

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 January 2011 (20.01.2011)

PCT

(10) International Publication Number
WO 2011/008589 A1

- (51) **International Patent Classification:**
C08F 297/08 (2006.01) *C08L 23/14* (2006.01)
C08F 8/50 (2006.01)
- (21) **International Application Number:**
PCT/US2010/041031
- (22) **International Filing Date:**
6 July 2010 (06.07.2010)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/225,417 14 July 2009 (14.07.2009) US
- (71) **Applicant (for all designated States except US):** **DOW GLOBAL TECHNOLOGIES INC.** [US/US]; 2040 Dow Center, Midland, MI 48674 (US).
- (72) **Inventor; and**
- (75) **Inventor/Applicant (for US only):** **ZUM MALLEN, Michael, P.** [US/US]; 1902 Rosewood Lane, Sugar Land, TX 77479 (US).
- (74) **Agent:** **PLOTECHER, Gary, R.**; Whyte Hirschboeck Dudek S.C., 555 East Wells Street, Suite 1900, Milwaukee, WI 53202 (US).
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report (Art. 21(3))



WO 2011/008589 A1

(54) **Title:** POLYPROPYLENE IMPACT COPOLYMERS HAVING HIGH MELT FLOW AND IZOD DUCTILITY

(57) **Abstract:** Impact copolymers that comprise a continuous phase comprising a propylene-based polymer and a discontinuous rubber phase comprising a propylene/ethylene copolymer. The impact copolymers can have a fraction copolymer value (Fc) of at least 35, an ethylene content (Ec) of at least 38, a melt flow rate of at least 50 g/10 min and a notched Izod impact strength at 23 C of at least 615 J/m.

POLYPROPYLENE IMPACT COPOLYMERS HAVING HIGH MELT FLOW AND IZOD DUCTILITY

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of US Provisional Application Number 61/225,417 filed July 14, 2009.

FIELD OF THE INVENTION

[0001] This invention relates to polypropylene impact copolymers having a high melt flow rate and a high impact strength and further relates to methods of making the impact copolymers.

BACKGROUND OF THE INVENTION

[0002] There is a continuing need for polypropylene heterophasic copolymers with improved properties, notably materials with high melt flow rates and impact characteristics, especially for automotive thermoplastic olefin (TPO) applications, molding, injection molding, thin wall packaging and engineering applications.

[0003] One approach commonly used to achieve polypropylenes with high melt flow rates (MFR) involves chemical treatment, i.e., visbreaking of molten polypropylene heterophasic copolymers. Unfortunately, the resulting visbroken copolymers, also called controlled rheology (CR) polymers, generally need improved impact properties.

BRIEF SUMMARY OF THE INVENTION

[0004] One aspect of the invention provides impact copolymers that comprise a continuous phase comprising a propylene-based polymer and a discontinuous rubber phase comprising a propylene/ethylene copolymer. The impact copolymers of this aspect of the invention have an fraction copolymer (F_c , expressed as weight percent (wt. %)) of at least 35, an ethylene content of the rubber fraction (E_c , expressed as weight percent (wt. %)) of at least 38, a melt flow rate of at least 50 g/10 min, and a notched Izod impact strength at 23 °C of at least about 615 J/m (about 11.5 ft-lb/in). In some embodiments, the impact copolymers have a melt flow rate of at least 100 g/10 min. In some embodiments, the impact copolymers have a notched Izod impact strength at 23 °C of at least about 630 J/m (about 11.8 ft-lb/in). In some embodiments the impact copolymers have an E_c of at least 41.

[0005] In some embodiments, the impact copolymers are nucleated. While in other embodiments the impact copolymers are non-nucleated. In particular, the impact copolymers can be non-nucleated and have a melt flow rate of at least 100 g/10 min.

[0006] In some embodiments, the impact copolymers have a visbreaking ratio of at least 3. This includes embodiments wherein the impact copolymers have a visbreaking ratio of at least 5 and further includes embodiments wherein the impact copolymers have a visbreaking ratio of at least 10. In some embodiments the impact copolymers have a visbreaking ratio in the range of 4 to 15.

[0007] In some embodiments, the impact copolymers have a flexural modulus of at least about 758 MPa (110,000 psi). This includes embodiments wherein the impact copolymers have a flexural modulus of at least about 827 MPa.

