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(54) Title: DUAL REACTOR POLYETHYLENE RESINS WITH BALANCED PHYSICAL PROPERTIES

(57) Abstract: Bags, such as for trash, pet excrement and dry cleaning, but not for use in food contact or medical bags, having a good balance of dart impact strength, machine direction (MD) tear strength and transverse direction (TD) tear strength and puncture energy may be prepared from linear low density polyethylene having a melt flow ratio (I_2/I_1) from about 23 to 32, prepared in a tandem dual reactor solution phase polymerization in the presence of a phosphinimine catalyst and an aluminum based activator in the first reactor and an ionic activator in the second reactor.



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DUAL REACTOR POLYETHYLENE RESINS WITH BALANCED PHYSICAL PROPERTIES

TECHNICAL FIELD

The present invention relates to polyethylene bags. More particularly the present invention relates to polyethylene bags having a good balance of puncture resistance, dart impact strength, machine direction tear and transverse direction tear strengths.

BACKGROUND ART

Films made from resins and particularly polyethylene resins manufactured using metallocene catalysts have higher dart impact strengths than the films made using Ziegler Natta resins. However, such metallocene resins tend to have a number of drawbacks including their difficulty in conversion to finished products and the tendency for films made from these resins to split in the machine direction. It is desirable to produce a resin and particularly polyethylene having a good balance of properties and which is relatively easy to process or convert into finished products.

One approach has been to blend resins and particularly polyethylenes made using different types of catalyst such as a dry blend of a polyethylene made using a Ziegler Natta catalyst and a polyethylene made using a metallocene catalyst or a single site catalyst. However, dry blending resin typically requires at least one additional pass of the component resins together through an extruder to form pellets of the blended resin. This can be costly particularly when one of the resins is difficult to process (e.g. the resin produced using the metallocene catalyst).

An alternate approach to avoid dry blending is the use of mixed catalyst systems in a single reactor. For example, U.S. Patent No. 4,530,914 (Ewen et al., to Exxon) teaches the use of two different metallocenes in a single reactor, and U.S. Patent No. 4,701,432 (Welborn, to Exxon) teaches the use of a supported catalyst prepared with a

metallocene catalyst and a Ziegler Natta catalyst. Many others have subsequently attempted to use similar mixed catalyst systems as described in U.S. Patent Nos. 5,767,031; 5,594,078; 5,648,428; 4,659,685; 5,145,818; 5,395,810; and 5,614,456.

However, the use of "mixed" catalyst systems is generally associated with operability problems. For example, the use of two catalysts on a single support (as taught by Welborn in U.S. Patent No. 4,701,432) may be associated with a reduced degree of process control flexibility (e.g. if the polymerization reaction is not proceeding as desired when using such a catalyst system, then it is difficult to establish which corrective action should be taken as the corrective action will typically have a different effect on each of the two different catalyst components). Moreover, the two different catalyst/co-catalyst systems may interfere with one another - for example, the organoaluminum component, which is often used in Ziegler Natta or chromium catalyst systems, may "poison" a metallocene catalyst.

United States Patent 6,372,864 issued April 16, 2002 to Brown teaches a dual reactor solution process for preparing a polyethylene in the presence of a phosphinimine catalyst and different co-catalysts in the first and second reactors. It discloses that some of the resulting polymers have a good balance of properties. However, the patent does not expressly teach any specific end use applications. Nor does the patent teach that by controlling the melt flow ratio (i.e. the ratio of I_{21}/I_2) or selecting a resin having a melt flow ratio from 23 to 32, preferably from 25 to 30 for such a resin, there is a convergence in the maxima or a good balance in a number of physical properties such as dart impact strength, tear strength in the machine direction (MD) and the direction perpendicular to the machine direction (transverse direction - TD) tear and puncture resistance.

The present invention seeks to provide bags or sacks having a good balance of properties and which are relatively easy to manufacture or process.

DISCLOSURE OF INVENTION

The present invention provides a bag made from a linear low density polyethylene having a density from 0.914 to 0.935, preferably from 0.915 to 0.926 g/cm³ and a melt flow ratio (MFR = I_{21}/I_2) determined according to ASTM D 1238 from 23 to 32 prepared by A) polymerizing ethylene optionally with one or more C₃₋₁₂ alpha olefins, in solvent in a first stirred polymerization reactor at a temperature of from 80 to 200°C and a pressure of from 10,500 to 35,000 KPa, (1,500 to 5,000 psi) in the presence of (a) a catalyst which is an organometallic complex of a group 3, 4 or 5 metal, characterized by having at least one phosphinimine ligand; and (b) a co-catalyst which contains an aluminoxane; and B) passing said first polymer solution into a second stirred polymerization reactor at a pressure from 10,500 to 35,000 KPa (1,500 to 5,000 psi) and a temperature at least 20°C higher than the first reactor and polymerizing further ethylene, optionally with one or more C₃₋₁₂ alpha olefins, in said second stirred polymerization reactor in the presence of (a) a catalyst which is an organometallic complex of a group 3, 4 or 5 metal, characterized by having at least one phosphinimine ligand; and (b) a co-catalyst which contains an ionic activator; said polyethylene when formed into a film at a blowup ratio from 2.0 to 4.0 and a thickness from 0.5 to 6.0 mils using a blown film line equipped with internal bubble cooling at a production rate that is greater than 10 typically 10 to 30 lbs per hour per inch of die circumference, has a good balance of dart impact strength, MD tear strength, TD tear strength and puncture energy.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows the GPC profiles of the resins used in the experiments.

Figure 2 shows the processing characteristics of the resins used in the experiments.

Figure 3 shows the dart impact strengths of 0.75 mil films made from the resins used in the experiments at a blow up ratio of 2.5 and a production rate of 16 lbs/hr/inch (2.8 kg/hr/cm) of die circumference.

Figure 4 shows the machine direction (MD) tear strengths of 0.75 mil films made from the resins used in the experiments at a blow up ratio of 2.5 and a production rate of 16 lbs/hr/inch (2.8 kg/hr/cm) of die circumference.

Figure 5 shows the puncture energy of 0.75 mil films made from the resins used in the experiments at a blow up ratio of 2.5 and a production rate of 16 lbs/hr/inch (2.8 kg/hr/cm) of die circumference.

Figure 6 shows the dart impact strengths of 0.75 mil films made from three bimodal single site resins used in the experiments at the blow up ratios of 2.5 and 3.5 and the production rates of 12 lbs/hr/inch (2.1 kg/hr/cm) and 16 lbs/hr/inch (2.8 kg/hr/cm) of die circumference.

Figure 7 shows the MD tear strength of 0.75 mil films made from three bimodal single site resins used in the experiments at the blow up ratios of 2.5 and 3.5 and the production rates of 12 lbs/hr/inch (2.1 kg/hr/cm) and 16 lbs/hr/inch (2.8 kg/hr/cm) of die circumference.

Figure 8 shows the transverse direction (TD) tear strengths of 0.75 mil films made from three bimodal single site resins used in the experiments at the blow up ratios of 2.5 and 3.5 and the production rates of 12 lbs/hr/inch (2.1 kg/hr/cm) and 16 lbs/hr/inch (2.8 kg/hr/cm) of die circumference.

Figure 9 shows the effect of blow up ratio (BUR) and output rate on MD/TD tear ratio of 0.75 mil films made from three bimodal single site resins used in the experiments at the blow up ratios of 2.5 and 3.5 and the production rates of 12 lbs/hr/inch (2.1 kg/hr/cm) and 16 lbs/hr/inch (2.8 kg/hr/cm) of die circumference.

Figure 10 shows the effects of BUR and output rate on puncture energy of 0.75 mil films made from three bimodal single site resins used in the experiments at the blow up ratios of 2.5 and 3.5 and the production rates of 12 lbs/hr/inch (2.1 kg/hr/cm) and 16 lbs/hr/inch (2.8 kg/hr/cm) of die circumference.

BEST MODE FOR CARRYING OUT THE INVENTION

The polyethylene polymers or resins which may be used in accordance with the present invention typically comprise not less than 60, preferably not less than 70, most preferably not less than 80 weight % of ethylene and the balance of one or more C₃₋₈ alpha olefins, preferably selected from the group consisting of 1-butene, 1-hexene and 1-octene.

The polymers suitable for use in the present invention are generally prepared using a solution polymerization process. Solution processes for the (co)polymerization of ethylene are well known in the art. These processes are conducted in the presence of an inert hydrocarbon solvent typically a C₅₋₁₂ hydrocarbon which may be unsubstituted or substituted by a C₁₋₄ 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" (C₈₋₁₂ aliphatic solvent, Exxon Chemical Co.).

The solution polymerization process for preparing the polymers suitable for use in the present invention must use at least two polymerization reactors one of which should be in tandem to the other. The first polymerization reactor preferably operates at a lower temperature ("cold reactor") using a "phosphinimine catalyst" described below.

