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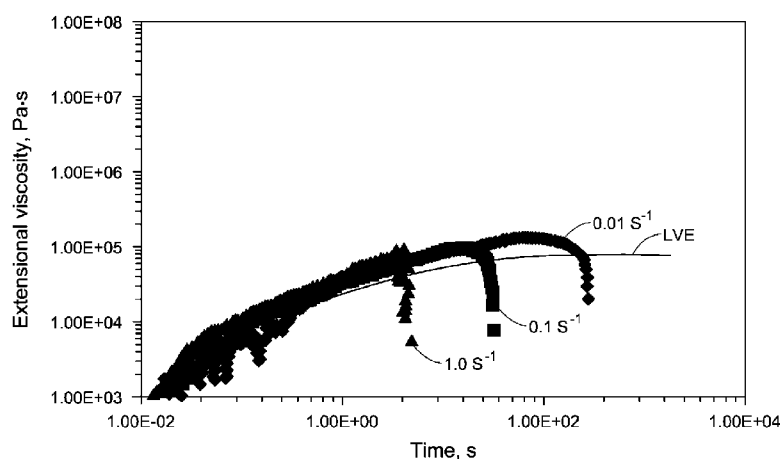


FIG. 1

(57) Abstract: A process to form a polypropylene composition comprising combining at a temperature within a range from 190°C to 320°C a polypropylene resin and within the range from 0.01 wt% to 3 wt% of at least one organic peroxide, by weight of the polypropylene composition and within a range from 100 to 4000 ppm each of phosphorous- and hindered phenol antioxidants; the polypropylene resin comprising at least 50 mol% propylene, and having a molecular weight distribution (Mw/Mn) greater than 6, a branching index (g') of at least 0.97, and a melt strength greater than 10 cN determined using an extensional rheometer at 190°C. The resulting polypropylene composition comprises at least 50 mol% propylene and has a peak extensional viscosity of greater than 500 kPa·s at a strain rate of 0.01 sec⁻¹ (190°C) and a melt strength of at least 40 determined using an extensional rheometer at 190°.



EXTRUSION OF POLYPROPYLENES WITH ORGANIC PEROXIDES**INVENTORS:** Mosha H. Zhao and George J. Pehlert**5 CROSS-REFERENCE TO RELATED APPLICATION**

[0001] The present application claims priority to U.S.S.N. 62/145,575, filed April 10, 2015, which is incorporated herein by reference.

BACKGROUND

[0002] Market demand for low cost, low environmental impact, and safe microwavable
10 containers for use in food and other packaging applications represents an opportunity for polypropylene ("PP") to replace polystyrene. However, common linear polypropylene grades display low melt strength and lack strain hardening behavior needed for foams. A polypropylene resin (see WO 2014/070386) with broad molecular weight distribution has shown some promise in terms of improved melt strength, but its strain hardening could be
15 improved. To expand the applications of high melt strength polypropylene resins the inventors have worked towards developing a new polypropylene product with high melt strength and strain hardening through a reactive extrusion process that is compatible with common production technologies. Part of such work involves development of the melt extrusion process, especially reactive extrusion of polypropylenes with organic peroxides and
20 ways to improve such processes. Thus, there is a need for an improved melt extrusion process to form high melt strength and strain hardened polypropylene. The inventors have surprisingly found that the higher processing temperatures impart favorable properties to the polypropylene.

[0003] Other relevant publications include EP 2 720 954 A1; EP 2 751 194 A1; EP 2 679
25 630 A1; EP 2 000 504 A1; EP 1 159 309 B1; US 5,180,751; US 5,883,151; US 6,323,289; US 6,573,343; US 6,875,826; US 2003/0157286; WO 1997/49759; WO 1999/27007; WO 1994/005707; WO 2012/049690; and WO 2014/070386; and

- N. Spisakova et al., in 15 J. MACRM. SCI. & APP. CHEM. 37 (2000);
- M.H. Wagner et al., "The strain-hardening behaviour of linear and long-chain-
30 branched polyolefin melts in extensional flows," in 39 RHEOL. ACTA 97-109 (2000);
- R.P. Lagendijk et al., in "Peroxydicarbonate modification of polypropylene and extensional flow properties," in 42 POLYMER 10035-10043 (2001);
- M. Ratzsch et al., 27 PROG. POLYM. SCI. 27 1195 (2002);

- A.D. Gotsis, "Effect of long branches on the rheology of polypropylene," in 48(4) J. RHEOLOGY 895-914 (2004);
- P. Iacobucci, "High melt strength polypropylene through reactive extrusion with Perkadox 24L," SPE POLYOLEFINS CONFERENCE, Houston, TX (February 2004);
- 5 • P. Spitael et al., in "Strain hardening in polypropylenes and its role in extrusion foaming," in 44(11) POLY. ENG. & SCI. 2090-2100 (2004);
- K. Jayaraman et al., "Entangling additives enhance polypropylene foam quality," in SPE PLASTICS RESEARCH ONLINE (2011); and
- H. Pol et al., "Microstructure and rheology of high-melt-strength poly-(propylene) impact copolymer," in SPE PLASTICS RESEARCH ONLINE (2014).

SUMMARY

[0004] Disclosed is a process to form a polypropylene composition comprising combining at a temperature within a range from 190°C to 320°C a polypropylene resin and within the range from 0.01 wt% to 3 wt% of at least one organic peroxide, by weight of the ingredients, and within a range from 100 to 4000 ppm each of phosphorous- and hindered phenol antioxidants, and isolating a polypropylene composition; the polypropylene resin comprising at least 50 mol% propylene, and having a molecular weight distribution (Mw/Mn) greater than 6, a branching index (g') of at least 0.97, and a melt strength greater than 10 cN determined using an extensional rheometer at 190°C.

20 [0005] Also disclosed is a process to form a polypropylene composition comprising combining at a temperature within a range from 190°C to 320°C a polypropylene resin and within the range from 0.01 wt% to 3 wt% of at least one organic peroxide, by weight of the ingredients, and within a range from 100 to 4000 ppm each of phosphorous- and hindered phenol antioxidants, and isolating a polypropylene composition; the polypropylene resin having a melt strength within the range from 10 to 40 cN, and the polypropylene composition having a melt strength within the range from greater than 40 to 100 cN, both as determined using an extensional rheometer at 190°C.

[0006] Also disclosed is a polypropylene composition comprising at least 50 mol% propylene and having a PEV (annealed) of greater than 500 kPa•s at a strain rate of 0.01 sec⁻¹ (190°C) and a melt strength of at least 40 determined using an extensional rheometer at 190°C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] **Figure 1** is a graph of Extensional Viscosity data as a function of time using the MCR501 Dynamic Stress/Strain Rheometer as described below for polypropylene resin at 240°C.

5 [0008] **Figure 2** is a graph of Extensional Viscosity data as a function of time for polypropylene resin reacted with an organic peroxide, as described below, at 240°C.

[0009] **Figure 3** is a graph of Extensional Viscosity data as a function of time for polypropylene resin reacted with an organic peroxide, as described below, at 260°C.

10 [0010] **Figure 4** is a graph of Shear Viscosity as a function of Angular Frequency for various polypropylene resins and reaction products at various temperatures.

[0011] **Figure 5** is a graph of Pull-off-Force as a function of draw ratio for various polypropylene resins and reaction products at various temperatures.

DETAILED DESCRIPTION

15 [0012] Disclosed here is a process to form a polypropylene composition having improved shear thinning and melt strength, making it highly suitable for application such as making foamed articles at commercial conditions (e.g., relatively high extrusion temperatures). The inventors have unexpectedly found that the shear viscosity of the reaction product of short half-life organic peroxides with certain polypropylenes, such as reaction during melt extrusion, can be effected by increasing reaction (e.g., melt extrusion) temperature. A higher reaction temperature between at least the organic peroxide and polypropylene will further improve shear viscosity over the same reaction product when combined at lower temperatures (e.g., 210°C versus 260°C), thus leading to a new method of improving shear viscosity in polypropylenes, and the higher shear viscosity product therefrom.

25 [0013] As evidenced by a number of factors such as (1) an increasing I_{21}/I_2 value of the reaction product polypropylene composition (or simply “polypropylene composition”) indicating improved shear thinning, (2) the high draw ratios evidencing extensional flow capabilities, and (3) increased extensional viscosity as directly measured and quantified in the Peak Extensional Viscosity (“PEV”) values, the inventors disclose in any embodiment a polypropylene composition comprising the reaction product at a temperature within the range from 190, or 200, or 220°C to 270, or 280, or 290, or 300, or 320°C of a polypropylene resin comprising at least 50 mol% propylene, and having a molecular weight distribution (M_w/M_n) greater than 6, a branching index (g') of at least 0.97, and a melt strength greater than 10 cN determined using an extensional rheometer at 190°C; and within the range from 0.01 to 3

wt% of at least one organic peroxide (or other quantities as described herein), by weight of the polypropylene composition.

