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(54) Title: PROCESS FOR MAKING GRAFT COPOLYMERS IN MOLTEN STATE USING A REACTIVE, PEROXIDE-CON-
TAINING OLEFIN POLYMER

(57) Abstract: A process for making graft copolymers by using a reactive, peroxide-containing polyolefin comprising: a) preparing a polymer mixture comprising: I. about 80.0 to about 99.5 wt% of a reactive, peroxide-containing olefin polymer material (A); and II. about 0.5 to about 20.0 wt% of at least one vinyl monomer capable of being polymerized or grafted in the presence of free radicals; b) extruding or compounding in molten state the polymer mixture, thereby producing a melt mixture; and optionally c) pelletizing the melt mixture after it is cooled.



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PROCESS FOR MAKING GRAFT COPOLYMERS IN MOLTEN STATE USING A REACTIVE, PEROXIDE-CONTAINING OLEFIN POLYMER

This invention relates to a method for making graft copolymers of olefin polymer materials with vinyl monomers in molten state by extrusion or other melt processing methods.

Polyolefin graft copolymers can be made by various methods known in the state of the art, such as by grafting reaction which may be conducted in polymer solutions, in the presence of solid polymer or with a polymer in molten state. The active sites on the polyolefin can be formed either in the presence of grafting monomers, or contacted with the monomers at a later stage. The grafting sites can be produced by treatment with a peroxide or any other chemical compound which is a free radical polymerization initiator capable of extracting a hydrogen free radical from the polymer backbone, or by irradiation with high energy ionizing radiation. The free radicals produced in the reaction as a result of the degradation of peroxides or irradiation treatment act as initiators for polymerization of the monomers, as well as active sites for grafting when the free radicals are formed on the olefin polymers.

For example, U.S. Patent No. 5,411,994 discloses a method for making polyolefin graft copolymers by irradiating olefin polymer particles and treating with a vinyl monomer in liquid form under a non-oxidizing environment which is maintained throughout the process. U.S. Patent No. 5,817,707 discloses a process for making a graft copolymer by irradiating a porous propylene polymer material in the absence of oxygen, adding a controlled amount of oxygen to produce an oxidized propylene polymer material and then heating, dispersing the oxidized polymer in water in the presence of a surfactant to react with a vinyl monomer by using a redox initiator system. In all the above-mentioned documents, the grafting reaction is carried out on the polymer in solid state, at a temperature lower than the softening point of the polymer itself.

Graft copolymers have also been made in an extruder as disclosed in U.S. Patent No. 3,862,265 in which an organic peroxide initiator was injected into the extruder to initiate the grafting reaction of polyolefins in molten state with vinyl monomers. The reactive extrusion, carried out on the polymer in molten state, offers many advantages such as a fast reaction rate and a simple reaction system. Nevertheless, such graft polymerization requires the use of organic peroxides during extrusion. Since peroxides are unstable and explosive chemicals, they require special safe handling procedures to minimize the risk. Moreover, the degradation products from the organic peroxide, such as t-butyl alcohol, undesirably remain in the final product and render the product unsuitable for certain applications. In addition, since the free

radical initiator used in such a process does not only initiate the graft copolymerization but also homopolymerization of the vinyl monomers, relatively low grafting efficiency often occurs and results in low degree of graft monomer content, thus reducing the value of the final products.

There is a need, therefore, for a process for making a graft copolymer in molten state with a low by-product concentration and a stable starting material, easy to handle and not requiring unusual safety procedures.

Accordingly, it is an object of this invention to produce a graft copolymer material without using an organic peroxide in order to eliminate the above-mentioned difficulties associated with the handling of organic peroxides and to avoid the toxic by-products resulting from their use.

In accordance with the present invention, a graft polymerization process for making graft copolymers in molten state by using a reactive, peroxide-containing olefin polymer as an initiator is disclosed.

In one embodiment, the present invention relates to a process making graft copolymers comprising:

a) preparing a polymer mixture comprising:

- I. about 80.0 to about 99.5 wt% of a reactive, peroxide-containing olefin polymer material (A); and
- II. about 0.5 to about 20.0 wt% of at least one vinyl monomer capable of being polymerized or grafted in the presence of free radicals;

wherein the sum of components I + II is equal to 100 wt%;

- b) extruding or compounding in molten state the polymer mixture, thereby producing a melt mixture; and optionally
- c) pelletizing the melt mixture after it is cooled, thereby producing a pelletized mixture.

In another embodiment, the present invention relates to a process for making graft copolymer mixtures comprising:

a) preparing a polymer mixture comprising:

- I. about 10.0 to about 80 wt% of a reactive, peroxide-containing olefin polymer material (A);
- II. about 0.5 to about 20.0 wt% of at least one vinyl monomer capable of being polymerized or grafted in the presence of free radicals; and
- III. about 10.0 to about 80.0 wt% of an olefin polymer material (B);

wherein the sum of components I + II + III is equal to 100 wt%;

- b) extruding or compounding in molten state the polymer mixture, thereby producing a melt mixture; and optionally
- c) pelletizing the melt mixture after it is cooled.