[0008] In one specific, non-limiting embodiment, the impact copolymer is a nucleated impact copolymer comprising a continuous phase comprising a propylene-based polymer and a discontinuous rubber phase comprising a propylene/ethylene copolymer, wherein the impact copolymer has an Fc of at least 35, an Ec of at least 41, a melt flow rate of at least 55 g/10 min and a notched Izod impact strength at 23 °C of at least 630 J/m (11.8 ft-lb/in). In this embodiment, the nucleated impact copolymer can have a visbreaking ratio of at least 5 and a flexural modulus of at least 882 MPa (128,000 psi). The nucleating agent used to produce this nucleated copolymer can be an organic phosphorous nucleating agent.

[0009] In another specific, non-limiting embodiment, the impact copolymer is a non-nucleated copolymer comprising a continuous phase comprising a propylene-based polymer and a discontinuous rubber phase comprising a propylene/ethylene copolymer comprising at least about 41 wt.% ethylene, wherein the impact copolymer has an Fc of at least 35, an Ec of at least 41, a melt flow rate of at least 100 g/10 min, and a notched Izod impact strength at 23 °C of at least 615 J/m (11.5 ft-lb/in). In this embodiment, the non-nucleated impact copolymer can have a visbreaking ratio of at least 5 and a flexural modulus of at least 772 MPa (112,000 psi). This includes embodiments wherein the non-nucleated impact copolymer has a visbreaking ratio of at least 10.

[0010] Another aspect of the invention provides methods of making impact copolymers. The methods include compounding a polypropylene impact copolymer with a visbreaking agent at a temperature of at least 210 C to provide a visbroken polypropylene

impact copolymer having a visbreaking ratio of at least 5. This includes embodiments in which the visbroken polypropylene impact copolymer has a visbreaking ratio of at least 10, and further includes embodiments in which the visbroken polypropylene impact copolymer has a visbreaking ratio in the range of 4 to 15. In some embodiments the compounding takes place at a temperature of at least 215°C. The visbroken polypropylene impact copolymers can be made without nucleating agents. Suitable visbreaking agents include organic peroxides, such as linear peroxides.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0011] Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight and all test methods are current as of the filing date of this disclosure. For purposes of United States patent practice, the contents of any referenced patent, patent application or publication are incorporated by reference in their entirety (or its equivalent US version is so incorporated by reference) especially with respect to the disclosure of synthetic techniques, definitions (to the extent not inconsistent with any definitions specifically provided in this disclosure), and general knowledge in the art.

[0012] Numerical ranges include all values from and including the lower and the upper values, in increments of one unit, provided that there is a separation of at least two units between any lower value and any higher value. As an example, if a compositional, physical or other property or process parameter, such as, for example, impact strength, viscosity, melt flow rate, temperature, etc., is from 100 to 1,000, it is intended that all individual values, such as 100, 101, 102, *etc.*, and sub ranges, such as 100 to 144, 155 to 170, 197 to 200, etc., are expressly enumerated. For ranges containing values which are less than one or containing fractional numbers greater than one (e.g., 1.1, 1.5, *etc.*), one unit is considered to be 0.0001, 0.001, 0.01 or 0.1, as appropriate. For ranges containing single digit numbers less than ten (e.g., 1 to 5), one unit is typically considered to be 0.1. These are only examples of what is specifically intended, and all possible combinations of numerical values between the lowest value and the highest value enumerated, are to be considered to be expressly stated in this disclosure. Numerical ranges are provided within this disclosure for, among other things, impact strength, melt flow rate and relative amounts of components in various compositions and blends.

[0013] Various properties of the present propylene-based polymers, propylene/ethylene copolymers and impact copolymers are recited and claimed in this application. For the purposes of this disclosure, the standard methods and conditions used to measure these properties are as follows:

- (1) Melt Flow Rate (MFR): ASTM D 1238-04, Procedure B, Condition 230 °C/2.16 kg;
- (2) Notched Izod Impact Strength: ASTM D 256A at 23 °C using an ASTM D 638 Type I test specimen; and
- (3) Flexural Modulus: 1% secant flexural modulus measured according to ASTM D 790A, method I at a testing speed of 1.3 mm/min. using an ASTM D 638 Type I test specimen.
- (4) Test specimens: Injection molded according to ASTM D4101.

[0014] The term “comprising” and its derivatives are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, any process or composition claimed through use of the term “comprising” may include any additional steps, equipment, additive, adjuvant, or compound whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, “consisting essentially of” excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term “consisting of” excludes any component, step or procedure not specifically delineated or listed. The term “or”, unless stated otherwise, refers to the listed members individually as well as in any combination.

