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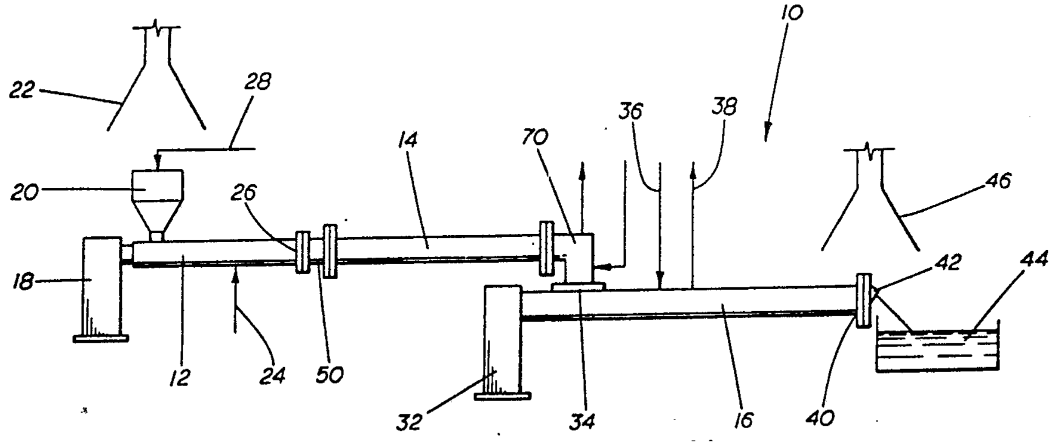

(57) Abstract

A polymer grafting process, apparatus and products obtained therewith are disclosed. The process comprises the melt-phase grafting of a polyolefin containing unsaturation sites with an enophile (such as maleic anhydride) under ene reaction conditions at 180°-265 °C in reactor with a mean residence time of 12-40 minutes and a relatively narrow residence time distribution such that 90 percent of the reactor throughput has a residence time within 75-175 percent of the mean. The apparatus comprises means for supplying molten, pressurized unsaturated polyolefin and enophile, a distributively mixed reactor for receiving the pressurized, molten reactants, for maintaining the ene reaction conditions and for producing a grafted polymer product, and a finishing extruder for removal of unreacted enophile. The grafted polymer product contains ene grafted enophile, and has an intact molecular structure substantially unchanged from that of the polymer prior to grafting.

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POLYMER GRAFTING PROCESS, APPARATUS AND PRODUCTS OBTAINED THEREWITH

Field of the Invention

This invention relates to a process and apparatus for the grafting of enophiles onto polymers at moderate temperatures and extended reaction times, and the grafted polymers obtained thereby. More particularly, the invention relates to the grafting of polyolefins containing unsaturation sites with an enophile such as maleic anhydride via the ene reaction in a tubular reactor employing distributive mixing.

Background Art

In U. S. Patent 4,026,967 to Flexman, Jr. et al., there is described a continuous process for grafting polyolefins with monomers at high temperatures for short reaction times. This patent discloses, for example, the grafting of fumaric acid onto high density polyethylene (HDPE) in an extruder equipped with a Kenics brand static mixer at a temperature of 275-550°C for a period of time of one-quarter to 10 minutes.

From U. S. Patent 4,010,223 to Caywood, Jr., it is known to graft maleic anhydride to ethylene-propylene-diene monomer (EPDM), without appreciable generation of free radicals, at a temperature of at least 225° up to 350°C.

U. K. patent specification 946,384 discloses the grafting of maleic anhydride onto polyethylene at 300°C in a 30 inch long annular reactor having an inside diameter of 1-7/8 inch and an outside diameter of 2 inches.

Other references which generally describe the grafting of carboxylic acids onto olefin and/or diene polymers include U. S. Patents 4,762,890 to Strait et al.; 4,639,495 to Waggoner; 4,616,059 to Motooka et al.; 4,517,104 to Bloch et al.; 4,082,817 to Imaizumi et al.; 3,997,487 to Rees et al.; 3,884,882 to Caywood, Jr.; and 3,868,433 to Bartz et al.

The ene reaction comprising the indirect substituting addition of a compound with a double bond (enophile) to an olefin with an allylic hydrogen (ene) is discussed in Hoffmann, Angew. Chem. Internat. Edit., vol. 8, no. 8, pp. 556-577 (1969).

Various static in-line mixers are described, for example, in U. S. Patents 4,179,222 to Strom et al.; 3,923,288 to King; 3,800,985 to Grout et al.; and 3,286,992 to Armeniades et al. In-line static mixers are also commercially available from various manufacturers such as Kenics Corporation and Koch Engineering Company, Inc. This latter manufacturer has advertised a melt blender for homogenization of melt streams from plastic extruders as described in Koch Bulletin KMB-5 (1986). Koch Bulletin KSM-5 (1986) also generally describes static mixing technology. Static mixing elements are also described in Rauwendaal, Polymer Extrusion (Hanser Publishers, Munich, 1986).