[0014] The polypropylene composition described herein has several measurable features. In any embodiment, the polypropylene composition has an $M_{z\text{MALLS}}/M_{w\text{MALLS}}$ value of greater than 3.0, or 3.2, or 3.6, or within a range from 3.0, or 3.2, or 3.6 to 5.0, or 6.0, or 8.0, or 12, or 16. Also in any embodiment, the polypropylene composition has an MWD ($M_{w\text{MALLS}}/M_n$) within the range from 10, or 12 to 16, or 20. Also in any embodiment, the polypropylene composition has a branching index (g') of less than 0.97, or 0.95, or 0.90, or within a range from 0.70, or 0.80 to 0.90, or 0.95, or 0.97, indicative of some branching and/or cross-linking of the polypropylene resin in the polypropylene composition.

[0015] The polypropylene composition has improved melt strength and extensional viscosity when compared to the polypropylene resins. In any embodiment the polypropylene composition has a melt strength greater than 40, or 45, or 50 cN, or within the range from 40, or 45, or 50, or 55 cN to 80, or 85, or 90, or 100 cN. In any embodiment, the polypropylene composition has a draw ratio of greater than 5, or 6, or within a range from 5, or 5.5 to 8, or 10, or 12. In any embodiment, the polypropylene composition has a PEV (annealed) of greater than 500, or 800, or 1000, or 1500, or 2000, or 2200, or 2400, or 2800, or 3000 kPa•s at a strain rate of 0.01 sec^{-1} (190°C), or within a range of from 500, or 800, or 1000, or 1500, or 2000 kPa•s to 5000, or 5500, or 6000, or 6500, or 7000, or 8000 kPa•s. The PEV is the difference between the highest value for the extensional viscosity and the LVE, as labeled in Figure 3.

[0016] As further evidence of any long chain branching and/or cross-linking in the organic peroxide-treated polypropylene resins, the melt flow properties were measured. In any embodiment the polypropylene composition has an I_{21}/I_2 value (ASTM D1238, 21.6 kg/2.16 kg, 190°C) of greater than 150, or 160, or 170, or within a range from 160, or 170 to 190, or 200, or 220, or 240, or 260. The I_2 value of the polypropylene composition in any embodiment is within a range from 0.1, or 0.2, or 0.5 g/10 min to 4, or 5, or 8, or 10 g/10 min.

[0017] The polypropylene composition can thus be described by any combination of features described herein. For instance, in any embodiment is disclosed a polypropylene composition comprising at least 50 mol% propylene-derived units ("propylene") and having a PEV (annealed) of greater than 500 kPa•s at a strain rate of 0.01 sec^{-1} (190°C) and a melt strength of at least 40 determined using an extensional rheometer at 190°C .

[0018] The individual components used to form the polypropylene composition is described in more detail here, elements of which can be easily interchanged with the description above.

Polypropylene Resin

5 [0019] As stated above, the polypropylene composition is derived from a polypropylene having a balanced melt strength (greater than 10 or 20 cN), referred herein simply as a “polypropylene resin” having certain desirable features. Some desirable features and its method of production are described in WO 2014/070386. In particular, in any embodiment the polypropylene resin useful in the present disclosure comprises at least 50, or 60, or 70, or
10 80, or 90 mol% propylene, or within a range from 50, or 60, or 80 to 95, or 99 mol% propylene-derived units. In any embodiment the polypropylene resin is a homopolymer of propylene-derived units. In any embodiment the polypropylene resin may comprise within the range from 0.1 to 10 mol% of a comonomer selected from the group consisting of ethylene and C₄ to C₂₀ olefins.

15 [0020] In any embodiment the polypropylene resin has an isotactic percentage of greater than 90, or 92, or 95%. Also in any embodiment the polypropylene resin has a melt flow rate (MFR) within the range from 0.1, or 1, or 2 g/10 min to 12, or 16, or 20, or 40 g/10 min, determined according to ASTM D1238 Condition L (230°C/2.16 kg).

[0021] In any embodiment the polypropylene resin has a molecular weight distribution (Mw/Mn) greater than 6, or 8, or 10, or within a range from 6, or 7, or 8 to 14, or 16, or 18 or
20 20. Also in any embodiment the polypropylene resin has an Mz/Mw value of less than or equal to 3.6, or 3.4, or 3.2, or 3.0. The polypropylene resins useful in the present disclosure tend to be highly linear as evidenced by a high branching index. Thus, in any embodiment the polypropylene resins have a branching index (g' , also referred to in the literature as g'_{vis}
25 $_{avg}$) of at least 0.97, or 0.98. In any embodiment the polypropylene resins useful herein have a melt strength greater than 10, or 20, or 30 cN determined using an extensional rheometer at 190°C, or within a range from 10, or 15, or 18 cN to 35, or 40 cN.

[0022] In any embodiment the polypropylene resins have a viscosity ratio within the range from 35 to 80 determined from the complex viscosity ratio at 0.01 to 100 rad/s angular
30 frequency at a fixed strain of 10% at 190°C. Also in any embodiment the polypropylene resin has a PEV (annealed) within a range from 10, or 20 kPa•s to 40, or 50, or 55, or 60 kPa•s at a strain rate of 0.01 /sec (190°C).

[0023] In any embodiment the polypropylene resin has a heat distortion temperature of greater than or equal to 100°C, determined according to ASTM D648 using a load of 0.45

MPa (66 psi). Finally, in any embodiment the polypropylene resin has a Modulus within the range from 1800, or 2000 MPa to 2400, or 2500 MPa determined according to ASTM D790A on nucleated samples with 0.1% α -nucleating agent.

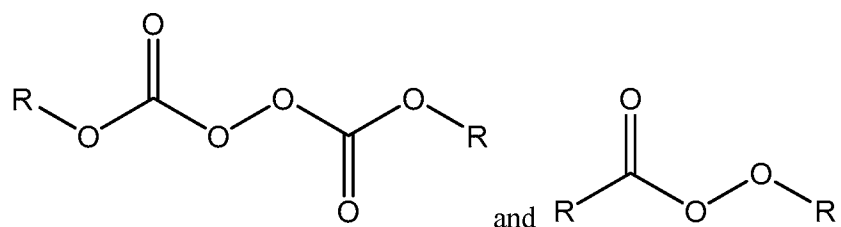
[0024] The polypropylene resin can be used in any embodiment, such as by combining
5 with other ingredients, in the form of reactor granules and/or flakes, or as extruder-formed pellets.

Organic Peroxides and Methods of forming the polypropylene composition

[0025] In any embodiment, the polypropylene composition is formed by combining under suitable conditions the polypropylene resin, phosphorous- and hindered phenol antioxidants,
10 and an organic peroxide, wherein the “organic peroxide” is any organic compound comprising at least one —(O)COO— group and/or at least one —O—O— group, and a 1 hour half-life temperature ($^1T_{1/2}$) of less than 100°C determined in an aromatic and/or halogenated aromatic hydrocarbon solvent, preferably a ($^1T_{1/2}$) within the range from 25, or 35, or 45°C to 65, or 75, or 85, or 100°C.

[0026] In any embodiment, reactor granules of the polypropylene resin used herein are preferred over extruded pellets. Such polypropylene resin granules are preferably dry blended with the organic peroxide before melt extrusion. In any embodiment, the organic peroxide melts (becomes liquid) before combining with the polypropylene resin so that the granules get evenly coated and the high specific surface area is utilized prior to the branching
20 and/or cross-linking reactions.

[0027] In any embodiment, the organic peroxide is selected from compounds having one or more structures selected from:



wherein each “R” group is independently selected from the group consisting of hydrogen, C1
25 or C5 to C24 or C30 linear alkyls, C1 or C5 to C24 or C30 secondary alkyls, C1 or C5 to C24 or C30 tertiary alkyls, C7 to C34 alkylaryl, C7 to C34 arylalkyls, and substituted versions thereof. By “substituted” what is meant are hydrocarbon “R” groups having substituents such as halogens, carboxylates, hydroxyl groups, amines, mercaptans, and phosphorous containing groups. In a particular embodiment, each “R” group is independently selected from C8 to

C20 or C24 linear, secondary, or tertiary alkyls, such as octyl, decyl, lauryl, myristyl, cetyl, arachidyl, behenyl, erucyl and ceryl groups and linear, secondary or tertiary versions thereof.

[0028] In any embodiment, the polypropylene resin may be dry blended (or, if the organic peroxide is a liquid, dry-liquid blended) with at least the organic peroxide prior to melt extrusion, and more preferably during such dry blending may be heated up to below its melting point temperature prior to melt extrusion (“combining”) with the organic peroxide, for instance, to a temperature within a range from 100, or 110, or 120°C up to the melting point temperature such as 150, or 155, or 160°C.

[0029] The formation of the polypropylene composition described herein is effected in any embodiment by “combining” (melt blending, reactive extrusion, or melt extrusion) at least the polypropylene resin and organic peroxide such that they are caused to react with one another through shear forces and applied radiative heating during blending/extrusion in an apparatus such as a single or twin barrel extruder, to a melt temperature of at least the melting point of the polypropylene resin, such as at least 140, or 150, or 160, or 180°C, or within a range from 150, or 160°C to 180, or 200, or 220, or 240, or 260, or 280, or 300, or 320°C. In any embodiment the polypropylene composition, directly from the extrusion process, is formed into reactor flakes and/or granules, or extruded pellets without being treated under vacuum and/or solvent washing.