[0015] “Composition” and like terms mean a mixture of two or more materials. Included in compositions are pre-reaction, reaction and post-reaction mixtures the latter of which will include reaction products and by-products as well as unreacted components of the reaction mixture and decomposition products, if any, formed from the one or more components of the pre-reaction or reaction mixture.

[0016] “Polymer” means a compound prepared by polymerizing monomers, whether of the same or a different type.

[0017] “Heterophasic polymers” are multiple phase polymers having a continuous polymer phase (also referred to as the matrix phase) and a discontinuous polymer phase (also referred to as the rubber phase or the elastomeric phase) dispersed within the continuous polymer phase. A heterophasic polymer may contain more than two polymer phases.

[0018] The term “propylene-based polymer,” as used herein, refers to a polymer that comprises a majority weight percent polymerized propylene monomer (based on the total weight of polymerizable monomers), and optionally may comprise at least one (or more) polymerized comonomer(s), such as ethylene. The propylene-based polymer can be a propylene homopolymer or an interpolymer. A propylene interpolymer means a polymer prepared by the polymerization of propylene with at least one other monomer, such as ethylene.

[0019] The term “propylene/ethylene copolymer,” as used herein, refers to a polymer that comprises polymer units derived from propylene monomers, polymer units derived from ethylene monomers and, optionally, polymer units derived from at least one other α -olefin monomer. In a propylene/ethylene copolymer, either the polymerized propylene monomers or the polymerized ethylene monomers constitute a majority weight percent of the polymer.

[0020] A “polypropylene impact copolymer” is a heterophasic copolymer typically having a high impact strength relative to a homopolymer of similar MFR. In a polypropylene impact copolymer, the continuous phase comprises a propylene-based polymer and the discontinuous phase comprises a propylene/ethylene copolymer.

[0021] The “fraction of copolymer” or “amount of rubber” of a heterophasic copolymer is the percent weight (wt. %) of the discontinuous phase. This is designated as “Fc.” The composition or “ethylene content” of the rubber phase is the percent weight (wt. %) of ethylene in the discontinuous phase. This is designated as “Ec”. The weight percent of ethylene based on the total weight of the propylene impact copolymer is designated as “Et.” The impact copolymer composition is measured by a Fourier Transformation Infrared (FTIR) procedure which measures the total amount of ethylene in the impact copolymer (Et in wt%) and the amount of ethylene in the rubber fraction (Ec in wt%). The method is used for impact copolymers that have pure propylene homopolymer as the first reactor component and pure EPR as the second reactor component. The amount of rubber fraction (Fc in wt%) follows from the relationship

$$Et = Ec * Fc / 100$$

Equivalent values of Et, Ec and Fc can be obtained by combining the amount of rubber fraction with the total ethylene content. As is well known in the art, the amount of rubber can be obtained from a mass balance of the reactors or from measurement of the titanium or

magnesium residues from the first and second reactor products employing well known analytical methods. The total ethylene content of the impact copolymer can be measured by a variety of methods which include

1. FTIR by ASTM D 5576-00;
2. ^{13}C NMR by S. Di Martino and M. Kelchtermans, "Determination of the Composition of Ethylene-Propylene Rubbers Using ^{13}C NMR Spectroscopy", Journal of Applied Polymer Science, Vol. 56, 1781-1787 (1995);
3. J.C. Randall, "A Review of High Resolution Liquid ^{13}C NMR Characterizations of Ethylene-Based Polymers", Journal of Macromolecular Science – Reviews of Macromolecular Chemical Physics, Ch. 29, 201-317 (1989); and
4. The methods detailed in United States Published Patent Application 2004/0215404.

[0022] The term β/α relates to the ratio of the molecular weight of the copolymer of the discontinuous phase to the molecular weight of the propylene-based polymer of the continuous phase where β and α are the values of the intrinsic viscosity of the copolymer and propylene-based polymer fractions, respectively, as measured in decalin at 135 °C (ASTM D 1601). For the purposes of this disclosure, the value of β/α is calculated from the MFR of the homopolymer fraction, the MFR of the whole impact copolymer and F_c before visbreaking, as follows:

$$B/\alpha = 1 + \frac{(\text{MFR}_{\text{homo}} / \text{MFR}_{\text{whole}})^{0.213} - 1}{F_c}$$

[0023] The term "visbreaking ratio" (also referred to as the crack ratio), as used herein, refers to the ratio of the final melt flow rate of a heterophasic copolymer that has undergone visbreaking to the initial melt flow rate of the heterophasic copolymer prior to visbreaking.

