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(54) Titre : METHODE POUR LA GREFFE DE MONOMERES VINYLIQUES SUR DES POLYMERES OLEFINIQUES PARTICULAIRES

(54) Title: PROCESS FOR GRAFTING VINYL MONOMERS ON PARTICULATE OLEFIN POLYMERS

(57) Abrégé/Abstract:
This invention provides a uniformly grafted particulate polyolefin material formed by the free radical-initiated grafting of at least one non-homopolymerizing vinyl monomer at free radical sites on a particulate olefin polymer material having (a) a pore volume fraction of at least about 0.07 wherein more than 40% of the pores have a diameter larger than 1 micron; and (b) a weight average diameter in the range of about 0.4 to 7 mm. The amount of vinyl monomer grafted to the as-polymerized particulate olefin polymer material is about 0.1 to 10%, preferably about 0.3 to 5.0%, of the total weight of the grafted olefin polymer product, and the grafted vinyl monomer is uniformly distributed throughout the particles of the olefin polymer material.

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PROCESS FOR GRAFTING VINYL
MONOMERS ON PARTICULATE OLEFIN POLYMERS

Abstract

This invention provides a uniformly grafted particulate polyolefin material formed by the free radical-initiated grafting of at least one non-homopolymerizing vinyl monomer at free radical sites on a particulate olefin polymer material having (a) a pore volume fraction of at least about 0.07 wherein more than 40% of the pores have a diameter larger than 1 micron; and (b) a weight average diameter in the range of about 0.4 to 7 mm. The amount of vinyl monomer grafted to the as-polymerized particulate olefin polymer material is about 0.1 to 10%, preferably about 0.3 to 5.0%, of the total weight of the grafted olefin polymer product, and the grafted vinyl monomer is uniformly distributed throughout the particles of the olefin polymer material.

It is known to graft non-polymerizable vinyl monomers such as maleic anhydride onto polyolefins. However, the various known methods have a number of disadvantages.

One known method involves dissolving the polyolefin in a solvent, typically a hydrocarbon solvent, followed by the addition of a peroxide initiator and maleic anhydride. The grafting is typically carried out at temperatures in excess of 125°C, more usually from 130 to 150°C. This method of grafting is costly, in part because of the need to recover the solvent. Moreover, the amount of monomer such as maleic anhydride which can be grated on the polyolefin is low, usually no more than 3% by weight. When the polyolefin is polypropylene, grafting by this process results in considerable degradation because of the relatively high temperatures employed. When polyethylene is the polyolefin to be grafted, there is undesirable cross-linking, again as a result of the relatively high grafting temperatures.

Another prior art grafting technique involves an extrusion operation, wherein the monomer, e.g., maleic anhydride, and the peroxide initiator, are compounded with the polyolefin and the resulting mixture is extruded. Inasmuch as the extrusion must be carried out at a relatively high temperature, there is, as with polypropylene, undesirable degradation, and with polyethylene, undesired cross-linking. Further, the grafting efficiency is poor, so that generally the amount of monomer, such as maleic anhydride, that can be grafted onto the polyolefin is 2% by weight or lower. Moreover, it is difficult and costly to remove unreacted monomer from the polyolefin.

Another prior art grafting technique, involves a dry process wherein the polyolefin in powder form is placed in a closed reactor with agitation and, in the absence of oxygen, the peroxide initiator and monomer are introduced. Relatively high temperatures are required, generally at least 130°C and frequently higher. This technique is disadvantageous because of undesired degradation (with polypropylene) or excessive cross-linking (with polyethylene).

In contrast, and as more fully described hereinafter, the present invention substantially overcomes the foregoing disadvantages (a) use of a porous polyolefin, (b) by conducting the grafting at considerably lower temperatures, typically 60 to 125°C when using a peroxide initiator, and/or (c) by conducting the grafting from room temperatures as 100°C when using radiation for the generation of free radicals for grafting, or, preferably, by a combination of (a) and (b) or (a) and (c). As a result, there is higher grafting efficiency, a reduction or elimination of degradation and/or cross-linking, and a retention of molecular weight. When the porous polyolefin is used, one is able to work with a free flowing powder that is capable of high liquid absorption, with little or no caking.

This invention provides a uniformly grafted particulate polyolefin material formed by the free radical-initiated grafting of at least one non-homopolymerizing vinyl monomer at free radical sites on a particulate olefin polymer material having (a) a pore volume fraction of at least about 0.07 wherein more than 40% of the pores have a diameter larger than 1 micron; and (b) a weight average diameter in the range of about 0.4 to 7 mm. The amount of vinyl monomer grafted to the particulate olefin polymer material is about 0.1 to 10%, preferably about 0.3 to 5.0%, of the total weight of the grafted olefin polymer product, and the grafted vinyl monomer is uniformly distributed throughout the particles of olefin polymer material.