[0030] Thus formed, the polypropylene composition described herein is ready to ship, transport, and/or store without further treatment, and be used in making any number of articles, both foamed and non-foamed. In any embodiment a foaming agent may be added during the heating/extrusion process described above such that the agent is not activated until after shipping and ready to form into a foamed article. As mentioned, the composition may be later heated/extruded again to form articles and effect foaming, if so desired.

[0031] Thus described herein is a process to improve sheer thinning and melt strength in a polypropylene composition comprising combining at a temperature, preferably, increasing temperatures, within the range from 190°C to 320°C a polypropylene resin comprising at least 50 mol% propylene, and having a molecular weight distribution (M_w/M_n) greater than 6, a branching index (g') of at least 0.97, and a melt strength greater than 10 cN determined using an extensional rheometer at 190°C; and within the range from 0.01 wt% to 3 wt% of at least one organic peroxide, by weight of the polypropylene composition. By the phrase “combining at increasing temperatures within a range from 190°C to 320°C” what is meant is that the properties of the claimed polypropylene composition can be further improved by incrementally increasing, by any incremental amount, the temperature above the claimed

level, such as above 190, or 200, or 210, or 220, or 240°C, up to 260, or 280, or 300, or 320°C. The “temperature” referred to here is the temperature of the polymer melt along with the other ingredients.

[0032] The process described herein is a means by which the extensional viscosity, or shear thinning, of the polypropylene composition can be improved (increased). This is evidenced by direct measurements of extensional viscosity, and indirectly by measuring melt flow properties. For instance, in any embodiment, as the melt temperature of the polypropylene composition—preferably at the final or die stage of the extrusion process—increases from 190, or 210, or 240°C, the I_{21}/I_2 value of the polypropylene composition increases. For instance, when combined at 200-220°C, the I_{21}/I_2 of the polypropylene composition in any embodiment is within a range from 100 to 140, and when combined at a temperature of 260-280°C the I_{21}/I_2 is within a range from 140 to 200.

[0033] In any embodiment, as the level of organic peroxide increases, the I_2 and I_{21} values of the polypropylene composition decrease and the I_{21}/I_2 value increases; preferably as the level of organic peroxide increases above 1.5 wt% the I_{21}/I_2 value becomes constant or goes down. By “constant” what is meant is that the value of the I_{21}/I_2 does not vary more than by ± 5 , or ± 10 , or $\pm 15\%$. Stated another way, the level of peroxide can be adjusted such that the optimal or peak value of I_{21}/I_2 is when the amount of organic peroxide combined when forming the polypropylene composition is within a range from 1.0, or 1.1 wt% to or 1.6, or 1.8, or 2.0 wt%. Thus, in any embodiment of the process of forming the polypropylene composition, a preferred level of organic peroxide is within a range from 1.0, or 1.1 wt% to or 1.6, or 1.8, or 2.0 wt% by weight of the polypropylene composition.

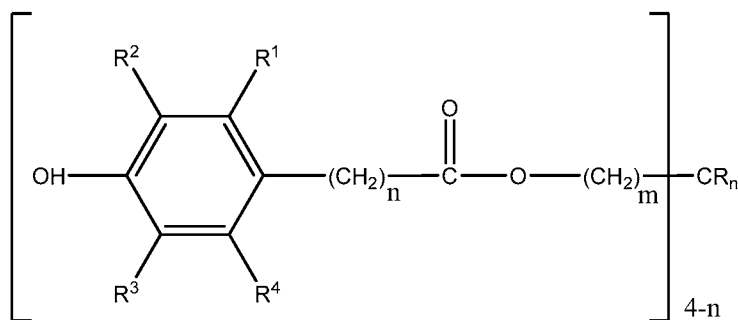
[0034] In any embodiment, the extensional viscosity of a polypropylene resin can be increased by melt extrusion of the polypropylene resin with at least one organic peroxide and increasing temperatures, preferably up to 260, or 280, or 300, or 320°C. In any embodiment, the PEV of the polypropylene resin can be increased by extruding with an organic peroxide as described to a value of greater than 500, or 800, or 1000, or 1500, or 2000, or 2200, or 2400, or 2800, or 3000 kPa•s at a strain rate of 0.01 sec^{-1} (190°C), or within a range of from 500, or 800, or 1000, or 1500, or 2000 kPa•s to 5000, or 5500, or 6000, or 6500, or 7000, or 8000 kPa•s by either or both of increasing the level of organic peroxide combined with the polypropylene resin and/or the temperature at which they are combined. For instance, when combined at 200-220°C, the PEV of the polypropylene composition in any embodiment is within a range from 500 to 1500 kPa•s, and when combined at a temperature of 260-280°C

the PEV is within a range from 1500 to 2500 kPa·s, as measured at a strain rate of 0.01 sec⁻¹ (190°C).

[0035] In any embodiment, other “additives” may also be present in the polypropylene composition as is known in the art, up to 1, or 2, or 3 wt% by weight of the polypropylene composition. These additives may be added before, during, or after the formation of the reaction products of the organic peroxide and polypropylene resins. Such additives include antioxidants (e.g., hindered phenol- and phosphorous-type compounds), nucleators, colorants (dyes, pigments, etc.), fillers (silica, talc, etc.), UV stabilizers, release agents, tackifiers, anti-static agents, acid scavengers (e.g., calcium stearate), anti-blocking agents, anti-blooming agents, alkyl-radical scavengers such as disclosed in WO 2015/200586, and other common additives as is known in the art. In a preferred embodiment, even when the polypropylene composition “consist of” the named components, the composition may nonetheless include within a range from 100 to 4000 ppm each of phosphorous- and hindered phenol antioxidants, or within a range from 100 to 4000 ppm of each of antioxidants (one or more) and foaming agents (one or more), or other amount as disclosed herein.

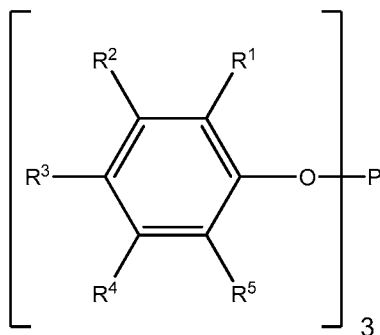
[0036] The polypropylene resin in any embodiment is preferably blended with hindered phenol and phosphorous-type antioxidants, and optionally at least one alkyl radical scavenger prior to or simultaneous with melt extrusion. “Hindered phenol” and “phosphorous-type” antioxidants (“primary” and “secondary” antioxidants) are well documented in the art, such as in Stricker et al. “New Stabilizer solutions for polyolefin film grades”, in European TAPPI PLACE Conference, Rome, Italy, May 12-14 (2003) (Ciba Specialty Chemicals); EP 1 736 506 A1; US 2005/0043450; and US 2006/0128849. Desirably, the polypropylene resin described herein is blended with at least one hindered phenol and at least one phosphorous-type antioxidant, and most preferably, with an alkyl radical scavenger as well.

[0037] More particularly, hindered phenol antioxidants, or “primary” antioxidants, comprise in any embodiment compounds having the structure HO—Ph—R, wherein “Ph” is a phenyl group which may or may not be substituted with alkyl groups, and “R” can be any alkyl, ketone, or carboxylate containing group. A particularly preferred structure in any embodiment for the hindered phenol antioxidant is selected from:



wherein each R^1 to R^4 is independently selected from hydrogens and C_1 to C_{12} alkyls, more preferably, hydrogen and C_4 to C_{10} alkyls, and most preferably hydrogen and C_3 to C_8 secondary or tertiary alkyls; and “n” is 0, 1, 2, or 3; n and m independently range from 1 to 5, or 10; and R is as defined for R^1 . An example of such a phosphorous-type antioxidant is Irganox™ 1010 from BASF.

[0038] More particularly, phosphorous-type antioxidants, or “secondary” antioxidants, comprise in any embodiment compounds having the structure $\text{P}(\text{OR})_3$, wherein each R is independently selected from hydrocarbyl groups, more particularly, a C_5 to C_{20} alkyls, aryls, alkylaryls, and arylalkyls. A particularly preferred structure in any embodiment for the phosphorous-type antioxidant is selected from:



wherein each R^1 to R^5 is independently selected from hydrogens and C_1 to C_{12} alkyls, more preferably, hydrogen and C_4 to C_{10} alkyls, and most preferably hydrogen and C_3 to C_8 secondary or tertiary alkyls. An example of such a phosphorous-type antioxidant is Irgofos™ 168 from Ciba, Inc. or BASF.

[0039] Preferably, these primary and secondary antioxidants are independently present in the polypropylene resin, or blend used in the process disclosed herein, within a range from 100, or 500 or 600 or 700 or 800 ppm to 1000 or 1200 or 1600 or 2000 or 2500 or 3000 or 4000 ppm relative to the total weight of the components. Optionally, from 20 to 600, or 800, or 1000 ppm of an acid scavenger (such as alkali or alkaline metal stearates, and others known in the art sold by trade name) is also combined during melt extrusion.