The polymerization temperature in the first reactor is from about 80°C to about 180°C (preferably from about 120°C to 160°C) and the second reactor or hot reactor is preferably operated at a higher temperature (up to about 220°C). Most preferably, the second polymerization reactor is operated at a temperature higher than the first reactor by at least 20°C, typically 30 to 80°C, generally 30 to 50°C. The most preferred reaction process is a "medium pressure process", meaning that the pressure in each reactor is preferably less than about 6,000 psi (about 42,000 kilopascals or kPa), most preferably from about 2,000 psi to 3,000 psi (about 14,000-21,000 kPa).

The monomers are dissolved/dispersed in the solvent either prior to being fed to the first or second reactor (or for gaseous monomers the

monomer may be fed to the reactor so that it will dissolve in the reaction mixture). Prior to mixing, the solvent and monomers are generally purified to remove potential catalyst poisons such as water, oxygen or metal impurities. The feedstock purification follows standard practices in the art, e.g. molecular sieves, alumina beds and oxygen removal catalysts are used for the purification of monomers. The solvent itself as well (e.g. methyl pentane, cyclohexane, hexane or toluene) is preferably treated in a similar manner.

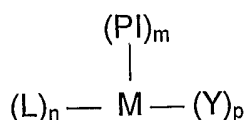
The feedstock may be heated or cooled prior to feeding to the first reactor. Additional monomers and solvent may be added to the second reactor, and it may be heated or cooled, preferably heated.

Generally, the catalyst components (i.e. the catalyst and co-catalyst) may be premixed in the solvent for the reaction or fed as separate streams to each reactor. In some instances of premixing it may be desirable to provide a reaction time for the catalyst components prior to entering the reaction. Such an "in line mixing" technique is described in a number of patents in the name of DuPont Canada Inc. (e.g. U.S. Patent No. 5,589,555, issued December 31, 1996).

The residence time in each reactor will depend on the design and the capacity of the reactor. Generally, the reactors should be operated under conditions to achieve a thorough mixing of the reactants. In addition, it is preferred that from 20 to 60 weight % of the final polymer is polymerized in the first reactor, with the balance being polymerized in the second reactor. On leaving the reactor system the solvent is removed and the resulting polymer is finished in a conventional manner.

In a highly preferred embodiment, the first polymerization reactor has a smaller volume than the second polymerization reactor.

The polymers useful in accordance with the present invention are prepared in the presence of a phosphinimine catalyst of the formula:



wherein M is a group 4 metal, preferably selected from the group Ti, Zr, and Hf, most preferably Ti; PI is a phosphinimine ligand; L is a monoanionic ligand selected from the group consisting of a cyclopentadienyl-type ligand; Y is an activatable ligand; m is 1 or 2; n is 0 or 1; and p is an integer and the sum of m+n+p equals the valence state of M.

The phosphinimine ligand has the formula $((\text{R}^{21})_3\text{P}=\text{N})-$ wherein each R^{21} is independently selected from the group consisting of C_{3-6} alkyl radicals. Preferably R^{21} is a t-butyl radical.

Preferably, L is a 5-membered carbon ring having delocalized bonding within the ring and bound to the metal atom through η^5 bonds and said ligand being unsubstituted or up to fully substituted with one or more substituents selected from the group consisting of C_{1-10} hydrocarbyl radicals which hydrocarbyl substituents are unsubstituted or further substituted by one or more substituents selected from the group consisting of a halogen atom and a C_{1-8} alkyl radical; a halogen atom; a C_{1-8} alkoxy radical; a C_{6-10} aryl or aryloxy radical; 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; silyl radicals of the formula $-\text{Si}-(\text{R})_3$ wherein each R is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, and C_{6-10} aryl or aryloxy radicals; and germanyl radicals of the formula $\text{Ge}-(\text{R})_3$ wherein R is as defined above. Most preferably, the cyclopentadienyl type ligand is selected from the group consisting of a cyclopentadienyl radical, an indenyl radical and a fluorenyl radical.

Y is selected from the group consisting of a hydrogen atom; a halogen atom, a C_{1-10} hydrocarbyl radical; a C_{1-10} alkoxy radical; a C_{5-10} aryl oxide radical; each of which said hydrocarbyl, alkoxy, and aryl oxide radicals may be unsubstituted or further substituted by one or more

substituents selected from the group consisting of a halogen atom; a C₁₋₈ alkyl radical; a C₁₋₈ alkoxy radical; a C₆₋₁₀ aryl or aryloxy radical; an amido radical which is unsubstituted or substituted by up to two C₁₋₈ alkyl radicals; and a phosphido radical which is unsubstituted or substituted by up to two C₁₋₈ alkyl radicals. Most preferably, Y is selected from the group consisting of a hydrogen atom, a chlorine atom and a C₁₋₄ alkyl radical.

The catalysts used to make the polymers useful in the present invention are activated with different activators.

In the first reactor (e.g. the cold reactor) the co-catalyst comprises an aluminoxane compound of the formula $R^{12}_2AlO(R^{12}AlO)_mAlR^{12}_2$ wherein each R^{12} is independently selected from the group consisting of C₁₋₂₀ hydrocarbyl radicals and m is from 3 to 50, and optionally a hindered phenol to provide a molar ratio of Al:hindered phenol from 2:1 to 5:1 if the hindered phenol is present. The catalyst in the cold reactor may also comprise an ionic activator as described below but it should form a lesser amount of the catalyst typically less than 40 weight %, preferably less than 20, most preferably less than 10 weight % of the catalyst.

In the second reactor (e.g. the hot reactor) the activator comprises an ionic activator. The ionic activator may be selected from the group consisting of:

(A) compounds of the formula $[R^{13}]^+ [B(R^{14})_4]^-$ wherein B is a boron atom, R^{13} is a cyclic C₅₋₇ aromatic cation or a triphenyl methyl cation and each R^{14} is independently selected from the group consisting of phenyl radicals which are unsubstituted or substituted with 3 to 5 substituents selected from the group consisting of a fluorine atom, a C₁₋₄ alkyl or alkoxy radical which is unsubstituted or substituted by a fluorine atom; and a silyl radical of the formula $-Si-(R^{15})_3$; wherein each R^{15} is independently selected from the group consisting of a hydrogen atom and a C₁₋₄ alkyl radical; and

(B) compounds of the formula $[(R^{18})_t ZH]^+ [B(R^{14})_4]^-$ 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^{18} is selected from the group consisting of C₁₋₈ alkyl

radicals, a phenyl radical which is unsubstituted or substituted by up to three C₁₋₄ alkyl radicals, or one R¹⁸ taken together with the nitrogen atom may form an anilinium radical and R¹⁴ is as defined above; and

(C) compounds of the formula B(R¹⁴)₃ wherein R¹⁴ is as defined above. The catalyst in the hot reactor may also comprise the aluminum catalyst noted above typically in an amount of less than 40 weight %, preferably less than 20, most preferably less than 10 weight % of the catalyst.

The residence time in each reactor will depend on the design and the capacity of the reactor. Generally the reactors should be operated under conditions to achieve a thorough mixing of the reactants. In addition, it is preferred that from 20 to 60 weight % of the final polymer is polymerized in the first reactor, with the balance being polymerized in the second reactor. On leaving the reactor system the solvent is removed and the resulting polymer is finished in a conventional manner.

In a highly preferred embodiment, the first polymerization reactor has a smaller volume than the second polymerization reactor. In addition, the first polymerization reactor is preferably operated at a colder temperature than the second reactor.

Following polymerization (i.e. on leaving the second reactor) the resulting polymer solution is passed through a flasher to flash the solvent. The resulting melt is pelletized and further steam stripped to remove residual solvent and monomers. In accordance with the present invention the polymer should have a melt index (i.e. I₂) less than 2, preferably less than 1, most preferably from 0.4 to 0.9 g/10 minutes as measured according to ASTM D 1238.

The resulting resin may be compounded with typical amounts of antioxidants and heat and light stabilizers such as combinations of hindered phenols and one or more of phosphates, phosphites and phosphonites typically in amounts of less than 0.5 weight % based on the weight of the resin. The resin may also be compounded with process aids, slip aids, and anti-blocking agents in conventional amounts.

The resulting resin may then be converted to blown film. Typically the resin is extruded as a melt and passed through an annular die and is biaxially stretched (e.g. is expanded in the transverse direction by compressed air within the extrudate having a circular cross section and is stretched in the machine direction by increasing the speed of the take off line). The blow up ratio (BUR – how much the diameter of the extrudate is increased in comparison to the die diameter) may be from about 2 to about 4, typically from 2.5 to 3.5. The resins of the present invention have good bubble stability and are largely machine independent in processing. That is the particular machines upon which the resin is processed do not have to be operated significantly different from the conditions using other resins.

The annular extrudate may be slit and collapsed to form a monolayer film. The resulting film typically has a thickness from about 0.5 to 6 mils, preferably from 0.75 to 3.0, most preferably from about 0.80 to 2.0 mils. The resulting film may be converted to bags such as trash bags, animal excrement bags (e.g. pooper scoopers – an application where puncture and split resistance is highly valued), dry cleaning bags and similar non-food applications.

The present invention will now be illustrated by the following non limiting examples.