Summary of the Invention

We have discovered a process for grafting a polyolefin containing unsaturation sites with an enophile wherein the melt-phase ene modification of the polyolefin is effected with improved grafting efficiency, but without excessive polyolefin thermal degradation. This has been achieved by using a reactor provided with distributive mixing elements, and by operating the reactor at a moderate temperature with a relatively long mean residence time, and a relatively narrow residence time distribution to simulate plug flow as nearly as possible. Such distributive mixing may be accomplished by any mixing device, satisfying the residence time and residence time distribution requirements described more fully hereinbelow, preferably by using static mixing elements such as those described in Rauwendaal, mentioned above, which is hereby incorporated herein by reference. This process, novel in itself, is employed to obtain a novel grafted polymer product. Also, the reactor used for the enophile grafting process may be employed in other polymer processing applications wherein long residence times and narrow residence time distributions are required.

Accordingly, the present invention provides a grafting process. The process comprises the steps of: (a) heating a polyolefin having unsaturation sites to a temperature at which the polyolefin is molten; (b) contacting the polyolefin with an enophile reactive therewith in a reactor under ene reaction conditions at a temperature from about 180°C to about 265°C, wherein the reactor has a mean residence time of from about 12 minutes to about 40 minutes and a residence time distribution wherein 90 percent of reactor throughput has a residence time between about 75 and about 175 percent of the mean residence time; and (c) recovering enophile-grafted polymer from the reactor.

In another aspect, the invention provides a polyolefin grafted with an enophile. The grafted polyolefin has a molecular structure that survives the grafting process substantially intact. The grafted polyolefin is preferably produced by a process which includes contacting a polyolefin containing unsaturation sites in melt phase with an enophile reactive therewith in a reactor under ene reaction conditions at a temperature of from about 180°C to about 265°C, wherein the reactor has a mean residence time of from about 12 minutes to about 40 minutes and a residence time distribution wherein 90 percent of reactor throughput has a residence time between 75 and about 175 percent of the mean residence time. In a preferred embodiment there is provided an ethylene- or propylene-diene copolymer grafted to a relatively high level with maleic anhydride and having a substantially unchanged molecular weight distribution.

In a further aspect, the invention provides apparatus for preparing graft polymers. Broadly, the apparatus includes a reactor equipped with distributive mixing elements and means for continuously supplying molten, pressurized polymer and an enophile graft reactant thereto. The reactor receives the molten polymer/enophile reactant mixture from the supply means, maintains the polymer and reactant at a temperature of from about 180°C to about 265°C, and produces a grafted polymer product. The reactor has a mean residence time for melt-phase ene grafting of from about 12 to about 40 minutes, and a residence time distribution wherein 90 weight percent of the product has a residence time between about 75 and about 175 percent of the mean residence time.

In a preferred embodiment, the apparatus includes a supply means comprising a first extruder, a tubular mixer-reactor and a finishing extruder. The first extruder continuously melts the polymer with an enophile graft reactant and produces a pressurized polymer-reactant mixture. The mixer-reactor receives the mixture from the first extruder and maintains the mixture at ene reaction conditions to produce a grafted polymer product. The mixer-reactor comprises a plurality of static distributive mixing elements. The finishing extruder receives the grafted polymer product from the mixer-reactor. The finishing extruder includes a devolatilization zone for stripping unreacted enophile from the product. The first extruder, the mixer-reactor and the finishing extruder are operable so that the polymer/enophile mixture has a mean residence time at ene reaction conditions between about 12 and about 40 minutes, and so that 90 percent of the mixture has a residence time between about 75 and about 175 percent of the mean residence time.

Brief Description of the Drawings

Fig. 1 is a schematic illustration of polymer processing equipment according to the present invention.

Fig. 2 is a longitudinal cross-sectional view of a connecting piece employed between the first extruder and mixer-reactor of the equipment seen in Fig. 1.

Fig. 3 is a cross-sectional elevation of a transfer piece provided between the mixer-reactor and finishing extruder of the equipment seen in Fig. 1.

Detailed Description of the Invention

Contrary to the prior art which teaches maximizing grafting efficiency and minimizing backbone polymer degradation by the employment of high temperature, short-residence-time grafting conditions, it has been discovered that, for certain types of polymer grafting reactions, quite surprisingly, grafting efficiency is maximized and polymer thermal degradation minimized by the use of relatively long residence times at relatively reduced temperatures. This is the case when, for example, a polyolefin containing unsaturation sites is grafted with an enophile such as maleic anhydride, and particularly in the case of grafting ethylene- or propylene-diene copolymers with maleic anhydride.

Polymers which may be suitably employed in the melt-phase ene reaction process according to the present invention generally include polyolefins having an allylic hydrogen, or "ene" as it is sometimes called, capable of participating in the ene reaction with a compound having an electron-deficient double bond "enophile," wherein a reaction mechanism proposed in Hoffman, mentioned above, may involve the allylic shift of one double bond, transfer of the allylic hydrogen to the enophile, and bonding between the two unsaturated termini. Such polyolefins generally include polyolefins having unsaturated side chains, such as, for example, olefin/diene copolymers, i.e. copolymers of an olefin and a diene prepared by interpolymerizing a mixture of the diene with the olefin, or by graft polymerization of the diene onto a backbone of the polyolefin.