Olefin polymer suitable as a starting material for the reactive, peroxide-containing olefin polymer material (A) and the olefin polymer material (B) is a propylene polymer material, an ethylene polymer material, a butene-1 polymer material, or mixtures thereof. The olefin polymer used in the present invention can be selected from:

- (a) a crystalline homopolymer of propylene having an isotactic index greater than about 80%, preferably about 90% to about 99.5%;
- (b) a crystalline, random copolymer of propylene with an olefin selected from ethylene and C₄-C₁₀ α -olefins wherein the polymerized olefin content is about 1-10% by weight, preferably about 2% to about 8%, when ethylene is used, and about 1% to about 20% by weight, preferably about 2% to about 16%, when the C₄-C₁₀ α -olefin is used, the copolymer having an isotactic index greater than about 60%, preferably at least about 70%;
- (c) a crystalline, random terpolymer of propylene and two olefins selected from ethylene and C₄-C₈ α -olefins wherein the polymerized olefin content is about 1% to about 5% by weight, preferably about 1% to about 4%, when ethylene is used, and about 1% to about 20% by weight, preferably about 1% to about 16%, when the C₄-C₁₀ α -olefins are used, the terpolymer having an isotactic index greater than about 35%; and
- (d) an olefin polymer composition comprising:
 - (i) about 10% to about 60% by weight, preferably about 15% to about 55%, of a crystalline propylene homopolymer having an isotactic index at least about 80%, preferably about 90 to about 99.5%, or a crystalline copolymer of monomers selected from (a) propylene and ethylene, (b) propylene, ethylene and a C₄-C₈ α -olefin, and (c) propylene and a C₄-C₈ α -olefin, the copolymer having a polymerized propylene content of more than about 85% by weight, preferably about 90% to about 99%, and an isotactic index greater than about 60%;

- (ii) about 3% to about 25% by weight, preferably about 5% to about 20%, of a copolymer of ethylene and propylene or a C₄-C₈ α -olefin that is insoluble in xylene at ambient temperature; and
- (iii) about 10% to about 80% by weight, preferably about 15% to about 65%, of an elastomeric copolymer of monomers selected from (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer optionally containing about 0.5% to about 10% by weight of a polymerized diene and containing less than about 70% by weight, preferably about 10% to about 60%, most preferably about 12% to about 55%, of polymerized ethylene, and being soluble in xylene at ambient temperature and having an intrinsic viscosity of about 1.5 to about 6.0 dl/g;

wherein the total of (ii) and (iii), based on the total olefin polymer composition is about 50% to about 90% by weight, and the weight ratio of (ii)/(iii) is less than about 0.4, preferably 0.1 to 0.3, and the composition is prepared by polymerization in at least two stages;

- (e) homopolymers of ethylene;
- (f) random copolymers of ethylene and an α -olefin selected from C₃-C₁₀ α -olefins having a polymerized α -olefin content of about 1 to about 20% by weight, preferably about 2% to about 16%;
- (g) random terpolymers of ethylene and two C₃-C₁₀ α -olefins having a polymerized α -olefin content of about 1% to about 20% by weight, preferably about 2% to about 16%;
- (h) homopolymers of butene-1;
- (i) copolymers or terpolymers of butene-1 with ethylene, propylene or C₅-C₁₀ α -olefin, the comonomer content ranging from about 1 mole % to about 15 mole %; and
- (j) mixtures thereof.

Preferably, the olefin polymer is selected from:

- (a) a crystalline homopolymer of propylene having an isotactic index greater than about 80%, preferably about 90% to about 99.5%; and
- (b) a crystalline, random copolymer of propylene with an olefin selected from ethylene and C₄-C₁₀ α -olefins wherein the polymerized olefin content is about

1-10% by weight, preferably about 2% to about 8%, when ethylene is used, and about 1% to about 20% by weight, preferably about 2% to about 16%, when the C₄-C₁₀ α -olefin is used, the copolymer having an isotactic index greater than about 60%, preferably at least about 70%;

Most preferably, the olefin polymer is a propylene homopolymer having an isotactic index greater than about 90%.

The useful polybutene-1 homo or copolymers can be isotactic or syndiotactic and have a melt flow rate (MFR) from about 0.1 to 150 dg/min, preferably from about 0.3 to 100, and most preferably from about 0.5 to 75.

These butene-1 polymer materials, their methods of preparation and their properties are known in the art. Suitable polybutene-1 polymers can be obtained, for example, by using Ziegler-Natta catalysts with butene-1, as described in WO 99/45043, or by metallocene polymerization of butene-1 as described in WO 02/102811, the disclosures of which are incorporated herein by reference.

Preferably, the butene-1 polymer materials contain up to about 15 mole % of copolymerized ethylene or propylene. More preferably, the butene-1 polymer material is a homopolymer having a crystallinity of at least about 30% by weight measured with wide-angle X-ray diffraction after 7 days, more preferably about 45% to about 70%, most preferably about 55% to about 60%.

The starting material for the reactive, peroxide-containing olefin polymer (A) and the olefin polymer material (B) can be the same or different from each other.