Three different ethylene octene bimodal single site LLDPE resins (Resins C, D and E) were made using a titanium complex of titanium one cyclopentadienyl ligand, one tritertiary butyl phosphinimine ligand and two chlorine atoms ($\text{CpTiNP}(\text{t-Bu})_3\text{Cl}_2$) prepared according to the procedures disclosed in *Organometallic* 1999,18,1116-1118. The co-catalyst in the first reactor was methylalumoxane purchased from Akzo-Nobel under the trade name MMAO-7[®] and the activator in the second reactor was triphenylcarbenium tetrafluorophenyl borate. Dual tandem reactors were used to make the polymer according to the teachings of U.S. Patent No. 6,372,864 B1 (Resins C, D and E). All three resins had essentially similar MI and density, but differed in terms of MWD (molecular weight distribution, M_w/M_n) and, therefore, melt flow ratio (I_{21}/I_2). Two

commercial LLDPE resins one made using Z-N catalyst in an ethylene - hexene gas phase process (Resin A) and one made using a Z-N catalyst in an ethylene - octene solution phase process (Resin B) were selected for comparison. Resins A and B had similar melt index and density to resins C, D and E. Table 1 shows the physical characteristics of all the samples used in this study.

Molecular Weight and Co-monomer Distributions

The average molecular weights and the MWDs were determined using a Waters Model 150 Gel Permeation Chromatography (GPC) apparatus equipped with a differential refractive index detector. The co-monomer distribution of the resins was determined through GPC-FTIR. All of the resins, A to E, exhibited normal co-monomer distributions, i.e., the amount of co-monomer incorporated in polymer chains decreased as molecular weight increased.

TABLE 1
Characteristics of Polyethylene Samples

Resin	Melt Index I_2	Density kg/m^3	MFR (I_2/I_1)	Polydispersity	Catalyst Type
A	0.50	918	27.7	3.3	Z-N
B	0.50	918	31.1	3.3	Z-N
C	0.65	918	22.9	2.4	Single site
D	0.65	918	28.8	2.8	Single site
E	0.65	918	35.5	3.8	Single site

Film Extrusion

The selected resins were extruded into 0.75 mil (19.05 micron) and 1.25 mil (31.75 micron) monolayer films at two different blow up ratios (BUR) using a 3.5-inch industrial size Macro Blown Film Line with an 8-inch die. The Macro line consisted of a general-purpose 88.9 mm (3.5 inch) barrier flight screw having L/D = 30 and a mixing head. The die outer diameter was 203.2 mm (8 inch) with a dual lip air ring and internal bubble cooling (IBC). The die had a 6-port spiral mandrel with inner bore heating and was designed for IBC. The resins were extruded at two different output rates, 12 lbs/hr/inch (2.1 kg/hr/cm) and 16 lbs/hr/inch (2.8 kg/hr/cm)

of die circumference and it was ensured that the films were free of melt fracture. A constant frost line height was maintained irrespective of changes in BUR and film gauge. The films were conditioned for a minimum of 48 hours under controlled environmental conditions before measuring dart impact and tear strengths. ASTM procedure D 1709-01 Method A was used for the measurements of the dart impact strength using a phenolic dart head. ASTM D 1922-03a procedure was used to measure the Elmendorf tear strengths of the films. The puncture resistance was measured using an in-house NOVA Chemicals procedure. In this procedure, the energy required to puncture a polyethylene film is measured using a $\frac{3}{4}$ inch diameter round faced probe at a 20-inch/minute-puncture rate.

A Rosand capillary rheometer with tensile module attachment was used for the measurement of melt strength for all the samples.

Figure 1 shows the GPC profiles for Resins A to E. Resins A and B show the expected unimodal MWDs. Resins C, D and E showed different MWDs depending on the molecular weight and amount of polymer produced in each reactor. The MWDs of resins C, D and E are consistent with their polydispersity and MFR measurements as shown in Table 1.

Figure 2 depicts the processing characteristics of Resins A to E. As expected, the extrusion pressure for Resins C, D and E decreases as the polydispersity or the MFR increases. The extrusion pressure for Resins A and B is also consistent with their MFR values. Resin E showed the lowest extrusion pressure and extruder current, and provided the highest specific power (kg/hr/amp) among all, due to its higher MFR and lower viscosity. The extrusion melt temperatures of resins C, D and E were found to be 5 to 8°C lower than resins A and B. This drop in melt temperature provided equivalent bubble stability for resins C, D, and E compared to resins A and B, even though Resins C, D, and E had slightly lower melt strength (4 versus 5 cN for Resins A and B at equivalent temperature of 190°C).

Figure 3 shows the Dart Impact Strengths of the 0.75 mil films made at 2.5 BUR and 16 lbs/hr/inch (2.8 kg/hr/cm) of die circumference output rate for all the resins. It is seen from this figure that the broadest MWD (MFR = 35.5) bimodal Resin E, provides similar Dart Impact values as obtained with the two Z-N catalyzed Resins A and B. However, when the MWD of the single site catalyzed bimodal LLDPE resins was narrowed, the Dart Impact Strength substantially increased with the peak value achieved for Resin D with MFR value of 28.8. It is interesting to note that at essentially similar MFR values, the bimodal Resin D provided Dart Impact Strength that was more than double the value achieved for the Z-N catalyzed Resins A and B.

Figure 4 depicts the Machine Direction (MD) Tear Strengths for the same film samples. The single site catalyzed bimodal LLDPE Resins C, D and E all showed higher MD Tear Strengths compared to the Z-N catalyzed unimodal Resins A and B. Furthermore, the MD Tear strength peaked for sLLDPE Resin D with MFR value of 28.8, that also showed highest Dart Impact Strength among all resins.

Figure 5 illustrates a comparison of Puncture Energy required to break the films for all the resins. The films of single site catalyzed bimodal LLDPE C, D and E showed significantly higher values of Puncture Energy required as compared to the Z-N catalyzed resin (A and B) film samples. For bimodal LLDPE films the Puncture Energy appeared to be relatively insensitive to MWD of the resins. Essentially similar trends in Dart Impact and MD Tear Strengths and Puncture Energy were obtained for the 1.25 mil films blown at 2.5 BUR and 16 lbs/hr/inch (2.8 kg/hr/cm) of die circumference output rate. These results show that the single site catalyzed bimodal LLDPE resins can provide superior film physical properties and excellent processing characteristics at the same time compared to the Z-N catalyzed resins processed under similar conditions (BUR and output rate). This should allow the film processors to achieve significantly higher film performance with single site catalyzed bimodal LLDPE resins. Alternatively, it may be possible to down gage the film

thickness with single site bimodal LLDPE resins and achieve similar film properties as realized with the conventional Z-N catalyzed resins.

Figure 6 shows the Dart Impact Strengths of films at two different BURs and output rates as a function of MFR of different resins (C, D and E). For films made at 2.5 BUR, it appears that high values of Dart Impact Strength are achieved when the MFR of the resin is between 25 and 30 and these values are essentially independent of the extruder output rates. At 3.5 BUR, however, high values of Dart Impact Strength are achieved with the single site LLDPE resins (C, D and E) irrespective of their MWD (in the MFR range of 22.8 to 35.5 that was examined in this study). Furthermore, at 3.5 BUR, a slight decrease in Dart Impact Strength was seen as extruder output was increased from 12 lbs/hr/inch (2.1 kg/hr/cm) to 16 lbs/hr/inch (2.8 kg/hr/cm) of die circumference. These results indicate that the molecular orientation and, perhaps more importantly, the resulting morphology (crystallite number, size and its orientation) play important roles in determining the Dart Impact Strength of films made with different MWD resins under different processing conditions.

Figure 7 illustrates the effect of BUR and extruder output rates on the MD Tear Strength of the 0.75-mil films made with single site LLDPE resins (C, D and E) having different MFR values. At 2.5 BUR, it appears that Resin D with MFR value of 28.8 gives the maximum value of MD Tear Strength. At 3.5 BUR, however, MD Tear Strength increases with an increase in resin MFR. In all cases, MD Tear Strength of films increased with an increase in extruder output rate. This result is somewhat surprising and opposite in relation to the observations generally made with the conventional Z-N catalyzed resins (and with LLDPE/LDPE blends) where an increase in output rates is thought to impart higher molecular orientation thus reducing machine direction tear strength. It implies that single site catalyzed, bimodal LLDPE resins (C, D and E) exhibit very different film morphology than the films made with the conventional Z-N catalyzed resins, and, therefore, previous understanding of the role of molecular orientation on film physical properties needs to be re-examined

in relation to the unique film morphological attributes in bimodal single site catalyzed LLDPE resins.

Figure 8 depicts the effects of BUR and output rates on the Transverse Direction (TD) Tear Strength for various single site catalyzed LLDPE resins (C, D and E). This figure shows that the TD Tear Strength of films of bimodal single site catalyzed LLDPE increases with an increase in resin MFR and extruder output rates. Furthermore, TD Tear Strength also increases with a decrease in BUR. Higher molecular orientation under these conditions is believed to increase TD Tear Strengths in these films.

