-R^2-(Ind))Ti(N=P(t-Bu)$_3$)X_2 where R^2 is an alkyl group, an aryl group or a benzyl group and wherein each of the alkyl group, the aryl group, and the benzyl group may be unsubstituted or substituted by at least one fluoride atom; and X is an activatable ligand.

In an embodiment of the invention, the phosphinimine catalyst has the formula: $(1\text{-}C_6F_5CH_2\text{-Ind})M(N{=}P(t\text{-Bu})_3)X_2$, where M is Ti, Zr or Hf; and X is an activatable ligand.

In an embodiment of the invention, the phosphinimine catalyst has the formula: $(1\text{-}C_6F_5CH_2\text{-Ind})Ti(N{=}P(t\text{-Bu})_3)X_2$, where X is an activatable ligand.

In the current invention, the term “activatable”, means that the ligand X may be cleaved from the metal center M via a protonolysis reaction or abstracted from the metal center M by suitable acidic or electrophilic catalyst activator compounds (also known as “co-catalyst” compounds) respectively, examples of which are described below. The activatable ligand X may also be transformed into another ligand which is cleaved or abstracted from the metal center M (e.g. a halide may be converted to an alkyl group). Without wishing to be bound by any single theory, protonolysis or abstraction reactions generate an active “cationic” metal center which can polymerize olefins.

In embodiments of the present invention, the activatable ligand, X is independently selected from the group consisting of a hydrogen atom; a halogen atom, a C_{1-10} hydrocarbyl radical; a C_{1-10} alkoxy radical; and a C_{6-10} aryl or aryloxy radical, where each of the hydrocarbyl, alkoxy, aryl, or aryl oxide radicals may be un-substituted or further substituted by one or more halogen or other group; a C_{1-8} alkyl; a C_{1-8} alkoxy, a C_{6-10} aryl or aryloxy; an amido or a phosphido radical, but where X is not a cyclopentadienyl. Two X ligands may also be joined to one another and form for example, a substituted or unsubstituted diene ligand (e.g. 1,3-butadiene); or a delocalized heteroatom containing group such as an acetate or acetamidinate group. In a convenient embodiment of the invention, each X is independently selected from the group consisting of a halide atom, a C_{1-4} alkyl radical and a benzyl radical.

Particularly suitable activatable ligands are monoanionic such as a halide (e.g. chloride) or a hydrocarbyl (e.g. methyl, benzyl).

The catalyst activator used to activate the phosphinimine polymerization catalyst can be any suitable activator including one or more activators selected from the group consisting of alkylaluminoxanes and ionic activators, optionally together with an alkylating agent.

Without wishing to be bound by theory, alkylaluminoxanes are thought to be complex aluminum compounds of the formula: $R^3_2Al^1O(R^3Al^1O)_mAl^1R^3_2$, wherein each R^3 is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and m is from 3 to 50. Optionally a hindered phenol can be added to the alkylaluminoxane to provide a molar ratio of Al^1:hindered phenol of from 2:1 to 5:1 when the hindered phenol is present.

In an embodiment of the invention, R^3 of the alkylaluminoxane, is a methyl radical and m is from 10 to 40.

In an embodiment of the invention, the cocatalyst is methylaluminoxane (MAO).

In an embodiment of the invention, the cocatalyst is modified methylaluminoxane (MMAO).

The alkylaluminoxanes are typically used in substantial molar excess compared to the amount of group 4 transition metal in the phosphinimine catalyst. The Al^1:group 4 transition metal molar ratios may be from about 10:1 to about 10,000:1, preferably from about 30:1 to about 500:1.

It is well known in the art, that the alkylaluminoxane can serve dual roles as both an alkylator and an activator. Hence, an alkylaluminoxane activator is often used in combination with activatable ligands such as halogens.

Alternatively, the catalyst activator of the present invention may be a combination of an alkylating agent (which may also serve as a scavenger) with an activator capable of ionizing the group 4 of the phosphinimine catalyst metal catalyst (i.e. an ionic activator). In this context, the activator can be chosen from one or more alkylaluminoxane and/or an ionic activator, since an alkylaluminoxane may serve as both an activator and an alkylating agent.

When present, the alkylating agent may be selected from the group consisting of $(R^4)_p\ MgX^2_{2-p}$ wherein X^2 is a halide and each R^4 is independently selected from the group consisting of C_{1-10} alkyl radicals and p is 1 or 2; R^4Li wherein in R^4 is as defined above, $(R^4)_qZnX^2_{2-q}$ wherein R^4 is as defined above, X^2 is halogen and q is 1 or 2; $(R^4)_s\ Al^2X^2_{3-s}$ wherein R^4 is as defined above, X^2 is halogen and s is an integer from 1 to 3. Preferably in the above compounds R^4 is a C_{1-4} alkyl radical, and X^2 is chlorine. Commercially available compounds include triethyl aluminum (TEAL), diethyl aluminum chloride (DEAC), dibutyl magnesium ($(Bu)_2Mg$), and butyl ethyl magnesium (BuEtMg or BuMgEt). Alkylaluminoxanes can also be used as alkylators.

The ionic activator may be selected from the group consisting of: (i) compounds of the formula $[R^5]^+ [B(R^6)_4]^-$ wherein B is a boron atom, R^5 is a cyclic C_{5-7} aromatic cation or a triphenyl methyl cation and each R^6 is independently selected from the group consisting of phenyl radicals which are unsubstituted or substituted with from 3 to 5 substituents selected from the group consisting of a fluorine atom, a C_{1-4} alkyl or alkoxy radical which is unsubstituted or substituted by a fluorine atom; and a silyl radical of the formula $\text{--Si--}(R^7)_3$; wherein each R^7 is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical; and (ii) compounds of the formula $[(R^8)_t\ ZH]^+ [B(R^6)_4]^-$ wherein B is a boron atom, H is a hydrogen atom, Z is a nitrogen atom or phosphorus atom, t is 2 or 3 and R^8 is selected from the group consisting of C_{1-8} alkyl radicals, a phenyl radical which is unsubstituted or substituted by up to three C_{1-4} alkyl radicals, or one R^8 taken together with the nitrogen atom may form an anilinium radical and R^6 is as defined above; and (iii) compounds of the formula $B(R^6)_3$ wherein R^6 is as defined above.

In the above compounds preferably R^6 is a pentafluorophenyl radical, and R^5 is a triphenylmethyl cation, Z is a nitrogen atom and R^8 is a C_{1-4} alkyl radical or R^8 taken together with the nitrogen atom forms an anilinium radical which is substituted by two C_{1-4} alkyl radicals.

Examples of compounds capable of ionizing the phosphinimine catalyst include the following compounds: triethylammonium tetra(phenyl)boron, tripropylammonium tetra(phenyl)boron, tri(n-butyl)ammonium tetra(phenyl)boron, trimethylammonium tetra(p-tolyl)boron, trimethylammonium tetra(o-tolyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tripropylammonium tetra (o,p-dimethylphenyl)boron, tributylammonium tetra(m,m-dimethylphenyl)boron, tributylammonium tetra(p-trifluoromethylphenyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tri(n-butyl)ammonium tetra (o-tolyl)boron, N,N-dimethylanilinium tetra(phenyl)boron, N,N-diethylanilinium tetra(phenyl)boron, N,N-diethylanilinium tetra(phenyl)n-butylboron, N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron, di-(isopropyl)ammonium tetra(pentafluorophenyl)boron, dicyclohexylammonium tetra (phenyl)boron, triphenylphosphonium tetra)phenyl)boron, tri(methylphenyl)phosphonium tetra(phenyl)boron, tri(dimethylphenyl)phosphonium tetra(phenyl)boron, tropillium tetrakispentafluorophenyl borate, triphenylmethylium tetrakispentafluorophenyl borate, benzene (diazonium) tetrakispentafluorophenyl borate, tropillium phenyltris-pentafluorophenyl borate, triphenylmethylium phenyl-trispentafluorophenyl borate, benzene (diazonium) phenyltrispentafluorophenyl borate, tropillium tetrakis (2,3,5,6-tetrafluorophenyl) borate, triphenylmethylium tetrakis (2,3,5,6-tetrafluorophenyl) borate, benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate, tropillium tetrakis (3,4,5-trifluorophenyl) borate, benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate, tropillium tetrakis (1,2,2-trifluoroethenyl) borate, trophenylmethylium tetrakis (1,2,2-trifluoroethenyl) borate, benzene (diazonium) tetrakis (1,2,2-trifluoroethenyl) borate, tropillium tetrakis (2,3,4,5-tetrafluorophenyl) borate, triphenylmethylium tetrakis (2,3,4,5-tetrafluorophenyl) borate, and benzene (diazonium) tetrakis (2,3,4,5-tetrafluorophenyl) borate.

Commercially available activators which are capable of ionizing the phosphinimine catalyst include:

N,N-dimethylaniliniumtetrakispentafluorophenyl borate ("$[Me_2NHPh][B(C_6F_5)_4]$");

triphenylmethylium tetrakispentafluorophenyl borate ("$[Ph_3C][B(C_6F_5)_4]$"); and

trispentafluorophenyl boron.

In an embodiment of the invention, the ionic activator compounds may be used in amounts which provide a molar ratio of group 4 transition metal to boron that will be from 1:1 to 1:6.

Optionally, mixtures of alkylaluminoxanes and ionic activators can be used as activators for the phosphinimine catalyst.

In the current invention, the polymerization catalyst system will preferably comprise an inert support (note: the terms "support" and "inert support" are used interchangeably in the present invention). In a particular embodiment of the invention, the polymerization catalyst system comprises a phosphinimine catalyst which is supported on an inert support.

The inert support used in the present invention can be any support known in the art to be suitable for use with polymerization catalysts. For example the support can be any porous or non-porous support material, such as talc, inorganic oxides, inorganic chlorides, aluminophosphates (i.e. $AlPO_4$) and polymer supports (e.g. polystyrene, etc). Hence, supports include Group 2, 3, 4, 5, 13 and 14 metal oxides generally, such as silica, alumina, silica-alumina, magnesium oxide, magnesium chloride, zirconia, titania, clay (e.g. montmorillonite) and mixtures thereof.

Agglomerate supports such as agglomerates of silica and clay may also be used as a support in the current invention.

Supports are generally used in calcined form. An inorganic oxide support, for example, will contain acidic surface hydroxyl groups which will react with a polymerization catalyst. Prior to use, the inorganic oxide may be dehydrated to remove water and to reduce the concentration of surface hydroxyl groups. Calcination or dehydration of a support is well known in the art. In an embodiments of the invention, the support is calcined at temperatures above 200°C, or above 300°C, or above 400°C, or above 500°C . In other embodiments, the support is calcined at from about 500 °C to about 1000°C, or from about 600°C to about 900°C. The resulting support may be free of adsorbed water and may have a surface hydroxyl content from about 0.1 to 5 mmol/g of support, or from 0.5 to 3 mmol/g. The amount of hydroxyl groups in a silica support may be determined according to the method disclosed by J. B. Peri and A. L. Hensley Jr., in *J. Phys. Chem.*, 72 (8), 1968, pg 2926.

The support material, especially an inorganic oxide, typically has a surface area of from about 10 to about 700 m^2/g, a pore volume in the range from about 0.1 to about 4.0 cc/g and an average particle size of from about 5 to about 500 μm. In a more specific embodiment, the support material has a surface area of from about 50 to about 500 m^2/g, a pore volume in the range from about 0.5 to about 3.5 cc/g and an average particle size of from about 10 to about 200 μm. In another more specific embodiment the support material has a surface area of from about 100 to about 400 m^2/g, a pore volume in the range from about 0.8 to about 3.0 cc/g and an average particle size of from about 5 to about 100 μm.

The support material, especially an inorganic oxide, typically has an average pore size (i.e. pore diameter) of from about 10 to about 1000 Angstroms(Å). In a more specific embodiment, the support material has an average pore size of from about 50 to about 500Å. In another more specific embodiment, the support material has an average pore size of from about 75 to about 350Å.

The surface area and pore volume of a support may be determined by nitrogen adsorption according to B.E.T. techniques, which are well known in the art and are described in the *Journal of the American Chemical Society*, 1938, v 60, pg 309-319.

A silica support which is suitable for use in the present invention has a high surface area and is amorphous. By way of example only, useful silicas are commercially available under the trademark of Sylopol® 958, 955 and 2408 by the Davison Catalysts, a Division of W. R. Grace and Company and ES-70W by Ineos Silica.

Agglomerate supports comprising a clay mineral and an inorganic oxide, may be prepared using a number techniques well known in the art including pelletizing, extrusion, drying or precipitation, spray-drying, shaping into beads in a rotating coating drum, and the like. A nodulization technique may also be used. Methods to make agglomerate supports comprising a clay mineral and an inorganic oxide include spray-drying a slurry of a clay mineral and an inorganic oxide. Methods to make agglomerate supports comprising a clay mineral and an inorganic oxide are disclosed in U.S. Patent Nos. 6,686,306; 6,399,535; 6,734,131; 6,559,090 and 6,958,375.

An agglomerate of clay and inorganic oxide which is useful in the current invention may have the following properties: a surface area of from about 20 to about 800 m^2/g, preferably from 50 to about 600 m^2/g; particles with a bulk density of from about 0.15 to about 1 g/ml, preferably from about 0.20 to about 0.75 g/ml; an average pore diameter of from about 30 to about 300 Angstroms (Å), preferably from about 60 to about 150 Å; a total pore volume of from about 0.10 to about 2.0 cc/g, preferably from about 0.5 to about 1.8 cc/g; and an average particle size of from about 4 to 250 microns (μm), preferably from about 8 to 100 microns.

Alternatively, a support, for example a silica support, may be treated with one or more salts of the type: $Zr(SO_4)_2 \cdot 4H_2O$, $ZrO(NO_3)_2$, and $Fe(NO_3)_3$ as taught in co-pending Canadian Patent Application No. 2,716,772. Supports that have been otherwise chemically treated are also contemplated for use with the catalysts and processes of the present invention.

The present invention is not limited to any particular procedure for supporting a phosphinimine catalyst or other catalyst system components. Processes for depositing such catalysts as well as an activator on a support are well known in the art (for some non-limiting examples of catalyst supporting methods, see “Supported Catalysts” by James H. Clark and Duncan J. Macquarrie, published online November 15, 2002 in the Kirk-Othmer Encyclopedia of Chemical Technology Copyright © 2001 by John Wiley & Sons, Inc.; for some non-limiting methods to support an single site catalysts see U.S. Patent No. 5,965,677). For example, a phosphinimine catalyst may be added to a support by co-precipitation with the support material. The activator can be added to the support before and/or after the phosphinimine catalyst or together with the phosphinimine catalyst. Optionally, the activator can be added to a supported phosphinimine catalyst in situ or a phosphinimine catalyst may be added to the support in situ or a phosphinimine catalyst can be added to a supported activator in situ. A phosphinimine catalyst may be slurried or dissolved in a suitable diluent or solvent and then added to the support. Suitable solvents or diluents include but are not limited to hydrocarbons and mineral oil. A phosphinimine catalyst for example, may be added to the solid support, in the form or a solid, solution or slurry, followed by the addition of the activator in solid form or as a solution or slurry. Phosphinimine catalyst, activator, and support can be mixed together in the presence or absence of a solvent.

A "catalyst modifier" made also be added to the phosphinimine based catalyst system and is a compound which, when added to a polymerization catalyst system or used in the presence of the same in appropriate amounts, can reduce, prevent or mitigate at least one: of fouling, sheeting, temperature excursions, and static level of a material in polymerization reactor; can alter catalyst kinetics; and/or can alter the properties of copolymer product obtained in a polymerization process.

Non limiting examples of catalyst modifiers which can be used in the present invention are Kemamine AS-990^{TM}, Kemamine AS-650^{TM}, Armostat-1800^{TM}, bis-hydroxy-cocoamine, 2,2′-octadecyl-amino-bisethanol, and Atmer-163^{TM}.

Other catalyst modifiers may be used in the present invention and include compounds such as carboxylate metal salts (see U.S. Patent Nos. 7,354,880; 6,300,436; 6,306,984; 6,391,819; 6,472,342 and 6,608,153 for examples), polysulfones, polymeric polyamines and sulfonic acids (see U.S. Patent Nos. 6,562,924; 6,022,935 and 5,283,278 for examples). Polyoxyethylenealkylamines, which are described in for example in European Pat. Appl. No. 107,127, may also be used. Further catalyst modifiers include aluminum stearate and aluminum oleate. Catalyst modifiers are supplied commercially under the trademarks OCTASTAT^{TM} and STADIS^{TM}. The catalyst modifier STADIS is described in U.S. Patent Nos. 7,476,715; 6,562,924 and 5,026,795 and is available from Octel Starreon. STADIS generally comprises a polysulfone copolymer, a polymeric amine and an oil soluble sulfonic acid.

A long chain amine type catalyst modifier may be added to a reactor zone (or associated process equipment) separately from the polymerization catalyst system, as part of the polymerization catalyst system, or both as described in co-pending CA Pat. Appl. No. 2,742,461. The long chain amine can be a long chain substituted monoalkanolamine, or a long chain substituted dialkanolamine as described in co-pending CA Pat. Appl. No. 2,742,461, which is incorporated herein in full.

Detailed descriptions of slurry polymerization processes are widely reported in the patent literature. For example, particle form polymerization, or a slurry process where the temperature is kept below the temperature at which the polymer goes into solution is described in U.S. Patent No. 3,248,179. Other slurry processes include those employing a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Further examples of slurry processes are described in U.S. Patent No. 4,613,484.

Slurry phase polymerization processes are conducted in the presence of a hydrocarbon diluent such as an alkane (including isoalkanes), an aromatic or a cycloalkane. The diluent may also be the alpha olefin comonomer used in copolymerizations. Alkane diluents include propane, butanes, (i.e. normal butane and/or isobutane), pentanes, hexanes, heptanes and octanes. The monomers may be soluble in (or miscible with) the diluent, but the polymer is not (under polymerization conditions). The polymerization temperature is preferably from about 5°C to about 200°C, most preferably less than about 120°C typically from about 10°C to 100°C. The reaction temperature is selected so that the ethylene copolymer is produced in the form of solid particles. The reaction pressure is influenced by the choice of diluent and reaction temperature. For example, pressures may range from 15 to 45 atmospheres (about 220 to 660 psi or about 1500 to about 4600 kPa) when isobutane is used as diluent (see, for example, U.S. Patent No. 4,325,849) to approximately twice that (i.e. from 30 to 90 atmospheres – about 440 to 1300 psi or about 3000 -9100 kPa) when propane is used (see U.S. Patent No. 5,684,097). The pressure in a slurry process must be kept sufficiently high to keep at least part of the ethylene monomer in the liquid phase. The reaction typically takes place in a jacketed closed loop reactor having an internal stirrer (e.g. an impeller) and at least one settling leg. Catalyst, monomers and diluents are fed to the reactor as liquids or suspensions. The slurry circulates through the reactor and the jacket is used to control the temperature of the reactor. Through a series of let-down valves the slurry enters a settling leg and then is let down in pressure to flash the diluent and unreacted monomers and recover the polymer generally in a cyclone. The diluent and unreacted monomers are recovered and recycled back to the reactor.