[0024] The term "nucleating agents," as used herein, refers to substances which, when incorporated into a polymer melt, form nuclei for the growth of polymer crystals in the polymer melt. Examples of nucleating agents for polypropylene include, talc, carboxylate salts (e.g., sodium benzoate), sorbital acetals and organic phosphorous compounds. The term

“nucleated polymer,” as used herein, refers to a polymer that is polymerized in the presence of a nucleating agent.

[0025] One aspect of the invention provides polypropylene impact copolymers characterized by high melt flow rates and high notched Izod impact strengths. The high melt flow rates can be achieved by visbreaking the copolymers with appropriate visbreaking agents in an extrusion reaction at elevated temperatures, as discussed in greater detail below.

[0026] In some embodiments, the present impact copolymers are visbroken to achieve melt flow rates at 23 °C, of at least 50 g/10 min. This includes impact copolymers having melt flow rates of at least 60 g/10 min, further includes impact copolymers having melt flow rates of at least 75 g/10 min, still further includes impact copolymers having melt flow rates of at least 90 g/10 min, and yet further includes impact copolymers having melt flow rates of at least 100 g/10 min.

[0027] Prior to visbreaking, the impact copolymers (“the starting copolymers”) can have relatively low initial melt flow rates. For example, the starting copolymers can have melt flow rates of 20 g/10 min or lower. This includes embodiments where the starting copolymers have melt flow rates of 15 g/10 min or lower, and further includes embodiments where the starting copolymers have melt flow rates at of 10 g/10 min or lower. Thus, the visbreaking ratios for various embodiments of the impact copolymers can be at least 3, at least 5, at least 7, or even at least 10. In some embodiments, the visbreaking ratios for the impact copolymers are no greater than 20. For example, the visbreaking ratio can be in the range of about 4 to about 15.

[0028] At these high melt flow rates, the impact copolymers exhibit high notched Izod impact strengths. In some embodiments, the impact copolymers have sufficiently high impact strengths to render them fully ductile. As used herein, the term “fully ductile” refers to an impact copolymer having a notched Izod impact strength at 23 °C of at least 534 J/m (10 ft-lb/in). For example, some embodiments of the impact copolymers have notched Izod impact strengths at 23 °C of at least 587 J/m (11 ft-lb/in), at least 615 J/m (11.5 ft-lb/in), or at least 635 J/m (11.8 ft-lb/in).

[0029] Some embodiments of the impact copolymers also exhibit a high flexural modulus. For example, the impact copolymers can have a flexural modulus of at least 689 MPa (100,000 psi), at least 758 MPa (110,000 psi), at least 772 MPa (112,000 psi), at least

827 MPa (120,000 psi), at least 861 MPa (125,000 psi), or at least 882 MPa (128,000 psi).

[0030] Without intending to be bound by any particular theory, the inventors believe that the high impact strengths of the impact copolymers may be due, at least in part, to the promotion of polymer crosslinking relative to degradation in the discontinuous rubber phase of the copolymers during visbreaking. Propylene-based polymer predominantly undergoes chain scission during visbreaking while, in the absence of oxygen, polyethylene undergoes crosslinking. Visbreaking also narrows the molecular weight distribution. The more rapid decrease in molecular weight of the continuous propylene-based polymer phase relative to the dispersed rubber phase results in an increase of β/α . It is believed that the combination of higher β/α and a more narrow propylene-based polymer molecular weight distribution can result in enhanced impact properties.

[0031] The impact copolymers are desirably characterized by F_c values of at least 30. This includes embodiments in which the impact copolymers are characterized by F_c values of at least 33 and further includes embodiments in which the impact copolymers are characterized by F_c values of at least 35.

[0032] The impact copolymers are desirably characterized by E_c values of at least 38. For example, in some embodiments the impact copolymers have an E_c value of 38 to 45, which promotes ductile failure. The impact copolymers can have a β/α ratio before visbreaking of, for example, 1.5 or greater. In some embodiments, the β/α ratio is at least 2.