Both the pore volume of at least about 0.07 and the pore diameter wherein m ore than 40% of the pores in the particle have a diameter in excess of 1 micron are critical to the preparation of the grafted olefin polymer material of this invention. In such olefin polymer materials grafting of the vinyl monomer takes place throughout the interior of the particulate material as well as on the external surface thereof, resulting in a substantially uniform distribution of the graft polymer throughout the olefin polymer particle. Aside from these materials, the commercially available ethylene and propylene polymers in particulate form, even those having a reasonably high surface area, and porosity, do not provide graft polymers with internal uniform distribution of the grafted vinyl monomer since they lack the combination of the requisite pore diameter and large pore volume fraction essential for producing the grafted olefin polymer product of this invention.

According to a further aspect of the invention, the grafted particulate olefin polymer material can be prepared by either of the following methods.

Initially, the grafted polyolefin material may be prepared by

(a) irradiating a particulate olefin polymer material at a temperature in the range of about 10° to 85°C with high-energy ionizing radiation to produce free-radical sites in the olefin polymer material;

(b) treating the irradiated particulate olefin polymer material at a temperature up to about 100°C for a period of at least about 3 minutes, with about 0.2 to 20 percent by weight, based on the total weight of olefin polymer and grafting monomer used, of at least one non-free radical homopolymerizing but free-radical graftable vinyl monomer;

(c) simultaneously or successively, in either order,

(1) deactivating substantially all residual free radicals in the resultant grafted particulate olefin polymer material, and

(2) removing any unreacted grafting monomer from said material;

the particulate olefin polymer material being maintained in a substantially non-oxidizing environment throughout said steps at least until after the deactivation of residual free radicals has been completed.

According to the second method of the invention, the particulate olefin polymer material is treated at a temperature of about 60° to 125°C with about 0.1 to 6.0 pph (parts by weight per 100 parts by weight of the olefin polymer material) of an organic chemical compound which is a free radical polymerization initiator and has a decomposition half-life of about 1 to 240 minutes at the temperature employe.

Over a time period which coincides with, or follows, the period of initiator treatment, with or without overlap, the polymer material is treated with about 0.2 to 20 percent by weight, based on the total weight of olefin polymer and grafting monomer used, of at least one grafting monomer. The temperature employed during any period of monomer treatment is within the same range as indicated above with respect to the initiator treatment.

After the grafting period, i.e., the period of treatment with the grafting monomer, and any subsequent holding period at the reaction conditions, any unreacted monomer is removed from the resultant grafted particulate olefin polymer material, and the decomposition of any unreacted initiator and deactivation of any residual free radicals are promoted, e.g., by a temperature increase. During the entire process the polymer material is maintained in a substantially non-oxidizing environment.

All parts and percentages used in this specification are by weight unless otherwise noted.

The olefin polymer material useful in the practice of the methods of this invention for making graft copolymers of olefin polymers is

(a) a homopolymer of a linear or branched C_2-C_8 1-olefin;

(b) a random copolymer of a linear or branched C_2-C_8 1-olefin with a second olefin selected from the group consisting of C_2-C_{10} 1-olefins, provided that, when the second olefin is ethylene the maximum polymerized ethylene content is about 10%, preferably about 4%, when the olefin is propylene and the second olefin is a C_4-C_{10} 1-olefin the maximum polymerized content thereof is about 20%, preferably about 16%, and when the olefin is ethylene and the second olefin is a C_3-C_{10} 1-olefin the maximum polymerized content thereof is about 10%, preferably about 5%;

(c) a terpolymer of a linear or branched C_3-C_8 1-olefin and two different olefins selected from the group consisting of ethylene and C_4-C_8 1-olefins, provided that, when ethylene is one of the two different olefins the maximum polymerized ethylene content is about 5%, preferably about 4%, and when each of the two different olefins is a C_4-C_{10} 1-olefin, the maximum polymerized content of the two different C_4-C_8 1-olefins is about 20%, preferably about 16%; or

(d) a homopolymer of (a) or a random copolymer of (b), impact-modified with about 10 to 60% of

(i) an ethylene-propylene rubber having an ethylene content of about 7 to 70%, preferably about 10 to 40%, and most preferably an ethylene-propylene rubber having an ethylene content of about 7 to 40%,

(ii) an ethylene/butene-1 copolymer rubber (EBR) having an ethylene content of about 30 to 70%,

(iii) a propylene/butene-1 copolymer rubber (PBR) having a butene-1 content of about 30 to 70%,

(iv) an ethylene/propylene diene monomer rubber (EPDM) having an ethylene content of about 30 to 70% and diene content of about 1 to 10%,

(v) an ethylene/propylene/butene terpolymer rubber (EPBR) having a propylene content of about 1 to 10% and butene content of about 30 to 70% or a propylene content of about 30 to 70% and a butene content of about 1 to 10%.