In a process to prepare the graft copolymers, the reactive, peroxide-containing olefin polymer material (A) can be present in an amount from about 80.0 to about 99.5 % by weight, preferably about 90 to about 99 %, more preferably about 92.0 to 98.0 %, and most preferably about 94.0 to about 96.0 %.

In a process to prepare the graft copolymer mixtures, the reactive, peroxide-containing olefin polymer material (A) can be present in an amount from about 10.0 to about 80.0 % by weight, preferably from about 40 to about 70 %, more preferably about 55.0 to 65.0 %. The olefin polymer material (B) can be present in an amount from about 10.0 % to about 80 % by weight, preferably from about 20 to about 50 %, more preferably about 30.0 to 40.0 %.

The reactive, peroxide-containing olefin polymer has a peroxide concentration typically ranging from about 10 to about 100 milli-equivalent per kilogram of the polymer (meq/kg), and preferably ranging from about 20 to about 50.

The reactive, peroxide-containing olefin polymer may be prepared by using an irradiation and oxidation process by exposing the polyolefin starting material to high energy ionizing radiation in an essentially oxygen-free environment, i.e., an environment in which the active oxygen concentration is established and maintained at 0.004% by volume or less. The olefin polymer starting material is exposed to high-energy ionizing radiation under a blanket of inert gas, preferably nitrogen. The ionizing radiation should have sufficient energy to penetrate the mass of polymer material being irradiated to the extent desired. The ionizing radiation can be of any kind, but preferably includes electrons and gamma rays. More preferred are electrons beamed from an electron generator having an accelerating potential of 500-4,000 kilovolts. Satisfactory results are obtained at a dose of ionizing radiation of about 0.1 to about 15 megarads ("Mrad"), preferably about 0.5 to about 9.0 Mrad.

The term "rad" is usually defined as that quantity of ionizing radiation that results in the absorption of 100 ergs of energy per gram of irradiated material regardless of the source of the radiation using the process described in U.S. Patent No. 5,047,446. Energy absorption from ionizing radiation is measured by the well-known convention dosimeter, a measuring device in which a strip of polymer film containing a radiation-sensitive dye is the energy absorption sensing means. Therefore, as used in this specification, the term "rad" means that quantity of ionizing radiation resulting in the absorption of the equivalent of 100 ergs of energy per gram of the polymer film of a dosimeter placed at the surface of the olefin material being irradiated, whether in the form of a bed or layer of particles, or a film, or a sheet.

The irradiated olefin polymer material is then oxidized in a series of steps. According to a preferred preparation method, the first treatment step consists of heating the irradiated polymer in the presence of a first controlled amount of active oxygen greater than 0.004% by volume but less than 21% by volume, preferably less than 15% by volume, more preferably less than 8% by volume, and most preferably from 0.5% to 5.0% by volume, to a first temperature of at least 25°C but below the softening point of the polymer, preferably about 25°C to 140°C, more preferably about 40°C to 100°C, and most preferably about 50°C to 90°C. Heating to the desired temperature is accomplished as quickly as possible, preferably in less than 10 minutes. The polymer is then held at the selected temperature, typically for about 5 to 90 minutes, to increase the extent of reaction of the oxygen with the free radicals in the polymer. The holding time, which can be determined by one skilled in the art, depends upon the properties of the starting material, the active oxygen concentration used, the irradiation

dose, and the temperature. The maximum time is determined by the physical constraints of the fluid bed used to treat the polymer.

In the second treatment step, the irradiated polymer is heated in the presence of a second controlled amount of oxygen greater than 0.004% by volume but less than 21% by volume, preferably less than 15% by volume, more preferably less than 8% by volume, and most preferably from 0.5% to 5.0% by volume to a second temperature of at least 25°C but below the softening point of the polymer. Preferably, the second temperature is from 80°C to less than the softening point of the polymer, and greater than the temperature of the first treatment step. The polymer is then held at the selected temperature and oxygen concentration conditions for about 10 to 300 minutes, preferably about 20 to 180 minutes, most preferably about 30 to 60 minutes, to minimize the recombination of chain fragments, i.e., to minimize the formation of long chain branches. The holding time is determined by the same factors discussed in relation to the first treatment step.

In the optional third step, the oxidized olefin polymer material is heated under a blanket of inert gas, preferably nitrogen, to a third temperature of at least 80°C but below the softening point of the polymer, and held at that temperature for about 10 to about 120 minutes, preferably about 60 minutes. A more stable product is produced if this step is carried out. It is preferred to use this step if the reactive, peroxide-containing olefin polymer material is going to be stored rather than used immediately, or if the radiation dose that is used is on the high end of the range described above. The polymer is then cooled to a fourth temperature of about below 50°C under a blanket of inert gas, preferably nitrogen, before being discharged from the bed. In this manner, stable intermediates are formed that can be stored at room temperature for long periods of time without further degradation.

As used in this specification, the expression "room temperature" or "ambient" temperature means approximately 25°C. The expression "active oxygen" means oxygen in a form that will react with the irradiated olefin polymer material. It includes molecular oxygen, which is the form of oxygen normally found in air. The active oxygen content requirement of this invention can be achieved by replacing part or all of the air in the environment by an inert gas such as, for example, nitrogen.