[0033] The impact copolymers may, or may not, be nucleated. In some instances, the impact copolymers are produced in the presence of nucleating agents. Where nucleating agents are used, suitable nucleating agents include, talc, carboxylate salts (e.g., sodium benzoate), sorbital acetals and organic phosphates. However, in other embodiments, the impact copolymers are produced in the absence of nucleating agents. Such embodiments are based on the inventors' discovery that the use of nucleating agents can have a significant negative impact on the notched Izod impact strength of the impact copolymers.

[0034] The impact copolymers can be produced in a two-stage process that includes a first stage, in which the propylene-based polymer of the continuous polymer phase is prepared, and a second stage, in which the discontinuous rubbery polymer phase is produced in the continuous polymer phase to provide a heterophasic copolymer. The first stage polymerization can be carried out in one or more bulk reactor(s) or in one or more gas phase

reactor(s). The second stage polymerization is typically carried out in one or more gas phase reactor(s). The second stage polymerization is typically carried out directly following the first stage polymerization, i.e., the polymerization product recovered from the first polymerization stage is conducted to the first gas phase reactor in the second polymerization stage.

[0035] The polymerizations are typically carried out in the presence of a stereoregular olefin polymerization catalyst. Such catalysts are well known. Ziegler Natta and metallocene or single site catalysts are appropriate for polymerizing olefins of three carbons or more. The Ziegler Natta catalysts are preferred. Suitable Ziegler-Natta catalysts are sold by The Dow Chemical Company under the tradename SHACTM (e.g., SHACTM 330 Propylene Catalyst).

[0036] The present impact copolymers can, optionally, include fillers such as calcium carbonate and kaolin clays. Other additives that can be used in the preparation of (and be present in) the copolymers of this invention, include, but are not limited to, antioxidants, processing aids, pigments, ultraviolet absorbers, flame retardants and lubricants. Suitable pigments include carbon black, titanium dioxide, cadmium-based or other inorganic or organic based pigments. Antioxidants include phenolic and phosphitic antioxidants which can be included to enhance the processing and end use stability of the product. Processing aids include, but are not limited to, low molecular weight polyethylene waxes, ester waxes, paraffin wax, paraffin oils, mineral oils, naphthenic oils, bis-stearamides, stearamides, calcium stearate, and stearic acid.

[0037] Once formed, the heterophasic impact copolymer is visbroken by adding a visbreaking agent, such as a peroxide, to the copolymer during extrusion to increase its melt flow rate. The visbreaking can be carried out in a pelletizing extruder. Alternatively, the heterophasic copolymer first can be pelletized and visbreaking can be carried out on the pelletized polymer. For example, a solution of peroxide in mineral oil or alcohol can be mixed with the polymer or added to the polymer at the throat of the extruder. The extruder should provide good mixing to ensure dispersion of the rubber phase into a fine rubber particle size. Typical quantities of the peroxide in the visbreaking reaction are from about 200 to about 1000 ppm. Extrusion temperatures will depend, at least in part, on the visbreaking agent employed. Generally, the visbreaking temperature should be sufficiently

high to ensure that substantially all the visbreaking agent reacts during the visbreaking process. Typical extruder temperatures during visbreaking are at least 210 °C. This includes embodiments where visbreaking is carried out at a melt temperature of at least 215 °C. For example the visbreaking temperature can be from about 215 to about 250 °C.

[0038] The visbreaking of the heterophasic copolymer can be conducted with organic peroxides. The peroxides may be linear or cyclic. The peroxide is desirably characterized in that it undergoes appreciable decomposition beginning at lower melt temperatures during the extrusion reaction. Without intending to be bound by any particular theory of the invention, the inventors believe such peroxides increase the proportion of crosslinking over degradation in the discontinuous rubber phase of the impact copolymers at lower melt temperatures. This may be due to a high, but short-lived, stationary macro radical concentration in the melt arising from rapid peroxide decomposition. This has the effect of minimizing the decrease in the molecular weight of the discontinuous rubber fraction and resulting in an increased overall impact strength of the impact copolymer.

[0039] One particularly suitable, commercially available peroxide is 2,5-bis (tert-butylperoxy)-2,5-dimethyl-hexane. Other suitable organic peroxides include those with one hour half lives at temperatures greater than 120 °C. Examples of useful organic peroxides include, but are not limited to, tert-butyl peroxy benzoate (TBPB), dicumyl peroxide, t-butyl-cumyl peroxide, di-t-butyl peroxide, cumene hydroperoxide, and 2,5-dimethyl-2,5-di-(t-butyl peroxy) hexyne. Additional teachings regarding organic peroxide crosslinking agents are available in the *Plastics Additives Handbook*, 5th edition, edited by Dr. Hans Zweifel, Hanser Gardner Publications.