The copolymer preferably has a diene or unsaturation content of from about 0.01 to about 5 mole percent, and more preferably from about 0.1 to about 2 mole percent. The polyolefin containing unsaturation sites is preferably at least partially crystalline, e.g. at least about 10 weight percent crystalline and more preferably from about 30 to about 70 weight percent crystalline. A "crystalline" polymer is readily understood by those in the art, and an exemplary definition is found in "Crystallinity" by R. L. Miller in Volume 4 of The Encyclopedia of Polymer Science and Engineering, H. F. Mark, et al., eds., J. Wiley, New York, 1966. Techniques for determining the percent crystallinity are described, for example, in "Crystallinity Determination" by J. P. Runt in Volume 4 of The Encyclopedia of Polymer Science and Engineering, 2d Ed., H. F. Mark, et al., eds., J. Wiley, New York, 1986.

Where a grafted product containing a uniformly distributed ene grafting is desired, the polyolefin preferably contains uniformly distributed unsaturation sites. Preferred olefin/diene copolymers include copolymers of ethylene or propylene and a diene. The ethylene/diene copolymers preferably have a density of from about 0.86 to about 0.96 g/cm^3. The propylene/diene copolymers preferably have a diene content of from about 0.01 to about 5 mole percent. Also preferred are partially crystalline terpolymers of ethylene or propylene, an α-olefin and a diolefin. Suitable α-olefins in this terpolymer are, for example, ethylene, propylene and C_4 to C_{12} α-olefins such as butene-1, hexene-1, octene-1, decene-1 and the like.

Suitable diene comonomers include any diene comonomer which is polymerizable with ethylene and/or propylene in the presence of a transition metal catalyst to produce residual unsaturation in the copolymer. Preferred dienes include 1,4-pentadiene, 1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 4,5-dimethyl-1,4-hexadiene, 2-methyl-1,7-octadiene, 7-methyl-1,6-octadiene, 1,9-decadiene, 1,13-tetradecadiene, norbornadiene, dicyclopentadiene, ethylidenenorbornene, and like dienes of from about 5 to about 24 carbon atoms. Of these, 1,4-hexadiene, 4,5-dimethyl-1,4-hexadiene and 7-methyl-1,6-octadiene are particularly preferred. In addition, mixtures of these dienes may be employed.

Enophiles contemplated as suitable graft reactants in the process according to the invention generally include compounds having electron-deficient double bonds such as certain substituted azo compounds, certain substituted ethylenically unsaturated hydrocarbons, and the like. A preferred class of enophiles comprises the substituted and unsubstituted α,β-ethylenically unsaturated dicarboxylic acids and anhydrides, such as, for example, maleic acid, fumaric acid, itaconic acid, maleic anhydride, itaconic anhydride, himic anhydride, chloromaleic acid, chloromaleic anhydride, dichloromaleic anhydride, sulfomaleic anhydride, trimethyl silyl sulfomaleic anhydride, ethoxymaleic anhydride, and the like. Of these, maleic acid, fumaric acid and maleic anhydride are particularly preferred.

The melt-phase ene grafting of the polyolefin containing unsaturation sites is preferably effected at a grafting level of from about 0.01 to about 5 mole percent of the graft reactant based on the total grafted polyolefin, more preferably from about 0.1 to about 3 mole percent, and especially from about 1 to about 2 mole percent.

In the grafting process according to the present invention, the polymer substrate and graft reactant are brought together under carefully controlled ene reaction conditions. The reaction generally includes the steps of heating and melting the polymer, contacting the molten polymer in a specially designed reactor at carefully controlled reaction conditions and recovering the grafted polymer from the reactor. The reactor is generally a statically mixed, tubular reactor operated at a temperature of from about 180°C to about 265°C, preferably from about 220°C to about 260°C. Below this temperature range, the ene reaction generally proceeds too slowly to be of commercial interest, whereas above this temperature range, the polymer suffers excessive thermal degradation.

The reaction time necessary for reaction in this invention generally depends upon the actual reaction temperature selected from the above range of suitable temperatures, lower temperatures generally requiring longer residence times to complete the desired extent of reaction. The reactor should have a mean residence time of from about 12 minutes to about 40 minutes, depending upon the reaction temperature and the desired grafting level. Residence times shorter than about 12 minutes do not generally achieve the desired grafting level, and temperatures above the desired temperature range can result in excessive thermal degradation of the polyolefin. On the other hand, residence times in excess of about 40 minutes are generally unnecessary to achieve the desired grafting level and tend to degrade the polyolefin. A mean residence time of from about 15 minutes to about 30 minutes is preferred, and especially from about 15 to 20 minutes.

It is also important in the operation of the reactor used in the process of the present invention to simulate as nearly as possible a plug flow reactor. Broad residence time distributions are to be avoided since this can result in a corresponding undesirably broad distribution of grafted polyolefin product properties such as grafting site distribution, molecular weight, and grafting level, for example. We have found that it is important to maintain the residence time distribution in the reactor such that the bulk of the reactor throughput has a residence time very near that of the average residence time. The residence time distribution should be such that 90 percent of the reactor throughput has a residence time between about 75 and about 175 percent of the mean residence time, preferably between about 85 and about 135 percent of the mean residence time, and more preferably between about 90 and about 125 percent of the mean residence time.