Solution processes for the homopolymerization or copolymerization of ethylene are well known in the art. These processes are conducted in the presence of an inert hydrocarbon solvent typically a C_{5-12} hydrocarbon which may be unsubstituted or substituted by a C_{1-4} alkyl group, such as pentane, methyl pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane and hydrogenated naphtha. An example of a suitable solvent which is commercially available is "Isopar E" (C_{8-12} aliphatic solvent, Exxon Chemical Co.).

The polymerization temperature in a conventional solution process is from about 80 to about 300°C (preferably from about 120 to 250°C). However, as is illustrated in the Examples, the polymerization temperature for the process of this invention is preferably above 160°C. The upper temperature limit will be influenced by considerations which are well known to those skilled in the art, such as a desire to maximize operating temperature (so as to reduce solution viscosity) while still maintaining good polymer properties (as increased polymerization temperatures generally reduce the molecular weight of the polymer). In general, the upper polymerization temperature will preferably be between 200 and 300°C (especially 220 to 250°C). The most preferred reaction process is a "medium pressure process", meaning that the pressure in the reactor is preferably less than about 6,000 psi (about

42,000 kiloPascals or kPa). Preferred pressures are from 10,000 to 40,000 kPa, most preferably from about 2,000 to 3,000 psi (about 14,000 - 22,000 kPa).

A gas phase polymerization process is commonly carried out in a fluidized bed reactor. Such gas phase processes are widely described in the literature (see for example U.S. Patent Nos. 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228). In general, a fluidized bed gas phase polymerization reactor employs a "bed" of polymer and catalyst which is fluidized by a flow of monomer, comonomer and other optional components which are at least partially gaseous. Heat is generated by the enthalpy of polymerization of the monomer (and comonomers) flowing through the bed. Un-reacted monomer, comonomer and other optional gaseous components exit the fluidized bed and are contacted with a cooling system to remove this heat. The cooled gas stream, including monomer, comonomer and optional other components (such as condensable liquids), is then re-circulated through the polymerization zone, together with "make-up" monomer (and comonomer) to replace that which was polymerized on the previous pass. Simultaneously, polymer product is withdrawn from the reactor. As will be appreciated by those skilled in the art, the "fluidized" nature of the polymerization bed helps to evenly distribute/mix the heat of reaction and thereby minimize the formation of localized temperature gradients.

The reactor pressure in a gas phase process may vary from about atmospheric to about 600 psig. In a more specific embodiment, the pressure can range from about 100 psig (690 kPa) to about 500 psig (3448 kPa). In another more specific embodiment, the pressure can range from about 200 psig (1379 kPa) to about 400 psig (2759 kPa). In yet another more specific embodiment, the pressure can range from about 250 psig (1724 kPa) to about 350 psig (2414 kPa).

The reactor temperature in a gas phase process may vary according to the heat of polymerization as described above. In a specific embodiment, the reactor temperature can be from about 30°C to about 130°C. In another specific embodiment, the reactor temperature can be from about 60°C to about 120°C. In yet another specific embodiment, the reactor temperature can be from about 70°C to about 110°C. In still yet another specific embodiment, the temperature of a gas phase process can be from about 70°C to about 100°C.

The fluidized bed process described above is well adapted for the preparation of polyethylene but other monomers (i.e. comonomers) may also be employed. Monomers and comonomers include ethylene and C_{3-12} alpha olefins respectively, where C_{3-12} alpha olefins are unsubstituted or substituted by up to two C_{1-6} alkyl radicals, C_{8-12} vinyl aromatic monomers which are unsubstituted or substituted by up to two substituents selected from the group consisting of C_{1-4} alkyl radicals, C_{4-12} straight chained or cyclic diolefins which are unsubstituted or substituted by a C_{1-4} alkyl radical. Illustrative non-limiting examples of such alpha-olefins are one or more of propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, and 1-decene, styrene, alpha methyl styrene, p-tert-butyl styrene, and the constrained-ring cyclic olefins such as cyclobutene, cyclopentene, dicyclopentadiene norbornene, alkyl-substituted norbornenes, alkenyl-substituted norbornenes and the like (e.g. 5-methylene-2-norbornene and 5-ethylidene-2-norbornene, bicyclo-(2,2,1)-hepta-2,5-diene).

In one embodiment, the invention is directed toward a polymerization process involving the polymerization of ethylene with one or more of comonomer(s) including linear or branched comonomer(s) having from 3 to 30 carbon atoms, preferably 3-12 carbon atoms, more preferably 3 to 8 carbon atoms.

The process is particularly well suited to the copolymerization reactions involving the polymerization of ethylene in combination with one or more of the comonomers, for example alpha-olefin comonomers such as propylene, butene-1, pentene-1,4-methylpentene-1, hexene-1, octene-1, decene-1, styrene and cyclic and polycyclic olefins such as cyclopentene, norbornene and cyclohexene or a combination thereof. Other comonomers for use with ethylene can include polar vinyl monomers, diolefins such as 1,3-butadiene, 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, norbornadiene, and other unsaturated monomers including acetylene and aldehyde monomers. Higher alpha-olefins and polyenes or macromers can be used also.

Preferably, the first polyethylene copolymer comprises ethylene and an alpha-olefin having from 3 to 15 carbon atoms, preferably 4 to 12 carbon atoms and most preferably 4 to 10 carbon atoms.

In an embodiment of the invention, ethylene comprises at least 75 wt% of the total weight of monomer (i.e. ethylene) and comonomer (i.e. alpha olefin) that is fed to a polymerization reactor.

In an embodiment of the invention, ethylene comprises at least 85 wt% of the total weight of monomer (i.e. ethylene) and comonomer (i.e. alpha olefin) that is fed to a polymerization reactor.

In an embodiment of the invention, the first polyethylene copolymer is a copolymer of ethylene and an alpha-olefin having from 3-8 carbon atoms and is made in a single reactor in the presence of a polymerization catalyst system comprising a phosphinimine catalyst, a support and a catalyst activator.

In an embodiment of the invention, the first polyethylene copolymer is a copolymer of ethylene and an alpha-olefin having from 3-8 carbon atoms and is made in a single gas phase reactor in the presence of a polymerization catalyst system comprising a phosphinimine catalyst, a support and a catalyst activator.

In an embodiment of the invention, the first polyethylene copolymer is a copolymer of ethylene and an alpha-olefin having from 3-8 carbon atoms and is made in a single gas phase reactor in the presence of a polymerization catalyst system comprising a phosphinimine catalyst, a support and a catalyst activator, wherein the phosphinimine catalyst has the formula:

$$(1\text{-}R^2\text{-Indenyl})Ti(N{=}P(t\text{-}Bu)_3)X_2;$$

wherein R^2 is a substituted or unsubstituted alkyl group, a substituted or an unsubstituted aryl group, or a substituted or unsubstituted benzyl group, wherein substituents for the alkyl, aryl or benzyl group are selected from the group consisting of alkyl, aryl, alkoxy, aryloxy, alkylaryl, arylalkyl and halide substituents; and wherein X is an activatable ligand.

In an embodiment of the invention, the first polyethylene copolymer is a copolymer of ethylene and an alpha-olefin having from 3-8 carbon atoms and is made in a single gas phase reactor with a polymerization catalyst system comprising: a phosphinimine catalyst; an alkylaluminoxane cocatalyst; and a support.

In an embodiment of the invention, the first polyethylene copolymer is a copolymer of ethylene and an alpha-olefin having from 3-8 carbon atoms and is made in a single gas phase reactor with a polymerization catalyst system comprising: a phosphinimine catalyst; an alkylaluminoxane cocatalyst; a support; and a catalyst modifier.

In an embodiment of the invention, the first polyethylene copolymer is a copolymer of ethylene and an alpha-olefin having from 3-8 carbon atoms and is made in a single gas phase reactor with a polymerization catalyst system comprising: a phosphinimine catalyst having the formula $(1\text{-}R^2\text{-Ind})Ti(N{=}P(t\text{-}Bu)_3)X_2$ where R^2 is an alkyl group, an aryl group or a benzyl group wherein each of the alkyl group, the aryl group, or the benzyl group may be unsubstituted or substituted by at least one halide atom, and where X is an activatable ligand; and an activator.

In an embodiment of the invention, the first polyethylene copolymer is a copolymer of ethylene and an alpha-olefin having from 3-8 carbon atoms and is made in a single gas phase reactor with a polymerization catalyst system comprising: a phosphinimine catalyst having the formula $(1\text{-}R^2\text{-Ind})Ti(N{=}P(t\text{-}Bu)_3)X_2$ where R^2 is an alkyl group, an aryl group or a benzyl group wherein each of the alkyl group, the aryl group, or the benzyl group may be unsubstituted or substituted by at least one halide atom, where X is an activatable ligand; an activator; and an inert support.

In an embodiment of the invention, the first polyethylene copolymer is a copolymer of ethylene and an alpha-olefin having from 3-8 carbon atoms and is made in a single gas phase reactor with a polymerization catalyst system comprising: a phosphinimine catalyst having the formula $(1\text{-}R^2\text{-Ind})Ti(N{=}P(t\text{-}Bu)_3)X_2$ where R^2 is an alkyl group, an aryl group or a benzyl group wherein each of the alkyl group, the aryl group, or the benzyl group may be unsubstituted or substituted by at least one halide atom, where X is an activatable ligand; an activator; an inert support; and a catalyst modifier.

In an embodiment of the invention, the first polyethylene copolymer is a copolymer is a copolymer of ethylene and an alpha-olefin having from 3-8 carbon atoms and is made in a single gas phase reactor with a polymerization catalyst system comprising: a phosphinimine catalyst having the formula $(1\text{-}C_6F_5CH_2\text{-}Ind)Ti(N{=}P(t\text{-}Bu)_3)X_2$ where X is an activatable ligand; an activator; and an inert support.

In an embodiment of the invention, the first polyethylene copolymer is a copolymer is a copolymer of ethylene and an alpha-olefin having from 3-8 carbon atoms and is made in a single gas phase reactor with a polymerization catalyst system comprising: a phosphinimine catalyst having the formula $(1\text{-}C_6F_5CH_2\text{-}Ind)Ti(N{=}P(t\text{-}Bu)_3)X_2$ where X is an activatable ligand; an activator; an inert support; and a catalyst modifier.

The polymerization catalyst system may be fed to a reactor system in a number of ways. If the phosphinimine catalyst is supported on a suitable support, the catalyst may be fed to a reactor in dry mode using a dry catalyst feeder, examples of which are well known in the art. Alternatively, a supported phosphinimine catalyst may be fed to a reactor as a slurry in a suitable diluent. If the phosphinimine catalyst is unsupported, the catalyst can be fed to a reactor as a solution or as a slurry in a suitable solvent or diluents. Polymerization catalyst system components, which may include a phosphinimine catalyst, an activator, a scavenger, an inert support, and a catalyst modifier, may be combined prior to their addition to a polymerization zone, or they may be combined on route to a polymerization zone. To combine polymerization catalyst system components on route to a polymerization zone they can be fed as solutions or slurries (in suitable solvents or diluents) using various feed line configurations which may become coterminous before reaching the reactor. Such configurations can be designed to provide areas in which catalyst system components flowing to a reactor can mix and react with one another over various “hold up” times which can be moderated by changing the solution or slurry flow rates of the catalyst system components.

Optionally, scavengers are added to a polymerization process. Scavengers are well known in the art.

In an embodiment of the invention, scavengers are organoaluminum compounds having the formula: $Al^3(X^3)_n(X^4)_{3-n}$, where (X^3) is a hydrocarbyl having from 1 to about 20 carbon atoms; (X^4) is selected from alkoxide or aryloxide, any one of which having from 1 to about 20 carbon atoms; halide; or hydride; and n is a number from 1 to 3, inclusive; or alkylaluminoxanes having the formula: $R^3_2Al^1O(R^3Al^1O)_mAl^1R^3_2$ wherein each R^3 is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and m is from 3 to 50. Some non-limiting preferred scavengers useful in the current invention include triisobutylaluminum, triethylaluminum, trimethylaluminum or other trialkylaluminum compounds.

The scavenger may be used in any suitable amount but by way of non-limiting examples only, can be present in an amount to provide a molar ratio of Al:M (where M is the metal of the organometallic compound) of from about 20 to about 2000, or from about 50 to about 1000, or from about 100 to about 500. Generally the scavenger is added to the reactor prior to the catalyst and in the absence of additional poisons and over time declines to 0, or is added continuously.

Optionally, the scavengers may be independently supported. For example, an inorganic oxide that has been treated with an organoaluminum compound or alkylaluminoxane may be added to the polymerization reactor. The method of addition of the organoaluminum or alkylaluminoxane compounds to the support is not specifically defined and is carried out by procedures well known in the art.

Preparation of the Polymer Blend

The polymer blend can be formed using conventional equipment and methods, such as by dry blending the individual components and subsequently melt mixing in a mixer or by mixing the components together directly in a mixer, such as, for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin-screw extruder, which can include a compounding extruder and a side-arm extruder used directly downstream of a polymerization process. A mixture or blend of the first and second polyethylene copolymers can be indicated by the uniformity of the morphology of the composition. In another example, the polymer blend can be produced in situ using a multistage polymerization reactor arrangement and process. In a multistage reactor arrangement two or more reactors can be connected in series where a mixture of a first polymer and catalyst can be transferred from a first reactor to a second reactor where a second polymer can be produced and blended in situ with the first polymer. A multi-stage polymerization reactor and methods for using the same can be similar to that discussed and described in for example, U.S. Pat. No. 5,677,375.

The polymer blend can include at least 1 percent by weight (wt%) and up to 99 wt% of the first polyethylene copolymer and at least 1 wt% and up to 99 wt% of the second polyethylene copolymer, based on the total weight of the first and second polyethylene copolymers. The amount of the first polyethylene copolymer in the polymer blend can range from a low of about 5 wt%, about 10 wt%, about 20 wt%, about 30 wt%, or about 40 wt% to a high of about 60 wt%, about 70 wt%, about 80 wt%, about 90 wt%, or about 95 wt%, based on the total weight of the first and second polyethylene copolymers. For example, the amount of the first polyethylene copolymer in the polymer blend can range from about 15 wt% to about 40 wt%, about 10 wt% to about 35 wt%, or about 20 wt% to about 45 wt%, based on the total weight of the first and second polyethylene copolymers. In another example, the amount of the first polyethylene copolymer in the polymer blend can be at least 5 wt%, at least 10 wt%, at least 15 wt%, at least 20 wt%, at least 25wt%, at least 30wt%, or at least 35wt% and less than about 50 wt%, based on the total weight of the first and second polyethylene copolymers.

In an embodiment of the invention, the polymer blend comprises 1-99 wt% of a first polyethylene copolymer and 99-1 wt% of a second polyethylene copolymer.

In an embodiment of the invention, the polymer blend comprises 5-95 wt% of a first polyethylene copolymer and 95-5 wt% of a second polyethylene copolymer.

In an embodiment of the invention, the polymer blend comprises 1-50 wt% of a first polyethylene copolymer and 99-50 wt% of a second polyethylene copolymer.

In an embodiment of the invention, the polymer blend comprises 5-50 wt% of a first polyethylene copolymer and 95-50 wt% of a second polyethylene copolymer.

Additives

The polymer blend or the polymer blend components (i.e. the first and/or second polyethylene copolymers) of the current invention, may also contain additives, such as for example, primary antioxidants (such as hindered phenols, including vitamin E); secondary antioxidants (such as phosphites and phosphonites); nucleating agents, plasticizers or process aids (such as fluoroelastomer and/or polyethylene glycol bound process aid), acid scavengers, stabilizers, anticorrosion agents, blowing agents, other ultraviolet light absorbers such as chain-breaking antioxidants, etc., quenchers, antistatic agents, slip agents, anti-blocking agent, pigments, dyes and fillers and cure agents such as peroxide.

These and other common additives in the polyolefin industry may be present in polymer blend at from 0.01 to 50 wt% in one embodiment, and from 0.1 to 20 wt% in another embodiment, and from 1 to 5 wt% in yet another embodiment, wherein a desirable range may comprise any combination of any upper wt% limit with any lower wt% limit.

In an embodiment of the invention, antioxidants and stabilizers such as organic phosphites and phenolic antioxidants may be present in the polymer blend (and/or the first and/or second polyethylene copolymers) in from 0.001 to 5 wt% in one embodiment, and from 0.01 to 0.8 wt% in another embodiment, and from 0.02 to 0.5 wt% in yet another embodiment. Non-limiting examples of organic phosphites that are suitable are tris(2,4-di-tert-butylphenyl)phosphite (IRGAFOS 168) and tris (nonyl phenyl) phosphite (WESTON 399). Non-limiting examples of phenolic antioxidants include octadecyl 3,5 di-t-butyl-4-hydroxyhydrocinnamate (IRGANOX 1076) and pentaerythrityl tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (IRGANOX 1010); and 1,3,5-Tri(3,5-di-tert-butyl-4-hydroxybenzyl-isocyanurate (IRGANOX 3114).

Fillers may be present in the polymer blend (and/or the first and/or second polyethylene copolymers) in from 0.1 to 50 wt% in one embodiment, and from 0.1 to 25 wt% of the composition in another embodiment, and from 0.2 to 10 wt% in yet another embodiment. Fillers include but are not limited to titanium dioxide, silicon carbide, silica (and other oxides of silica, precipitated or not), antimony oxide, lead carbonate, zinc white, lithopone, zircon, corundum, spinel, apatite, Barytes powder, barium sulfate, magnesiter, carbon black, dolomite, calcium carbonate, talc and hydrotalcite compounds of the ions Mg, Ca, or Zn with Al, Cr or Fe and CO_3 and/or HPO_4, hydrated or not; quartz powder, hydrochloric magnesium carbonate, glass fibers, clays, alumina, and other metal oxides and carbonates, metal hydroxides, chrome, phosphorous and brominated flame retardants, antimony trioxide, silica, silicone, and blends thereof. These fillers may particularly include any other fillers and porous fillers and supports which are known in the art.