SPECIFIC EMBODIMENTS

[0040] This example describes methods of making polypropylene impact copolymers in accordance with the present invention, and illustrates the improved impact and flow properties of said impact copolymers.

[0041] SHACTM 320/330 catalyst system available from The Dow Chemical Company is used in the preparation of the impact copolymers of these examples. The system comprises TiCl₄/MgCl₂ in combination with an external stereo-control agent (dicyclopentyl dimethoxy silane or DCPDMS) and an activator (triethylaluminum).

[0042] Six impact copolymers are prepared in a UNIPOL pilot plant gas phase reactor under standard gas phase polymerization conditions. The polymerizations are carried out in two sequential reactors. Homopolymerization of propylene is conducted in the first reactor. Hydrogen is used to obtain the desired MFR value. The catalyst system components are added at a rate to obtain the desired rate of polymerization. DCPDMS is added at a rate to obtain a nominal 1.5% xylene solubles.

[0043] The homopolymer powder containing active catalyst residues is intermittently transferred to a depressurization vessel to remove unreacted propylene monomer and other gaseous components. The depressurization vessel is pressurized with nitrogen to convey the homopolymer powder into the second reactor for polymerization with ethylene to make the ethylene-propylene rubber (EPR). Ethylene and propylene monomers are added in a ratio to obtain the desired EPR composition. Hydrogen is also used to obtain the desired MFR value. Impact copolymer powder is intermittently removed from the second reactor for subsequent compounding once the target compositions are obtained and the reactor system is lined out. For each composition, homopolymer reactor powder from the first reaction is collected for subsequent dilution of the impact copolymer composition to obtain samples of lower rubber fraction (Fc).

[0044] The impact copolymer composition is measured by a Fourier Transformation Infrared (FTIR) procedure which measures the total amount of ethylene in the impact copolymer (Et in wt%) and the amount of ethylene in the rubber fraction (Ec in wt%). The method is used for impact copolymers that have pure propylene homopolymer as the first reactor component and pure EPR as the second reactor component. The amount of rubber fraction (Fc in wt%) follows from the relationship

$$Et = Ec * Fc / 100$$

Equivalent values of Et, Ec and Fc can be obtained by combining the amount of rubber fraction with the total ethylene content. As is well known in the art, the amount of rubber can be obtained from a mass balance of the reactors or from measurement of the titanium or magnesium residues from the first and second reactor products employing well known analytical methods. The total ethylene content of the impact copolymer can be measured by a variety of methods. However, for the purposes of this disclosure, the selected method for measuring total ethylene content will be FTIR by ASTM D 5576-00.

[0045] Table 1 reports the impact copolymer base compositions made in the pilot plant and employed in the preparation of the working examples and comparative examples that follow.

Table 1
Base Compositions from Pilot Plant

Base Composition	Reactor 1 MFR	Reactor 2 MFR	Ec	Fc
A	46	10	42.4	35.2
B	46	10	42.8	35.2
C	47	10	42.2	35.6
D	77	20	43.0	33.2
E	78	20	43.4	33.5
F	78	20	43.2	33.6

[0046] Additional base compositions for visbreaking were obtained from the base compositions of Table 1 by diluting those compositions with the respective homopolymer to lower the rubber content (Fc). (See Table 3.) The impact copolymer compositions are stabilized with 1,000 parts per million (ppm) Irganox 1010 (tetrakis-(methylene-(3,5-di-(tert)-butyl-4-hydrocinnamate))-methane available from Ciba Specialty Chemicals Corporation), 1,000 ppm Irgafos PEP-Q (tetrakis(2,4-di-tert-butylphenyl)[1,1-biphenyl]-4,4'-diylbisphosphonite also available from Ciba Specialty Chemicals Corporation), and 250 ppm DHT-4A (hydrotalcite available from Kyowa Chemical). Some of the base compositions were nucleated with either 1000 ppm NA-11 (methylene bis-(4,6-di-tert-butylphenyl)phosphate sodium salt) available from Amfine Chemical Corporation) or 750 ppm sodium benzoate. The impact copolymer powders with dispersed additives are compounded into pellets on a 30 mm Werner Pfleiderer co-rotating intermeshing twin screw extruder having a length to diameter (L/D) ratio of 24/1. Extrusion conditions are shown in Table 2.