Figure 9 provides the MD/TD Tear Ratios for the 0.75-mil films made under different BURs and output rates using various bimodal single site catalyzed LLDPE resins having different MFR values. MD/TD Tear Ratio of 1.0 indicates a good balance of tear strength in both directions. This figure shows that Resin D having MFR of 28.8 provides a very good balance of Tear Strengths (within $\pm 10\%$) in both directions and the MD/TD Tear ratio is relatively insensitive to the processing conditions (BUR and output rates). From a film processor's viewpoint, this is a very good feature to have, since it eliminates the line-to-line dependency on film tear balance. Whereas, for resins C and E having lower and higher MFR values than Resin D, the line conditions would need to be optimized to achieve a better balance in tear properties.

Figure 10 shows the Puncture Energy required to break the films made under different processing conditions using various single site catalyzed bimodal LLDPE resins (C, D and E). The processing conditions (BUR and output rate) seem to have little influence on Puncture Energy of film for a particular resin. Resin C with the lowest MFR appear to provide slightly higher values of Puncture Energy under all processing conditions that were used here.

The results show that the bimodal single site catalyzed LLDPE resins (C, D and E) exhibit superior film physical properties and excellent resin processability compared to comparable films made using

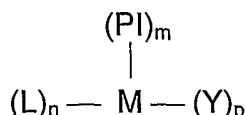
conventional Z-N catalyzed resins (A and B). The bimodal single site catalyzed LLDPE resins having a MFR between 23 and 32, preferably between 25 and 30 provide high Dart Impact Strength, MD Tear Strength and balanced tear strengths in both the MD and TD directions. Furthermore, the film properties are found to be relatively insensitive to processing conditions.

INDUSTRIAL APPLICABILITY

The present invention provides bags of line low-density polyethylenes adding improved puncture and impact resistance.

CLAIMS

1. A bag made from a linear low density polyethylene having a density from 0.914 to 0.935 g/cm³ and a melt flow ratio (MFR (I_{21}/I_2)) determined according to ASTM D 1238 from 23 to 32 prepared by A) polymerizing ethylene optionally with one or more C₃₋₁₂ alpha olefins, in solvent in a first stirred polymerization reactor at a temperature of from 80 to 200°C and a pressure of from 10,500 to 35,000 KPa, (1,500 to 5,000 psi) in the presence of (a) a catalyst which is an organometallic complex of a group 3, 4 or 5 metal, characterized by having at least one phosphinimine ligand; and (b) a cocatalyst which contains an alumoxane; and B) passing said first polymer solution into a second stirred polymerization reactor at a pressure from 10,500 to 35,000 KPa (1,500 to 5,000 psi) and a temperature at least 20°C higher than the first reactor and polymerizing further ethylene, optionally with one or more C₃₋₁₂ alpha olefins, in said second stirred polymerization reactor in the presence of (a) a catalyst which is an organometallic complex of a group 3, 4 or 5 metal, characterized by having at least one phosphinimine ligand; and (b) a co-catalyst which contains an ionic activator; said polyethylene, having a melt index less than 2 as measured by ASTM D 1238, when formed into a film at a blowup ratio from 2 to 4 and a thickness from 0.5 to 6 mils using a blown film line equipped with internal bubble cooling at a production rate that is greater than 10 lbs/hr/inch (1.7 kg/hr/cm) of die circumference has a good balance of dart impact strength, machine direction (MD) tear strength and transverse direction (TD) tear strength and puncture energy.
2. A bag according to claim 1, wherein said polyethylene is polymerized in the presence of a catalyst of the formula:



wherein M is a group 4 metal; PI is a phosphinimine ligand; L is a monoanionic ligand selected from the group consisting of a cyclopentadienyl-type ligand; Y is an activatable ligand; m is 1 or 2; n is 0

or 1; and p is an integer and the sum of m+n+p equals the valence state of M.

3. A bag according to claim 2, wherein said resin is polymerized in said first reactor in the presence of a co-catalyst comprising a complex aluminum compound of the formula $R^{12}_2AlO(R^{12}AlO)_mAlR^{12}_2$ wherein each R^{12} is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and m is from 3 to 50, and optionally a hindered phenol to provide a molar ratio of Al:hindered phenol from 2:1 to 5:1 if the hindered phenol is present.

4. A bag according to claim 3, wherein said resin is polymerized in said second reactor in the presence of a co-catalyst comprising an ionic activator selected from the group consisting of:

(A) compounds of the formula $[R^{13}]^+ [B(R^{14})_4]^-$ wherein B is a boron atom, R^{13} is a cyclic C_{5-7} aromatic cation or a triphenyl methyl cation and each R^{14} is independently selected from the group consisting of phenyl radicals which are unsubstituted or substituted with 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 $-Si-(R^{15})_3$; wherein each R^{15} is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical; and

(B) compounds of the formula $[(R^{18})_t ZH]^+ [B(R^{14})_4]^-$ 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^{18} 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^{18} taken together with the nitrogen atom may form an anilinium radical and R^{14} is as defined above; and

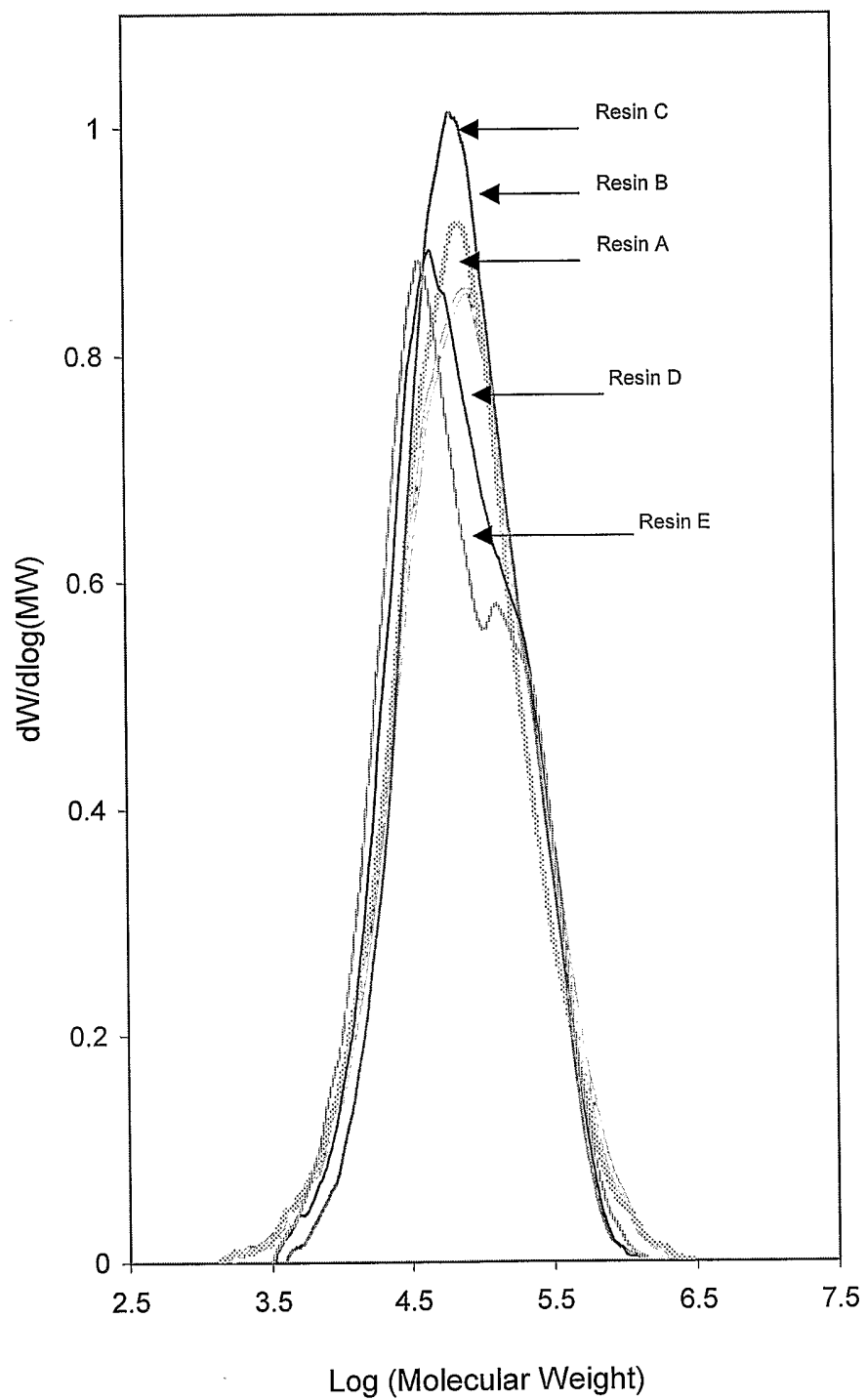
(C) compounds of the formula $B(R^{14})_3$ wherein R^{14} is as defined above.