Fatty acid salts may also be present in the polymer blends (and/or the first and/or second polyethylene copolymers). Such salts may be present from 0.001 to 2 wt% in the polymer blend or in the polymer blend components in one embodiment, and from 0.01 to 1 wt% in another embodiment. Examples of fatty acid metal salts include lauric acid, stearic acid, succinic acid, stearyl lactic acid, lactic acid, phthalic acid, benzoic acid, hydroxystearic acid, ricinoleic acid, naphthenic acid, oleic acid, palmitic acid, and erucic acid, suitable metals including Li, Na, Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn, Pb and so forth. Desirable fatty acid salts are selected from magnesium stearate, calcium stearate, sodium stearate, zinc stearate, calcium oleate, zinc oleate, and magnesium oleate.

With respect to the physical process of introducing to the polymer blend (and/or the first and/or second polyethylene copolymers) one or more additives, sufficient mixing should take place to assure that a uniform blend will be produced prior to conversion into a finished product. The polymer blend (and/or the first and/or second polyethylene copolymers) can be in any physical form when used to blend with the one or more additives. In one embodiment, reactor granules, defined as the granules of the polymer blend (and/or the first and/or second polyethylene copolymers) that are isolated and used to blend with the additives. The reactor granules have an average diameter of from 10 µm to 5 mm, and from 50 µm to 10 mm in another embodiment. Alternately, the polymer blend or its components may be in the form of pellets, such as, for example, having an average diameter of from 1 mm to 6 mm that are formed from melt extrusion of the reactor granules.

One method of blending the additives with the polymer blend (and/or the first and/or second polyethylene copolymers) is to contact the components in a tumbler or other physical blending means, the copolymer being in the form of reactor granules. This can then be followed, if desired, by melt blending in an extruder. Another method of blending the components is to melt blend the polymer blend or polymer blend component pellets with the additives directly in an extruder, or any other melt blending means.

Film Production

The extrusion-blown film process is a well-known process for the preparation of plastic film. The process employs an extruder which heats, melts and conveys the molten plastic (e.g. the polymer blend) and forces it through an annular die. Typical extrusion temperatures are from 330 to 500°F, especially 350 to 460°F.

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

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

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

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

The above description relates to the preparation of monolayer films. Multilayer films may be prepared by 1) a "co-extrusion" process that allows more than one stream of molten polymer to be introduced to an annular die resulting in a multi-layered film membrane or 2) a lamination process in which film layers are laminated together.

In an embodiment of the invention, the films of this invention are prepared using the above described blown film process.

An alternative process is the so-called cast film process, wherein a polyethylene copolymer (or polymer blend) is melted in an extruder, then forced through a linear slit die, thereby "casting" a thin flat film. The extrusion temperature for cast film is typically somewhat hotter than that used in the blown film process (with typically operating temperatures of from 450 to 550°F). In general, cast film is cooled (quenched) more rapidly than blown film.

In an embodiment of the invention, the films of this invention are prepared using a cast film process.

The films of the invention may be single layer or multiple layer films. The multiple layers films may comprise one or more layers formed from the polymer blend. The films may also have one or more additional layers formed from other materials such as other polymers, linear low density polyethylene (LLDPE), medium density polyethylene, polypropylene, polyester, low density polyethylene (HPLDPE), high density polyethylene (HDPE), ethylene vinyl acetate, ethylene vinyl alcohol and the like.

Multiple layer films may be formed by methods well known in the art. If all layers are polymer, the polymers may be coextruded through a coextrusion feed block and die assembly to yield a film with two or more layers adhered together but differing in composition. Multiple layer films may also be formed by extrusion coating whereby a substrate material is contacted with the hot molten polymer as it exits the die.

Polymer Blend Film Properties.

The films of the present invention are made from the polymer blends as defined above. Generally, an additive as described above is mixed with the polymer blends prior to film production. The polymer blends and films have a balance of processing and mechanical properties as well as good optical properties. Accordingly, a 1 mil monolayer film of the present invention will have a dart impact strength of ≥ 250 g/mil, and a 1% MD secant modulus of greater than 140 MPa in combination with good film optical properties.

In embodiments of the invention, the film will have a dart impact of ≥ 250 g/mil, or ≥ 350 g/mil, or ≥ 550 g/mil, or ≥ 600 g/mil, or ≥ 650 g/mil, or ≥ 700 g/mil. In another embodiment of the invention, the film will have a dart impact of from 250 g/mil to 750 g/mil. In a further embodiment of the invention, the film will have dart impact of from 350 g/mil to 750 g/mil. In yet another embodiment of the invention, the film will have dart impact of from 550 g/mil to 750 g/mil. In still yet another embodiment of the invention, the film will have dart impact of from 600 g/mil to 750 g/mil. In a further embodiment of the invention, the film will have dart impact of from 650 g/mil to 750 g/mil.

In embodiments of the invention, the film will have a ratio of MD tear to TD tear (MD tear/TD tear) of less than 0.75, but greater than 0.10. In another embodiment of the invention, the film will have a ratio of MD tear to TD tear of from 0.10 to 0.75. In yet another embodiment of the invention, the film will have a ratio of MD tear to TD tear of from 0.1 to 0.6. In still another embodiment of the invention, the film will have a ratio of MD tear to TD tear of from 0.2 to 0.55. In still yet embodiment of the invention, the film will have a ratio of MD tear to TD tear of from 0.25 to 0.55.

In embodiments of the invention, a 1 mil film will have a machine direction (MD) secant modulus at 1% strain of ≥ 140 MPa, or ≥ 150 MPa, or ≥ 160 MPa. In an embodiment of the invention, a 1 mil film will have a machine direction (MD) secant modulus at 1% strain of between 130 MPa and 200 MPa. In an embodiment of the invention, a 1 mil film will have a machine direction (MD) secant modulus at 1% strain of between 140 MPa and 200 MPa. In another embodiment of the invention, a 1 mil film will have a machine direction (MD) secant modulus at 1% strain of between 140 MPa and 190 MPa.

In an embodiment of the invention, a 1 mil film will have a transverse direction (TD) secant modulus at 1% strain of ≥ 140 MPa, or ≥ 150 MPa, or ≥ 160 MPa, or ≥ 170 MPa. In an embodiment of the invention, a 1 mil film will have a transverse direction (TD) secant modulus at 1% strain of between 130 MPa and 200 MPa. In another embodiment of the invention, a 1 mil film will have a transverse direction (TD) secant modulus at 1% strain of between 140 MPa and 200 MPa. In yet another embodiment of the invention, a 1 mil film will have a transverse direction (TD) secant modulus at 1% strain of between 150 MPa and 220 MPa.

In an embodiment of the invention, a 1 mil film will have a haze of less than 12% and a gloss at 45° of at least 55. In an embodiment of the invention, a 1 mil film will have a haze of less than 10% and a gloss at 45° of at least 60. In another embodiment of the invention, a 1 mil film will have a haze of less than 7% and a gloss at 45° of at least 60. In another embodiment of the invention, a 1 mil film will have a haze of less than 7% and a gloss at 45° of at least 65. In another embodiment of the invention, a 1 mil film will have a haze of less than 7% and a gloss at 45° of at least 70. In an embodiment of the invention, a film has a haze of less than 10% and a gloss at 45° of greater than 60.

The film may, by way of example, have a total thickness ranging from 0.5 mils to 4 mils (note: 1 mil = 0.0254 mm), which will depend on for example the die gap employed during film casting or film blowing.

The above description applies to monolayer films. However, the film of the current invention may be used in a multilayer film. Multilayer films can be made using a co-extrusion process or a lamination process. In co-extrusion, a plurality of molten polymer streams are fed to an annular die (or flat cast) resulting in a multi-layered film on cooling. In lamination, a plurality of films are bonded together using, for example, adhesives, joining with heat and pressure and the like. A multilayer film structure may, for example, contain tie layers and/or sealant layers.

The film of the current invention may be a skin layer or a core layer and can be used in at least one or a plurality of layers in a multilayer film. The term “core” or the phrase “core layer”, refers to any internal film layer in a multilayer film. The phrase “skin layer” refers to an outermost layer of a multilayer film (for example, as used in the production of produce packaging). The phrase “sealant layer” refers to a film that is involved in the sealing of the film to itself or to another layer in a multilayer film. A “tie layer” refers to any internal layer that adheres two layers to one another.

By way of example only, the thickness of the multilayer films can be from about 0.5 mil to about 10 mil total thickness.

In an embodiment of the invention, a monolayer or multilayer film structure comprises at least one layer comprising a polymer blend comprising the first and second polyethylene copolymers described above.

EXAMPLES

General

All reactions involving air and or moisture sensitive compounds were conducted under nitrogen using standard Schlenk and cannula techniques, or in a glovebox. Reaction solvents were purified either using the system described by Pangborn et. al. in *Organometallics* 1996, v*15*, p.1518 or used directly after being stored over activated 4 Å molecular sieves. The methylaluminoxane used was a 10% MAO solution in toluene supplied by Albemarle which was used as received. The support used was silica Sylopol 2408 obtained from W.R. Grace. & Co. The support was calcined by fluidizing with air at 200 °C for 2 hours followed by nitrogen at 600°C for 6 hours and stored under nitrogen.

Melt index, I_2, in g/10 min was determined on a Tinius Olsen Plastomer (Model MP993) in accordance with ASTM D1238 condition F at 190°C with a 2.16 kilogram weight. Melt index, I_{10}, was determined in accordance with ASTM D1238 condition F at 190° C with a 10 kilogram weight. High load melt index, I_{21}, in g/10 min was determined in accordance with ASTM D1238 condition E at 190° C with a 21.6 kilogram weight. Melt flow ratio or "MFR" for short (also sometimes called melt index ratio) is I_{21}/I_2.

Polymer density was determined in grams per cubic centimeter (g/cc) according to ASTM D1928.

Molecular weight information (M_w, M_n and M_z in g/mol) and molecular weight distribution (M_w/M_n), and z-average molecular weight distribution (M_Z/M_W) were analyzed by gel permeation chromatography (GPC), using an instrument sold under the trade name "Waters 150c", with 1,2,4-trichlorobenzene as the mobile phase at 140°C. The samples were prepared by dissolving the polymer in this solvent and were run without filtration. Molecular weights are expressed as polyethylene equivalents with a relative standard deviation of 2.9% for the number average molecular weight ("Mn") and 5.0% for the weight average molecular weight ("Mw"). Polymer sample solutions (1 to 2 mg/mL) were prepared by heating the polymer in 1,2,4-trichlorobenzene (TCB) and rotating on a wheel for 4 hours at 150°C in an oven. The antioxidant 2,6-di-tert-butyl-4-methylphenol (BHT) was added to the mixture in order to stabilize the polymer against oxidative degradation. The BHT concentration was 250 ppm. Sample solutions were chromatographed at 140°C on a PL 220 high-temperature chromatography unit equipped with four Shodex columns (HT803, HT804, HT805 and HT806) using TCB as the mobile phase with a flow rate of 1.0 mL/minute, with a differential refractive index (DRI) as the concentration detector. BHT was added to the mobile phase at a concentration of 250 ppm to protect the columns from oxidative degradation. The sample injection volume was 200 mL. The raw data were processed with Cirrus GPC software. The columns were calibrated with narrow distribution polystyrene standards. The polystyrene molecular weights were converted to polyethylene molecular weights using the Mark-Houwink equation, as described in the ASTM standard test method D6474.

The branch frequency of copolymer samples (i.e. the short chain branching, SCB per 1000 carbons) and the C_6 comonomer content (in wt%) was determined by Fourier Transform Infrared Spectroscopy (FTIR) as per the ASTM D6645-01 method. A Thermo-Nicolet 750 Magna-IR Spectrophotometer equipped with OMNIC version 7.2a software was used for the measurements.

The determination of branch frequency as a function of molecular weight (and hence the comonomer distribution) was carried out using high temperature Gel Permeation Chromatography (GPC) and FT-IR of the eluent. Polyethylene standards with a known branch content, polystyrene and hydrocarbons with a known molecular weight were used for calibration.

Hexane extractables compression molded plaques were determined according to ASTM D5227.

To determine the composition distribution breadth index $CDBI_{50}$, which is also designated CDBI(50) in the present invention, a solubility distribution curve is first generated for the copolymer. This is accomplished using data acquired from the TREF technique. This solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilized as a function of temperature. This is converted to a cumulative distribution curve of weight fraction versus comonomer content, from which the $CDBI_{50}$ is determined by establishing the weight percentage of a copolymer sample that has a comonomer content within 50% of the median comonomer content on each side of the median (see WO 93/03093 for the definition of $CDBI_{50}$). The weight percentage of copolymer eluting at from 90-105°C, is determined by calculating the area under the TREF curve at an elution temperature of from 90 to 105°C. The weight percent of copolymer eluting below at or 40°C and above 100°C was determined similarly. For the purpose of simplifying the correlation of composition with elution temperature, all fractions are assumed to have a $Mn \geqq 15,000$, where Mn is the number average molecular weight of the fraction. Any low weight fractions present generally represent a trivial portion of the polymer. The remainder of this description and the appended claims maintain this convention of assuming all fractions have $Mn \geqq 15,000$ in the $CDBI_{50}$ measurement.

The specific temperature rising elution fractionation (TREF) method used herein was as follows. Homogeneous polymer samples (pelletized, 50 to 150 mg) were introduced into the reactor vessel of a crystallization-TREF unit (Polymer ChAR^{TM}). The reactor vessel was filled with 20 to 40 ml 1,2,4-trichlorobenzene (TCB), and heated to the desired dissolution temperature (e.g. 150°C) for 1 to 3 hours. The solution (0.5 to 1.5 ml) was then loaded into the TREF column filled with stainless steel beads. After equilibration at a given stabilization temperature (e.g. 110 °C) for 30 to 45 minutes, the polymer solution was allowed to crystallize with a temperature drop from the stabilization temperature to 30°C (0.1 or 0.2 °C/minute). After equilibrating at 30°C for 30 minutes, the crystallized sample was eluted with TCB (0.5 or 0.75 mL/minute) with a temperature ramp from 30°C to the stabilization temperature (0.25 or 1.0 °C/minute). The TREF column was cleaned at the end of the run for 30 minutes at the dissolution temperature. The data were processed using Polymer ChAR software, Excel spreadsheet and TREF software developed in-house.

The TREF procedures described above are well known to persons skilled in the art and can be used to determine the modality of a TREF profile, a $CDBI_{50}$, a copolymer wt% eluting at or below 40°C, a copolymer wt% eluting at above 100°C, a copolymer wt% eluting at from 90°C to 105°C, a T(75)-T(25) value, as well as the temperatures or temperature ranges where elution intensity maxima (elution peaks) occur.

The melting points including a peak melting point (T_m) and the percent crystallinity of the copolymers are determined by using a TA Instrument DSC Q1000 Thermal Analyzer at 10°C/min. In a DSC measurement, a heating-cooling-heating cycle from room temperature to 200°C or vice versa is applied to the polymers to minimize the thermo-mechanical history associated with them. The melting point and percent of crystallinity are determined by the primary peak temperature and the total area under the DSC curve respectively from the second heating data. The peak melting temperature T_m is the higher temperature peak, when two peaks are present in a bimodal DSC profile (typically also having the greatest peak height).

The melt strength of a polymer is measured on Rosand RH-7 capillary rheometer (barrel diameter = 15mm) with a flat die of 2-mm Diameter, L/D ratio 10:1 at 190°C. Pressure Transducer: 10,000 psi (68.95 MPa). Piston Speed: 5.33 mm/min. Haul-off Angle: 52°. Haul-off incremental speed: 50 – 80 m/min^2 or 65 ± 15 m/min^2. A polymer melt is extruded through a capillary die under a constant rate and then the polymer strand is drawn at an increasing haul-off speed until it ruptures. The maximum steady value of the force in the plateau region of a force versus time curve is defined as the melt strength for the polymer.

Dynamic Mechanical Analysis (DMA). Dynamic Mechanical Analysis (DMA). Rheological measurements (e.g. small-strain (10%) oscillatory shear measurements) were carried out on a dynamic Rheometrics SR5 Stress rotational rheometer with 25 mm diameter parallel plates in a frequency sweep mode under full nitrogen blanketing. The polymer samples are appropriately stabilized with the anti-oxidant additives and then inserted into the test fixture for at least one minute preheating to ensure the normal force decreasing back to zero. All DMA experiments are conducted at 10%

strain, 0.05 to 100 rad/s and 190°C. Orchestrator Software is used to determine the viscoelastic parameters including the storage modulus (G'), loss modulus (G"), phase angle (δ), complex modulus (G*) and complex viscosity (η^*).

The complex viscosity $|\eta^*(\omega)|$ versus frequency (ω) data were then curve fitted using the modified three parameter Carreau-Yasuda (CY) empirical model to obtain the zero shear viscosity η_0, characteristic viscous relaxation time τ_η, and the breadth of rheology parameter-*a*. The simplified Carreau-Yasuda (CY) empirical model used is as follows:

$$|\eta^*(\omega)| = \eta_0 / [1 + (\tau_\eta \omega)^a]^{(1-n)/a}$$

wherein: $|\eta^*(\omega)|$ = magnitude of complex shear viscosity; η_0 = zero shear viscosity; τ_η = characteristic relaxation time; *a* = "breadth" of rheology parameter (which is also called the "Carreau-Yasuda shear exponent" or the "CY *a*-parameter" or simply the "*a*-parameter" in the current invention); n = fixes the final power law slope, fixed at 2/11; and ω = angular frequency of oscillatory shearing deformation. Details of the significance and interpretation of the CY model and derived parameters may be found in: C. A. Hieber and H. H. Chiang, *Rheol. Acta,* 28, 321 (1989); C. A. Hieber and H. H. Chiang, *Polym. Eng. Sci.,* 32, 931 (1992); and R. B. Bird, R. C. Armstrong and O. Hasseger, *Dynamics of Polymeric Liquids, Volume* 1, *Fluid Mechanics,* 2nd Edition, John Wiley & Sons (1987); each of which is incorporated herein by reference in its entirety.

The Shear Thinning Index (SHI) was determined according to the method provided in U.S. Pat. Appl. No. 2011/0212315: the SHI is defined as $SHI(\omega)=\eta^*(\omega)/\eta^0$ for any given frequency (ω) for dynamic viscosity measurement, wherein $\eta 0$ is zero shear viscosity @190°C determined via the empiric Cox-Merz-rule. η^* is the complex viscosity @190°C determinable upon dynamic (sinusoidal) shearing or deformation of a copolymer as determined on a Rheometrics SR5 Stress rotational rheometer using parallel-plate geometry. According to the Cox-Merz-Rule, when the frequency (ω) is expressed in Radiant units, at low shear rates, the numerical value of η^* is equal to that of conventional, intrinsic viscosity based on low shear capillary measurements. The skilled person in the field of rheology is well versed with determining η^0 in this way. The shear thinning ratio shear thinning ratio ($\eta^*_{0.1}/\ \eta^*_{10}$) can be determined similarly using DMA by determining the complex viscosity at frequencies 0.1 and 10 rad/sec.