It is preferred to carry out the treatment by passing the irradiated polymer through a fluid bed assembly operating at a first temperature in the presence of a first controlled amount oxygen, passing the polymer through a second fluid bed assembly operating at a second temperature in the presence of a second controlled amount of oxygen, and then maintaining

the polymer at a third temperature under a blanket of nitrogen, in a third fluid bed assembly. In commercial operation, a continuous process using separate fluid beds for the first two steps, and a purged, mixed bed for the third step is preferred. However, the process can also be carried out in a batch mode in one fluid bed, using a fluidizing gas stream heated to the desired temperature for each treatment step. Unlike some techniques, such as melt extrusion methods, the fluidized bed method does not require the conversion of the irradiated polymer into the molten state and subsequent re-solidification and comminution into the desired form. The fluidizing medium can be, for example, nitrogen or any other gas that is inert with respect to the free radicals present, e.g., argon, krypton, and helium.

The concentration of peroxide groups formed on the polymer can be controlled easily by varying the radiation dose during the preparation of the reactive, peroxide-containing olefin polymer and the amount of oxygen to which such polymer is exposed after irradiation. The oxygen level in the fluid bed gas stream is controlled by the addition of dried, filtered air at the inlet to the fluid bed. Air must be constantly added to compensate for the oxygen consumed by the formation of peroxides in the polymer.

Alternatively, the reactive, peroxide-containing olefin polymer materials could be prepared according to the following procedures. In the first treatment step, the polymer starting material was treated with 0.1 to 10 wt% of an organic peroxide initiator while adding a controlled amount of oxygen so that the olefin polymer material is exposed to greater than 0.004% but less than 21% by volume, preferably less than 15%, more preferably less than 8% by volume, and most preferably 1.0% to 5.0% by volume, at a temperature of at least 25 °C but below the softening point of the polymer, preferably about 25 °C to about 140 °C. In the second treatment step, the polymer is then heated to a temperature of at least 25 °C up to the softening point of the polymer, preferably from 100 °C to less than the softening point of the polymer, at an oxygen concentration that is within the same range as in the first treatment step. The total reaction time is typically about 0.5 hour to four hours. After the oxygen treatment, the polymer is treated at a temperature of at least 80 °C but below the softening point of the polymer, typically for 0.5 hour to about two hours, in an inert atmosphere such as nitrogen to quench any active free radicals.

Suitable organic peroxides include acyl peroxides, such as benzoyl and dibenzoyl peroxides; dialkyl and aralkyl peroxides, such as di-tert-butyl peroxide, dicumyl peroxide; cumyl butyl peroxide; 1,1-di-tert-butylperoxy-3,5,5-trimethylcyclohexane; 2,5-dimethyl-1,2,5-tri-tert-butylperoxyhexane, and bis(alpha-tert-butylperoxy isopropylbenzene), and

peroxy esters such as bis(alpha-tert-butylperoxy pivalate; tert-butylperbenzoate; 2,5-dimethylhexyl-2,5-di(perbenzoate); tert-butyl-di(perphthalate); tert-butylperoxy-2-ethylhexanoate, and 1,1-dimethyl-3-hydroxybutylperoxy-2-ethyl hexanoate, and peroxycarbonates such as di(2-ethylhexyl) peroxy dicarbonate, di(n-propyl)peroxy dicarbonate, and di(4-tert-butylcyclohexyl)peroxy dicarbonate. The peroxides can be used neat or in diluent medium.

The reactive, peroxide-containing olefin polymers used in the process of the invention are easy to handle and may be stored for long periods of time without the need of specific storage requirement. The resulting graft copolymer has low degradation by-product and high grafting efficiency.

The vinyl monomer includes any monomeric vinyl compound that is capable of being polymerized or grafted by free radicals, wherein the vinyl compound could contain straight or branched aliphatic chain or a substituted or unsubstituted aromatic, heterocyclic, or alicyclic ring in a mono- or polycyclic compound. Typical substituent groups can be alkyl, hydroxyalkyl, aryl, and halo. Usually the vinyl monomer will be a member of one of the following classes: (1) vinyl-substituted aromatic, heterocyclic, or alicyclic compounds, including styrene, vinylnaphthalene, vinylpyridine, vinylpyrrolidone, vinylcarbazole, and homologs thereof, e.g., alpha- and para-methylstyrene, methylchlorostyrene, p-tert-butylstyrene, methylvinylpyridine, and ethylvinylpyridine, (2) unsaturated aliphatic nitriles and carboxylic acids and their esters including acrylonitrile; methacrylonitrile; acrylic acid; acrylate esters such as the methyl, ethyl, hydroxyethyl, 2-ethylhexyl, and butyl acrylate esters; methacrylic acid; methacrylate esters, such as the methyl, ethyl, butyl, benzyl, phenylethyl, phenoxyethyl, epoxypropyl, and hydroxypropyl methacrylate esters, (3) unsaturated acid anhydrides and salts, such as, maleic anhydride, and zinc methacrylic acid and (4) halogenated vinyl compounds, such as, halogenostyrenes. Multiple monomers from the same or different classes can be employed.