As used herein unless otherwise indicated, the term "residence time" is in reference to the duration for which the polymer has been in contact with a substantial amount of the reactive enophile at ene reaction conditions, i.e. at a temperature above about 180°C, between the point of enophile introduction and enophile stripping and/or depletion to an insubstantial level. The enophile may be introduced to the polymer either before or after the polymer is heated to reactive conditions, and the enophile may likewise be depleted and/or removed either before or after cooling of the polymer product to non-reactive conditions. Thus, the "reactor" for the purpose of residence time distribution could, for example, include a portion of an extruder barrel feeding the distributive mixer-reactor and/or an extruder barrel receiving the mixer-reactor discharge.

The carefully controlled reaction conditions in the present process obtain a polymer grafted predominantly by the ene reaction pathway. It is preferred to conduct the grafting reaction in a melt phase of the polymer which is essentially free of peroxides, oxygen, radiation, and similar sources of free radicals to avoid grafting by the free radical route. Preferably, oxygen can be excluded, for example, by passing the polymer through an inert gas blanket, e.g. nitrogen, argon, etc. prior to the onset of ene reaction conditions. More preferably, the polymer also includes antioxidant additives which tend to reduce free radical effects. Such antioxidants are well known in the art and include, for example, hindered phenols, phosphites, phosphonites, hindered amines and the like, generally at concentrations of from about 100 to about 5000 ppm.

The enophile-grafted polyolefin of the present invention is characterized by enophile grafting which is substantially the graft reaction product of the ene reaction. This novel grafted polyolefin has more uniformly distributed grafting sites than in the corresponding free-radically grafted polyolefin taught by the prior art. Grafted polymers of the present invention exhibit a relatively uniform distribution of the grafted moieties along the individual chains and a uniform content of grafted moieties between polymer molecules. This latter feature is only obtained in reactors with narrow residence time distributions. This uniformity of graft functionality is crucially important in various applications such as adhesion to reactive substrates.

In addition, the present grafted polyolefin has less degradation because the ene reaction does not effect substantial changes in the polymer molecular structure, and this retention of molecular characteristics can be enhanced by conducting the grafting at relatively reduced temperatures, e.g. 180°C to 265°C. Thus, a relatively high molecular weight, high graft level polyolefin is possible, in contrast to the prior art polyolefin grafts wherein high grafting levels are invariably accompanied by substantial changes in molecular structure. As used herein, the phrase "substantially intact molecular structure" is used in reference to a grafted polyolefin wherein the properties of molecular weight, molecular weight distribution and degree of long chain branching are substantially more similar to the polyolefin prior to grafting, than they are to the polyolefin predominantly free-radically and/or thermally (i.e. substantially above 265°C) grafted to the same enophile level.

The apparatus of the present invention constitutes a preferred embodiment of the reactor for carrying out the process of the present invention and for obtaining the enophile-grafted polymer of the invention. With reference to the drawings wherein like reference numerals depict like parts, a polymer grafting apparatus 10 according to one embodiment of the invention has a first extruder 12, a mixer-reactor 14 and a second extruder 16 connected in series for processing a polymer. The first extruder 12 is preferably a single screw extruder equipped with a drive unit 18, hopper 20, vent hood 22, injection port 24, and discharge end 26. Single screw extruders such as first extruder 12 illustrated in Fig. 1 are well known in the art and typically receive a feed material at inlet 28 of the hopper 20. By shear forces and heat applied, generally along the outside of first extruder 12, the extruder 12 melts the polymer feed, mixes the polymer with any additives which may be included as a masterbatch with the polymer feed in inlet 28 or as a material injected at injection port 24, and discharges the molten mixture at an elevated pressure at discharge end 26. As an example of the first extruder 12, there may be mentioned a single screw extruder of 36 mm diameter, 30:1 L/D with a maximum screw speed up to approximately 300 rpm, depending on screw diameter, and a maximum head pressure capability of up to 35 MPa which is capable of processing 5-15 kg per hour of polymer. The extruder screw is preferably a two-stage screw with a pressure release section at approximately 22:1 L/D, corresponding to a vent port location in the cylinder.

The barrel of extruder 12 is fitted with the injection port 24 at the vent and is adapted for a liquid additive injection. The discharge end 26 of the extruder 12 is also desirably fitted with ports for pressure and melt temperature measurement. The barrel is desirably fitted for liquid water cooling in the throat area located under hopper 20, and the balance of the barrel is laid out for a plurality of temperature control zones, heated by electric band heaters and cooled by fan-forced air, or other conventional heating and cooling means. The monomer to be grafted may be injected through the injection port 24, as aforementioned, preferably in liquid form. In the case of maleic anhydride, injection may be via a twin plunger pump for pressure injection (not shown) such as a Waters brand programmable solvent delivery module wherein the mechanical pump components are in a hot box for being maintained at a 60°C minimum temperature for receiving a maleic anhydride melted in a nitrogen or other inert gas-padded melting pot (not shown).