The C_2-C_8 1-olefins which can be sued in the preparation of the above olefin polymer materials include ethylene, propylene, 1-

butene, 3-methyl-1-butene, 3,4-dimethyl-1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 3-methyl-1-hexene, 1-heptene, and the like.

C_3-C_{10} 1-olefins which can be used to prepare olefin polymer materials as described above include linear and branched olefins which have at least 3 carbon atoms.

When the olefin polymer is an ethylene homopolymer it has a density of 0.91 g/cm^3 or greater, and when the olefin polymer is an ethylene copolymer with a C_{3-10} alpha-olefin it has a density of 0.,91 g/cm^3 or greater. Suitable ethylene copolymers include ethylene/butene-1, ethylene/hexene-1 and ethylene/4-methyl-1-pentene. The ethylene copolymer can be a HDPE or a LLDPE, and the ethylene homopolymer can be a HDPE or a LDPE. Typically the LLDPE and LDPE have densities of 0.91 g/cm^3 or greater and the HDPE have densities of 0.95 g/cm^3 or greater.

Homopolymers and random copolymers of ethylene, propylene and 1-butene are preferred. With respect to ethylene, HDPE and LLDPE are preferred.

Suitable particulate forms of the olefin polymer material used in the present method include powder, flake, granulate, spherical, cubic and the like. Spherical particulate forms having a pore volume fraction of at least about 0.07, preferably at least about 0,.2, are preferred. The spherical particulate olefin polymers having pore volume fractions of at least about 0.2 are obtainable using catalysts of the type described in Examples 2, 3 and 4 of European Patent Application EP 0395083.

According to the radiation method of this invention, free radical or active sites are formed on the particulate olefin polymer material by irradiation before the polymer is exposed to the grafting monomer(s). Irradiation in the absence of monomer is advantageous although the degree of benefit varies from monomer to monomer.

The radiation is carried about according to the method and procedure described in U.S. Patent Nos. 5,411,994 and 5,652,281 (Canadian Patent No. 2,031,406).

The peroxide treatment used in this invention is carried out in accordance with the method and procedure described in U.S. Patent No. 5,140,074 (Canadian Patent No. 2,033,671).

The method of this invention embodies a combination of steps which together permit olefin grafted polymers to be obtained not only in high conversions (monomer consumption) but also with a high degree of graft efficiency. Moreover, degradation of the backbone olefin polymer is minimized, thereby avoiding the production of a grafted polymer having a melt flow rate which is substantially higher than that of the starting backbone olefin polymer, a condition that can adversely affect the processing behavior of the grafted polymer.

Examples of grafting monomers useful in accordance with this invention are unsaturated cyclic anhydrides and their aliphatic diester and diacid derivatives. Suitable grafting monomers are selected from the group consisting of maleic anhydride, C_{1-10} linear and branched dialkyl maleate, C_{1-10} linear and branched dialkyl fumarate, itaconic anhydride, C_{1-10} linear and branched dialkyl esters of itaconic acid, maleic acid, fumaric acid, itaconic acid, and mixtures thereof.

Example 1

Four hundred grams of a finely divided porous propylene homopolymer (LBD-406A* commercially available from HIMONT Italia S.r.l.) are placed in a 1-liter glass reactor equipped with a heating jacket and a helical impeller. The polymer is in the form of generally spherical particles having the following characteristics: nominal melt flow rate (ASTM Method D 1238-82, Condition L) 8 dg/min; intrinsic viscosity (method of J. H. Elliott

*Trade-mark

et al., J. Applied Polymer Sci. 14, 2947-2963 (1970) - polymer dissolved in decahydronaphthalene at 135°C) 2.4 dl/g; weight average diameter 2.0 mm; and pore volume fraction (mercury porosimetry method) 0.33. More than 90% of the pores in the porous particles are larger than 1 micron in diameter.