Table 2
Basestock Compositions Extrusion Conditions

Heater Band Set Points (°C)						Backpressure (psi)	Screw Speed (rpm)	Melt Temp. (°C)
1	2	3	4	5	6			
180	185	190	190	195	195	360-510	400	220-251

[0047] The resulting base pellets are measured for melt flow according to ASTM D1238. Test specimens for notched Izod impact and flexural modulus are injection molded in accordance with ASTM D4101. Details of the base compositions including impact and stiffness properties are reported in Table 3. Table 3 also indicates whether the copolymers are nucleated.

Table 3
Base Compositions before Visbreaking

Sample Designation	A-1	A-2	B-1	B-2	C-1	C-2	D-1	E-1	F-1	F-2
Base Composition ¹	A	A	B	B	C	C	D	E	F	F
Homopolymer Dilution ²	none	77	none	80	none	28	none	52	none	50
Nucleation ³	none	none	NaBz	NaBz	NA-11	NA-11	none	NaBz	NA-11	NA-11
Final MFR	10	19	10	19	10	14	20	34	21	33
Fc	35.2	19.9	35.2	19.6	35.6	27.8	33.2	22.0	32.9	22.0
Ec	42.4	42.4	42.8	42.8	42.2	42.2	43.0	43.4	43.2	43.2
Notched Izod ⁴	732	80	694	91	705	294	107	75	598	75
Flexural Modulus ⁵	940	1309	976	1343	1027	1212	921	1367	1118	1461

¹ See Table 1

² Parts per hundred dilution with corresponding homopolymer

³ NaBz = 750 ppm Sodium Benzoate; NA-11 = 1000 ppm Amfine NA-11

⁴ Values in J/m

⁵ Values in MPa

[0048] The working and comparative examples are prepared by visbreaking the base compositions shown in Table 3 with Lupersol 101. To ensure compositional uniformity between the base and visbroken samples, each powder composition shown in Table 3 is blended in sufficient quantity to prepare the non-visbroken compositions and visbroken working and comparative examples. For visbreaking, the peroxide is diluted with acetone and broadly applied to the stabilized reactor powder with a syringe. Following peroxide application, the reactor powder is placed in a polyethylene bag and shaken to obtain a uniform distribution of peroxide and additives. Compounding into pellets is carried out in the 30 mm Werner Pfleiderer co-rotating intermeshing twin screw extruder having a length to diameter (L/D) ratio of 24/1. Table 4 details the compounding conditions.

Table 4
Extrusion Conditions for Visbreaking

Heater Band Set Points (°C)						Backpressure (psi)	Screw Speed (rpm)	Melt Temp. (°C)
1	2	3	4	5	6			
180	185	190	190	195	195	200-280	400	217-240

[0049] Values of MFR, impact and stiffness are given in Table 5 for the working and comparative (“comp.”) examples. By tracing back the visbroken properties to the base properties it is possible to evaluate the effect of visbreaking on the impact and stiffness properties.

Table 5
Visbroken Working and Comparative Examples

Example ¹	Base ²	Nucleation ³	MFR	VBR ⁴	Ec	Fc	Notched Izod at 23 °C (J/m)	Flexural Modulus (Mpa)
comp-1	E-1	NaBz	111	3.3	43.4	22.0	59	1317
comp-2	F-2	NA-11	105	3.2	43.2	22.0	59	1398
comp-3	B-2	NaBz	92	4.9	42.8	19.6	91	1324
comp-4	A-2	none	101	5.3	42.4	19.9	102	1274
working-1	A-1	none	107	10.7	42.4	35.2	619	779
comp-5	B-1	NaBz	92	9.2	42.8	35.2	139	818
comp-6	C-1	NA-11	107	10.7	42.2	35.6	203	852
comp-7	D-1	none	96	4.8	43.0	33.2	107	898
working-2	C-1	NA-11	55	5.5	42.2	35.6	636	889
comp-8	F-1	NA-11	69	3.3	43.2	32.9	134	1073
comp-9	C-2	NA-11	65	4.6	42.2	27.8	166	1140

¹ comp = comparative example

² Composition from Table 3

³ NaBz = 750 ppm Sodium Benzoate; NA-11 = 1000 ppm Amfine NA-11

⁴ Visbreak ratio

[0050] A comparison of the notched Izod impact values for the visbroken comparative examples of Table 5 with the notched Izod impact of the corresponding base compositions of Table 3 reveals a trend toward substantial loss of impact strength for visbroken copolymers made from base copolymers having very high (ductile) impact strengths. In contrast the

reduction in impact strength for visbroken copolymers made from base copolymers having relatively low (e.g., < 110 J/m) impact strengths is much less. Notably and unexpectedly, the visbroken working examples defy this trend by maintaining very high post-visbreaking notched Izod impact strengths.