The films of the current examples were made on a blown film line manufactured by Battenfeld Gloucester Engineering Company of Gloucester, Mass using a die diameter of 4 inches, and a die gap of 35 or 100 mil. This blown film line has a standard output of more than 100 pounds per hour and is equipped with a 50 horsepower motor. Screw speed was 35 to 50 RPM. The extender screw has a 2.5 mil diameter and a length/diameter (L/D) ratio of 24/1. Melt Temperature and Frost Line Height (FLH) are 420 to 430°F and 16 to 18 inches respectively. The blown film bubble is air cooled. Typical blow up ratio (BUR) for blown films prepared on this line are from 1.5/1 to 4/1. An annular die having a gap of 35 mils was used for these experiments. The films of this example were prepared using a BUR aiming point of 2.5:1 and a film thickness aiming point of 1.0 mils.

The haze (%) was measured in accordance with the procedures specified in ASTM D 1003-07, using a BYK-Gardner Haze Meter (Model Haze-gard plus).

Dart impact strength was measured on a dart impact tester (Model D2085AB/P) made by Kayeness Inc. in accordance with ASTM D-1709-04 (method A).

Machine (MD) and transverse (TD) direction Elmendorf tear strengths were measured on a ProTear^{TM} Tear Tester made by Thwing-Albert Instrument Co. in accordance with ASTM D-1922.

Puncture resistance was measured on a MTS Systems Universal Tester (Model SMT(HIGH)-500N-192) in accordance with ASTM D-5748

MD or TD secant modulus was measured on an Instrument 5-Head Universal Tester (Model TTC-102) at a crosshead speed of 0.2 in/min up to 10 % strain in accordance with ASTM D-882-10. The MD or TD secant modulus was determined by an initial slope of the stress-strain curve from an origin to 1% strain.

Film tensile testing was conducted on an Instrument 5-Head Universal Tester (Model TTC-102) in accordance with ASTM D-882-10.

Gloss was measured on a BYK-Gardner 45° Micro-Gloss unit in accordance with ASTM D2457-03.

A seal was prepared by clamping two 2.0 mil film strips between heated upper and lower seal bars on a SL-5 Sealer made by Lako Tool for 0.5 seconds, 40 psi seal bar clamping pressure for each temperature in the range from onset of seal to melt through. Seal strength or sealability parameter was measured as a function of seal temperature on an Instrument 5-Head Universal Tester (Model TTC-102) in accordance with ASTM F88-09.

Polymer Blend Components

Resin 1A: The First Polyethylene Copolymer

Synthesis of (1-$C_6F_5CH_2$-Indenyl)((t-Bu)$_3$P=N)TiCl_2. To distilled indene (15.0 g, 129 mmol) in heptane (200 mL) was added BuLi (82 mL, 131 mmol, 1.6 M in hexanes) at room temperature. The resulting reaction mixture was stirred overnight. The mixture was filtered and the filter cake washed with heptane (3 x 30 mL) to give indenyllithium (15.62 g, 99% yield). Indenyllithium (6.387 g, 52.4 mmol) was added as a solid over 5 minutes to a stirred solution of $C_6F_5CH_2$-Br (13.65 g, 52.3 mmol) in toluene (100 mL) at room temperature. The reaction mixture was heated to 50 °C and stirred for 4 h. The product mixture was filtered and washed with toluene (3 x 20 mL). The combined filtrates were evaporated to dryness to afford 1-$C_6F_5CH_2$-indene (13.58 g, 88%). To a stirred slurry of $TiCl_4$.2THF (1.72 g, 5.15 mmol) in toluene (15 mL) was added solid (t-

Bu)$_3$P=N-Li (1.12 g, 5 mmol) at room temperature. The resulting reaction mixture was heated at 100 °C for 30 min and then allowed to cool to room temperature. This mixture containing ((t-Bu)$_3$P=N)TiCl$_3$ (1.85 g, 5 mmol) was used in the next reaction. To a THF solution (10 mL) of 1-$C_6F_5CH_2$-indene (1.48 g, 5 mmol) cooled at -78 °C was added n-butyllithium (3.28 mL, 5 mmol, 1.6 M in hexanes) over 10 minutes. The resulting dark orange solution was stirred for 20 minutes and then transferred via a double-ended needle to a toluene slurry of ((t-Bu)$_3$P=N)TiCl$_3$ (1.85 g, 5 mmol). The cooling was removed from the reaction mixture which was stirred for a further 30 minutes. The solvents were evaporated to afford a yellow pasty residue. The solid was re-dissolved in toluene (70 mL) at 80 °C and filtered hot. The toluene was evaporated to afford pure (1-$C_6F_5CH_2$-Indenyl)((t-Bu)$_3$P=N)TiCl$_2$ (2.35 g, 74%).

Preparation of Supported Catalyst. Sylopol 2408 silica purchased from Grace Davison was calcined by fluidizing with air at 200 °C for 2 hours and subsequently with nitrogen at 600°C for 6 hours. 114.273 grams of the calcined silica was added to 620 mL of toluene. 312.993 g of a MAO solution containing 4.5 weight % Al purchased from Albemarle was added to the silica slurry quantitatively. The mixture was stirred for 2 hours at ambient temperature. The stirring rate should be such so as not to break-up the silica particles. 2.742 grams of (1-$C_6F_5CH_2$-Indenyl)((t-Bu)$_3$P=N)TiCl$_2$ (prepared as above in Example 1) was weighed into a 500-mL Pyrex bottle and 300 mL of toluene added. The metal complex solution was added to the silica slurry quantitatively. The resulting slurry was stirred for 2 hours at ambient temperature. 21.958 g of 18.55wt% toluene solution of Armostat® 1800 was weighed into a small vessel and transferred quantitatively to the silica slurry. The resulting mixture was stirred for a further 30 minutes after which the slurry was filtered, yielding a clear filtrate. The solid component was washed with toluene (2 x 150 mL) and then with pentane (2 x 150 mL). The final product was dried in vacuo to between 450 and 200 mtorr and stored under nitrogen until used. The finished catalyst had a pale yellow to pale orange color. The catalyst had 2.7 wt% of Armostat present.

Polymerization. Continuous ethylene/1-hexene gas phase copolymerization experiments were conducted in a 56.4L Technical Scale Reactor (TSR) in continuous gas phase operation (for an example of a TSR reactor set up see Eur. Pat. Appl. No. 659,773A1). Ethylene polymerizations were run at 75°C-90°C with a total operating pressure of 300 pounds per square inch gauge (psig). Gas phase compositions for ethylene and 1-hexene were controlled via closed-loop process control to values of 65.0 and 0.4-2.0 mole%, respectively. Hydrogen was metered into the reactor in a molar feed ratio of 0.0008-0.0018 relative to ethylene feed during polymerization. Nitrogen constituted the remainder of the gas phase mixture (approximately 38 mole%). A typical production rate for these conditions is 2.0 to 3.0 kg of polyethylene per hour. A seed-bed was used and prior to polymerization start-up was washed with a small amount of triethylaluminum, TEAL to scavenge impurities. Prior to introduction of the catalyst TEAL was flushed from the reactor. The catalyst was fed to the reactor together with small amount of dilute TEAL solution (0.25 wt%) during the start-up phase. The addition of TEAL was discontinued once the desired polymer production rate was reached. Alternatively, the reactor can be started with the catalyst feed line alone during the polymerization start-up phase (that is, without initially feeding the TEAL solution). The polymerization reaction was initiated under conditions of low comonomer concentration, followed by gradual adjustment of the comonomer to ethylene ratio to provide the targeted polymer density. Steady state polymerization conditions are provided in Table 1 (C2 = ethylene; C6 = 1-hexene; C6/C2 is the molar feed ratio of each component to the reactor; H2/C2 is the mol/mol feed ratio to the reactor). Polymer data for the resulting resin 1A are provided in Table 2. The data for resin 1A in Table 2, are representative of the first polyethylene copolymer as used in blends of the present invention.

Resin 2A: The Second Polyethylene Copolymer

Synthesis of (1,2-(n-propyl)(C_6F_5)Cp)Ti(N=P(t-Bu)$_3$)Cl$_2$. The phosphinimine catalyst compound (1,2-(n-propyl)(C_6F_5)Cp)Ti(N=P(t-Bu)$_3$)Cl$_2$ was made in a manner similar to the procedure given in U.S. Pat. No. 7,531,602 (see Example 2).

Supported Catalyst. To a slurry of dehydrated silica (122.42 g) in toluene (490 mL) was added a 10 wt% MAO solution (233.84 g of 4.5 wt % Al in toluene) over 10 minutes. The vessel containing the MAO was rinsed with toluene (2x10 mL) and added to the reaction mixture. The resultant slurry was stirred with an overhead stirrer assembly (200 rpm) for 1 hour at ambient temperature. To this slurry was added a toluene (46 mL) solution of (1,2-(n-propyl)(C_6F_5)Cp)Ti(N=P(t-Bu)$_3$)Cl$_2$ (2.28 g) over 10 minutes. This solution may need to be gently heated to 45°C for a brief period (5 minutes) to fully dissolve the molecule. The vessel containing the molecule was rinsed with toluene (2 x 10 mL) and added to the reaction mixture. After stirring for 2 hours (200 rpm) at ambient temperature a toluene (22 mL) solution of Armostat-1800 (18.55wt%) was added to the slurry which was further stirred for 30 minutes. The slurry was filtered and rinsed with toluene (2 x 100 mL) and then with pentane (2 x 100 mL). The catalyst was dried *in vacuo* to less than 1.5 wt% residual volatiles. The solid catalyst was isolated and stored under nitrogen until further use. The catalyst had 2.7 wt% of Armostat present.

Polymerization. Continuous ethylene/1-hexene gas phase copolymerization experiments were conducted in a 56.4L Technical Scale Reactor (TSR) in continuous gas phase operation. Ethylene polymerizations were run at 75°C-90°C with a total operating pressure of 300 pounds per square inch gauge (psig). Gas phase compositions for ethylene and 1-hexene were controlled via closed-loop process control to values of 50.0 and 0.5-2.0 mole%, respectively. Hydrogen was metered into the reactor in a molar feed ratio of 0.0012-0.0035 relative to ethylene feed during polymerization. Nitrogen constituted the remainder of the gas phase mixture (approximately 48 mole%). A typical production rate for these conditions is 2.0 to 3.0 kg of polyethylene per hour. Relevant polymerization data are provided in Table 1. Polymer data for the resulting resin 2A are provided in Table 2. Resin 2A may be used as the second polyethylene copolymer in blends of the present invention.

TABLE 1

TSR Conditions

LLDPE No.	Resin 1A	Resin 2A
Productivity (g PE/g Cat)	3400	7700
Hydrogen (mol%)	0.0350	0.0298
Hexene (mol%)	0.8603	1.2110
C6/C2 (mol/mol feed)	0.0232	0.0215
Temp (°C)	80	85
Production rate (kg/hr)	2.58	2.53
Residence Time (hrs)	1.81	1.62
Bulk Density (lb per cubic foot)	22.5	17.9

Also included in Table 2 are resins 2B, 2C, and 2D each of which may be used as the second polyethylene copolymer in the blends of the current invention. Resin 2B is an Exceed 1018™ ethylene copolymer of 1-hexene, which is commercially available from ExxonMobil. Resin 2C is a linear low density polyethylene having a melt index I_2 of 0.93 g/10min and a density of 0.917 g/cm^3 which is available from NOVA Chemicals as FPs-117-C™. Resin 2D is a linear low density polyethylene having a melt index I_2 of

1 g/10min and a density of 0.92 g/cm^3, which is available from NOVA Chemicals as FP-120-C^{TM}.

TABLE 2

Copolymer Properties

	First Polyethylene Copolymer	Second Polyethylene Copolymer			
Resin No.	**1A**	**2A**	**2B**	**2C**	**2D**
density (g/cm^3)	0.9208	0.9173	0.9212	0.9168	0.9198
MI, I_2 (g/10 min)	0.60	0.95	0.97	0.93	1.04
MFR, I_{21}/I_2	44.5	15.5	16.0	30.1	29.0
I_{10}/I_2	10.9	5.61	5.65	7.52	8.0
Comonomer	1-hexene	1-hexene	1-hexene	1-octene	1-octene
TREF profile	trimodal T(low) = 71.5°C T(med) = 81.3°C	bimodal T(low) = 81.0°C T(high) = 91.8°C	Bimodal T(low) = 83.3°C T(high) = 93.0°C	Bimodal T(low) = 78.5°C T(high) = 94.7°C	bimodal T(low) = 81.1°C T(high) = 95.4°C

	T(high) = 92.3°C				
T(med)−T(low), °C	9.8	NA	NA	NA	NA
T(high)-T(med), °C	11.0	NA	NA	NA	NA
T(high)−T(low), °C	20.8	10.8	9.7	16.2	14.3
wt% at 90-105°C	12.2	9.7	7.9%	5.6	15.9
T(75)-T(25) (°C)	14.6	9.7	10.6	8.25	14.4
$CDBI_{50}$ (wt%)	65.6	74.5	70.5	74.5	58.1
comonomer profile	reverse	flat	slightly reverse	Negative	negative
DSC melt temp (°C)	104.2, 120.3	109.5, 119.6	110.8, 118.9	108.2, 112.3	109.4, 119.6
% crystallinity	46.1	44.3	43.0	42.5	44.5
CY *a*-parameter	0.0947	0.642	0.733	0.593	0.402
M_w ($x 10^{-3}$)	97.3	98.3	103.3	96.6	103.4

M_n (x 10^{-3})	20.3	56.6	46.0	29.3	28.9
M_z (x10^{-3})	226.4	154.6	174.1	229.4	298.9
M_w / M_n	4.78	1.74	2.25	3.30	3.58
M_z / M_w	2.33	1.57	1.69	2.38	2.89
comonomer content (wt%)	7.3	6.0	6.0	10.4	9.2
SCB/1000 C	12.7	10.5	10.4	14.1	12.3
hexane extractables (%)	0.94	0.15	0.34	0.42	0.54
melt strength (cN)	5.74	3.07	2.60	2.48	3.24
processability enhancement index (χ)	1.10	0.93	0.89	0.89	0.92

VGP crossover phase angle (δ^{XO})	59.6	84.5	84.8	78.5	74.6
96 – 2.14 [($MFR^{0.5}$) + 1 × 10^{-4} (M_w – M_n)]	65.3	78.65	75.18	69.86	68.53
SCB/1000 at MW of 200,000 – SCB/1000 at MW of 50,000	6.1	0.6	1.2	- 2.0	- 0.6
Shear Thinning Index (SHI)	0.01	0.98	0.99	0.94	0.81
($CDBI_{50}$ – 3)	62.6	71.5	67.5	71.5	55.1
[15/ (a + 0.12)]	69.8	19.7	17.6	21.0	28.7
[80 – 1.22 ($CDBI_{50}$) / (M_w/M_n)]	63.26	27.76	41.77	52.45	60.2

68 $[(I_{21}/I_2)^{-1} + 10^{-6}$ $(M_n)]$	2.89	8.24	7.38	4.25	4.31

As shown in Table 2, the first polyethylene copolymer, resin 1A has a melt flow ratio that is distinct from resins 2A-2D. The resin 1A (as well as the resins 1B-1H discussed below) have a MFR (I_{21}/I_2) of greater than 32, while the resins 2A and 2B each have a melt flow ratio of less than 16.5. Resins 2C and 2D have an MFR (I_{21}/I_2) close to 30. The TREF profile of resin 1A (as well as resins 1B-1H discussed below) is multimodal (or trimodal with three prominent peaks separated by 5°C or more). The resin 1A (as well as the resins 1B-1H discussed below) have a composition distribution breadth index $CDBI_{50}$ of less than 70 wt%.

Resins 1B-1H (The First Polyethylene Copolymers)

The catalyst systems employed to make reins 1B-1H were prepared substantially the same way and using the same phosphinimine based catalyst system described and used above to make resin 1A, except that the levels of Armostat-1800, phosphinimine metal (Ti loading) or catalyst activator (Al loading) were altered (see Table 4). The i) the amount of Armostat-1800 present in the catalyst system (in weight % based on the total weight of the polymerization catalyst system); ii) the phosphinimine metal catalyst loading on a silica support (in Ti mmol/gram of the polymerization catalyst system); and iii) the amount of catalyst activator, methylaluminoxane MAO (in weight % Al based on the total weight of the polymerization catalyst system) were changed to see how the catalyst system responded to changes in its formulation. A total of seven catalyst system formulations (Table 3) were prepared and an ethylene copolymer of 1-hexene was prepared in a manner similar to that described above for resin 1A.

The catalyst system formulation data and polymerization data are given in Table 3 and Table 4 respectively and correspond to resins 1B through 1H which are further examples of the first polyethylene copolymer blend component. The properties of these polyethylene copolymers are provided in Table 5 (C2 = ethylene; C6 = 1-hexene; N2 = nitrogen; H2 = hydrogen).