The total amount of vinyl monomer or monomers used in the graft copolymerization is about 0.5 wt% to about 20 wt%, preferably about 1 wt% to about 10 wt%, more preferably about 2 wt% to about 8%, and most preferably about 4 wt% to about 6 wt%.

The polymer composition of the present invention may also contain conventional additives, for instance, anti-acid stabilizers, such as, calcium stearate, hydrotalcite, zinc stearate, calcium oxide, and sodium stearate.

In preparation of the polymer mixture of the present invention, the reactive, peroxide-containing olefin polymer material, the olefin polymer material if any and the vinyl monomer can be combined at ambient temperature in conventional operations well known in the art; including but not limited to, drum tumbling, manual mixing, or with low or high speed mixers.

The resulting mixture is then extruded or compounded in the molten state to carry out the grafting reaction in any conventional manner well known in the art, in batch or continuous mode; for example, by using a Banbury mixer, a kneading machine, a single screw extruder, a twin screw extruder or an autoclave equipped with adequate agitation.

According to an alternative procedure, the vinyl monomer may be added to the peroxide-containing olefin polymer material and to the olefin polymer material, if any, during the extrusion or compounding process, when the polymer materials are already in the molten state.

The melt mixture can then be optionally pelletized according to conventional methods well known in the art.

Unless otherwise specified, the properties of the olefin polymer materials, compositions and other characteristics that are set forth in the following examples have been determined according to the test methods reported below:

- Melt Flow Rate ("MFR"): ASTM D1238, units of dg/min; 230° C; 2.16 kg;
Polymer material with a MFR below 100, using full die;
Polymer material with a MFR equal or above 100, using ½ die; unless otherwise specified.
- Isotactic Index ("I.I."): Defined as the percent of olefin polymer insoluble in xylene. The weight percent of olefin polymer soluble in xylene at room temperature is determined by dissolving 2.5 g of polymer in 250 ml of xylene at room temperature in a vessel equipped with a stirrer, and heating at 135°C with agitation for 20 minutes. The solution is cooled to 25°C while continuing the agitation, and then left to stand without agitation for 30 minutes so that the solids can settle. The solids are filtered with filter paper, the remaining solution is evaporated by treating it with a nitrogen stream, and the solid residue is vacuum dried at 80°C until a constant weight is reached. These values correspond

substantially to the isotactic index determined by extracting with boiling n-heptane, which by definition constitutes the isotactic index of polypropylene.

Peroxide Concentration: Quantitative Organic Analysis via Functional Groups, by S. Siggia et al., 4th Ed., NY, Wiley 1979, pp. 334-42.

Grafted Monomer Content: 5 g of grafted polymer is dissolved in 100 g xylene at 135 °C and then cool the solution to ambient temperature. The solution was poured into 500 g of acetone in a container under agitation to precipitate the polymer. The solution with precipitated polymer was then filtered to recover the polymer solid. After vacuum drying, the solid polymer sample was collected and analyzed by using Elemental Analysis to determine the grafted monomer content.

Grafted maleic

anhydride content: 5 g of grafted polymer is dissolved in 100 g xylene at 135 °C and then cool the solution to ambient temperature. The solution was poured into 500 g of acetone in a container under agitation to precipitate the polymer. The solution with precipitated polymer was then filtered to recover the polymer solid. After vacuum drying, the solid polymer sample was collected and then analyzed by Fourier Transform Infrared Spectroscopy (FTIR).

In this specification, all parts, percentages and ratios are by weight unless otherwise specified. The reactive, peroxide-containing olefin polymer materials are prepared according to the following procedures.

Preparation 1

A polypropylene homopolymer having a MFR of 0.3 dg/min, and I.I. of 95.6%, commercially available from Basell USA Inc. was irradiated at 1.0 Mrad under a blanket of nitrogen. The irradiated polymer was then treated with 2.0% by volume of oxygen at ambient temperature for 60 minutes and then with 2.0% by volume of oxygen at 140°C for an additional 60 minutes. The oxygen was then removed. The polymer was then heated at 140°C under a blanket of nitrogen for 60 minutes, cooled and collected. The MFR of the resultant polymer material was 865 dg/min.

Preparation 2

A reactive, peroxide-containing propylene polymer was prepared from a propylene copolymer having a MFR of 0.1 dg/min, I.I. of 37.5%, and ethylene content of 21.7 wt%, commercially available from Basell USA Inc. The polymer was irradiated at 1.0 Mrad under a blanket of nitrogen. The irradiated polymer was then treated with 5.0% by volume of oxygen at ambient temperature for 60 minutes and then with 4.0% by volume of oxygen at 120°C for an additional 60 minutes. The oxygen was then removed. The polymer was then heated at 120°C under a blanket of nitrogen for 60 minutes, cooled and collected. The MFR of the resultant polymer material was 6.5 dg/min.

Preparation 3

A reactive, peroxide-containing propylene polymer was prepared from a propylene copolymer having a MFR of 3.8 dg/min, I.I. of 88.6% and ethylene content of 9.4 wt%, commercially available from Basell USA Inc. The polymer was irradiated at 2.0 Mrad and the irradiated polymer was treated with air (20.9% by volume of oxygen) at ambient temperature for 60 minutes. The resultant polymer material was then placed in an air-tight bag and stored at ambient temperature before use. The MFR of the reactive, peroxide-containing polymer material was 43.6 dg/min measured at 190 °C. The peroxide concentration was 22.2 meq/kg of polymer.