[0040] In any embodiment, the polypropylene composition described herein comprises within a range from 100 to 4000 ppm each of phosphorous- and hindered phenol antioxidants and the reaction products thereof. The “reaction product thereof” recognizes that one or both of the antioxidants may react with oxygenate or other radical species during melt extrusion.

5 [0041] In any embodiment, so called “comonomers” such as C4 to C20 α -olefins, diolefins, and conjugated dienes such as butadiene or butadiene oligomers, isoprene, etc., and α - ω -linear dienes such as 1,9-decadiene are substantially absent from the polypropylene resin and/or the polypropylene composition described herein, meaning that if the comonomers are present at all, they are present to a level of less than 1 wt%, 0.1 wt%, or 0.01 wt% of the resin
10 or composition, and are preferably not added to a reactor and/or extruder during any stage of the process.

[0042] The polypropylene composition has certain desirable features that make processing into pellets and/or articles of manufacture ideal. In any embodiment, a step of exposing the polypropylene composition to external radiation (e.g., gamma rays, microwaves,
15 electron beams, neutron beams) is absent at all stages of manufacturing. The term “external radiation” refers to man-made sources of radiation and excludes natural background radiation and/or sunlight. Most preferably, the polypropylene composition is not heated after melt extrusion to form the polypropylene composition. Thus, once the granules or pellets are isolated, there is no need to heat the granules or pellets to effect any other change to alter its
20 properties (e.g., activating a cross-linking agent, etc.).

[0043] In any embodiment, the polypropylene resin and organic peroxide, and any other ingredients, additives, etc., are heated up to below the polymer’s melting point temperature prior to or concurrently with blending together prior to the “combining” step of melt extrusion, preferably heated to between 50, or 60, or 70°C to 100, or 120°C. Such blending
25 can occur, for example, in the feed hopper of the extruder.

[0044] Also, in any embodiment the polypropylene composition comprises minimal side products from the process to form them, most preferably comprising decomposition products consisting of carbon dioxide and alcohol, especially alcohols having a lower molecular weight than the organic peroxide used to form the composition, preferably less than 3, or 2,
30 or 1 wt% (or within a range from 0.1, or 0.5 wt% to 1, or 2, or 3 wt%) of C10 to C20 or C30 alcohols, most preferably alcohols selected from the group consisting of octyl, decyl, lauryl, myristyl, cetyl, arachidyl, behenyl, erucyl and ceryl alcohols, and combinations thereof.

[0045] The polypropylene composition may further comprise a foaming agent as is known in the art to effect the formation of air containing pockets or cells within the

composition. In any embodiment is disclosed the reaction product of the foaming agent and polypropylene composition. This reaction product may be formed into any number of suitable foamed articles such as cups, plates, other food containing items, and food storage boxes, toys, handle grips, and other articles of manufacture.

- 5 [0046] The various descriptive elements and numerical ranges disclosed herein for the polypropylene composition and methods of forming such can be combined with other descriptive elements and numerical ranges to describe the invention(s); further, for a given element, any upper numerical limit can be combined with any lower numerical limit described herein, including the examples for jurisdictions that allow such combinations. The
10 features of the inventions are demonstrated in the following non-limiting examples.

EXAMPLES

Molecular Weights and Melting Temperatures

- [0047] Polymer molecular weight (weight-average molecular weight, M_w , number-average molecular weight, M_n , and z-averaged molecular weight, M_z) and molecular weight
15 distribution (M_w/M_n) are determined using Size-Exclusion Chromatography. Equipment consists of a High Temperature Size Exclusion Chromatograph (either from Waters Corporation or Polymer Laboratories), with a differential refractive index detector (DRI), an online light scattering detector, and a viscometer (SEC-DRI-LS-VIS), and also a Multi-Angle Light Scattering detector (MALLS), where mono-dispersed polystyrene is the standard in all
20 cases. The Mark-Houwink constants used were $K=0.000229$, and $a=0.705$. Three Polymer Laboratories PLgel 10mm Mixed-B columns are used. The nominal flow rate is $0.5 \text{ cm}^3/\text{min}$ and the nominal injection volume is $300 \text{ }\mu\text{L}$. The various transfer lines, columns and differential refractometer (the DRI detector) are contained in an oven maintained at 135°C . Solvent for the SEC experiment is prepared by dissolving 6 grams of butylated hydroxy
25 toluene as an antioxidant in 4 liters of reagent grade 1,2,4-trichlorobenzene (TCB). The TCB mixture is then filtered through a $0.7 \text{ }\mu\text{m}$ glass pre-filter and subsequently through a $0.1 \text{ }\mu\text{m}$ Teflon filter. The TCB is then degassed with an online degasser before entering the SEC. MALLS analysis is relied upon for M_w and M_z when calculating, for example, M_w/M_n , or M_z/M_n for the hyperbranched polypropylene, which is a more accurate method for
30 measuring highly branched polymers, while DRI values are used for M_n , which is more sensitive and detects smaller molecules. For purposes of the claims and specification, SEC-DRI shall be used for all M_n , M_w , and M_z unless otherwise specified.

[0048] The branching index (g'_{vis} , also referred to as $g'_{vis\ avg}$) is calculated using the output of the SEC-DRI-LS-VIS method described in WO 2014/070386 at paragraphs 30 to 35.

Sheer Thinning and Strain Hardening

5 [0049] A MCR501 Dynamic Stress/Strain Rheometer was used to measure sheer thinning of the polypropylene samples. A TA Instruments ARES-G2 mechanical spectrometer was used to measure strain hardening of the polypropylene samples. The polymer samples were prepared for measurements as follows: each polymer sample was heated to about 200°C for 3 min to melt the sample without pressure. Then, 1500 psi pressure was applied while the
10 sample was kept heated for another 3 min between two plates. Afterwards, the pressure applied to the sample was removed while the sample was kept heated at 200°C for another 20 min. After 20 min, the sample was cooled with water circulation without any pressure applied for an additional 20 min. In the experiments described herein, all samples were annealed. The temperature can vary from 120°C to 190°C for extensional measurements but was set
15 190°C for testing polymer samples herein. The Hencky strain rate was run at 0.01 s⁻¹, 0.1 s⁻¹ and 1.0 s⁻¹.

Melt Strength and Elongational Viscosity

[0050] The melt strength and elongational viscosity were measured using a Rheotester 1000 capillary rheometer in combination with the Rheotens 71.97 (Göttfert) as described in
20 established test method RHEO4-3.3 ("Measurement of the elongational viscosity of molten polymers"). The conditions for testing melt strength and extensional viscosity using the Rheotens 71-97 in combination with the Rheotester 1000 are described in RHEO4-3.3 are as follows:

Rheotester 1000:

- 25
- Temperature: 190°C
 - Die: 30/2
 - Piston speed: 0.278 mm/s
 - Shear rate: 40.050 sec⁻¹

Strand:

- 30
- Length: 100 mm
 - Vo: 10 mm/s

Rheotens:

- Gap: 0.7 mm

- Wheels: grooved
- Acceleration: 12.0 mm/s²

[0051] For each polymer sample, several measurements are performed. The complete amount of material present in the barrel of the Rheotester was extruded through the die and was picked up by the rolls of the Rheotens. Once the strand was placed between the rolls, the roll speed was adjusted until a force of “zero” was measured. This beginning speed “Vs” was the speed of the strand through the nip of the wheels at the start of the test. Once the test was started, the speed of the rolls was increased with a 12.0 mm/s² acceleration and the force was measured for each given speed. After each strand break, or strand slip between the rotors, the measurement was stopped and the polymer sample was placed back between the rolls for a new measurement. A new curve was recorded. Measuring continued until all sample in the barrel was used. After testing, all the obtained curves were saved. Curves which were out of line were deactivated. The remaining curves were cut at the same point at break or slip (maximum force measured), and were used for the calculation of a mean curve. The numerical data of the calculated mean curves are reported.

Melt Flow Characteristics

[0052] The melt index (I₂) and high melt flow index (I₂₁) were measured according to ASTM D1238 at 2.16 kg, and 21.6 kg, respectively, both at 190°C.

Experiments

[0053] Experiments were conducted to test the strain hardening, shear thinning and melt strength of PP resin melt blended at various temperatures and concentrations of organic peroxide. The starting polypropylene resin was a Ziegler-Natta produced homopolymer having an I₂ of 3.1 g/10 min, an I₂₁ of 352 g/10 min, a Mz/Mw (DRI) of 2.9, and a melt strength of 22.2 cN. Also, the starting polypropylene resin used in the examples have a Mw/Mn (MWD, by DRI) of 8.4, an Mn value of 41,300 g/mol, an Mw value of 347,400 g/mole, and an Mz value of 1,100,000 g/mole.