The mixer-reactor 14 receives the heated polymer from the discharge end 26 of the extruder 12. Any tubular static mixing apparatus may be employed as the mixer-reactor 14, provided that it is capable of achieving the required residence time and residence time distribution. Such static mixing units are available, for example, from the Kenics Corporation or Koch Engineering Company, Inc. and others, and are preferably sized and arranged for maintaining a minimum flow velocity of the reactant mixture of the mixer-reactor 14 to avoid flow stagnation and loss of mixing. A flow velocity of at least 4 inches per minute is usually sufficient for this purpose, preferably at least 5 inches per minute, and especially at least 6 inches per minute. It has been found, for example, that a copolymer processing rate of from 8 to 15 kg/h can be suitably obtained with a mixer-reactor having an inside diameter of 53.9 mm and a length of 1910 mm and containing 34 individual static mixing elements obtained from Sulzer Bros. Ltd., Winterthur Switzerland, under the trade designation SMX DN 50. In general, a sufficient number of mixing elements should be used to sufficiently promote radial mixing such that the homogeneity of the material processed expressed as a variation coefficient $\sigma/\bar{x}$ is less than 0.05, where σ is the standard deviation from the arithmetic mean $\bar{x}$ of the concentration of the material being mixed.

The mixer-reactor 14 usually will receive polymer which has been partially processed or reacted in the feeding means such as extruder 12, i.e. a portion of the reaction occurs prior to entry into the mixer-reactor 14 and the polymer feed thus has a broadened residence time distribution. Therefore, the residence time distribution of the mixer-reactor 14 is desirably sufficiently narrow to compensate for the broadening in the polymer feed means 12. The mixer-reactor 14 should have a residence time distribution such that 90 percent of the throughput exits within 80 percent and 150 percent of the mean residence time. More preferably, the 90 percent bulk of the throughput has a residence time in the mixer-reactor 14 of from about 85 percent to about 135 percent of the mean residence time therein, and especially from about 90 percent to about 125 percent of the mean residence time therein. The length to diameter ratio (L/D) of the mixer-reactor 14 is preferably at least about 15:1, more preferably at least about 30:1.

The product from the mixer-reactor 14 is received in a finishing extruder 16 which generally devolatilizes the grafted polymer product, and if desired, mixes the polymer product with any additional additives. The finishing extruder 16 is driven by drive unit 32 and is provided with inlet port 34 for receiving polymer from mixer-reactor 14 adjacent an inlet end, inlet port 36 and vent 38 disposed between inlet 34 and discharge end 40. Discharge end 40 may include conventional die 42, water bath 44 and vent 46. The inlet port 36 is provided for introducing a stripping gas such as nitrogen, argon or another inert gas, and removing the gas at devolatilization port 38. If desired, additional injection ports may be provided along the length of the finishing extruder 16 for the injection of other additaments in a conventional manner in the art. Finishing extruder 16 may, for example, be a twin screw extruder. It is preferred to provide a rear shaft seal or seals on the extruder 16 to exclude air from entering the extruder 16 since such air/polymer contact at elevated temperature may undesirably introduce free radicals and concomitant reactions thereof.

In a preferred embodiment, a connecting piece 50 may be provided between the first extruder 12 and the mixer-reactor 14. The connecting piece 50 is provided with flanges 52 and 54 for flanged connection between first extruder 12 adjacent discharge end 26 thereof and the inlet to mixer-reactor 14 as illustrated in Fig. 2. The connecting piece 50 has a generally cylindrical housing 56 and a central longitudinal bore 58 therethrough. An insert 60 is secured in annular recesses formed between discharge end 26 and flange 52. The insert 60 includes conventional screen pack 62 and breaker plate 64. A torpedo 66 is threadedly engaged in the insert 60 and extends downstream of the breaker plate 64 to fill the central longitudinal region of the connecting piece 50 to provide an annulus for polymer flow. The connecting piece 50 thus provides a minimum inventory for the polymer and a concomitantly minimum broadening of residence time distribution. The connecting piece 50 serves to maintain back pressure in the extruder 12, and also functions as a pressure reducer so that the polymer is fed from the first extruder 12 into the mixer-reactor 14 at a pressure which is below the maximum pressure of the mixer-reactor 14, but of sufficiently high pressure to overcome the pressure drop through the mixer-reactor 14. If desired, a port 68 may be provided for suitable pressure and temperature probes.

It is also preferred to employ a transfer piece 70 positioned in line between the mixer-reactor 14 of the finishing extruder 16. The transfer piece 70 is generally provided with a connecting face 72 for flanging or otherwise connecting to the discharge end of mixer-reactor 14. A central bore 74 is provided in the transfer piece housing body 76 for supplying molten polymer from the mixer-reactor 14 to a die insert 78 which is jacketed with a heating element 80. The transfer piece 70 is insulated and heated to an appropriate temperature to prevent plate out of maleic anhydride and other reactants therein. The die insert 78 terminates in a cone shaped strand die 82 to inhibit strand curling which can result in the polymer strand sticking to metal surfaces in the inlet 34, and possibly plugging the inlet 34 and/or otherwise adversely affecting the operation of the extruder 16. An annular space 84 is provided adjacent the die 82 for introduction of a heated purge gas, such as nitrogen, via port 86. The inlet 34 is vented via annular channel 88 and vent port 90. An annular baffle member is disposed between annular channels 84 and 88 to inhibit plugging of the vent.