Preparation 4

A reactive, peroxide-containing propylene polymer was prepared from a propylene homopolymer having a MFR of 0.4 dg/min, and I.I. of 95.4%, commercially available from Basell USA Inc. The polymer was irradiated at 4.0 Mrad and the irradiated polymer was treated with air (20.9% by volume of oxygen) at ambient temperature for 60 minutes. The resultant polymer material was then placed in an air-tight bag and stored at ambient temperature before use. The MFR of the reactive, peroxide-containing polymer material was 110 dg/min measured at 190 °C.

Examples 1 and 2

These examples show the graft polymerization of a reactive, peroxide-containing polymer with 2-acrylamido-2-methyl propanesulfonic acid (Acid I), or with the sodium salt of 2-acrylamido-2-methyl propanesulfonic acid (50 wt% aqueous solution) (Salt I) in a twin screw extruder.

The reactive, peroxide-containing olefin polymer was prepared from propylene homopolymer according to Preparation 1; 2-acrylamido-2-methyl propanesulfonic acid, and

the sodium salt of 2-acrylamido-2-methyl propanesulfonic acid (50 wt% aqueous solution) were obtained from Lubrizol Corporation and used without further purification.

Irganox B225 antioxidant is a 1:1 blend of Irganox 1010 antioxidant and Irgafos 168 tris(2,4-di-*t*-butylphenyl) phosphite antioxidant and is commercially available from Ciba Specialty Chemicals Corporation. The amounts given for the stabilizers are in parts per hundred parts of the polymer composition.

The materials were dry-blended and bag mixed with Irganox B225 antioxidant and calcium stearate. The obtained polymer mixtures were then compounded in a 30 mm co-rotating intermeshing Leistritz LSM 34 GL twin-screw extruder commercially available from Leistritz AG, with a barrel temperature of 190°C and a screw speed of 150 r.p.m. The barrel temperature at the die was of 160°C and the throughput was of 11.4 kg/h.

The composition and properties of the grafted polymers obtained in Examples 1 and 2 are reported in Table 1.

Example 3

This example shows the graft polymerization of a reactive, peroxide-containing copolymer with 2-acrylamido-2-methyl propanesulfonic acid (Acid I) in a twin screw extruder.

The reactive, peroxide-containing olefin copolymer was prepared from propylene copolymer according to Preparation 2, and 2-acrylamido-2-methyl propanesulfonic acid was obtained from Lubrizol Corporation and used without further purification.

The materials were blended and compounded under the same conditions as those reported in Example 1. The composition and properties of the obtained grafted polymer are reported in Table 1.

Example 4

This example shows the graft polymerization of a reactive, peroxide-containing polymer with maleic anhydride in a twin screw extruder.

The reactive, peroxide-containing olefin polymer was prepared from propylene copolymer according to Preparation 3. Maleic anhydride was received from Aldrich Chemical Company, Inc. and used without further purification.

The materials were blended and compounded under the same conditions as those reported in Example 1. The composition and properties of the obtained grafted polymer are reported in Table 1.

Example 5

This example shows the graft polymerization of a reactive, peroxide-containing polymer with maleic anhydride in a twin screw extruder.

The reactive, peroxide-containing olefin polymer was prepared from propylene homopolymer according to Preparation 4. Maleic anhydride was received from Aldrich Chemical Company, Inc. and used without further purification.

The materials were blended and compounded under the same conditions as those reported in Example 1. The composition and properties of the obtained grafted polymer are reported in Table 1.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5
Reactive, peroxide-containing polymer of Preparation 1 (g)	2931	2931			
Reactive, peroxide-containing polymer of Preparation 2 (g)			2811		
Reactive, peroxide-containing polymer of Preparation 3 (g)				2850	
Reactive, peroxide-containing polymer of Preparation 4 (g)					2850
Acid I (g)	60		180		
Salt I (g)		120			
Maleic anhydride (g)				150	150
Irganox B225 (pph)	0.2	0.2	0.2	0.2	0.2
Calcium Stearate (pph)	0.1	0.1	0.1	0.1	0.1
Added monomer content (wt%)	2.0	2.0	6.0	5.0	5.0
Grafted monomer content (wt%)	1.17	1.65	4.27	0.52	0.68

Other features, advantages and embodiments of the invention disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosures. In this regard, while specific embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.

CLAIMS

1. A process for making graft copolymers comprising:

a) preparing a polymer mixture comprising:

- I. about 80.0 to about 99.5 wt% of a reactive, peroxide-containing olefin polymer material (A); and
- II. about 0.5 to about 20.0 wt% of at least one vinyl monomer capable of being polymerized or grafted in the presence of free radicals;

wherein the sum of components I + II is equal to 100 wt%;

b) extruding or compounding in molten state the polymer mixture, thereby producing a melt mixture; and optionally

c) pelletizing the melt mixture after it is cooled, thereby producing a pelletized mixture.