[0054] The organic peroxide, Perkadox 24L™ (dicetyl peroxydicarbonate, from Akzo-Nobel), was tumble blended with all other additives as well as the base granule at room temperature (25°C). In the examples, different levels of Perkadox 24L, together with 2000 ppm of Irganox™ 1010, 2000 ppm of Irgafos™ 168 and 500 ppm of CaSt (acid scavenger), were added. All the samples were extruded in a ZSK 30 mm twin screw extruder from Werner Pfleiderer at the temperatures listed in Table 1. The listed temperatures are the set “temperatures” at the die portion of the extruder, or the temperature at which the equipment

was set. The melt flow testing results are consistent with later rheology testing results, as summarized in Table 1.

[0055] Various amounts of organic peroxide were dry blended then melt extruded with the polypropylene resin at various temperatures. It was observed that Perkadox 24L can be effective when present in an amount as low as 0.3 wt%. In this instance, the I_2 was lower than the control (without Perkadox 24L) sample, which indicates that the molecular weight of the polypropylene composition increases due to chain branching and/or cross-linking initiated by Perkadox 24L. And the higher the concentration of Perkadox, the lower the I_2 value becomes (the data set for 1.3% Perkadox 24L extruded at 210°C is believed to not follow the pattern because it had an issue with the stabilizing additives dosage amount).

[0056] Temperature also had an influence on the resulting polypropylene composition. At the same concentration of Perkadox 24L of 1.3%, the higher temperature 260°C extrusion resulted in a composition with lower I_2 but the highest I_{21}/I_2 ratio, which suggested the highest Mw and strongest shear thinning over all. The melt index testing results are consistent with the rheology testing results. These data are summarized in Table 1.

Table 1. Melt Extrusion experiments at different temperatures and organic peroxide concentrations

Organic peroxide (wt%)	Melt Temperature (°C)	I_2	I_{21}	I_{21}/I_2	Peak Extensional Viscosity (kPa-sec) at 0.01 s ⁻¹	melt strength (cN)	Draw Ratio
0	210	3.1	352	112	25	22.2	3.6
0.3	210	2.1	304	148	485	20.7	4.4
0.5	210	2.3	296	131	885	22.7	4.5
1.3	210	3.4	380	112	-	-	-
2	210	1.2	191	158	2083	48.8	5.2
1.3	240	1.3	206	156	2000	50.8	5.6
1.3	260	0.9	147	158	2900	56.3	7.4

[0057] Rheology testing was performed on the polypropylene compositions to test strain hardening, shear thinning and melt strength effects. As shown in **Figure 1**, **Figure 2** and **Figure 3**, and Table 1, the highest extensional viscosity, which is correlated to the strain hardening effect reached the highest when the PP resin was extruded with 1.3% of Perkadox 24L at 260°C.

[0058] The viscosity curves, shown in **Figure 4** from rheology testing, are consistent with the I_{21}/I_2 observations. The polypropylene resin was extruded with 1.3% of Perkadox 24L at 260°C also has the second steepest, as well as second highest Eta^* curve which represents a high shear thinning effect.

- 5 [0059] The polypropylene resin extruded with 1.3% of Perkadox 24L at 260°C also has the highest melt strength and a draw ratio, which is close to Borealis' WB140 resins, as shown in **Figure 5**.

[0060] Having described the various aspects of the polypropylene composition and process of making it, described here in numbered paragraphs is:

- 10 P1. A polypropylene composition comprising at least 50 mol% propylene and having a PEV (annealed) of greater than 500 kPa•s at a strain rate of 0.01 sec^{-1} (190°C) and a melt strength of at least 40 determined using an extensional rheometer at 190°C.
- P2. The polypropylene composition of numbered paragraph 1, the polypropylene composition having an $M_{Z\text{MALLS}}/M_{W\text{MALLS}}$ value of greater than 3.0.
- 15 P3. The polypropylene composition of numbered paragraphs 1 or 2, the polypropylene composition having an MWD within the range from 10 to 20.
- P4. The polypropylene composition of any one of the previous numbered paragraphs, the polypropylene composition having a branching index (g') of less than 0.97.
- P5. The polypropylene composition of any one of the previous numbered paragraphs, the
20 polypropylene composition having a draw ratio of greater than 5.0.
- P6. The polypropylene composition of any one of the previous numbered paragraphs, the polypropylene composition having an I_{21}/I_2 value of greater than 150.
- P7. A foamed article comprising the polypropylene composition of any one of the previous numbered paragraphs.
- 25 P8. A process to form the polypropylene composition of any one of the previous numbered paragraphs comprising (or consisting of, or consisting essentially of) or, alternatively, a method of increasing the I_{21}/I_2 in a polypropylene composition comprising:
- combining at (preferably increasing) a temperature within a range from 190°C to
30 320°C a polypropylene resin and within the range from 0.01 wt% to 3 wt% of at least one organic peroxide by weight of the ingredients, and within a range from 100 to 4000 ppm each of phosphorous- and hindered phenol antioxidants, and isolating a polypropylene composition;

the polypropylene resin comprising at least 50 mol% propylene, and having a molecular weight distribution (Mw/Mn) greater than 6, a branching index (g') of at least 0.97, and a melt strength greater than 10 cN determined using an extensional rheometer at 190°C; and

5 optionally wherein as the melt temperature increases from 190°C, the I_{21}/I_2 of the composition increases then levels off.

P9. A process to form a polypropylene composition of any one of the previous numbered paragraphs 1 to 7 comprising (or consisting of, or consisting essentially of), or, alternatively, a method of increasing the PEV in a polypropylene composition comprising:

10 combining at (preferably increasing) a temperature within a range from 190°C to 320°C a polypropylene resin and within the range from 0.01 wt% to 3 wt% of at least one organic peroxide by weight of the ingredients, and within a range from 100 to 4000 ppm each of phosphorous- and hindered phenol antioxidants, and isolating a polypropylene composition;

15 the polypropylene resin comprising at least 50 mol% propylene, and having a molecular weight distribution (Mw/Mn) greater than 6, a branching index (g') of at least 0.97, and a melt strength greater than 10 cN determined using an extensional rheometer at 190°C; and

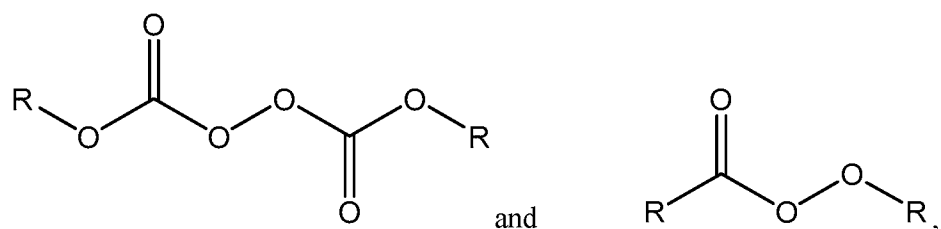
20 optionally wherein as the melt temperature of the polypropylene composition increases from 190°C the PEV increases then levels off.

P10. A process to form a polypropylene composition of any one of the previous numbered paragraphs 1 to 7 comprising (or consisting of, or consisting essentially of), or, in the alternative, a method of increasing the melt strength of a polypropylene composition comprising:

25 combining at (preferably increasing) a temperature within a range from 190°C to 320°C a polypropylene resin and within the range from 0.01 wt% to 3 wt% of at least one organic peroxide by weight of the ingredients, and within a range from 100 to 4000 ppm each of phosphorous- and hindered phenol antioxidants, and isolating a polypropylene composition;

30 the polypropylene resin having a melt strength within the range from 10 to 40 cN, and the polypropylene composition having a melt strength within the range from greater than 40 to 100 cN, both as determined using an extensional rheometer at 190°C.

- P11. The process of numbered paragraphs 8, 9 or 10, wherein the polypropylene resin has an MWD (M_w/M_n) within the range from 6 to 18.
- P12. The process of any one of the previous numbered paragraphs 8 to 11, wherein the polypropylene resin has a melt strength within the range from 10 cN to 40 cN.
- 5 P13. The process of any one of the previous numbered paragraphs 8 to 12, wherein the polypropylene resin has a PEV (annealed) within a range from 15 kPa•s to 60 kPa•s at a strain rate of 0.01 sec^{-1} (190°C).
- P14. The process of any one of the previous numbered paragraphs 8 to 13, wherein the polypropylene resin comprises at least 90 mol% propylene.
- 10 P15. The process of any one of the previous numbered paragraphs 8 to 14, wherein the polypropylene resin has an M_z/M_w value of less than 3.6.
- P16. The process of any one of the previous numbered paragraphs 8 to 15, wherein the organic peroxide is selected from compounds having one or more structures selected from:



wherein each “R” group is independently selected from the group consisting of hydrogen, C1 to C30 linear alkyls, C1 to C30 secondary alkyls, C1 to C30 tertiary alkyls, C7 to C34 alkylaryl, C7 to C34 arylalkyls, and substituted versions thereof.

- 20 P17. The process of numbered paragraph 16, wherein each “R” group is independently selected from C8 to C24 linear, secondary, or tertiary alkyls.
- P18. The process of any one of the previous numbered paragraphs 8 to 17, the polypropylene composition having a melt strength within the range from greater than 40 cN to 100 cN.
- 25 P19. The process of any one of the previous numbered paragraphs 8 to 18, the polypropylene composition having an I_{21}/I_2 value of greater than 150.
- P20. The process of any one of the previous numbered paragraphs 8 to 19, wherein as the melt temperature of the polypropylene composition increases from 190°C the PEV increases.