5. The bag according to claim 4, wherein the second reactor is 30 to 80°C hotter than the first reactor.

6. The bag according to claim 5, wherein in the catalyst the cyclopentadienyl ligand is selected from the group consisting of a cyclopentadienyl radical, an indenyl radical and a fluorenyl radical.
7. The bag according to claim 6, wherein in the catalyst the phosphinimine ligand has the formula $((R^{21})_3P=N)$ — wherein each R^{21} is independently selected from the group consisting of C_{3-6} alkyl radicals.
8. The bag according to claim 7, wherein in the catalyst Y is selected from the group consisting of a hydrogen atom, a chlorine atom and a C_{1-4} alkyl radical.
9. The bag according to claim 8, wherein the polyethylene has a melt flow ratio (MFR (I_{21}/I_2)) as determined according to ASTM D 1238 from 25 to 30.
10. The bag according to claim 9, wherein the polyethylene when formed into a film at a blowup ratio from 2.5 to 3.5 and a thickness from 0.75 to 3 mils at a production rate from 10 lbs/hr/inch (1.7 kg/hr/cm) to 30 lbs/hr/inch (5.3 kg/hr/cm) of die circumference has a good balance of dart impact strength, MD tear strength, TD tear strength and puncture energy.
11. A bag according to claim 10, which is a trash bag.
12. A bag according to claim 10, which is a dry cleaning bag.
13. A bag according to claim 10, which is a pet excrement bag.

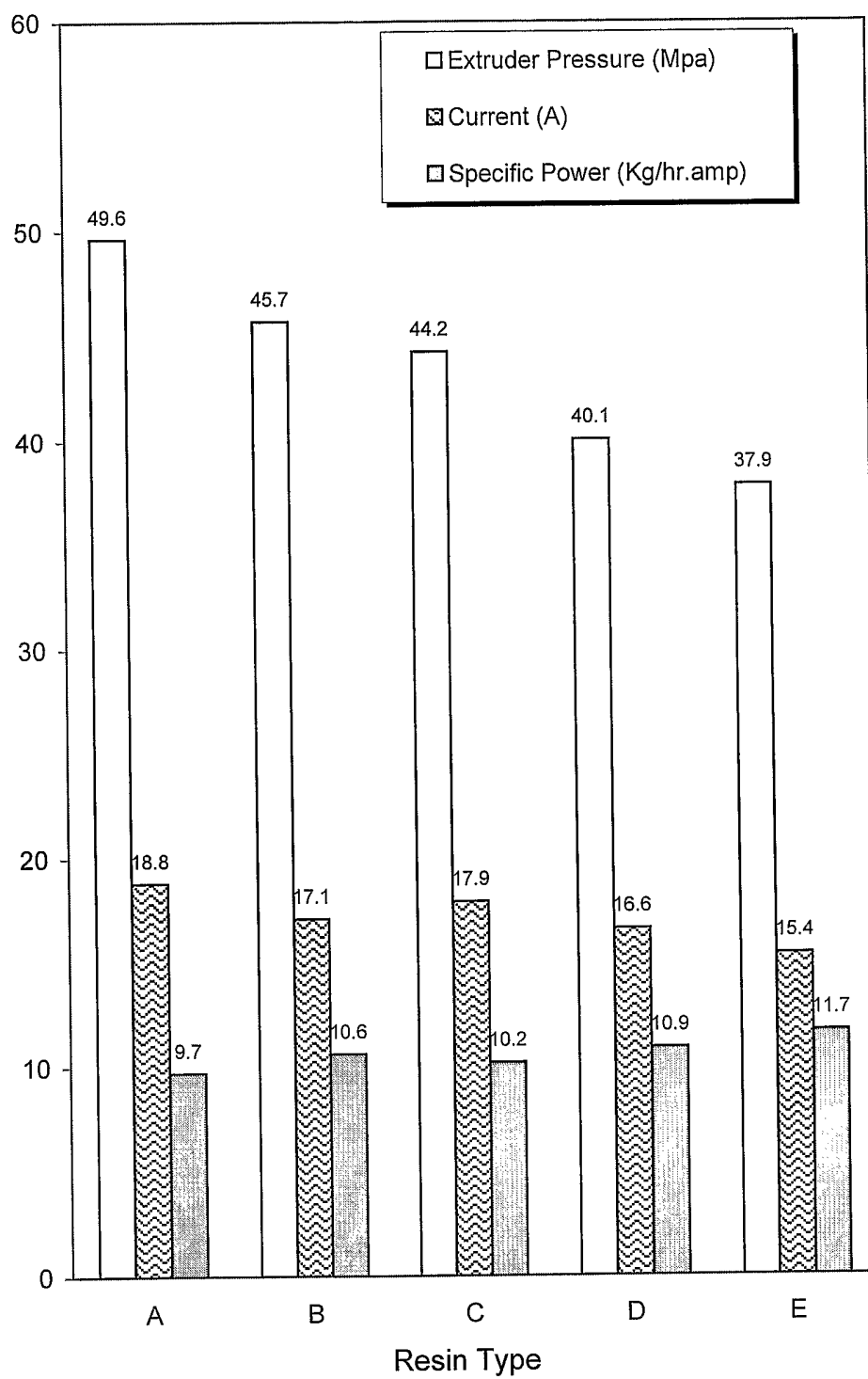
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Figure 1



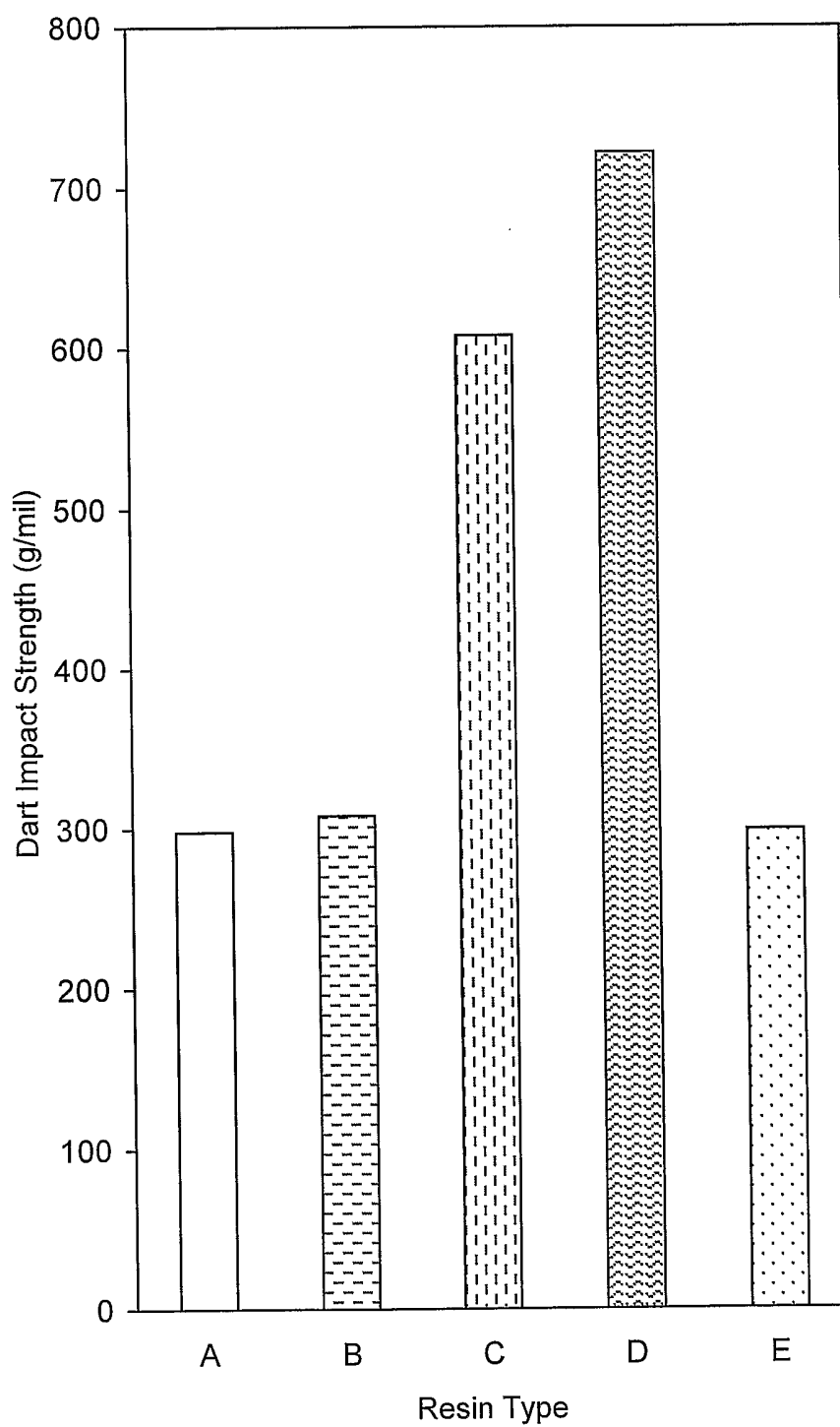
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Figure 2