The transfer piece 70 thus connects the outlet of the mixer-reactor 14 to the inlet opening 34 of the finishing extruder 16. The transfer piece 70 accepts melt from the mixer-reactor 14 and effectively subjects the melt to an atmospheric pressure venting environment in order to accomplish removal of most of the unreacted monomer at this location. The hot nitrogen or other inert gas purge lowers the partial pressure of the unreacted monomer to enhance stripping.

The invention is illustrated by way of the examples which follow.

Example 1

A 30 mm twin-screw Welding Engineers extruder with an L/D ratio of 42 in a counter-rotating, tangential extrusion arrangement was used to feed a mixer-reactor. The screw speed was maintained at 300 rpm, and one of the screws had an extended length to feed the mixer-reactor. A copolymer of propylene and 1,4-hexadiene containing 0.73 mole percent 1,4-hexadiene was fed into the open hopper of the extruder at a rate of 9.06 kg/hr using a loss-in-weight feeder. The copolymer contained 900 ppm Irganox 1010 and 600 ppm Ultranox 626 and had a melt flow rate (MFR) of 1.8 dg/min measured according to ASTM D-1238, condition B. Nourymix MA 912 was used as the source of maleic anhydride in the form of a porous granular polypropylene supporting 25 weight percent maleic anhydride, fed to the open hopper of the extruder at 0.94 kg/hr using a loss-in-weight feeder. The mixer-reactor contained 34 individual Sulzer SMX DN 50 elements, had an inside diameter of 53.9 mm and a length of 1910 mm. A screen pack and die were positioned on the discharge end of the mixer-reactor and added an additional 135 mm to its length. The temperature profile along the extruder was adjusted such that the polymer mixture exiting therefrom was at 264°C. The mixer-reactor temperature was kept at 260°C. The residence time in the mixer-reactor was measured to be 17 minutes, while that in the extruder was measured to be 2 minutes, yielding an overall residence time of 19 minutes. The polymer exited from the die of the mixer-reactor and was passed through a water bath and pelletized. The MFR was 17.2, and the amount of grafted maleic anhydride was 0.74 weight percent as determined by infrared analysis of a compression molded film prepared at 200°C and 10,000 psi with a dwell time of 1 minute. The absorbance of the 1780 cm^{-1} band was measured after a 10 minute soak of the compression-molded film in chloroform, and the amount of maleic anhydride was calculated from the equation:

$$\text{Wt.\% MAH} = 0.007418 * [\text{Abs}(1780\ \text{cm-1})]/[\text{film thickness (in.)}].$$

The mole percentage of maleic anhydride (MAH) in the copolymer can be calculated using the following equation:

$$\text{Mole \% MAH} = \frac{100(W_{MAH}/M_{MAH})}{W_{MAH}/M_{MAH} + \dfrac{100 - W_{MAH}}{\sum_i X_i M_i}}$$

wherein W_{MAH} is the weight percent of MAH, M_{MAH} is the molecular weight of grafted MAH (98.06 g/mole), X_i is the mole percentage of the *i*th component in the starting polymer, wherein the components are ethylene, propylene, α-olefins or dienes, not including MAH, and M_i is the molecular weight of *i*th component.

In order to demonstrate that the maleic anhydride was truly grafted onto the polymer, selected samples were dissolved in xylene and reprecipitated by pouring the solution into acetone. Following filtration and drying under vacuum for 16 hours at 70°C, the samples were analyzed again for grafted maleic anhydride, and the results agreed with those measurements made from the compression molded films.

Examples 2-8

Example 1 was repeated with varied temperature, residence time, and copolymer and maleic anhydride feed rates to demonstrate the effect of these variables on the extent of maleic anhydride grafting and the polymer MFR. All other conditions in Examples 2-8 were identical to those described in Example 1. The conditions and results of these examples are illustrated in Table I along with Example 1.

TABLE I

EXAMPLE	COPOLYMER FEED RATE (kg/hr)	NOURYMIX FEED RATE (kg/hr)	MIXER-REACTOR TEMPERATURE (°C)	MIXER-REACTOR RESIDENCE TIME (min)	MAH LEVEL (wt. %)	MFR (dg/min)
1	9.06	0.94	260	17	0.74	17.2
2	9.37	0.63	250	17	0.41	8.4
3	9.37	0.63	260	17	0.60	13.0
4	8.80	1.23	260	17	0.85	18.7
5	12.68	1.32	260	12	0.54	11.5
6	9.97	0.21	260	17	0.19	8.9
7	7.26	0.74	260	21	0.85	21.6
8	9.06	0.94	240	17	0.56	7.9

Example 9

The techniques and apparatus of Example 1 were used to graft maleic anhydride onto a diene-modified polyethylene. The ethylene copolymer contained 1.15 mole percent trans-1,4-hexadiene and had a melt index (MI) of 50 dg/min, measured according to ASTM D-1238, condition A. The copolymer contained 900 ppm Irganox 1010 and 600 ppm of Ultranox 626, and was fed through the mixer-reactor system at a rate of 8.8 kg/hr. Nourymix MA 901 (25 weight percent maleic anhydride on a porous HDPE support) was fed at a rate of 1.2 kg/hr. The temperature profile along the extruder was adjusted such that the polymer mixture exited from the extruder at 242°C, while the mixer-reactor temperature was maintained at 230°C. The residence time in the mixer-reactor was measured to be 17 minutes, and in the extruder, 2 minutes. The ethylene copolymer product had a maleic anhydride graft level of 1.10 weight percent and a MI of 13.8 dg/min.