TABLE 3

Catalyst System Formulations

Invent. Example No.	**Armostat-1800 (wt%)**	**(1-$C_6F_5CH_2$-Indenyl)((t-Bu)$_3$P=N)$TiCl_2$ (mmol Ti per g catalyst)**	**MAO (wt% Al)**
1B	3.2	0.029	9.4%
1C	2.7	0.025	8.1%
1D	2.2	0.021	6.8%
1E	3.2	0.021	6.8%
1F	2.2	0.029	9.4%
1G	2.7	0.025	8.1%
1H	2.7	0.025	6.7%

Table 4

Polymerization Conditions

Invent. Ex. No.	**Prod Rate, kg/hr**	**Residence Time, hr**	**Rx Temp, °C**	**C2 mol%**	**C6 mole%**	**N2 mole%**	**C6/C2 Molar Flow**	**H2/C2 Molar Flow**
1B	2.45	1.8	80	66	1.2	33.4	0.021	0.0011
1C	2.41	1.8	80	65	1.2	35.0	0.022	0.0011

1D	1.82	2.5	80	65	1.4	35.1	0.023	0.0012
1E	2.18	2.1	80	65	1.3	35.3	0.022	0.0012
1F	2.35	2.0	80	66	1.2	34.6	0.022	0.0011
1G	2.11	2.1	80	65	1.2	35.8	0.022	0.0012
1H	2.15	2.2	80	similar to above			0.022	0.0012

TABLE 5

Copolymer Properties

	First Polyethylene Copolymer						
Resin No.	1B	1C	1D	1E	1F	1G	1H
density (g/cm^3)	0.9204	0.9208	0.9211	0.9215	0.9206	0.9212	0.9216
MI, I_2 (g/10 min)	0.67	0.62	0.78	0.68	0.63	0.71	0.72
MFR, I_{21}/I_2	39.2	40.5	40.8	41.2	37.1	41.1	40.6
I_{10}/I_2	10.0	10.3	10.3	10.6	10.3	10.4	10.4
TREF profile, °C	trimodal T(low) = 70.4 T(med) = 82.1 T(high) = 93.6	trimodal T(low) = 70.6 T(med) = 81.6 T(high) = 93.6	trimodal T(low) = 68.0 T(med) = 82.1 T(high) = 93.4	Trimodal T(low) = 69.3 T(med) = 81.8 T(high) = 93.5	trimodal T(low) = 70.8 T(med) = 81.4 T(high) = 93.3	trimodal T(low) = 69.7 T(med) = 81.8 T(high) = 93.4	trimodal T(low) = 69.1 T(med) = 83.6 T(high) = 93.3
T(med)−T(low), °C	11.7	11.0	14.1	12.5	10.6	12.1	14.5
T(high)-T(med), °C	11.5	12.0	11.3	11.7	11.9	11.6	9.7

T(high)-T(low), °C	23.2	23.3	25.4	24.2	22.5	23.7	24.2
wt% at 90-105°C	18.1	18.6	16.9	18.8	19.3	17.5	20.1
wt% at > 100°C	0	0	0.85	0	0	0.14	0.03
T(75)-T(25) (°C)	19.21	18.64	19.77	19.06	19.46	19.09	20.29
$CDBI_{50}$ (wt%)	52.4	53.7	52.7	52.7	50.4	53.7	49.2
comonomer profile	reverse	reverse	reverse	Reverse	reverse	reverse	reverse
DSC melt temp (°C)	107.7, 121.7	108.2, 121.4	108.3, 121.2	106.2, 121.4	109.4, 121.4	106.7, 121.1	108.7, 121.6
% crystallinity	44.1	45.9	46.4	46.3	45.6	46.5	46.5
CY *a*-parameter	0.1832	0.1823	0.1814	0.1706	0.1928	0.1781	0.1980
M_w (x 10^{-3})	108738	109688	96771	113303	104054	107510	107736
M_n (x 10^{-3})	25484	24768	19835	20619	23148	23719	21641
M_z (x10^{-3})	307791	305388	265065	383405	296306	313382	321028
M_w / M_n	4.27	4.43	4.88	4.91	4.50	4.53	4.98

M_z / M_w	2.83	2.78	2.74	3.38	2.85	2.92	2.98
C_6 content (wt%)	7.3	7.1	7.3	7.1	7.3	7.3	7.2
SCB/1000 C	12.7	12.5	12.8	12.4	12.8	12.8	12.6
hexane extractables (%)	0.84	0.82	1.03	0.93	0.75	0.81	0.85
melt strength (cN)	5.92	6.17	5.58	5.90	6.12	5.45	5.53
processability enhancement index (χ)	1.06	1.07	1.08	1.05	1.08	1.06	1.04
VGP crossover phase angle (δ^{XO})	61.1	60.3	60.9	59.5	61.1	60.8	61.6
$96 - 2.14\ [(MFR^{0.5}) + 1 \times 10^{-4}\ (M_w - Mn)]$	64.8	64.2	65.9	62.4	65.7	64.4	63.9
SCB/1000 at MW of	7.97	7.39	6.86	8.39	8.06	8.10	8.30

200,000 – SCB/1000 at MW of 50,000							
Shear Thinning Index (SHI)	0.21	0.20	0.21	0.16	0.25	0.19	0.26
$(CDBI_{50} - 3)$	49.4	50.7	49.7	49.7	47.4	50.7	46.2
$[15/ (a + 0.12)]$	49.5	49.6	49.8	51.6	40.54	48.39	39.47
$[80 - 1.22 (CDBI_{50}) / (M_w/M_n)]$	65.03	65.21	66.83	66.91	66.34	65.54	68.41
$68 [(I_{21}/I_2)^{-1} + 10^{-6} (M_n)]$	3.47	3.36	3.02	3.22	3.41	3.27	3.15

As can be seen in Tables 2 and 5, all the resins 1A-1H have a reverse comonomer distribution, a multimodal (e.g. trimodal) TREF profile, a $CDBI_{50}$ within a range of from 40 to 70 wt%, a MFR (I_{21}/I_2) within a range of 32 to 50, a M_w/M_n within a range of from 3.5 to 6.0 and a fractional melt index (I_2 of less than 1.0). Each of the resins 1A-1H shown in Tables 2 and 5 also have a broad unimodal molecular weight distribution.

A representative TREF curve is shown in Figure 1 for resin 1A. A representative GPC curve is shown for resin 1A in Figure 2. A representative GPC-FTIR curve is shown for resin 1A in Figure 3.

The good processability of resins 1A-1H is also manifest in a model of polymer architecture which is based on van Gurp-Palmen (VGP) melt rheology behavior as determined by dynamic mechanical analysis (DMA), gel permeation chromatography (GPC) refractive Index (RI) data and melt flow ratio (I_{21}/I_2) information. The model is a polymer processability model, and provides a polymer "processability enhancement index" (χ) which may be usefully applied to distinguish resins having relatively low and relatively high processability.

A van Gurp-Palmen analysis is a means by which to study a polymer architecture (e.g. molecular weight distribution, linearity, etc.) as reflected by the polymer melt morphology. A VGP curve is simply a plot of the phase angle (δ) versus complex modulus (G*), where the two rheology parameters are obtained using the frequency sweep test in dynamic mechanical analysis (DMA). The processability model accounts for the effects of resin architecture on VGP parameters such as complex modulus (G*) and phase angle (δ). A shift of a VGP curve from a baseline curve or a decrease in the phase angles at the mid-range of complex modulus may indicate changes in the polymer melt morphology.

The present processability model further requires the determination of a VGP crossover rheology parameter which is defined as the intersecting point obtained between the phase angle (δ) vs. complex modulus (G^*) plot and a phase angle (δ) vs. complex viscosity (η^*) plot. Based on a linear viscoelasticity theory, the VGP crossover rheology parameter (δ^{XO}) occurs at a frequency (ω) which is equal to unity. It is the phase angle at which the G^* and the η^* are equivalent. Hence the VGP crossover rheology parameter can be determined in a single DMA test.

The VGP crossover plots for resin 2A and for a resin sold under the trade-name Exceed 1018 (resin 2B) is included in Figures 4A. The VGP crossover plots for the resin 1A is shown in Figure 4B. The VGP crossover points are dependent upon the copolymer architecture. Generally, for resins which are easier to process such as resin 1A, the VGP phase angle at which crossover occurs defined as δ^{XO} is lower than for resins which are more difficult to process such as resins 2A and 2B (compare Figures 4A and 4B). For resins that are easier to process, the shape of the phase angle-complex viscosity curves and the shape of the phase-angle complex modulus curves, are deflected somewhat and more closely resemble mirror images of each other, relative to the curves obtained for resins which are more difficult to process (compare the curves in Figure 4A with the curves in Figure 4B).

The crossover complex modulus (G^{*XO}) (or alternatively the crossover complex viscosity, η^{*XO}) was found to relate to melt index, I_2 in the following way:

(1) $G^{*XO} = 6798.3\ (I_2)^{-0.9250}$

Hence, a polymer with a higher molecular weight would have a greater crossover complex modulus. The relationship in equation 1 was found to hold regardless of the polymer density or molecular weight distribution.

The VGP phase angle δ^{XO} will be a function of several resin parameters. The polymer density was found to have a limited effect on the crossover phase angle, independent of other polymer architectural (or microstructural) effects. The molecular weight distribution (M_w/M_n) was found to have an effect on the VGP crossover phase angle.

The crossover phase angle and crossover complex modulus plot shows that resins having good processability and poor processability can be differentiated fairly well by imposing a constraint on the two VGP crossover parameters. Accordingly, resins which are relatively easy to process will satisfy inequality (2):

(2) $\delta^{XO} \leq 76.6 - 9 \times 10^4 (G^{*XO})$.

In order to remove the effects of molecular weight distribution (M_W/M_n) and weight average molecular weight (M_w) on the δ^{XO} and hence to determine polymer architectural (or microstructural) effects on processability, these effects must be decoupled from the determination of δ^{XO} to allow the ranking of resins of different M_w/M_n and M_w on the same semi-qualitative scale. For a semi-qualitative measurement of polymer architectural (or microstructural) effects, one has to design experiments to decouple the molecular weight and molecular weight distribution effects on the melt rheology parameters.

A composite structural constraint of the δ^{XO} is derived in order to separate resin into two groups according to their melt rheology behavior. By expressing δ^{XO} as a function of melt flow ratio (I_{21}/I_2), and number average (M_n) and weight average (M_w) molecular weights according to the inequality (3), the inventive and comparative resins are again separated into two groups having different relative processability:

(3) $\delta^{XO} \leq 96 - 2.14 [(MFR^{0.5}) + 1 \times 10^{-4} (M_w - M_n)]$.

Figure 5 shows a plot of the line for equation: $\delta^{XO} = 96 - 2.14\ [(MFR^{0.5}) + 1 \times 10^{-4}\ (M_w - M_n)]$ as well as plotted data corresponding to the VGP crossover phase angle (δ^{XO}) and $96 - 2.14\ [(MFR^{0.5}) + 1 \times 10^{-4}\ (M_w - M_n)]$ values for resins 1A-1H and resins 2A-2D.

Inequality (3) allows the decoupling of molecular weight and molecular weight distribution effects on δ^{XO} by including melt flow data and GPC data. As a result, resins of divergent molecular weight and molecular weight distribution can be ranked against one another using only melt flow, DMA and GPC data.

The crossover phase angle δ^{XO} generally follows a liner relationship with a composite function of the melt flow ratio and molecular weights for linear ethylene-α-olefin copolymers. Thus, without wishing to be bound by theory, any changes to the VGP crossover phase angle measured by DMA is herein attributed to other aspects of the polymer architecture affecting the melt rheology. The relative effect of such aspects of architecture (or microstructure) on the δ^{XO} value is manifest in a greater negative deviation from the baseline defined by inequality (3). Hence, inequality (3) allows one to rank ethylene copolymers according to undefined architectural or microstructural effects on the crossover phase angle, where those architectural/microstructural effects do not include molecular weight or molecular weight distribution.

The degree to which the VGP phase angle δ^{XO} is different for resins which are easier to process, may be assessed by using a "processability enhancement index (χ)". According to the present model, the processability enhancement index is defined in a semi-quantitative manner in the following equation 4:

$$(4) \qquad \chi = 96 - 2.14\ [(MFR^{0.5}) + 1 \times 10^{-4}\ (M_w - Mn)] / \delta^{XO}.$$

The χ values are close to or greater than unity for polymers showing significant processability enhancement from polymer architectural/microstructural affects and less than unity for polymers showing no or little processability enhancement from polymer architectural/microstructural affects (e.g. less than about 0.97). As the data in Tables 2 and 5 show, resins 1A-1H, each have a processability enhancement index χ of greater than 1.0, while resins 2A-2D have a processability enhancement index χ or less than 1.0.

In addition to the above, and as shown in Tables 2 and 5, is the fact that the first polyethylene copolymer (e.g. resins 1A-1H) and employed in the blends of the current invention were found to satisfy the following relationships:

(i) $(M_w/M_n) \geq 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$; and

(ii) $\delta^{XO} \leq [\ 80 - 1.22\ (CDBI_{50})\ /\ (M_w/M_n)\ ]$;

where δ^{XO} is the crossover phase angle, M_w, M_n, I_{21}, I_2 and $CDBI_{50}$ are all as defined as above. The data provided in Table 2, further shows that none of the resins 2A-2D satisfy either of the conditions: (i) $(M_w/M_n) \geq 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$ or (ii) $\delta^{XO} \leq [\ 80 - 1.22\ (CDBI_{50})\ /\ (M_w/M_n)\ ]$.

For further comparison purposes, the resins 1A-1H have been plotted against several known commercial resins in Figure 6. Figure 6 shows a plot of the equation: $(M_w/M_n) = 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$, as well as a plot of the Mw/Mn vs. $68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$ values for resins 1A-1H and several known commercial resins. The commercial resins included in Figure 6 for comparison purposes are all resins having an melt index I_2 of 1.5 or less and a density of between 0.916 and 0.930 g/cm^3 and which are sold under trade names such as, Elite™, Exceed™, Marflex™, Starflex™, Dowlex™, SURPASS™, SCLAIR™, NOVAPOL™ and Enable™. As can be seen from Figure 6, none of these commercial grades satisfy the condition: $(M_w/M_n) \geq 68$

$[(I_{21}/I_2)^{-1} + 10^{-6} (M_n)]$. In contrast all of the resins 1A-1H satisfy the condition: $(M_w/M_n) \geq 68 [(I_{21}/I_2)^{-1} + 10^{-6} (M_n)]$. This work demonstrates the distinct architecture of the resins used as the first polyethylene copolymer in the blends of the current invention.

For further comparison purposes, resins 1A-1H have been plotted against several known commercial resins in Figure 7. Figure 7 shows a plot of the equation: $\delta^{XO} = [80 - 1.22 (CDBI_{50}) / (M_w/M_n)]$, as well as a plot of the δ^{XO} vs. $[80 - 1.22 (CDBI_{50}) / (M_w/M_n)]$ values for resins 1A-1H and several known commercial resins. The commercial resins included in Figure 7 for comparison purposes are all resins having an melt index I_2 of 1.5 or less and a density of between 0.916 and 0.930 g/cm^3 and which are sold under trade names such as, Elite™, Exceed™, Marflex™, Starflex™, Dowlex™, SURPASS™, SCLAIR™, NOVAPOL™ and Enable™. As can be seen from the figure, none of these commercial grades satisfy the condition: $\delta^{XO} \leq [80 - 1.22 (CDBI_{50}) / (M_w/M_n)]$. In contrast, all of the resins 1A-1H satisfy the condition: $\delta^{XO} \leq [80 - 1.22 (CDBI_{50}) / (M_w/M_n)]$. This work further demonstrates the distinct architecture of the resins used as the first polyethylene copolymer in the blends of the current invention.

Polymer Blends

Inventive polymer blends were made by blending a first polyethylene copolymer (e.g. resins 1A-1H) with a second polyethylene copolymer (e.g. resins 2A-2D). The blends were made by dry blending the components in appropriate amounts using a metering device upstream of an extruder used to feed a blown film line. Tables 6-9 show the film properties of 1 mil (thickness) films comprising 100 wt% first or second polyethylene copolymers as well as the film properties for 15 wt%:85 wt% polymer blends.

Comparative polymer blends were made by blending LF-Y819-A^{TM} (a high pressure low density polyethylene (HPLDPE) material having a melt index I_2 of 0.75 g/10min and a density of 0.919 g/cm^3, available from NOVA Chemicals) with the second polyethylene copolymer (e.g. resins 2B, 2C and 2D). The film properties of these 15 wt%:85 wt% comparative blends are provided in Tables 7-9.

TABLE 6

Film Properties (Resin 1A, 2A and Inventive Blend of 1A/2A)

	First Polyethylene Copolymer	**Second Polyethylene Copolymer**	**Inventive Blend**
	1A **100%**	**2A** **100%**	**15 wt% 1A /** **85% wt% 2A**
Dart Impact (g/mil)	638	508	**686**
MD Tear (g/mil)	121	244	**200**
TD Tear (g/mil)	455	330	**415**
Puncture (J/mm)	53	68	**63**
1% MD Secant Modulus (MPa)	198	153	**160**
1% TD Secant Modulus (MPa)	220	173	**174**
2% MD Secant Modulus (MPa)	180	139	**141**
2% TD Secant Modulus (MPa)	194	148	**147**
MD Tensile Strength (MPa)	51.0	58.9	**59.9**
TD Tensile Strength (MPa)	48.8	50.4	**56.5**
MD Elongation at	477	568	**570**

Break (%)			
TD Elongation at Break (%)	696	675	**744**
MD Yield Strength (MPa)	10.9	9.5	**9.3**
TD Yield Strength (MPa)	11.2	9.9	**9.7**
MD Elongation at Yield (%)	14	14	**14**
TD Elongation at Yield (%)	15	19	**15**
Haze (%)	11.2	7.4	**4.7**
Gloss (%)	50	63	**75**
Cold Seal Strength:			
SIT (°C)	112	103	**108**
Maximum Force (N)	14.3	10.9	**12.3**
Temperature at Max. Force (°C)	130	150	**140**

Table 7

Film Properties (Resin 1A, 2B, Inventive Blend of 1A/2B and Comparative Blend HPLDPE/2B)

	First Polyethylene Copolymer	**Second Polyethylene Copolymer**	**Inventive Blend**	**Comparative Blend**
	1A **100%**	**2B** **100%**	**15 wt% 1A / 85 wt% 2B**	**15 wt% LF-Y819-A / 85 wt% 2B**
Dart Impact (g/mil)	638	707	**743**	224
MD Tear (g/mil)	121	235	**222**	106
TD Tear (g/mil)	455	370	**439**	652
Puncture (J/mm)	53	37	**43**	27
1% MD Secant Modulus (MPa)	198	144	**163**	170

1% TD Secant Modulus (MPa)	220	176	**168**	216
2% MD Secant Modulus (MPa)	180	131	**146**	156
2% TD Secant Modulus (MPa)	194	149	**145**	189
MD Tensile Strength (MPa)	51.0	57.3	**48**	41.8
TD Tensile Strength (MPa)	48.8	40.7	**44.9**	36.5
MD Elongation at Break (%)	477	574	**552**	536
TD Elongation at Break (%)	696	658	**661**	665
MD Yield Strength (MPa)	10.9	8.9	**9.8**	10.8

TD Yield Strength (MPa)	11.2	9.4	**10.5**	10.3
MD Elongation at Yield (%)	14	13	**14**	19
TD Elongation at Yield (%)	15	16	**17**	12
Haze (%)	11.2	13.6	**8.9**	4.7
Gloss (%)	50	46	**63**	78
Cold Seal Strength:				
SIT (°C)	112	108	**108**	107
Maximum Force (N)	14.3	10.9	**12.3**	15.5
Temperature at Max. Force (°C)	130	150	**160**	150

Table 8

Film Properties (Resin 1A, 2C, Inventive Blend of 1A/2C and Comparative Blend HPLDPE/2C)

	First Polyethylene Copolymer	**Second Polyethylene Copolymer**	**Inventive Blend**	**Comparative Blend**
	1A **100%**	**2C** **100%**	**15 wt% 1A / 85 wt% 2C**	**15 wt% LF-Y819-A / 85 wt% 2C**
Dart Impact (g/mil)	638	435	**392**	296
MD Tear (g/mil)	121	326	**269**	129
TD Tear (g/mil)	455	475	**525**	645
Puncture (J/mm)	53	84	**87**	59
1% MD Secant Modulus (MPa)	198	136	**141**	158
1% TD Secant	220	144	**159**	201