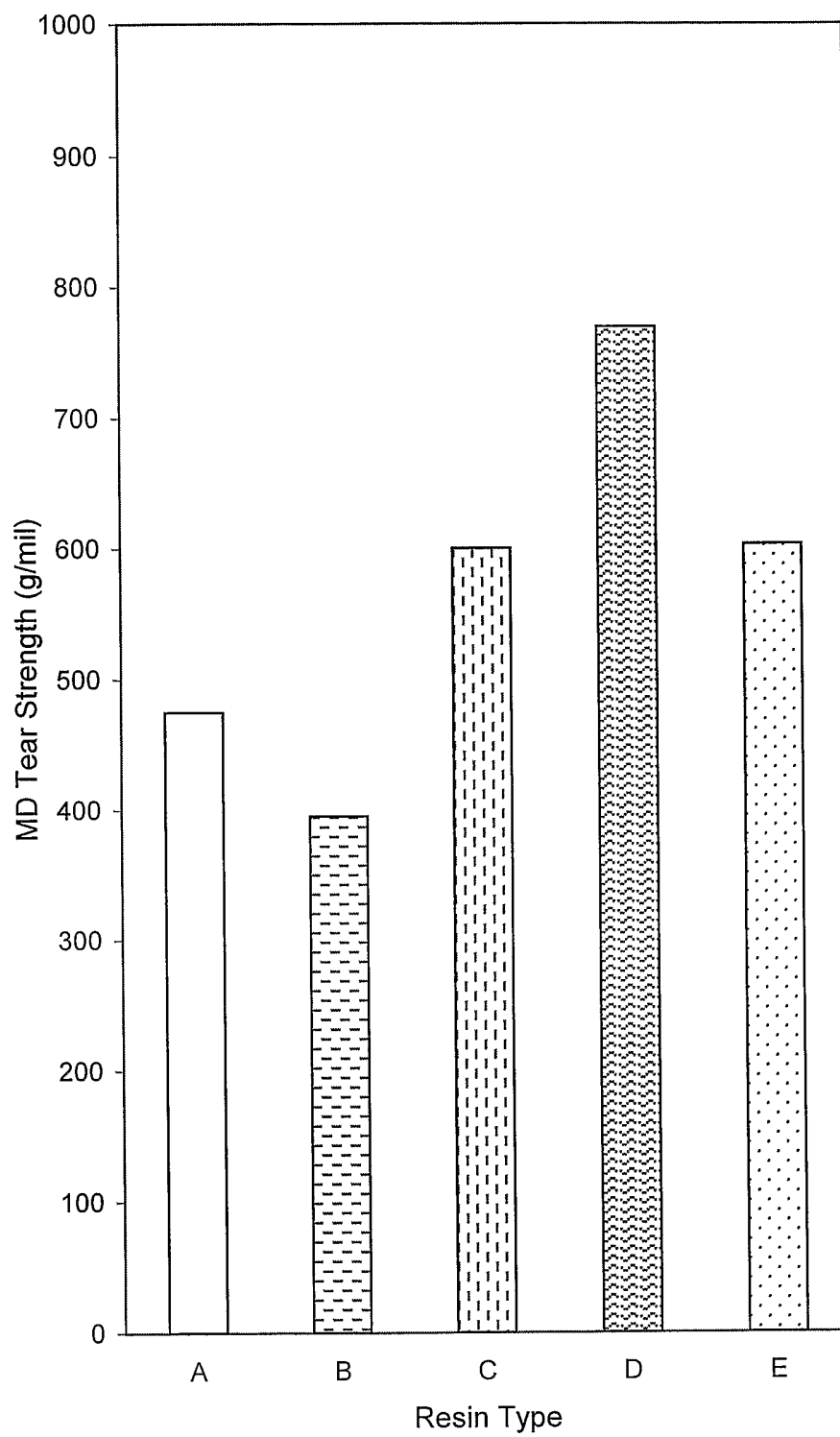
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Figure 3



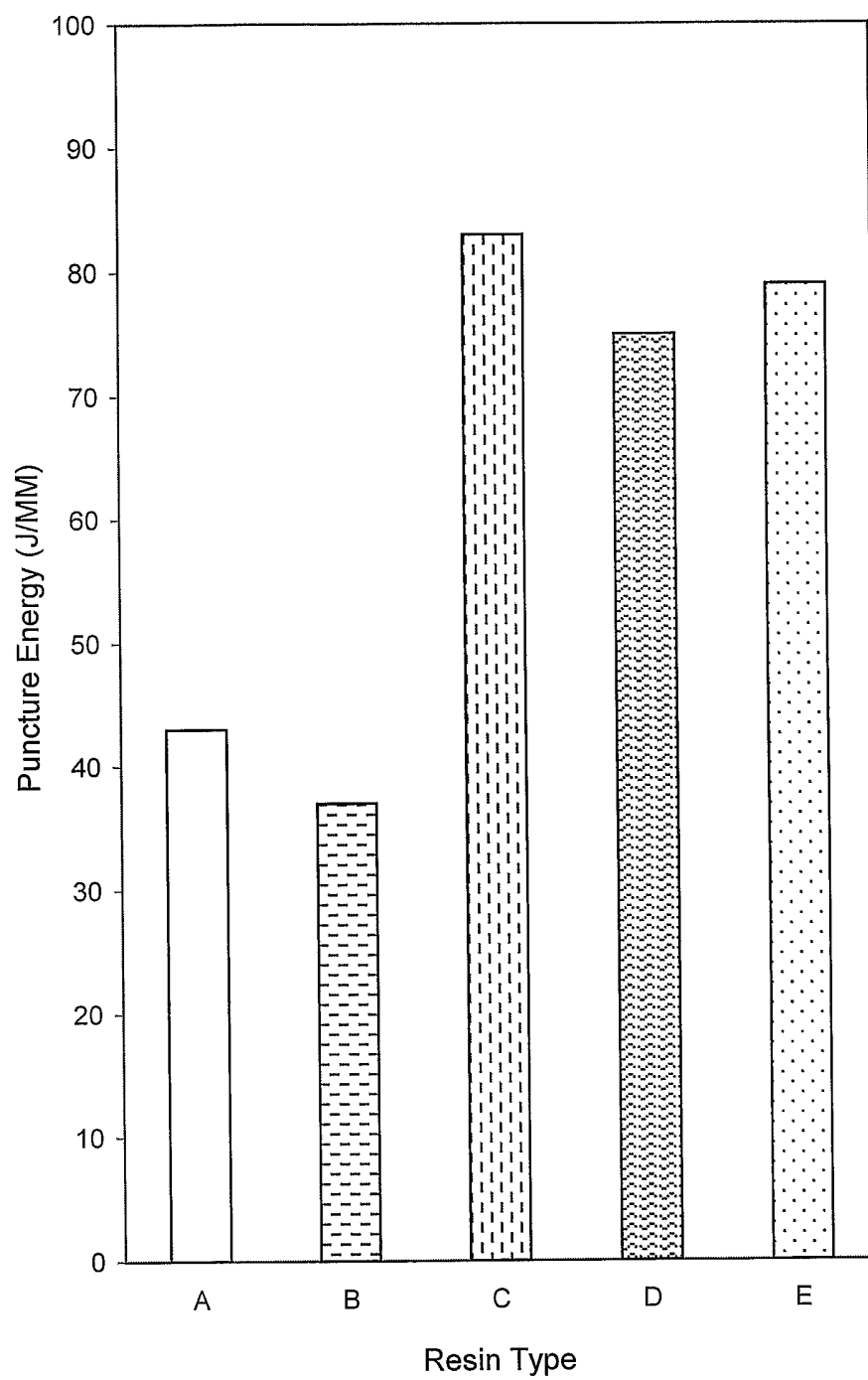
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Figure 4