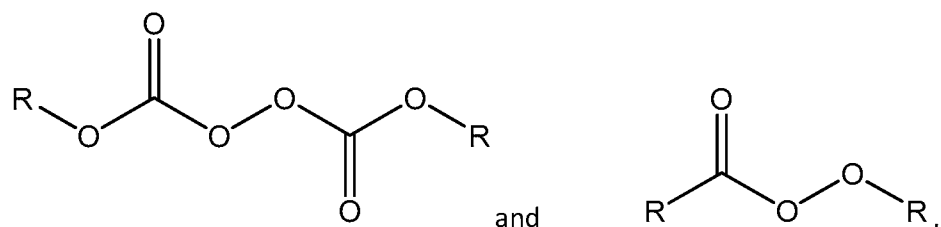
- P21. The process of any one of the previous numbered paragraphs 8 to 20, wherein as the level of organic peroxide increases, the I_2 and I_{21} values of the polypropylene composition decrease and the I_{21}/I_2 value of the polypropylene composition increases.
- 5 P22. The process of any one of the previous numbered paragraphs 8 to 21, wherein as the level of organic peroxide increases above 1.5 wt% the I_{21}/I_2 value of the polypropylene composition becomes constant or goes down.
- P23. The process of any one of the previous numbered paragraphs 8 to 22, wherein a step of exposing the composition to external radiation is absent at all stages of manufacturing.
- 10 P24. The process of any one of the previous numbered paragraphs 8 to 23, comprising decomposition products consisting of carbon dioxide and alcohol.
- P25. The process of any one of the previous numbered paragraphs 8 to 24, further comprising a foaming agent.
- 15 P26. A foamed article comprising the reaction product of the foaming agent and polypropylene composition of any one of the previous numbered paragraphs.
- P27. The foamed article of numbered paragraph 26, the article selected from the group of cups, plates, and food storage boxes.
- [0061] Also disclosed is the use of a polypropylene resin as described herein in a process to combine with an organic peroxide as described herein to form a polypropylene composition, preferably having the improved properties as described herein.
- 20 [0062] Also disclosed is the use of a polypropylene composition made as described in any one of the previous numbered paragraphs in an article, foamed or non-foamed.
- [0063] The phrase “consisting essentially of” in a polymer composition or components in a process means that no other additives, monomers, and/or catalysts are present in the composition or process being referred to other than those named, or, if present, are present to a level no greater than 0.5, or 1.0, or 2.0, or 4.0 wt% by weight of the composition; in a polymer, the phrase “consisting essentially of” means that only the named monomer-derived units are present, and if any others are present, they are present to a level no greater than 0.5, or 0.2 wt% by weight of the polymer; and also in a process, “process . . . consisting
- 25 essentially of” means that no other major process step is present that effects the formation of covalent chemical bonds between two or more moieties, for example, exposure to external radiation, addition of reactive cross-linking agents, another polymerization step, etc., but
- 30 minor process features and changes that effect the rate of covalent bond formation as is

claimed may be present, such as, for example, a change in temperature or pressure or concentration of components.

[0064] For all jurisdictions in which the doctrine of “incorporation by reference” applies, all of the test methods, patent publications, patents and reference articles are hereby
5 incorporated by reference either in their entirety or for the relevant portion for which they are referenced.

CLAIMS

1. A process to form a polypropylene composition comprising:
combining at a temperature within a range from 190°C to 320°C a polypropylene
resin and within the range from 0.01 wt% to 3 wt% of at least one organic
peroxide by weight of the ingredients, and within a range from 100 to 4000
ppm each of phosphorous- and hindered phenol antioxidants, and isolating a
polypropylene composition;
the polypropylene resin comprising at least 50 mol% propylene, and having a
molecular weight distribution (Mw/Mn) greater than 6, a branching index (g')
of at least 0.97, and a melt strength greater than 10 cN determined using an
extensional rheometer at 190°C.
2. The process of claim 1, wherein the polypropylene resin has an MWD (Mw/Mn)
within the range from 6 to 18.
3. The process of claim 1, wherein the polypropylene resin has a melt strength within the
range from 10 cN to 40 cN.
4. The process of claim 1, wherein the polypropylene resin has a peak extensional
viscosity ("PEV", annealed) within a range from 15 kPa•s to 60 kPa•s at a strain rate
of 0.01 sec⁻¹ (190°C).
5. The process of claim 1, wherein the polypropylene resin comprises at least 90 mol%
propylene.
6. The process of claim 1, wherein the polypropylene resin has an Mz/Mw value of less
than 3.6.
7. The process of claim 1, wherein the organic peroxide is selected from compounds
having one or more structures selected from:



wherein each “R” group is independently selected from the group consisting of hydrogen, C1 to C30 linear alkyls, C1 to C30 secondary alkyls, C1 to C30 tertiary alkyls, C7 to C34 alkylaryl, C7 to C34 arylalkyls, and substituted versions thereof.

8. The process of claim 7, wherein each “R” group is independently selected from C8 to C24 linear, secondary, or tertiary alkyls.
9. The process of claim 1, the polypropylene composition having an M_{ZMALLS}/M_{WMALLS} value of greater than 3.0.
10. The process of claim 1, the polypropylene composition having an MWD within the range from 10 to 20.
11. The process of claim 1, the polypropylene composition having a branching index (g') of less than 0.97.
12. The process of claim 1, the polypropylene composition having a melt strength within the range from greater than 40 cN to 80 cN.
13. The process of claim 1, the polypropylene composition having a draw ratio of greater than 5.0.
14. The process of claim 1, the polypropylene composition having a PEV (annealed) of greater than 500 kPa•s at a strain rate of 0.01 sec^{-1} (190°C).
15. The process of claim 1, the polypropylene composition having an I_{21}/I_2 value of greater than 150.

16. The process of claim 1, wherein a step of exposing the composition to external radiation is absent at all stages of manufacturing.
17. The process of claim 1, comprising decomposition products consisting of carbon dioxide and alcohol.
18. The process of claim 1, further comprising addition of a foaming agent either while combining the other ingredients or after isolating the polypropylene composition.
19. A foamed article comprising the reaction product of the foaming agent and polypropylene composition of claim 18.
20. A process to form a polypropylene composition comprising:
combining at a temperature within a range from 190°C to 320°C a polypropylene resin and within the range from 0.01 wt% to 3 wt% of at least one organic peroxide by weight of the ingredients, and within a range from 100 to 4000 ppm each of phosphorous- and hindered phenol antioxidants, and isolating a polypropylene composition;
the polypropylene resin having a melt strength within the range from 10 to 40 cN, and the polypropylene composition having a melt strength within the range from greater than 40 to 100 cN, both as determined using an extensional rheometer at 190°C.
21. A polypropylene composition comprising at least 50 mol% propylene and having a PEV (annealed) of greater than 500 kPa•s at a strain rate of 0.01 sec⁻¹ (190°C) and a melt strength of at least 40 determined using an extensional rheometer at 190°C.
22. The polypropylene composition of claim 21, the polypropylene composition having an M_{ZMALLS}/M_{WMALLS} value of greater than 3.0.
23. The polypropylene composition of claim 21, the polypropylene composition having an I_{21}/I_2 value of greater than 150.

24. The polypropylene composition of claim 21, further comprising within a range from 100 to 4000 ppm each of phosphorous- and hindered phenol antioxidants and the reaction products thereof.
- 5 25. A foamed article comprising the polypropylene composition of claim 21.