The reactor is purged with nitrogen at room temperature for 15 minutes (to an active oxygen content of less than 0.004% by volume), heated to 100°C by circulating hot oil through the reactor jacket, and equilibrated to that temperature with continued nitrogen purging and stirring at 225 rpm. Thereafter, purging is stopped, the reactor pressure is adjusted to 14 Kpa, and 20 ml of an oxygen-free mineral spirit solution of tert-butylperoxy-2-ethylhexanoate containing 10 g of the peroxy ester having a half life of 26 minutes at 100°C is added. After 15 minutes, 13.2 g of maleic anhydride, which is previously heated to 60°C to convert it to a liquid state, is sprayed into the reactor at a rate of 0.2 pph (parts per 100 parts polypropylene, by weight) per minute. The total time of addition is about 16 minutes. The reactor is maintained at 100°C and stirring continued for 60 minutes after all the maleic anhydride has been added.

At the end of the grafting period, the reactor is purged with nitrogen for 15 minutes, and the reactor contents are then heated to 130°C by purging with heated nitrogen. The reactor temperature is maintained at 130°C for 30 minutes during which time any unreacted maleic anhydride is swept out of the reactor in the nitrogen flow. After cool-down under a nitrogen blanket, the free-flowing solid product remaining in the reactor is discharged therefrom. The product is isolated in good yield. The product is characterized by excellent molecular weight retention.

Comparative Example

The procedure and ingredients of Example 1 are used with the exception that the reaction temperature is 150°C. The peroxide is Lupersol* 101 with a half-life of 30 minutes at the reaction

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temperature, and the quantity of peroxide used in 5.6 ml. The peroxide is 98% pure. The product is characterized as having a substantial degree of degradation.

Example 2

This example illustrates the grafted olefin polymer of this invention and a method of making same.

(a) Irradiation of the Polymer

A finely divided porous propylene homopolymer (LBD-520A* commercially available from HIMONT Italia S.r.l.) having the following characteristics: nominal melt flow rate (ASTM Method D 1238-82, Condition L) 8 dg/min; intrinsic viscosity (method of J. H. Elliott et al., J. Applied Polymer Sci. 14, 2947-2963 (1970) - polymer dissolved in decahydronaphthalene at 135°C) 1.89 dl/g; extractability in methylene chloride 2.0 wt. %; weight average diameter 1.88 mm; and pore volume fraction (mercury porosimetry method) 0.45. More than 90% of the pores in the porous particles are larger than 1 micron in diameter.

The polypropylene (400 grams), substantially free of active oxygen, is placed on a moving conveyor belt to form a powder bed, approximately 2 cm thick, which is passed by conveyor belt through an electron beam generated by a 2 MeV Van de Graaf generator operating at a 312 microamp beam current. The conveyor belt speed is adjusted to dose rate of about 30 Mrad/min. The environment or atmosphere within the enclosed radiation chamber consists essentially of nitrogen gas, the active oxygen content being maintained at less than 0.004% by volume. The chamber is at ambient temperature (about 23°C).

(b) Treatment with Grafting Monomer

The irradiated polypropylene is conveyed from the radiation chamber into a graft polymerization reactor at ambient temperature (23°C) where it is agitated and sprayed with 13.2 grams of liquid maleic anhydride monomer (3.3% maleic anhydride based on the total weight of monomer and polypropylene), added to the

*Trade-mark

agitated powder at a rate of about 1.0 g/min. A nitrogen environment or atmosphere is maintained in the grafting reactor and in the transfer system for conveying the irradiated particles from the radiation chamber to the grafting reactor so that the active oxygen content is less than 0.004% by volume. The time elapsing between the exposure of the polypropylene to the electron beam and its treatment with the monomer is about 2 minutes.

Agitation of the maleic anhydride/polypropylene mixture is continued for 30 minutes.

(c) Deactivation of Residual Free Radicals

After completion of the grafting reaction, the reactor contents are heated to 140°C by purging the reactor with heated nitrogen (supplemented by an electric heating mantle), and held at 140°C for 30 minutes. The nitrogen flow rate is high enough to provide sufficient heat transfer to minimize heat-up time as well as sufficient mass transfer to remove any unreacted monomer present. The product is isolated in good yield and is characterized by excellent molecular weight retention.

Variations from the foregoing detailed description can of course be made without departing from the spirit of the invention as set out in the following claims.