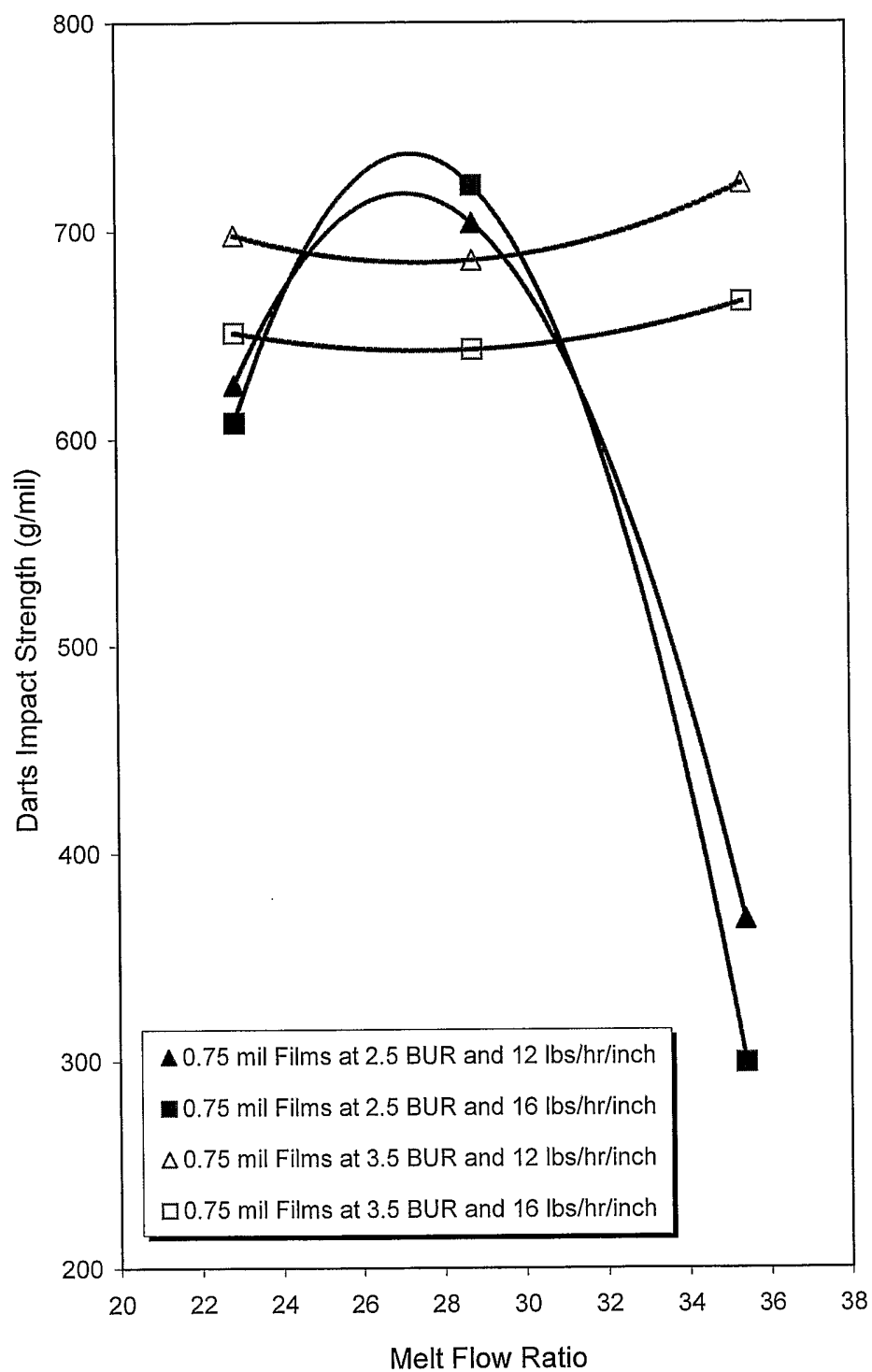
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Figure 5



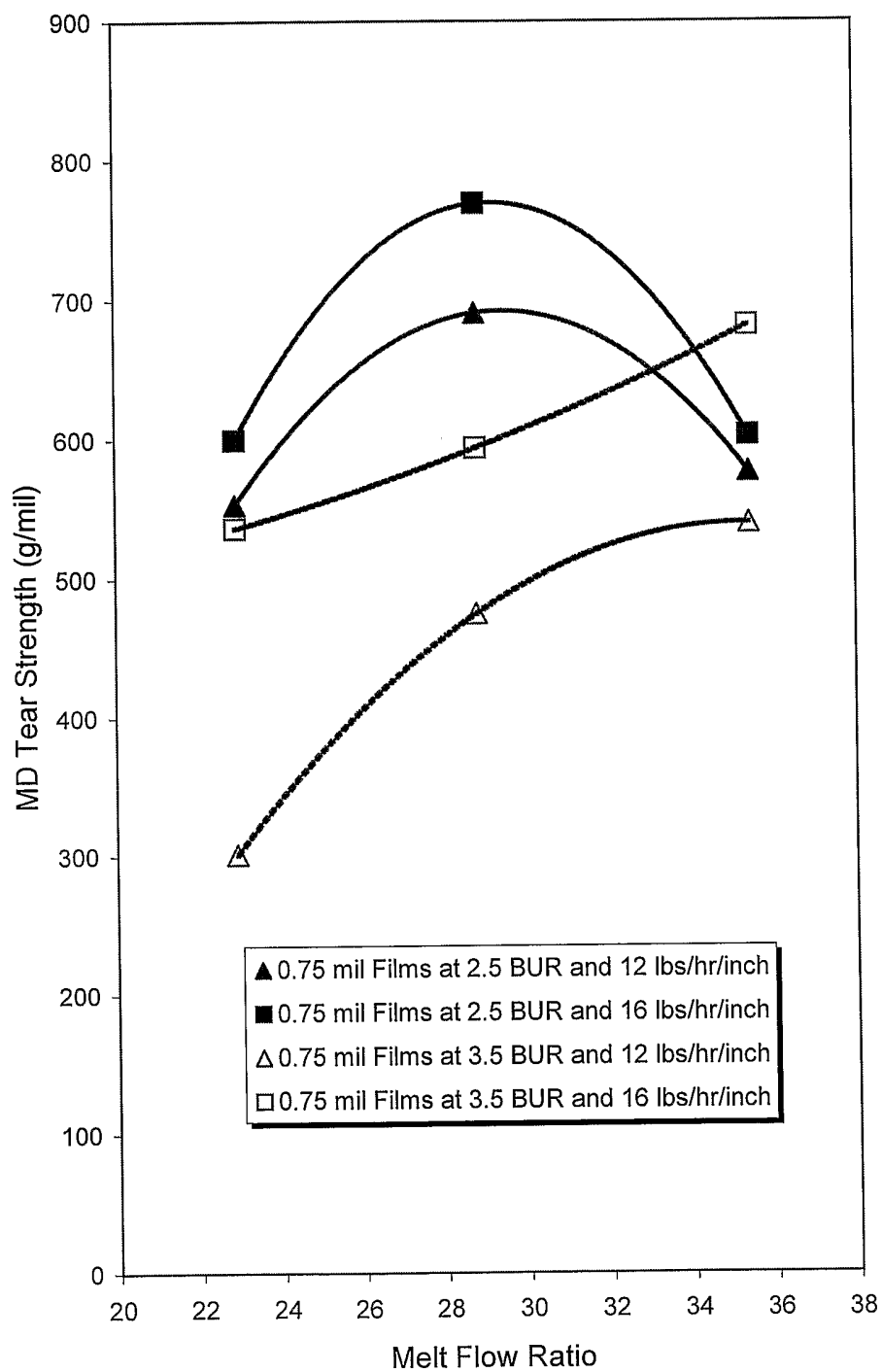
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Figure 6



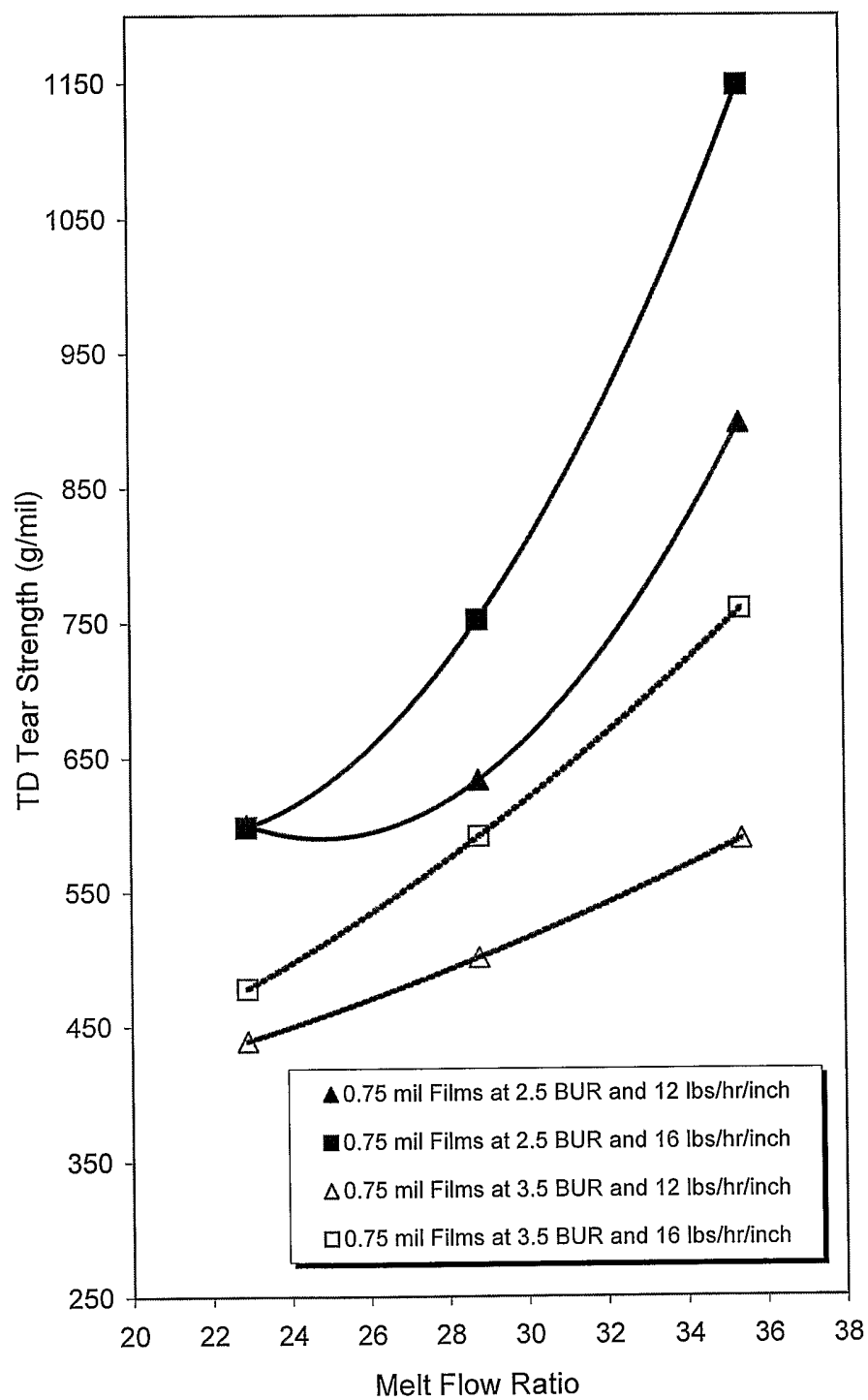
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Figure 7