Examples 10-11

The procedure and techniques of Example 9 were used to determine the effects of varying temperature and polyethylene/maleic anhydride feed rates on the extent of maleic anhydride grafting and the polymer MI. All other conditions were maintained identical to those described in Example 9. The results of these examples are illustrated in Table II along with Example 9.

TABLE II

EXAMPLE	COPOLYMER FEED RATE (kg/hr)	NOURYMIX FEED RATE (kg/hr)	MIXER-REACTOR TEMPERATURE (°C)	MIXER-REACTOR RESIDENCE TIME (min)	MAH LEVEL (wt. %)	MFR (dg/min)
9	8.80	1.20	230	17	1.10	13.8
10	8.80	1.20	240	17	1.61	13.7
11	8.30	1.70	240	17	1.98	9.6

Comparative Example 1

This Comparative Example 1 is presented to show the level of maleic anhydride grafting that can be achieved when an extruder is used alone without the mixer-reactor. The grafting was conducted on a 30 mm, twin-screw Werner & Pfleiderer ZSK-30 extruder with an L/D ratio of 43. The extruder was a co-rotating, intermeshing extruder and the screw was designed such that melt seals were placed immediately after the hopper and just before the vent. The vent was in turn positioned immediately prior to the extruder die. Vacuum was placed on the vent through use of a water-ring vacuum pump, and maximum shear was obtained by including 4 sets of kneading blocks along the length of the screws. The screw speed was 100 rpm, and product from the extruder was cooled in a water bath and pelletized. A propylene-1,4-hexadiene copolymer, containing 0.75 mole percent 1,4-hexadiene, stabilized with 1000 ppm BHT and having an MFR of 3.0 dg/min, was grafted with maleic anhydride in the absence of a conventional free radical source. Maleic anhydride was dry blended into the polymer at a level of 2 weight percent prior to feeding the dry blend to the extruder at a rate of 5.2 kg/hr. The temperature profile along the extruder was adjusted to come to 290°C as rapidly as possible, and the die temperature was maintained at 161°C. The average residence time in the extruder was measured to be 2.58 minutes. The MFR of the product was 9.4 dg/min and the amount of grafted maleic anhydride was 0.14 weight percent, indicating the excessive thermal degradation and low grafting levels achieved by using a short residence time and high reaction temperature.

Comparative Examples 2-4

Comparative Example 1 was repeated with varied temperature, residence time and extruder rpm. All other conditions were identical to those described in Comparative Example 1. The grafting conditions and results are illustrated in Table III along with Comparative Example 1.

TABLE III

COMPARATIVE EXAMPLE	COPOLYMER FEED RATE (kg/hr)	TEMPERATURE (°C)	EXTRUDER RESIDENCE TIME (min)	GRAFTED MAH LEVEL (wt. %)	MFR (dg/min)	RPM
1	5.20	290	2.58	0.14	9.4	100
2	8.63	260	2.03	0.06	5.6	100
3	5.45	230	2.50	0.02	3.0	100
4	5.45	260	3.42	0.07	3.0	50

The foregoing data in Table III illustrate that the use of a temperature which is too high results in polymer degradation (Comparative Example 1), while the use of residence times which are too short results in low grafting levels (Comparative Examples 1-4).

Comparative Example 5

This Comparative Example 5 demonstrates that conducting the grafting reaction at relatively low temperatures for long reaction times results in less polymer degradation than at short times and high temperatures. Whereas high temperatures favor grafting, low temperatures minimize thermal degradation, but require longer reaction times to achieve the desired grafting level. Since the activation energy for the ene reaction is 15 kcal/mole (Trivedi, et al., Maleic Anhydride (Plenum Press, New York 1982)), the same extent of reaction obtained at 250°C for 7 minutes should also be obtained at 300°C for 2 minutes. To demonstrate the effects of reaction temperature and times on polymer degradation, polymer samples were heated in a Brabender mixer at either 300°C for 2 minutes or 250°C for 7 minutes. When a polypropylene containing 0.9 weight percent 1,9-decadiene and having a MFR of 30 dg/min was processed at 300°C for 2 minutes, it had a MFR of 218 dg/min, whereas when processed at 250°C for 7 minutes, it had a MFR of 128, indicating significantly less polymer degradation at the lower temperature, longer reaction time condition even though the same level of maleic anhydride grafting would be expected. Similarly for a polypropylene containing no diene and having a MFR of 2 dg/min, processing at 300°C for 2 minutes resulted in a MFR increase to 30.0 dg/min, whereas the same polymer processed at 250°C for 7 minutes had a MFR increase only to 21 dg/min, again indicating that there is less polymer degradation at the lower temperature for a longer period of time than at the corresponding high temperature for a shorter period of time required for the same extent of maleic anhydride grafting.