2. The process of claim 1 wherein the reactive, peroxide-containing olefin polymer material (A) is prepared from an olefin polymer starting material selected from:

- (a) a crystalline homopolymer of propylene having an isotactic index greater than about 80%;
- (b) a crystalline, random copolymer of propylene with an olefin selected from ethylene and C₄-C₁₀ α -olefins wherein the polymerized olefin content is about 1-10% by weight when ethylene is used, and about 1% to about 20% by weight when the C₄-C₁₀ α -olefin is used, the copolymer having an isotactic index greater than about 60%;
- (c) a crystalline, random terpolymer of propylene and two olefins selected from ethylene and C₄-C₈ α -olefins wherein the polymerized olefin content is about 1% to about 5% by weight when ethylene is used, and about 1% to about 20% by weight when the C₄-C₁₀ α -olefins are used, the terpolymer having an isotactic index greater than about 85%;
- (d) an olefin polymer composition comprising:
 - (i) about 10% to about 60% by weight of a crystalline propylene homopolymer having an isotactic index at least about 80% or a crystalline copolymer of monomers selected from (a) propylene and ethylene, (b) propylene, ethylene and a C₄-C₈ α -olefin, and (c) propylene and a C₄-C₈ α -olefin, the copolymer having a polymerized propylene content of more than about 85% by weight, and an isotactic index greater than about 60%;

- (ii) about 3% to about 25% by weight of a copolymer of ethylene and propylene or a C₄-C₈ α -olefin that is insoluble in xylene at ambient temperature; and
- (iii) about 10% to about 80% by weight of an elastomeric copolymer of monomers selected from (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer optionally containing about 0.5% to about 10% by weight of a polymerized diene and containing less than about 70% by weight of polymerized ethylene, and being soluble in xylene at ambient temperature and having an intrinsic viscosity of about 1.5 to about 6.0 dl/g;

wherein the total of (ii) and (iii), based on the total olefin polymer composition is about 50% to about 90% by weight, and the weight ratio of (ii)/(iii) is less than about 0.4, and the composition is prepared by polymerization in at least two stages;

- (e) homopolymers of ethylene;
 - (f) random copolymers of ethylene and an α -olefin selected from C₃-C₁₀ α -olefins having a polymerized α -olefin content of about 1 to about 20% by weight;
 - (g) random terpolymers of ethylene and C₃-C₁₀ α -olefins having a polymerized α -olefin content of 1 to 20% by weight;
 - (h) homopolymers of butene-1;
 - (i) copolymers or terpolymers of butene-1 with ethylene, propylene or C₅-C₁₀ α -olefin, the comonomer content from about 1 mole % to about 15 mole %; and
 - (j) mixtures thereof.
3. The process of claim 2 wherein the starting material is a crystalline homopolymer of propylene having an isotactic index greater than 80%.
 4. A process for making graft copolymer mixture comprising:
 - a) preparing a polymer mixture comprising:
 - I. about 10.0 to about 80.0 wt% of a reactive, peroxide-containing olefin polymer material (A);
 - II. about 0.5 to about 20.0 wt% of at least one vinyl monomer capable of being polymerized or grafted in the presence of free radicals; and
 - III. about 10 to about 80.0 wt% of an olefin polymer material (B);

wherein the sum of components I + II + III is equal to 100 wt%;

- b) extruding or compounding in molten state the polymer mixture, thereby producing a melt mixture; and optionally
 - c) pelletizing the melt mixture after it is cooled.
5. The process of claim 4 wherein the reactive, peroxide-containing olefin polymer material (A) is prepared from an olefin polymer starting material selected from:
- (a) a crystalline homopolymer of propylene having an isotactic index greater than about 80%;
 - (b) a crystalline, random copolymer of propylene with an olefin selected from ethylene and C₄-C₁₀ α -olefins wherein the polymerized olefin content is about 1-10% by weight when ethylene is used, and about 1% to about 20% by weight when the C₄-C₁₀ α -olefin is used, the copolymer having an isotactic index greater than about 60%;
 - (c) a crystalline, random terpolymer of propylene and two olefins selected from ethylene and C₄-C₈ α -olefins wherein the polymerized olefin content is about 1% to about 5% by weight when ethylene is used, and about 1% to about 20% by weight when the C₄-C₁₀ α -olefins are used, the terpolymer having an isotactic index greater than about 85%;
 - (d) an olefin polymer composition comprising:
 - (i) about 10% to about 60% by weight of a crystalline propylene homopolymer having an isotactic index at least about 80% or a crystalline copolymer of monomers selected from (a) propylene and ethylene, (b) propylene, ethylene and a C₄-C₈ α -olefin, and (c) propylene and a C₄-C₈ α -olefin, the copolymer having a polymerized propylene content of more than about 85% by weight, and an isotactic index greater than about 60%;
 - (ii) about 3% to about 25% by weight of a copolymer of ethylene and propylene or a C₄-C₈ α -olefin that is insoluble in xylene at ambient temperature; and
 - (iii) about 10% to about 80% by weight of an elastomeric copolymer of monomers selected from (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈

α -olefin, the copolymer optionally containing about 0.5% to about 10% by weight of a polymerized diene and containing less than about 70% by weight of polymerized ethylene, and being soluble in xylene at ambient temperature and having an intrinsic viscosity of about 1.5 to about 6.0 dl/g;

wherein the total of (ii) and (iii), based on the total olefin polymer composition is about 50% to about 90% by weight, and the weight ratio of (ii)/(iii) is less than about 0.4, and the composition is prepared by polymerization in at least two stages;

- (e) homopolymers of ethylene;
 - (f) random copolymers of ethylene and an α -olefin selected from C₃-C₁₀ α -olefins having a polymerized α -olefin content of about 1% to about 20% by weight;
 - (g) random terpolymers of ethylene and two C₃-C₁₀ α -olefins having a polymerized α -olefin content of about 1% to about 20% by weight;
 - (h) homopolymers of butene-1;
 - (i) copolymers or terpolymers of butene-1 with ethylene, propylene or C₅-C₁₀ α -olefin, the comonomer content from about 1 mole % to about 15 mole %; and
 - (j) mixtures thereof.
6. The process of claim 5 wherein the starting material is a crystalline homopolymer of propylene having an isotactic index greater than 80%.
7. The process of claim 4 wherein the olefin polymer material (B) is selected from:
- (a) a crystalline homopolymer of propylene having an isotactic index greater than about 80%;
 - (b) a crystalline, random copolymer of propylene with an olefin selected from ethylene and C₄-C₁₀ α -olefins wherein the polymerized olefin content is about 1-10% by weight when ethylene is used, and about 1% to about 20% by weight when the C₄-C₁₀ α -olefin is used, the copolymer having an isotactic index greater than about 60%;
 - (c) a crystalline, random terpolymer of propylene and two olefins selected from ethylene and C₄-C₈ α -olefins wherein the polymerized olefin content is about 1% to about 5% by weight when ethylene is used, and about 1% to about 20% by weight when the C₄-C₁₀ α -olefins are used, the terpolymer having an isotactic index greater than about 85%;

- (d) an olefin polymer composition comprising:
- (i) about 10% to about 60% by weight of a crystalline propylene homopolymer having an isotactic index at least about 80% or a crystalline copolymer of monomers selected from (a) propylene and ethylene, (b) propylene, ethylene and a C₄-C₈ α -olefin, and (c) propylene and a C₄-C₈ α -olefin, the copolymer having a polymerized propylene content of more than about 85% by weight, and an isotactic index greater than about 60%;
 - (ii) about 3% to about 25% by weight of a copolymer of ethylene and propylene or a C₄-C₈ α -olefin that is insoluble in xylene at ambient temperature; and
 - (iii) about 10% to about 80% by weight of an elastomeric copolymer of monomers selected from (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer optionally containing about 0.5% to about 10% by weight of a polymerized diene and containing less than about 70% by weight of polymerized ethylene, and being soluble in xylene at ambient temperature and having an intrinsic viscosity of about 1.5 to about 6.0 dl/g;

wherein the total of (ii) and (iii), based on the total olefin polymer composition is about 50% to about 90% by weight, and the weight ratio of (ii)/(iii) is less than about 0.4, and the composition is prepared by polymerization in at least two stages;

- (e) homopolymers of ethylene;
- (f) random copolymers of ethylene and an α -olefin selected from C₃-C₁₀ α -olefins having a polymerized α -olefin content of about 1% to about 20% by weight;
- (g) random terpolymers of ethylene and two C₃-C₁₀ α -olefins having a polymerized α -olefin content of about 1% to about 20% by weight;
- (h) homopolymers of butene-1;
- (i) copolymers or terpolymers of butene-1 with ethylene, propylene or C₅-C₁₀ α -olefin, the comonomer content from about 1 mole % to about 15 mole %; and
- (j) mixtures thereof.

8. The process of claim 4 wherein the olefin polymer material (B) is a crystalline homopolymer of propylene having an isotactic index greater than 80%.
9. The process of claim 1 or claim 4 wherein the vinyl monomer is selected from:
 - (a) vinyl-substituted aromatic, heterocyclic, or alicyclic compounds;
 - (b) unsaturated aliphatic nitriles, carboxylic acids and their esters;
 - (c) unsaturated acid anhydrides and salts; and
 - (d) halogenated vinyl compounds.
10. The process of claim 9 wherein the vinyl monomer is selected from:
styrene, alpha-methylstyrene, and divinyl benzene.
11. The process of claim 9 wherein the vinyl monomer is selected from:
alkyl acrylates, alkyl acrylic acid, alkyl methacrylate, alkyl methacrylic acids, glycol alkyl acrylates and glycol alkyl methacrylates.
12. The process of claim 9 wherein the vinyl monomer is selected from:
maleic anhydride, 2-acrylamido-2-methyl propanesulfonic acid, sodium salt, 2-acrylamido-2-methyl propanesulfonic acid, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No

IB2004/001963

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F255/00 C08F8/06

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	GB 878 443 A (MONTEDISON SPA) 27 September 1961 (1961-09-27) claims; examples -----	1-12
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A	US 5 561 196 A (KOTLAR HANS K ET AL) 1 October 1996 (1996-10-01) claim 1 -----	1-12



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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