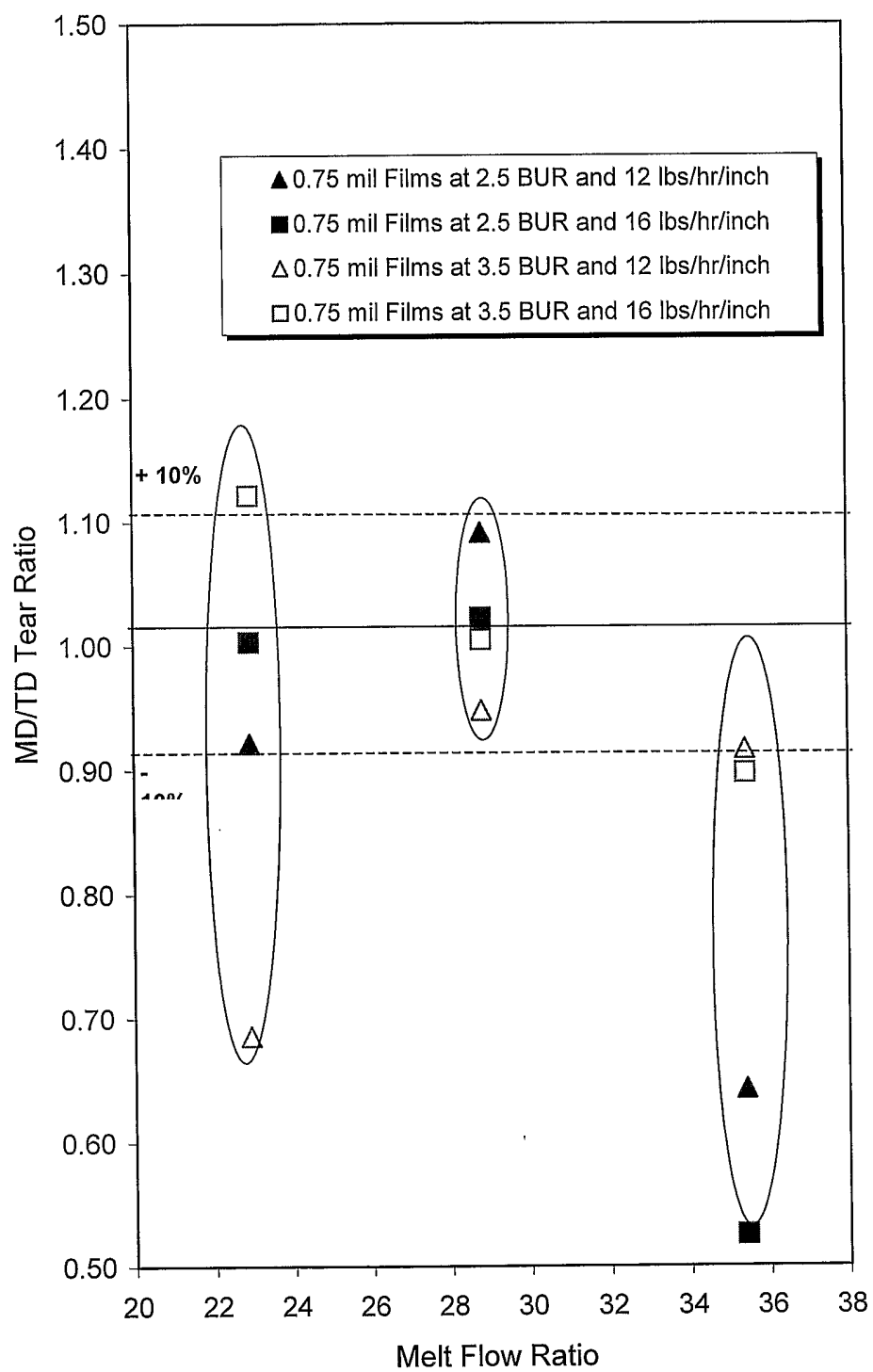
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Figure 8



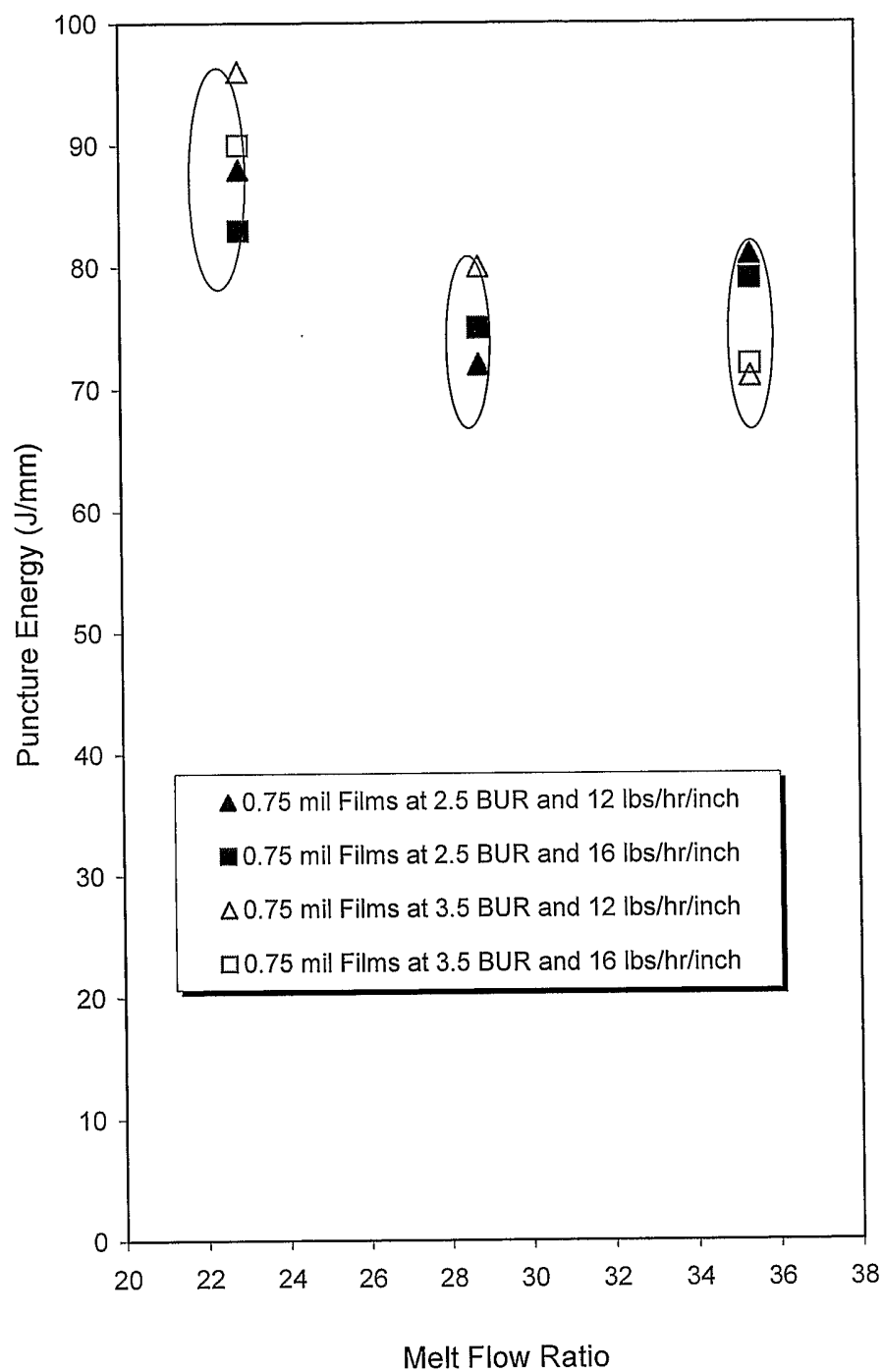
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Figure 9



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Figure 10



INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2006/000067

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C08J 5/00** (2006.01) , **B65D 30/02** (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C08J 5/00 (2006.01) , B65D 30/02 (2006.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Canadian Patent Database, Delphion, USPTO, Espacenet, STN-CAPLUS ("LLDPE", "linear low density polyethylene", alumoxane", "phosphinimine", "film", "bag")

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CA 2,245,375 (NOVA CHEM.) 19 February 2000 abstract, pages 4-5	1-13
Y	CA 2,411,183 (NOVA CHEM.) 05 May 2004 abstract, pages 8-10, 15-16 and 21	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 March 2006 (01-03-2006)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/CA2006/000067

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