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CLAIMS:

1. A process for preparing a uniformly grafted particulate olefin polymer material formed by the free radical-initiated grafting of at least one non-homopolymerizing vinyl monomer at free radical sites on a particulate olefin polymer material having (a) a pore volume fraction of at least about 0.07 wherein more than 40% of the pores have a diameter larger than 1 micron; and (b) a weight average diameter in the range of about 0.4 to 7 mm, which comprises:

the process of:

(a) irradiating the particulate olefin polymer material at a temperature in the range of about 10° to 85°C with high-energy ionizing radiation to produce free-radical sites in the olefin materials;

(b) treating the irradiated particulate olefin polymer material at a temperature up to about 100°C for a period of at least about 3 minutes, with about 0.2 to 20% by weight, based on the total weight of olefin polymer and grafting monomer used, of at least one non-free radical homopolymerizing but free-radical graftable vinyl monomer;

(c) simultaneously or successively, in either order,

(1) deactivating substantially all residual free radicals in the resultant grafted particulate olefin polymer material; and

(2) removing any unreacted grafting monomer from said material; or

the process of:

(a') treating the polymer material at a temperature of about 60° to 125°C with about 0.1 to 6.0 pph (parts by weight per 100 parts by weight of the olefin polymer material) of an organic chemical compound which is a free radical polymerization initiator and has a decomposition half-life of about 1 to 240 minutes at the temperature employed; and

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(b') over a time period which coincides with, or follows, the period of initiator treatment, with or without overlap, treating the olefin polymer material with about 0.2 to 20 percent by weight, based on the total weight of olefin polymer and grafting monomer used, with at least one grafting monomer;

wherein during the entire process (a) to (c) or (a') and (b') the polymer material is maintained in a substantially non-oxidizing environment.

2. The process according to claim 1, in which the non-homopolymerizing vinyl monomer is selected from the group consisting of unsaturated cyclic anhydrides and their aliphatic diesters.

3. Particulate olefin polymer material substantialy uniformly grafted with a non-homopolymerizing vinyl monomer, wherein the uniformly grafted particulate olefin polymer material has: (a) a pore volume fraction of at least about 0.07 wherein more than 40% of the pores have a diameter larger than 1 micron; and (b) a weight average diameter in the range of about 0.4 to 7 mm.

4. Particulate olefin polymer material substantially uniformly grafted with maleic anhydride, wherein the uniformly grafted particulate olefin polymer material has: (a) a pore volume fraction of at least about 0.07 wherein more than 40% of the pores have a diameter larger than 1 micron; and (b) a weight average diameter in the range of about 0.4 to 7 mm.

5. The process according to claim 1, wherein the non-homopolymerizing vinyl monomer is maleic anhydride.

6. The process according to claim 1, 2 or 5, wherein the olefin polymer material is polypropylene.

7. The process according to claim 1, 2 or 5, wherein the olefin polymer material is

(a) a homopolymer of a linear or branched C_2-C_8 1-olefin;

(b) a random copolymer of a linear or branched C_2-C_8 1-olefin with a second olefin selected from the group consisting of C_2-C_{10} 1-olefins, provided that, when the second olefin is ethylene the maximum polymerized ethylene content is about 10%, when the olefin is propylene and the second olefin is a C_4-C_{10} 1-olefin the maximum polymerized content thereof is about 20%, and when the olefin is ethylene and the second olefin is a C_3-C_{10} 1-olefin the maximum polymerized content thereof is about 10%;

(c) a terpolymer of a linear or branched C_3-C_8 1-olefin and two different olefins selected from the group consisting of ethylene and C_4-C_8 1-olefins, provided that, when ethylene is one of the two different olefins the maximum polymerized ethylene content is about 5%, and when each of the two different olefins is a C_4-C_{10} 1-olefin, the maximum polymerized content of the two different C_4-C_8 1-olefins is about 20%; or

(d) a homopolymer of (a) or a random copolymer of (b), impact-modified with about 10 to 60% of

(i) an ethylene-propylene rubber having an ethylene content of about 7 to 70%,

(ii) an ethylene/butene-1 copolymer rubber (EBR) having an ethylene content of about 30 to 70%,

(iii) a propylene/butene-1 copolymer rubber (PBR) having a butene-1 content of about 30 to 70%,

(iv) an ethylene/propylene diene monomer rubber (EPDM) having an ethylene content of about 30 to 70% and diene content of about 1 to 10%,

(v) an ethylene/propylene/butene terpolymer rubber (EPBR) having a propylene content of about 1 to 10% and butene content of about 30 to 70% or a propylene content of about 30 to 70% and a butene content of about 1 to 10%.

8. The process according to claim 1, 2, 5, 6 or 7, wherein the process comprising (a), (b) and (c) is adopted.

9. The process according to claim 1, 2, 5, 6 or 7, wherein the process comprising (a′) and (b′) is adopted.

10. The process according to claim 1 or 2 or any one of claims 5 to 9, wherein the olefin polymer material has a pore volume fraction of 0.07 to 0.45.

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