Modulus (MPa)				
2% MD Secant Modulus (MPa)	180	122	**126**	143
2% TD Secant Modulus (MPa)	194	126	**138**	173
MD Tensile Strength (MPa)	51.0	57.6	**55.1**	45.2
TD Tensile Strength (MPa)	48.8	52.1	**47.8**	42.6
MD Elongation at Break (%)	477	580	**563**	530
TD Elongation at Break (%)	696	811	**780**	839
MD Yield Strength (MPa)	10.9	8.6	**9.1**	9.8

TD Yield Strength (MPa)	11.2	8.9	**9.2**	9.1
MD Elongation at Yield (%)	14	13	**14**	15
TD Elongation at Yield (%)	15	20	**16**	12
Haze (%)	11.2	10.3	**5.9**	3.9
Gloss (%)	50	48	**70**	78
Cold Seal Strength:				
SIT (°C)	112	100	**102**	101
Maximum Force (N)	14.3	11.5	**12.4**	14.6
Temperature at Max. Force (°C)	130	130	**160**	150

Table 9

Film Properties (Resin 1A, 2D, Inventive Blend of 1A/2D and Comparative Blend HPLDPE/2D)

	First Polyethylene Copolymer	**Second Polyethylene Copolymer**	**Inventive Blend**	**Comparative Blend**
	1A **100%**	**2D** **100%**	**15 wt% 1A / 85 wt% 2D**	**15 wt% LF-Y819-A / 85 wt% 2D**
Dart Impact (g/mil)	638	223	**258**	170
MD Tear (g/mil)	121	350	**266**	120
TD Tear (g/mil)	455	584	**599**	682
Puncture (J/mm)	53	73	**75**	51
1% MD Secant Modulus (MPa)	198	158	**169**	208
1% TD Secant	220	202	**193**	238

Modulus (MPa)				
2% MD Secant Modulus (MPa)	180	146	**151**	184
2% TD Secant Modulus (MPa)	194	169	**162**	204
MD Tensile Strength (MPa)	51.0	55.5	**49.0**	52.3
TD Tensile Strength (MPa)	48.8	41.5	**44.3**	44.0
MD Elongation at Break (%)	477	524	**553**	564
TD Elongation at Break (%)	696	748	**760**	852
MD Yield Strength (MPa)	10.9	10.3	**9.9**	10.5

TD Yield Strength (MPa)	11.2	10.6	**10.5**	10.6
MD Elongation at Yield (%)	14	13	**14**	13
TD Elongation at Yield (%)	15	14	**16**	12
Haze (%)	11.2	8.3	**8.1**	4.3
Gloss (%)	50	62	**63**	77
Cold Seal Strength:				
SIT (°C)	112	108	**108**	107
Maximum Force (N)	14.3	9.4	**13.6**	15.3
Temperature at Max. Force (°C)	130	125	**150**	150

As shown in Table 6, a blend of resin 1A and resin 2A (a linear low density polyethylene with relatively low MFR (I_{21}/I_2) and having a narrow MWD (M_w/M_n) and a melt index I_2 of 0.95 g/10min) have improved dart impact relative to either of the blend components. The blend also has a TD tear value which is more than 10% higher than the weighted average of the blend components. In addition the blend has a haze of 4.7% and a gloss at 45° of 75, each of which is significantly improved over either of the blend components. Finally, the MD tear, and the MD and TD 1% secant modulus are not impacted in a hugely negative way.

With reference to Table 7, a blend of resin 1A and resin 2B (a linear low density polyethylene having a relatively low MFR (I_{21}/I_2) and having a narrow MWD (M_w/M_n) and a melt index I_2 of 1.0 g/10min) has dart impact and puncture resistance values which are greater than weighted average of the blend components, a TD tear which increases more than 10% over the weighted average of the blend components, and haze and gloss values which improve to levels beyond that expected for the weighted average of the blend components. Further, when compared to a blend containing HPLDPE (e.g. LF-Y819-A) in the same amount as the first polyethylene copolymer 1A, film made from the inventive blend has better MD tear, dart impact and puncture resistance properties.

With reference to Table 8, a blend of resin 1A with 2C (a linear low density polyethylene having a melt index I_2 of 0.93 g/10min and a density of 0.917 g/cm^3) has TD tear, puncture resistance, haze and gloss values which are all improved beyond that expected for a weighted average of the blended components. Further, the addition of resin 1A improves optical properties without reducing the dart impact and MD tear as much as using HPLDPE (e.g. LF-Y819-A) as a blend component in equivalent amounts. Thus, compared to a blend containing HPLDPE in the same amount as the first polyethylene copolymer 1A, film made from the inventive blend has better MD tear, dart impact and puncture resistance properties.

Table 9 shows that a blend of resin 1A and resin 2D (a linear low density polyethylene having a melt index I_2 of 1 g/10min and a density of 0.92 g/cm^3) has TD tear and puncture resistance values which are higher than the weighted average expected for the blended components. It is also evident that addition of resin 1A improves optical properties without reducing the dart impact and MD tear as much as does the addition of HPLDPE (e.g. LF-Y819-A) in equivalent amounts. Thus, when compared to a blend containing HPLDPE in the same amount as the first polyethylene copolymer 1A, film made from the inventive blend has much better MD tear, dart impact and puncture resistance properties.

Overall, the films made from the polymer blends of the current invention have dart impact values of at least 250 g/mil, have MD tear strengths of greater than 200 g/mil, an MD tear to TD tear ratio of at least 0.4, an MD or TD secant modulus at 1% strain of at least 130 MPa, a haze of less than 10%, and a gloss at 45° of at least 60.

Figure 8 shows that the use of the first polyethylene copolymer (e.g. resin 1A) in blends with a linear low density polyethylene material (e.g. resins 2B, 2C or 2D), improves the shear thinning ratio ($\eta^*_{0.1}/\eta^*_{10}$) as determined by DMA, which is a measure of processability, as the amount of the first polyethylene copolymer is increased in the blend. Such a trend indicates improvements in melt fracture tendency and hence processability.

Figure 9, shows how the melt strength (in centiNewtons, cN) of a blend with a linear low density material (e.g. resins 2B, 2C or 2D) also increases as the amount of first polyethylene copolymer (e.g. resin 1A) is increased in the blend. The improvement can be as much as from 20 to 45%, depending on the nature of the first and second polyethylene copolymer components.

In view of the above data, the resin blends of the present invention have improved optical properties relative to either of the blend components when each is blown into film. See Tables 6, 7, 8 and 9. As shown in Table 7, 8 and 9 blending HPLDPE into a linear low density polyethylene can also improve optical properties, but this comes at the expense of other film properties, namely the dart impact resistance, puncture resistance and the MD direction tears.

The overall result is a polymer blend having good processability which when blown into film affords good physical properties, such as impact resistance, puncture strength, tear strength and stiffness, as well as good optical properties.

In addition, use of an equivalent amount of the first polyethylene copolymer in place of a high pressure linear low density material, leads to blends having far better MD tear strength, dart impact resistance, and puncture strength.

In view of the forgoing, the first polyethylene copolymers described herein (e.g. resins 1A-1H) can be used as a highly successful alternative blend component to a HPLDPE material, in order to alleviate the processing deficiencies of a linear low density polyethylene material (such as for example, those having narrow molecular weight distributions and/or fractional melt indices).

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A polymer blend comprising:

a) 5-95 wt% of a first polyethylene copolymer having a density of from 0.916 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of from 32 to 50, a molecular weight distribution (M_w/M_n) of from 3.6 to 6.5, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, a composition distribution breadth index $CDBI_{50}$ of from 35 wt% to 70 wt% as determined by TREF and which satisfies the following relationships:

(i) $\delta^{XO} \leq [\, 80 - 1.22\, (CDBI_{50}) \,/\, (M_w/M_n)]$ and

(ii) $(M_w/M_n) \geq 68\, [(I_{21}/I_2)^{-1} + 10^{-6}\, (M_n)]$;

and

b) 95-5 wt% of a second polyethylene copolymer which is a linear low density polyethylene (LLDPE) different from the first polyethylene copolymer and having a density of from 0.910 to 0.940 g/cm^3, a melt index (I_2) of 0.2 to 5.0 g/10min, and a melt flow ratio (I_{21}/I_2) of less than 35.

2. The polymer blend of claim 1, wherein the first polyethylene copolymer has a multimodal TREF profile defined by three intensity peaks occurring at elution temperatures T(low), T(med) and T(high); wherein T(low) is from 62°C to 82°C, T(med) is from 76°C to 89°C but higher than T(low), and T(high) is from 90°C to 100°C.

3. The polymer blend of claim 1, wherein the blend comprises from 5 to 50 wt% of the first polyethylene copolymer and from 95 to 50 wt% of the second polyethylene copolymer.

4. The polymer blend of claim 1, wherein the first polyethylene copolymer has a molecular weight distribution (M_w/M_n) of from 4.0 to 6.0.

5. The polymer blend of claim 1, wherein the first polyethylene copolymer has a $CDBI_{50}$ of from 45 wt% to 69 wt%.

6. The polymer blend of claim 1, wherein the first polyethylene copolymer has a melt index (I_2) of from 0.25 to 0.80 g/10min.

7. The polymer blend of claim 1, wherein the first polyethylene copolymer has a density of from 0.917 to 0.927 g/cm^3.

8. The polymer blend of claim 1, wherein the first polyethylene copolymer has a Z-average molecular weight distribution (M_Z/M_w) of from 2.0 to 4.0.

9. The polymer blend of claim 1, wherein the first polyethylene copolymer has an amount eluting at a temperature of from 90°C to 105°C of from 5 to 40 weight percent as determined by TREF.

10. The polymer blend of claim 1, wherein the first polyethylene copolymer has an amount eluting at a temperature of above 100°C of 0 weight percent as determined by TREF.

11. The polymer blend of claim 1, wherein the second polyethylene copolymer has a density of from 0.916 to 0.930 g/cm^3.

12. The polymer blend of claim 1, wherein the second polyethylene copolymer has a $CDBI_{50}$ of at least 50 wt%.

13. The polymer blend of claim 1, wherein the second polyethylene copolymer has a molecular weight distribution (M_w/M_n) of from 1.7 to 5.0.

14. The polymer blend of claim 1, wherein the first polyethylene copolymer is made in a single gas phase reactor by contacting ethylene and at least one alpha olefin having from 3-8 carbon atoms with a polymerization catalyst system comprising a phosphinimine catalyst, a support, and a catalyst activator.

15. The polymer blend of claim 14, wherein the phosphinimine catalyst has the formula:

$$(1\text{-}R^2\text{-Indenyl})Ti(N{=}P(t\text{-}Bu)_3)X_2;$$

wherein R^2 is a substituted or unsubstituted alkyl group, a substituted or an unsubstituted aryl group, or a substituted or unsubstituted benzyl group, wherein substituents for the alkyl, aryl or benzyl group are selected from the group consisting of alkyl, aryl, alkoxy, aryloxy, alkylaryl, arylalkyl and halide substituents; and wherein X is an activatable ligand.

16. The polymer blend of claim 1, wherein the first polyethylene copolymer further satisfies the following relationship:

$\delta^{XO} \leq 96 - 2.14\ [(MFR^{0.5}) + 1 \times 10^{-4}\ (M_w - M_n)]$.

17. A film structure comprising a least one layer comprising the polymer blend of any of claims 1-16.

18. A blown film comprising the polymer blend of claim 1, the film having a haze of less than 10% and a gloss at 45° of greater than 60.

19. A polymer blend comprising:

a) 5-95 wt% of a first polyethylene copolymer having a density of from 0.916 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of from 32 to 50, a molecular weight distribution (M_w/M_n) of from 3.6 to 6.5, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, a composition distribution breadth index $CDBI_{50}$ of from 35 wt% to 70 wt% as determined by TREF and which satisfies the following relationships:

(i) $\delta^{XO} \leq [\ 80 - 1.22\ (CDBI_{50})\ /\ (M_w/M_n)]$; and

(ii) $(M_w/M_n) \geq 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$;

and

b) 95-5 wt% of a second polyethylene copolymer which is a linear low density polyethylene (LLDPE) having a density of from 0.910 to 0.940 g/cm^3, a melt index (I_2) of 0.2 to 5.0 g/10min, and a melt flow ratio (I_{21}/I_2) of less than 32.

20. The polymer blend of claim 19, wherein the first polyethylene copolymer further satisfies the following relationship:

$\delta^{XO} \leq 96 - 2.14 [(MFR^{0.5}) + 1 \times 10^{-4} (M_w - M_n)]$.

21. A film structure comprising a least one layer comprising the polymer blend of claim 19.

22. A blown film comprising the polymer blend of claim 19, the film having a haze of less than 10% and a gloss at 45° of greater than 60.

23. A polymer blend comprising:

a) 5-95 wt% of a first polyethylene copolymer having a density of from 0.916 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of from 35 to 50, a molecular weight distribution (M_w/M_n) of from 3.6 to 6.5, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, a composition distribution breadth index $CDBI_{50}$ of from 35 wt% to 70 wt% as determined by TREF and which satisfies the following relationships:

(i) $\delta^{XO} \leq [\ 80 - 1.22\ (CDBI_{50}) / (M_w/M_n)]$; and

(ii) $(M_w/M_n) \geq 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$;

and

b) 95-5 wt% of a second polyethylene copolymer which is a linear low density polyethylene (LLDPE) having a density of from 0.910 to 0.940 g/cm^3, a melt index (I_2) of 0.2 to 5.0 g/10min, and a melt flow ratio (I_{21}/I_2) of less than 35.

24. The polymer blend of claim 23, wherein the first polyethylene copolymer further satisfies the following relationship:

$$\delta^{XO} \leq 96 - 2.14 [(MFR^{0.5}) + 1 \times 10^{-4} (M_w - M_n)].$$

25. A film structure comprising a least one layer comprising the polymer blend of claim 23.

26. A blown film comprising the polymer blend of claim 23, the film having a haze of less than 10% and a gloss of greater than 60.

27. A polymer blend comprising:

a) 5-95 wt% of a first polyethylene copolymer having a density of from 0.916 to 0.935 g/cm^3, a melt index (I_2) of from 0.1 to 1.0 g/10min, a melt flow ratio (I_{21}/I_2) of at least 30, a molecular weight distribution (M_w/M_n) of from 3.0 to 6.5, a reverse comonomer distribution profile as determined by GPC-FTIR, a multimodal TREF profile, a composition distribution breadth index $CDBI_{50}$ of from 35 wt% to 70 wt% as determined by TREF and which satisfies the following relationships:

(i) $\delta^{XO} \leq [80 - 1.22 (CDBI_{50}) / (M_w/M_n)];$

(ii) $(M_w/M_n) \geq 68\ [(I_{21}/I_2)^{-1} + 10^{-6}\ (M_n)]$; and

(iii) $\delta^{XO} \leq 96 - 2.14\ [(MFR^{0.5}) + 1 \times 10^{-4}\ (M_w - M_n)]$;

and

b) 95-5 wt% of a second polyethylene copolymer which is a linear low density polyethylene (LLDPE) different from the first polyethylene copolymer and having a density of from 0.910 to 0.940 g/cm^3, a melt index (I_2) of 0.2 to 5.0 g/10min, and a melt flow ratio (I_{21}/I_2) of less than 35.

28. A film structure comprising a least one layer comprising the polymer blend of claim 27.

FIGURE 1

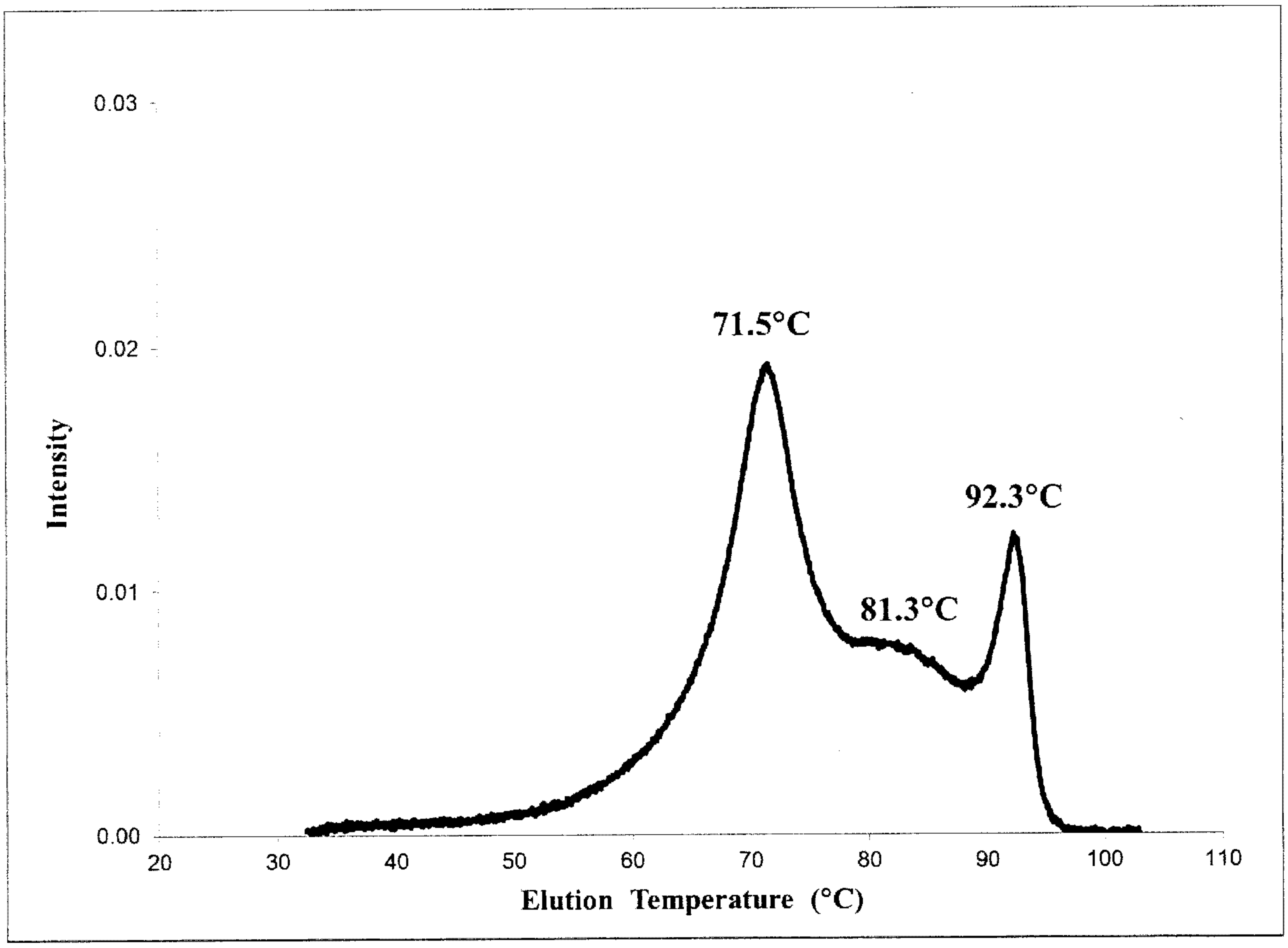

0.03
0.02
0.01
0.00
Intensity
71.5°C
81.3°C
92.3°C
20
30
40
50
60
70
80
90
100
110
Elution Temperature (°C)