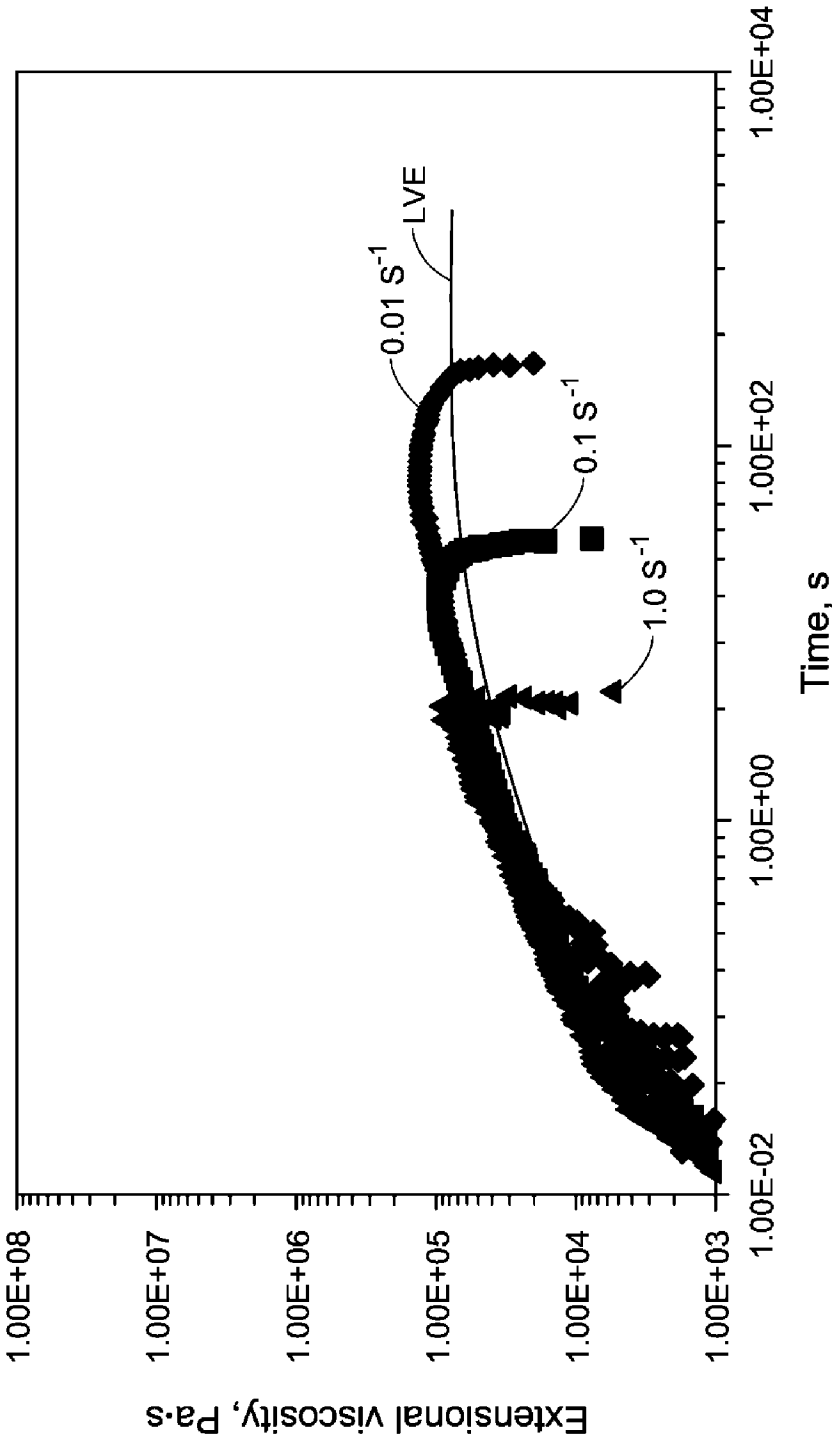


FIG. 1

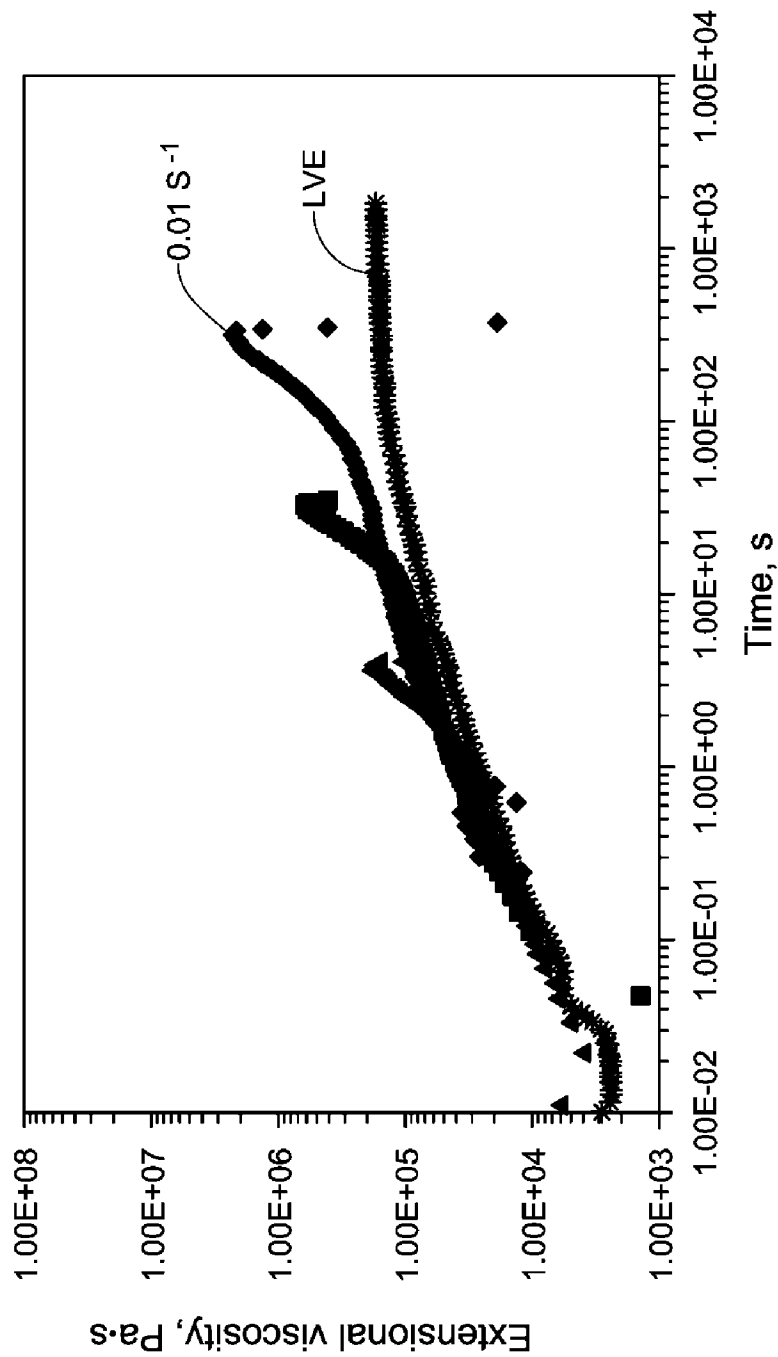


FIG. 2

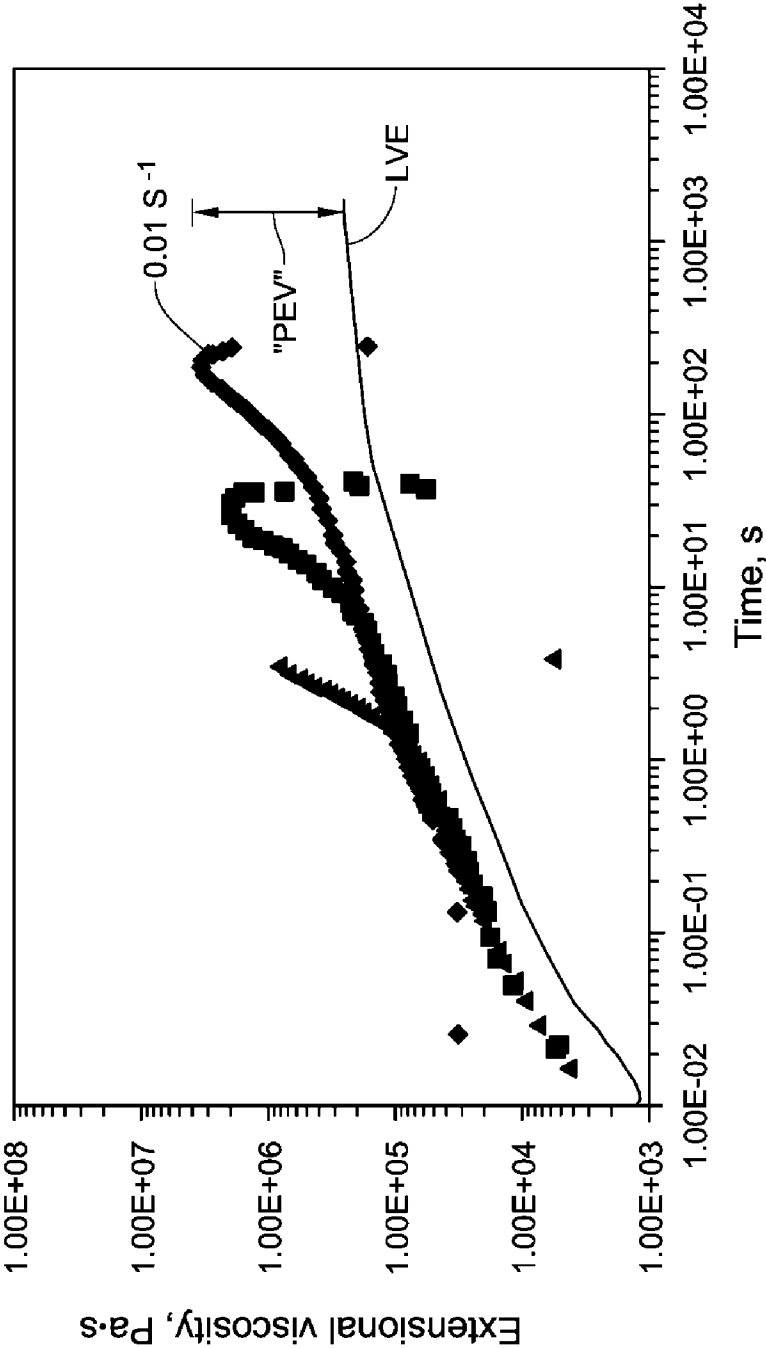


FIG. 3

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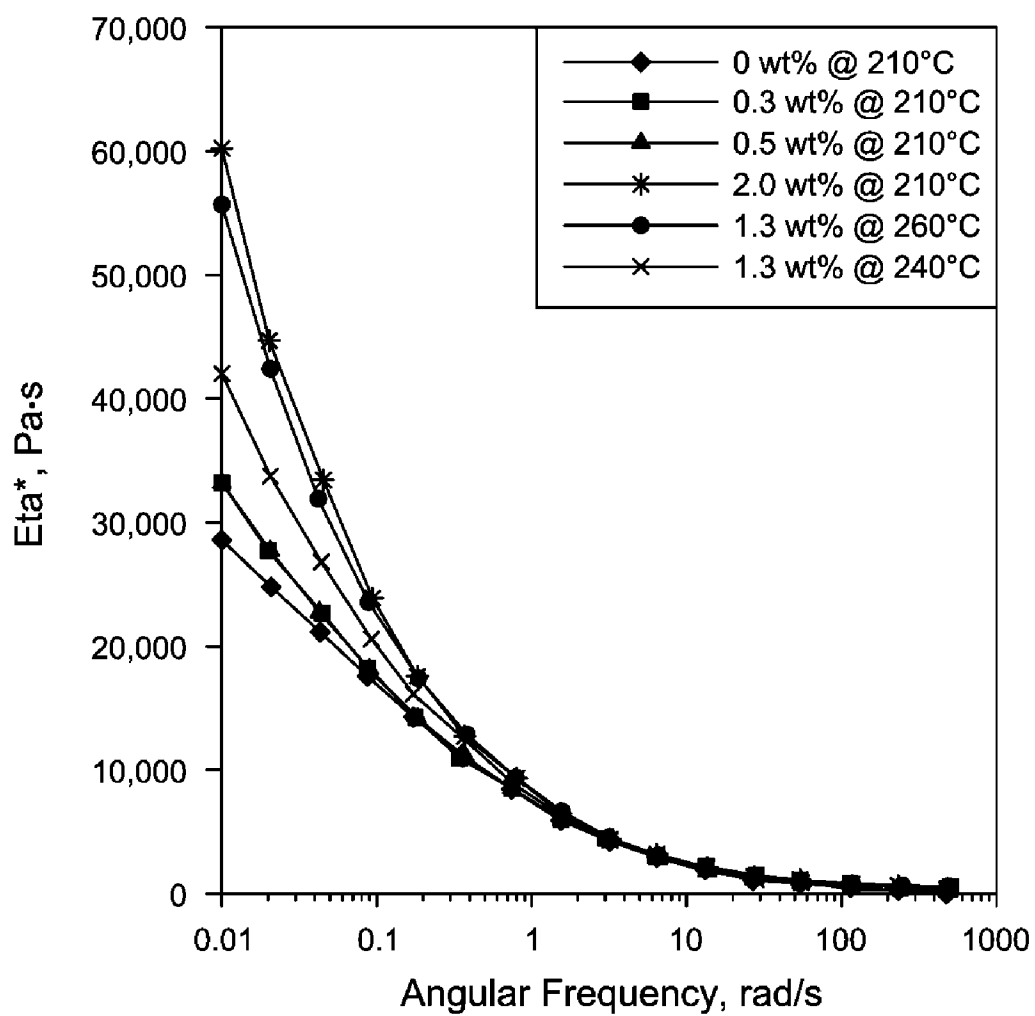


FIG. 4

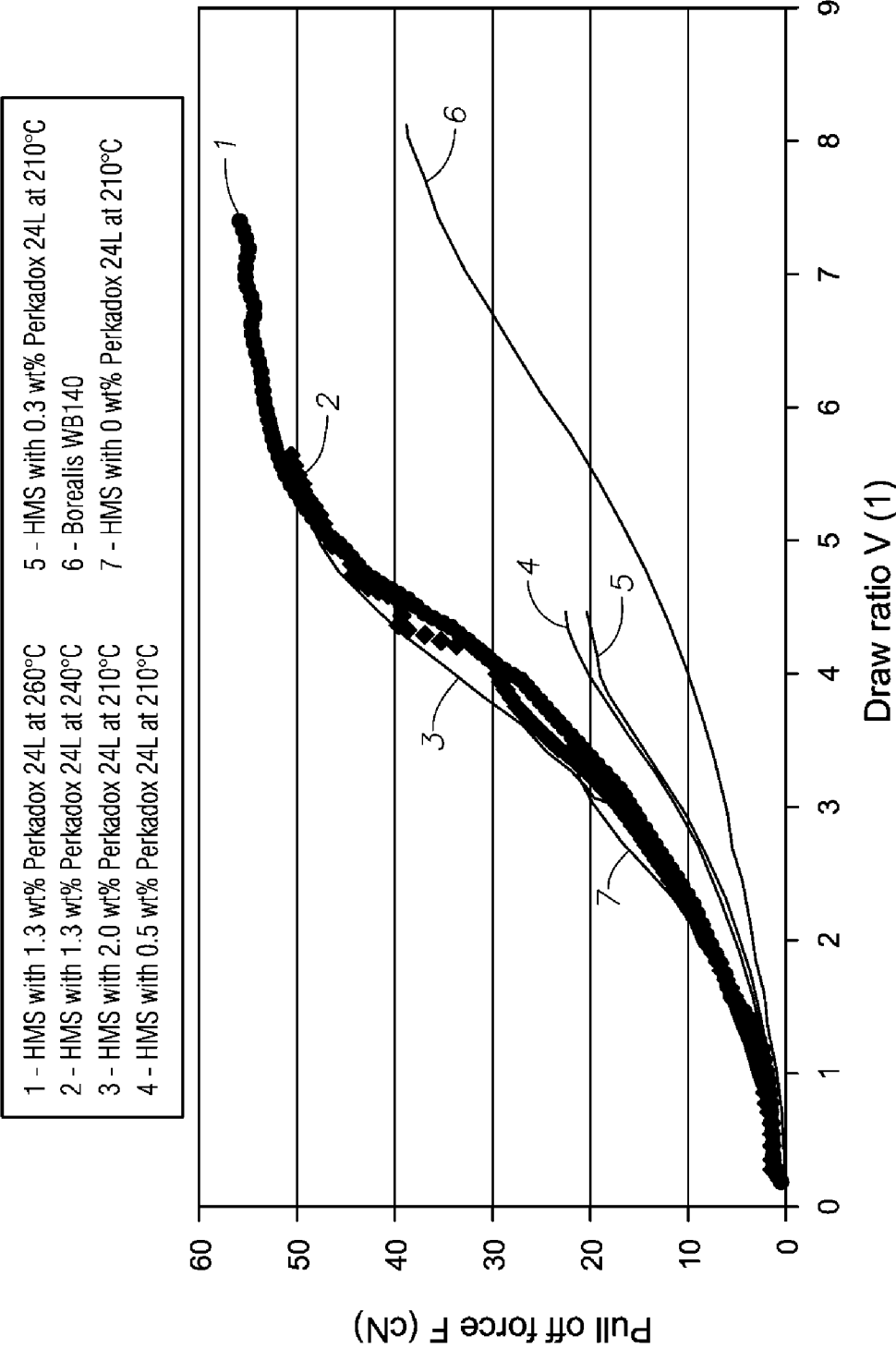


FIG. 5

A. CLASSIFICATION OF SUBJECT MATTER**C08L 23/12(2006.01)i, C08K 5/14(2006.01)i, C08J 5/00(2006.01)i**

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)

C08L 23/12; C08F 8/50; C08K 5/098; C08K 5/5393; C08F 8/00; C08F 8/06; C08L 23/26; C08K 5/14; C08J 5/00

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: polypropylene, melt strength, melt tension, peroxide, dicetyl peroxydicarbonate, antioxidant, phenol, phosphite

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015-0018463 A1 (COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH) 15 January 2015 See paragraphs [0029], [0031], [0046], [0047], [0061]; Example 1; claims 1-9; Tables 1, 2; Figures 1-5.	1-11, 13-19
A		12, 20-25
A	US 2003-0119996 A1 (KITANO, K. et al.) 26 June 2003 See paragraph [0049]; Example 1; claims 1-5; Table 1.	1-25
A	EP 1159309 B1 (BOREALIS A/S) 02 September 2009 See Examples 1, 2.	1-25
A	US 4897452 A (BERRIER, B. et al.) 30 January 1990 See column 4, line 55 - column 5, line 8; Examples 1-3.	1-25
A	US 6103833 A (HOGT, A. H. et al.) 15 August 2000 See column 2, lines 5-14; column 7, lines 28-47.	1-25



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

31 May 2016 (31.05.2016)

Date of mailing of the international search report

31 May 2016 (31.05.2016)

Name and mailing address of the ISA/KR

International Application Division

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/018272

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