[0051] Comparison examples comp-1 to comp-4 demonstrate the effect of VBR on impact strength. These examples have similar rubber contents (Fc) but vary somewhat in VBR and nucleation. All four comparative examples have values of notched Izod impact that would impart a large amount of brittle character in the failure modes of the impact copolymers. As VBR increases the value of notched Izod impact increases. The presence or absence of nucleation has little effect on the notched Izod impact strengths of these copolymers.

[0052] Working example 1 exhibits an unexpectedly high value of notched Izod impact strength for a nominal MFR of about 100 when judged against comparative examples comp-5 to comp-7. Comparative examples comp-5 and comp-6 are essentially equivalent to Example 1 in Fc and VBR but have surprisingly lower values of notched Izod impact strength. These two comparative examples show that the presence of nucleation can substantially decrease the post-visbreaking notched Izod impact strength of impact copolymers made from base copolymers characterized by failure modes having a large degree of ductility. Comparison example comp-7 illustrates a large reduction in notched Izod impact strength corresponding to a relatively low VBR coupled with only a modest decrease in Fc relative to working example 1.

[0053] Working example 2 illustrates that certain embodiments of the present impact copolymers can achieve a ductile Izod in a nucleated formulation at a high MFR. Comparison example comp-8 shows a substantial loss of impact strength for an impact copolymer having a very modest decrease in Fc but a significant decrease in VBR relative to working example 2. Comparison example comp-9 shows the effect of Fc on notched Izod impact strength.

[0054] Although the invention has been described in considerable detail through the preceding description and examples, this detail is for the purpose of illustration and is not to be construed as a limitation on the scope of the invention as it is described in the appended claims.

What is claimed is:

1. An impact copolymer comprising:
 - (a) a continuous phase comprising a propylene-based polymer; and
 - (b) a discontinuous rubber phase comprising a propylene/ethylene copolymer;the impact copolymer having an Fc of at least 35, an Ec of at least 38, a melt flow rate of at least 50 g/10 min and a notched Izod impact strength at 23 °C of at least 615 J/m (11.5 ft-lb/in).
2. The impact copolymer of claim 1, wherein the impact copolymer is non-nucleated.
3. The impact copolymer of claim 1, further comprising a nucleating agent.
4. The impact copolymer of claim 6, wherein the nucleating agent is an organic phosphorous nucleating agent.
5. The impact copolymer of any of claims 1-4 having a flexural modulus of at least 758 MPa.
6. The impact copolymer of any of claims 1-5 further comprising a linear peroxide.
7. A method of making an impact copolymer, the method comprising compounding a polypropylene impact copolymer with a visbreaking agent at a temperature of at least 210° C to provide a visbroken polypropylene impact copolymer having a visbreaking ratio of at least 5.
8. The method of claim 7, in which the visbroken polypropylene impact copolymer has a visbreaking ratio of at least 10.
9. The method of claim 8, in which the visbroken polypropylene impact copolymer is made without a nucleating agent.
10. The method of any of claims 7-9, in which the visbreaking agent is a linear peroxide.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/041031

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08F297/08 C08F8/50 C08L23/14
 ADD.

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)
 C08F C08L

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005/107558 A1 (PONCELET ROBERT [BE] ET AL) 19 May 2005 (2005-05-19) the whole document	1-10
A	US 2007/128388 A1 (LE DANG [US] ET AL) 7 June 2007 (2007-06-07) the whole document	1-10

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>
--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------

Date of the actual completion of the international search 6 September 2010	Date of mailing of the international search report 10/09/2010
------------------------------------------------------------------------------------------	-----------------------------------------------------------------------------

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Knutzen-Mies, Karen
----------------------------------------------------------------------------------------------------------------------------------------------------------------------	------------------------------------------------------

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2010/041031

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005107558 A1	19-05-2005	NONE	
US 2007128388 A1	07-06-2007	US 2009088531 A1	02-04-2009