FIGURE 2

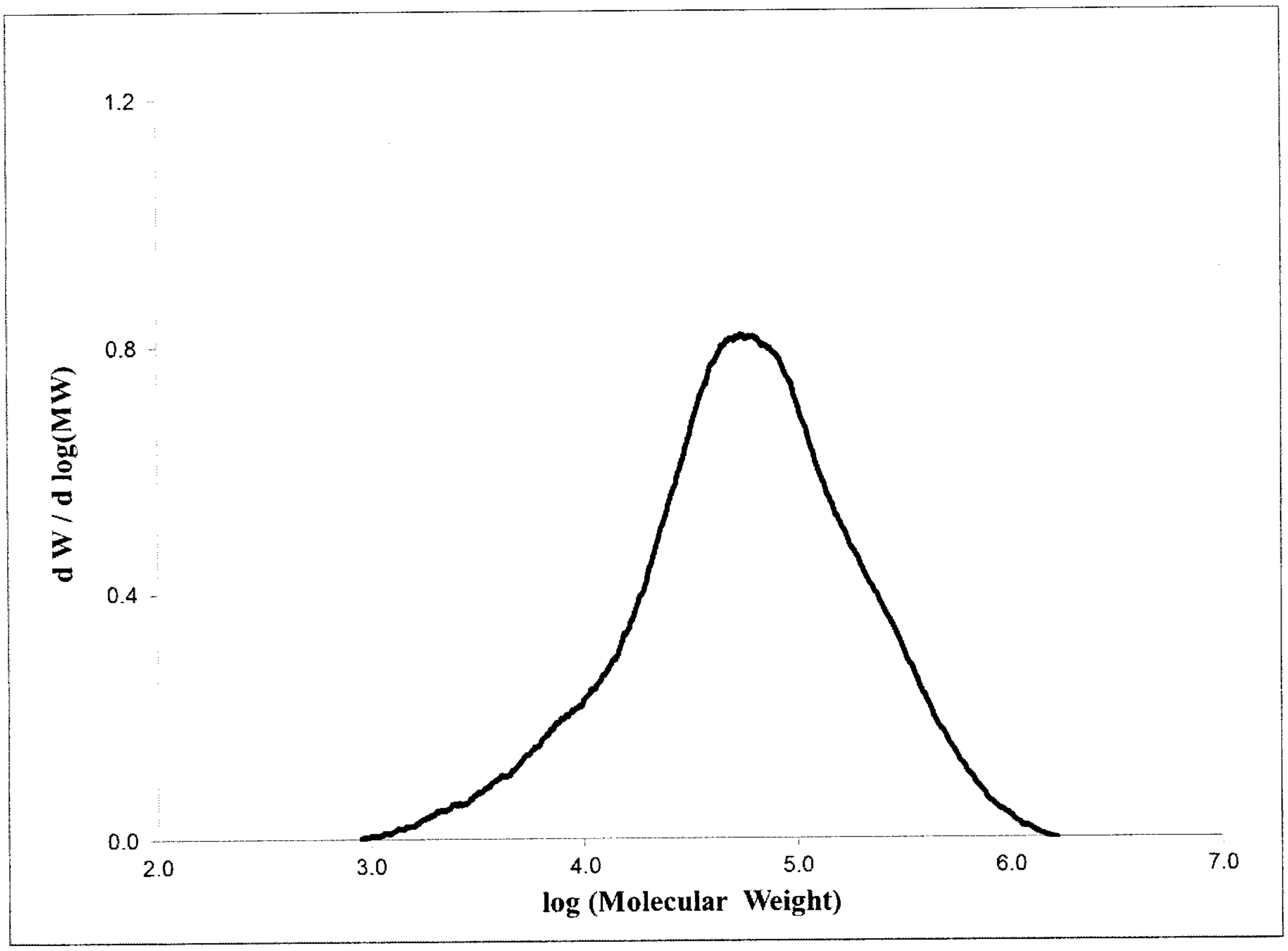


FIGURE 3

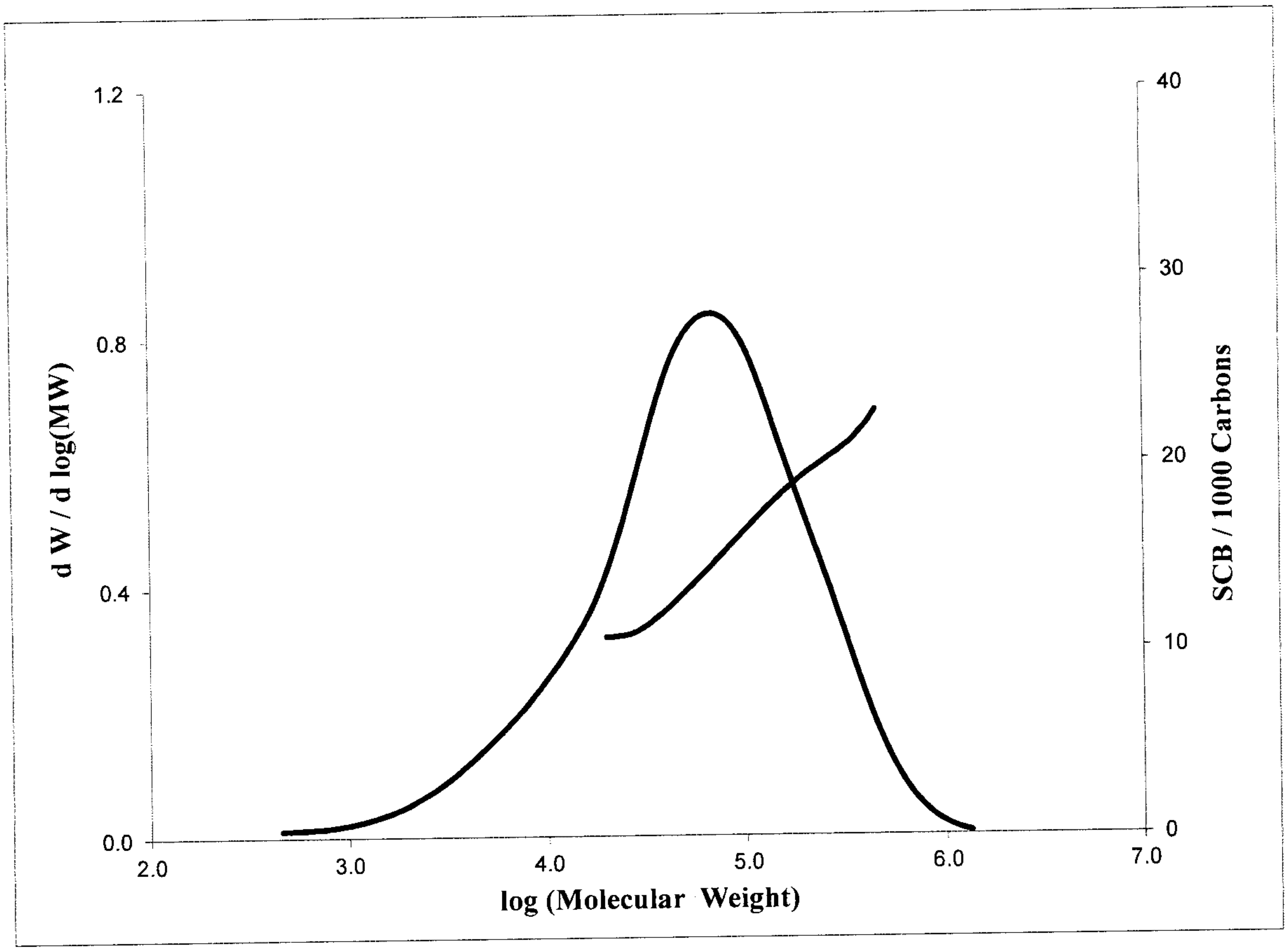

1.2
0.8
0.4
0.0
d W / d log(MW)
40
30
20
10
0
SCB / 1000 Carbons
2.0
3.0
4.0
5.0
6.0
7.0
log (Molecular Weight)

FIGURE 4A

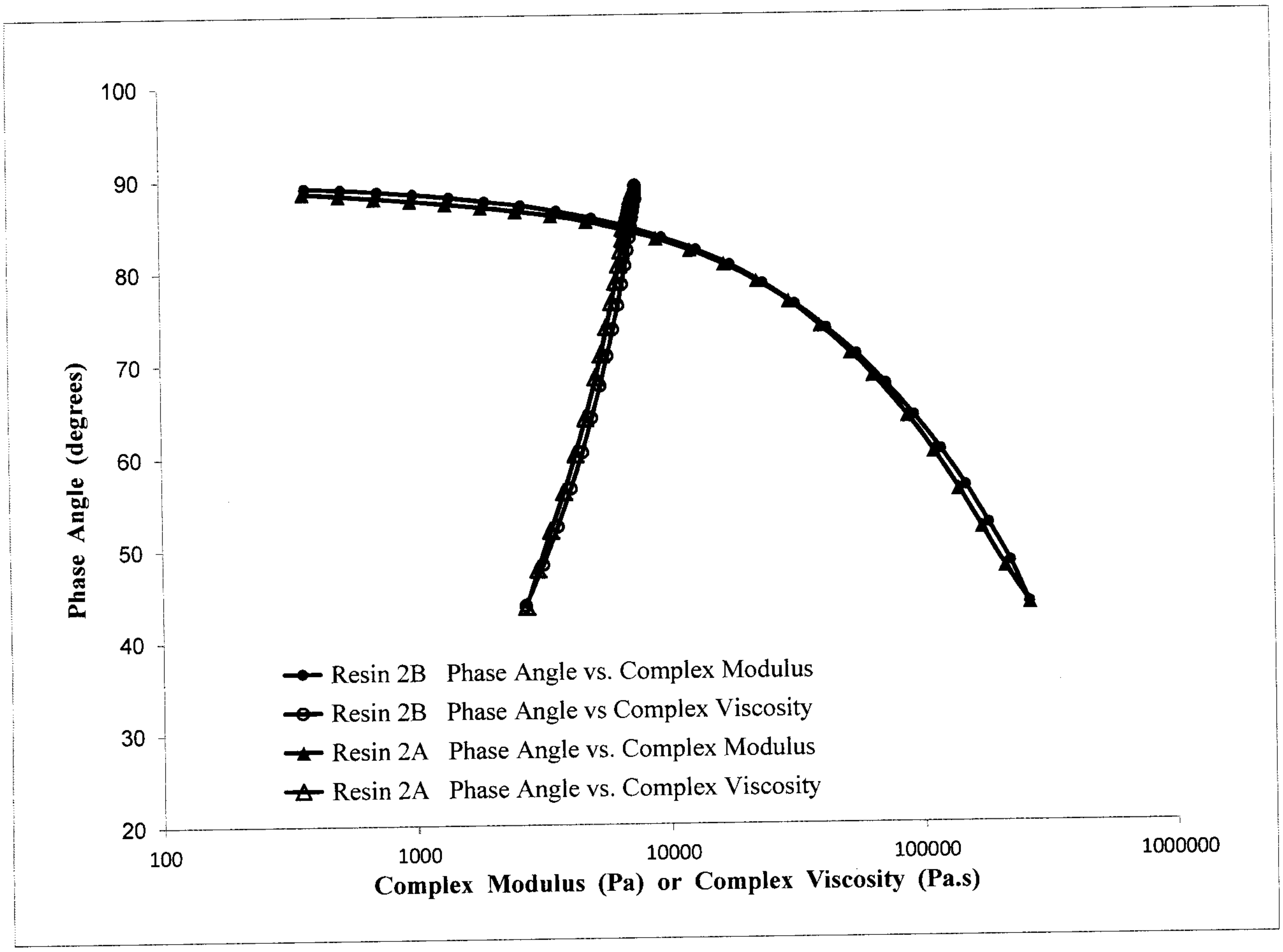

100
90
80
70
60
50
40
30
20
Phase Angle (degrees)
100
1000
10000
100000
1000000
Complex Modulus (Pa) or Complex Viscosity (Pa.s)
Resin 2B Phase Angle vs. Complex Modulus
Resin 2B Phase Angle vs Complex Viscosity
Resin 2A Phase Angle vs. Complex Modulus
Resin 2A Phase Angle vs. Complex Viscosity

FIGURE 4B

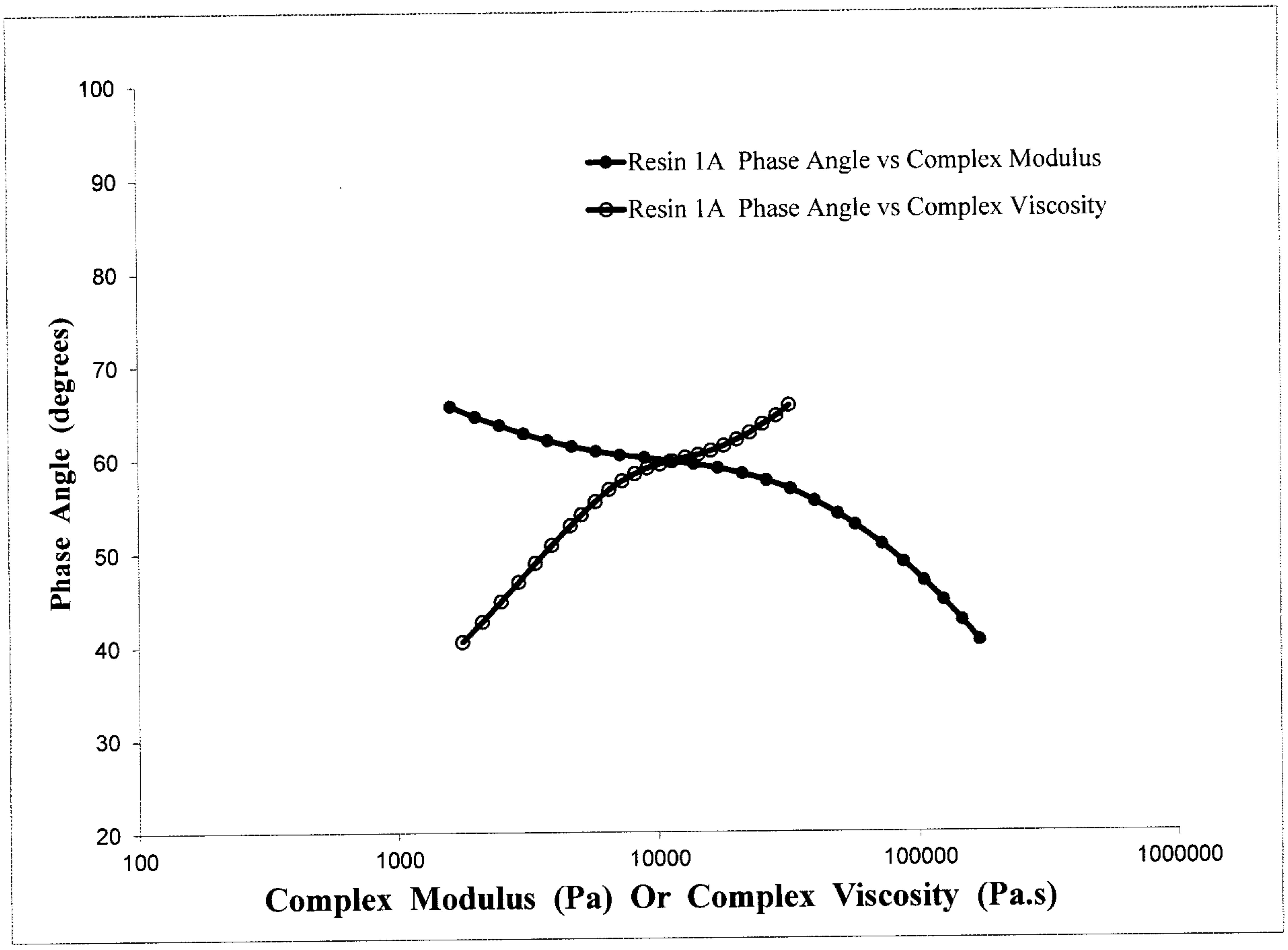

Resin 1A Phase Angle vs Complex Modulus
Resin 1A Phase Angle vs Complex Viscosity
Phase Angle (degrees)
100
90
80
70
60
50
40
30
20
100
1000
10000
100000
1000000
Complex Modulus (Pa) Or Complex Viscosity (Pa.s)

FIGURE 5

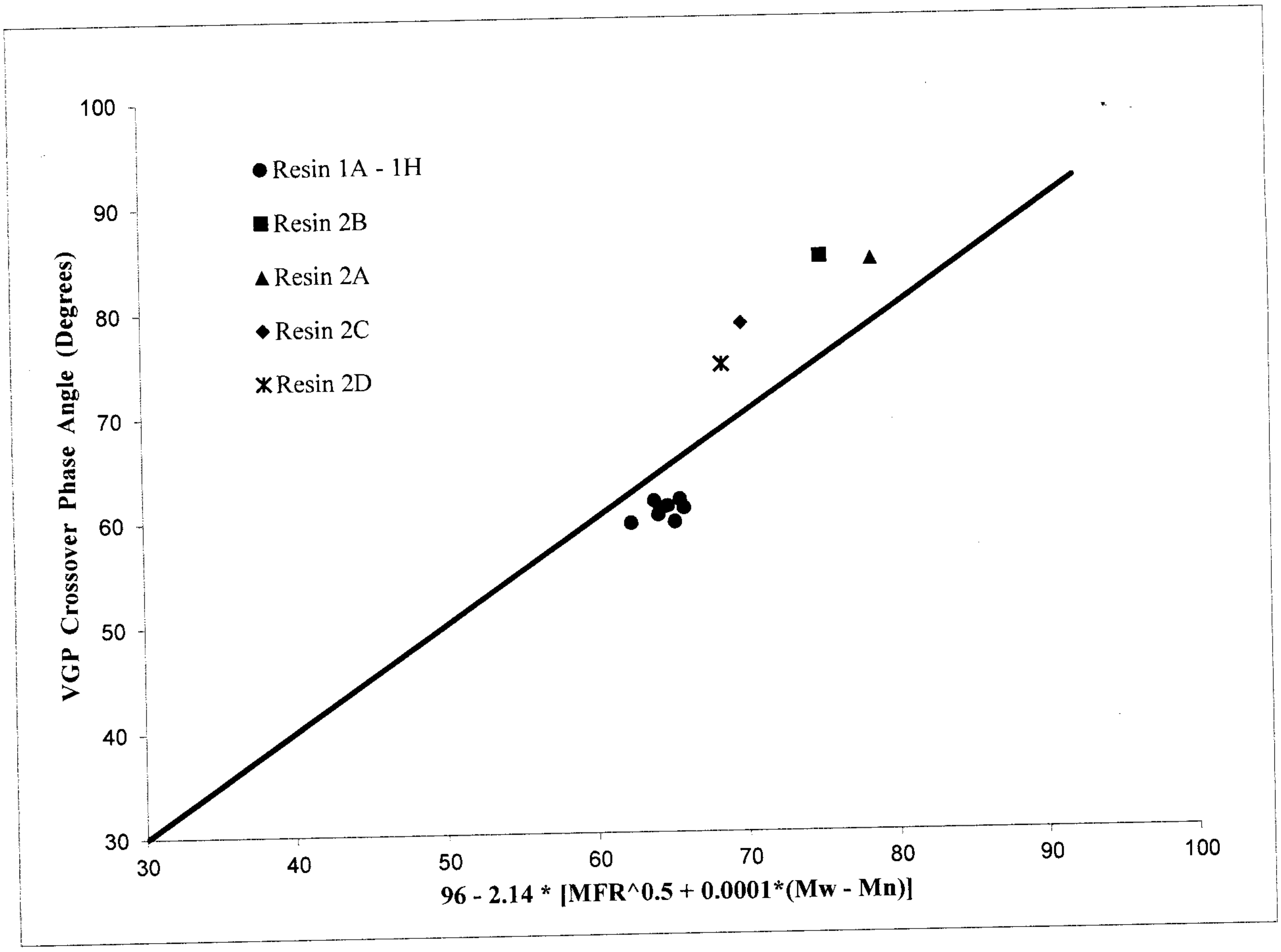

VGP Crossover Phase Angle (Degrees)
100
90
80
70
60
50
40
30
30
40
50
60
70
80
90
100
96 - 2.14 * [MFR^0.5 + 0.0001*(Mw - Mn)]
● Resin 1A - 1H
■ Resin 2B
▲ Resin 2A
◆ Resin 2C
✱ Resin 2D

FIGURE 6

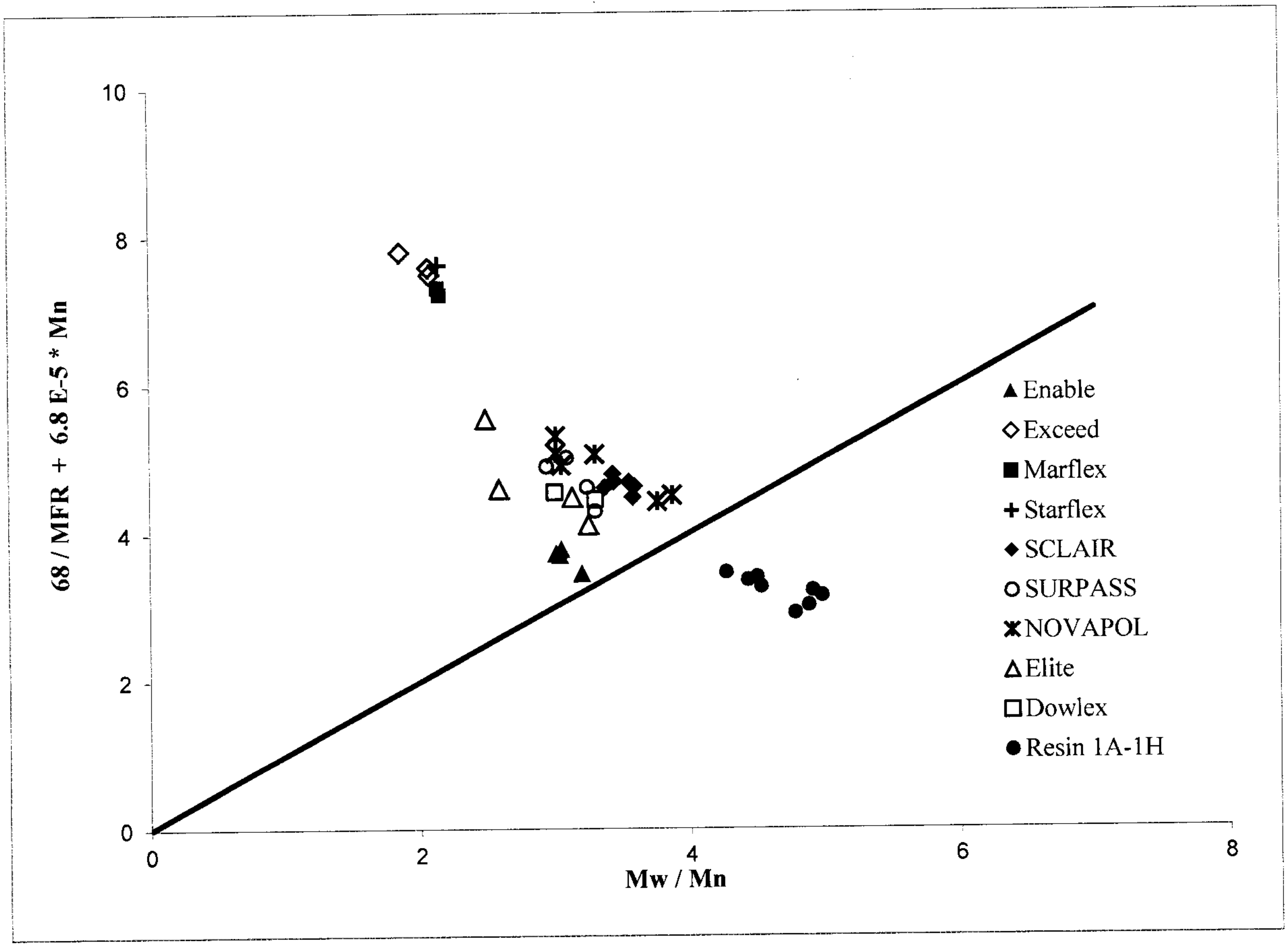

10
8
6
4
2
0
68 / MFR + 6.8 E-5 * Mn
0
2
4
6
8
Mw / Mn
▲ Enable
◇ Exceed
■ Marflex
+ Starflex
◆ SCLAIR
○ SURPASS
✱ NOVAPOL
△ Elite
□ Dowlex
● Resin 1A-1H

FIGURE 7

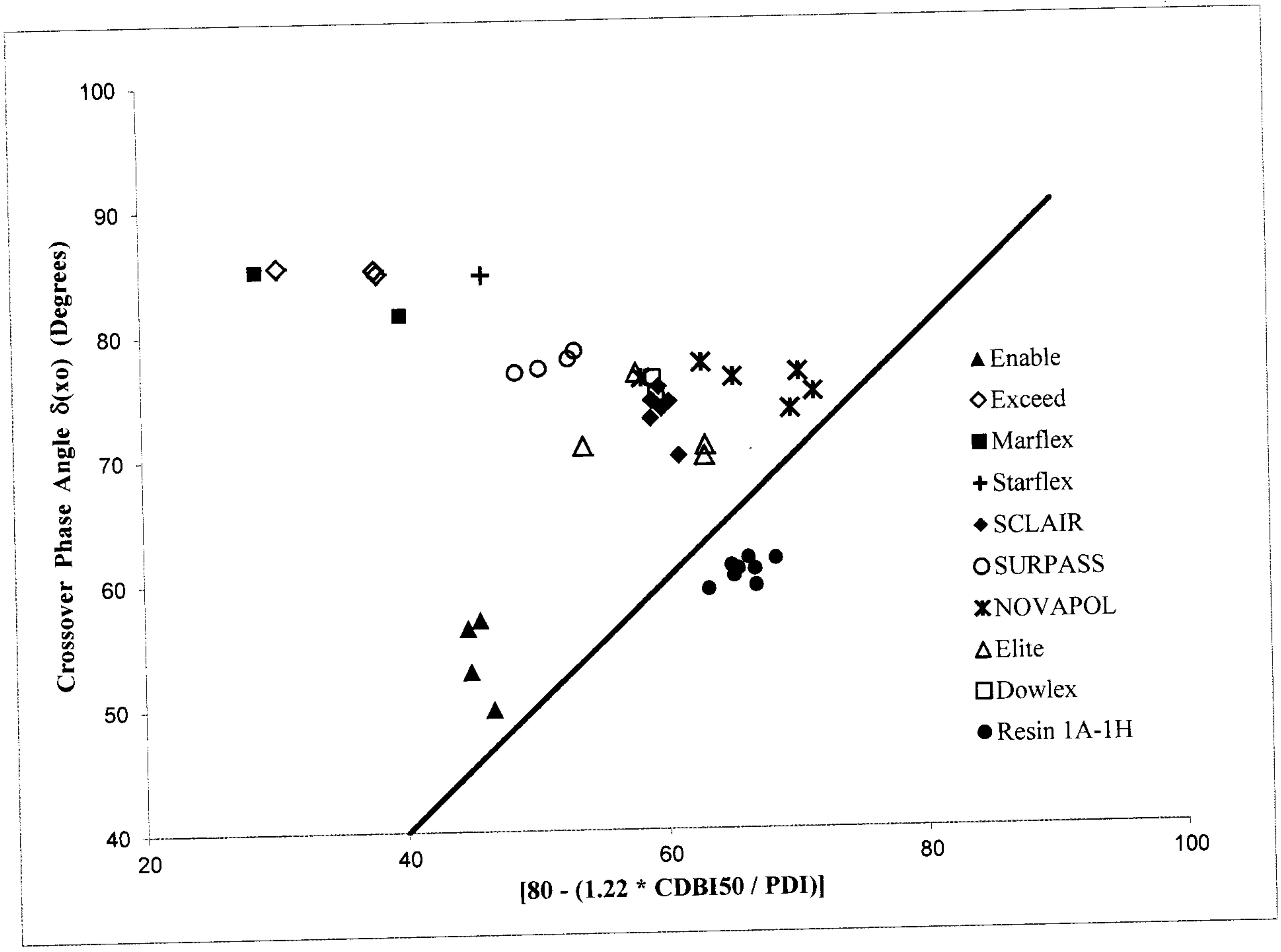

Crossover Phase Angle δ(xo) (Degrees)
100
90
80
70
60
50
40
20
40
60
80
100
[80 - (1.22 * CDBI50 / PDI)]
▲Enable
◇Exceed
■Marflex
+Starflex
◆SCLAIR
○SURPASS
✱NOVAPOL
△Elite
□Dowlex
●Resin 1A-1H

FIGURE 8

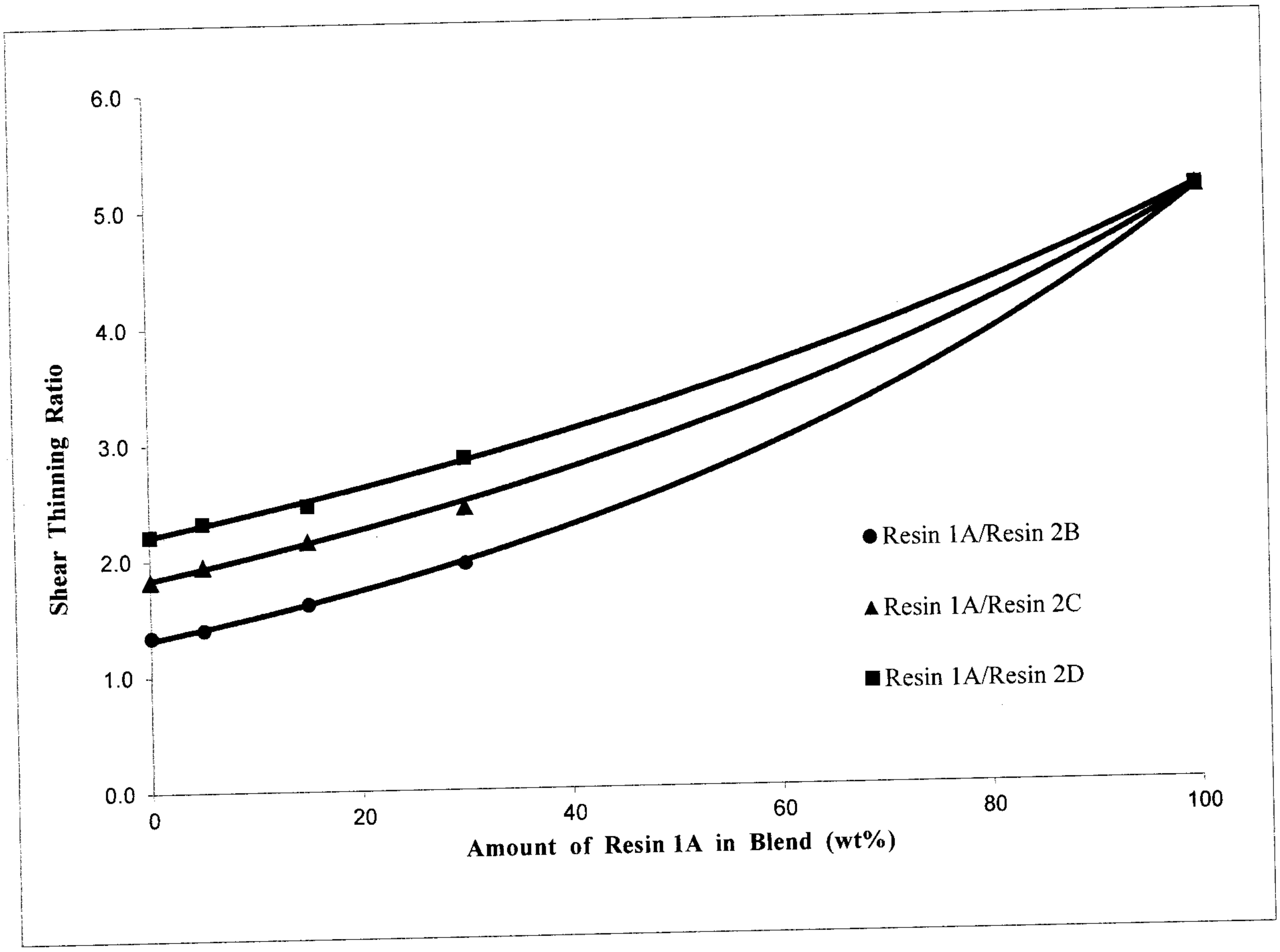
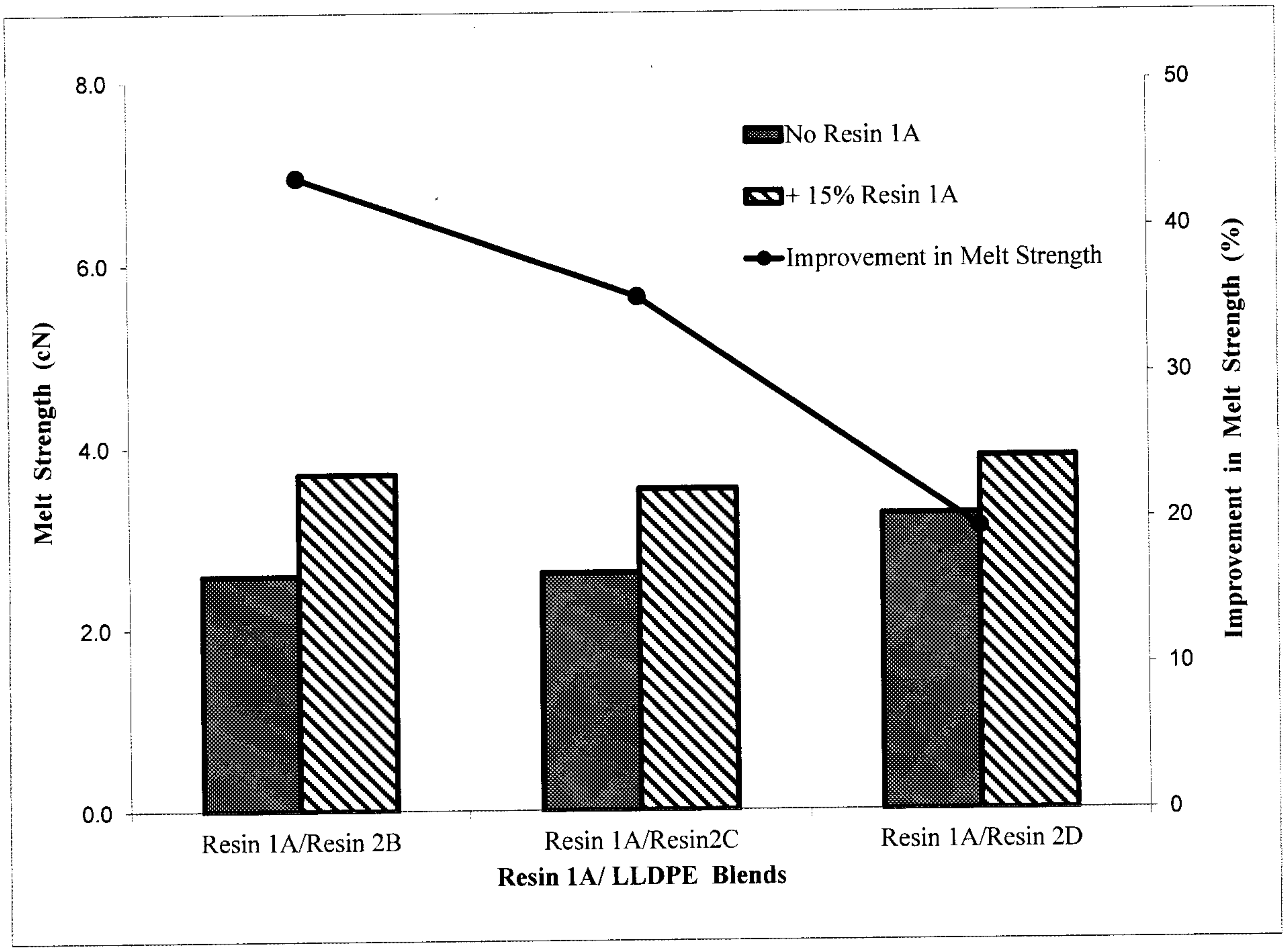

6.0
5.0
4.0
3.0
2.0
1.0
0.0
Shear Thinning Ratio
0
20
40
60
80
100
Amount of Resin 1A in Blend (wt%)
● Resin 1A/Resin 2B
▲ Resin 1A/Resin 2C
■ Resin 1A/Resin 2D

FIGURE 9


8.0
6.0
4.0
2.0
0.0
Melt Strength (cN)
50
40
30
20
10
0
Improvement in Melt Strength (%)
No Resin 1A
+ 15% Resin 1A
Improvement in Melt Strength
Resin 1A/Resin 2B
Resin 1A/Resin2C
Resin 1A/Resin 2D
Resin 1A/ LLDPE Blends