Comparative Example 6

This Comparative Example 6 is presented to demonstrate the effect of unsaturation sites within the polyolefin used in the process of this invention. The procedures and techniques described in Example 9 were used except that a linear low density polyethylene (LLDPE) was used in place of the diene-modified polyethylene. The LLDPE was an ethylene-butene copolymer having a melt index (ASTM D-1238, Condition A) of 50 dg/min and density of 0.918 g/cc. The LLDPE contained 900 ppm Irganox 1010 and 600 ppm Ultranox 626. The product from the described process had a maleic anhydride graft content of 0.06 weight percent and a MI of 34.7 dg/min. This contrasts with Example 9 wherein the diene-modified polyethylene was grafted at a level of 1.10 weight percent maleic anhydride, and shows that significant grafting does not occur unless unsaturation sites are present in the polymer.

Comparative Example 7

This comparative example is presented to demonstrate the uniformity of grafting achieved with the present invention. The concentration of maleic anhydride was measured as a function of molecular weight for the polymer prepared in Example 1 and for a sample of Epolene® E-43 from Eastman Kodak. E-43 is a commercial product prepared by grafting maleic anhydride onto polypropylene via a melt phase free radical reaction. Since it is prepared by a free radical route, its maleic anhydride distribution is similar to that obtained by any other route which generates free radicals, e.g., very high temperatures or high shear rates.

A 0.6 weight percent solution of polymer from Example 1 was prepared in 1,2,5-trichlorobenzene (TCB) and injected into a Waters 150 gel permeation chromatograph (GPC) operating at 135°C at 0.3 ml/min. The GPC was equipped with four Shodex columns of crosslinked polystyrene beads (8025, 8035, 8045, 8055). The polymer retention time in the chromatograph ranged from 60 to 110 minutes. Six equal samples of polymer were collected on KBr plates over the retention time range and the reflectance IR spectrum of the samples collected was measured by a FTIR spectrometer. The first sample exiting from the chromatograph has the highest molecular weight and the last sample has the lowest molecular weight. The 2920 cm^{-1} peak was used as an internal reference to the quantity of polymer in the sample. The concentration of grafted maleic anhydride, in both the anhydride and acid forms, is proportional to the ratio:

$$[Abs(1730\ cm^{-1}) + Abs(1780\ cm^{-1})]/Abs(2920\ cm^{-1})$$

wherein Abs(1730 cm^{-1}) is the absorbance at 1730 cm^{-1} of grafted succinic acid, Abs(1780 cm^{-1}) is the absorbance at 1780 cm^{-1} of grafted succinic anhydride, and Abs(2920 cm^{-1}) is the absorbance at 2920 cm^{-1}.

The same experiment was done with a 0.22 weight percent solution of E-43 in TCB. E-43 contains 5.0 weight percent maleic anhydride overall, so the absorbance ratio values are higher than the product from Example 1, which contained 0.74 weight percent maleic anhydride overall. The results of these experiments are shown in Table IV.

TABLE IV

	ABSORBANCE RATIO		
FRACTION	EXAMPLE 1	E-43	MOLECULAR WEIGHT
1	0.030	0.06	Highest
2	0.025	0.08	↑
3	0.023	0.13	
4	0.029	0.17	
5	0.019	0.34	↓
6	0.020	0.63	Lowest
Mean ($\bar{x}$)	0.024	0.24	
Standard Deviation (σ)	0.004	0.22	
$\sigma/\bar{x}$	0.180	0.92	

This comparative example demonstrates the uniform composition distribution of enophile obtained with the present invention (Example 1). In contrast, the maleic anhydride concentration increases as the molecular weight of the E-43 fractions decreases. Therefore, the maleic anhydride distribution is very non-uniform when grafted by free radicals. This variation (expressed as a ratio of the standard deviation of maleic anhydride concentration and the mean concentration) is over 90%.

In comparison, the distribution is much more uniform for maleic anhydride grafted via the process of the present invention in Example 1. The variation is about 18% and there is no increase in maleic anhydride concentration in those fractions having lower molecular weight.

The foregoing description of the invention is illustrative and explanatory thereof, and various modifications in the details will become apparent to those skilled in the art in view of the foregoing disclosure. It is intended that all such modifications and variations within the scope or spirit of the appended claims be embraced thereby.

Claims

1. A polymer grafting process, comprising the steps of:
   (a) heating a polyolefin containing unsaturation sites to a temperature at which the copolymer is molten;
   (b) contacting the molten polyolefin with an enophile reactive therewith in a distributively mixed reactor under ene reaction conditions at a temperature of from about 180°C to about 265°C, said reactor having a mean residence time of from about 12 minutes to about 40 minutes and a residence time distribution such that 90 weight percent of reactor throughput has a residence time between about 75 and about 175 percent of the mean residence time; and
   (c) recovering from the reactor polyolefin grafted with said enophile.
2. The process of claim 1, wherein said heated polyolefin comprises a copolymer of an α-olefin and a diene.
3. The process of claim 2, wherein said α-olefin comprises ethylene or propylene.
4. The process of claim 2, wherein said copolymer comprises from about 0.01 to about 5 mole percent of said diene.
5. The process of claim 2, wherein said polyolefin is at least about 10 weight percent crystalline.
6. The process of claim 1, wherein said enophile comprises α,β-ethylenically unsaturated dicarboxylic acid or anhydride.
7. The process of claim 1, wherein said reactor has an extruder zone which feeds said polyolefin into a static mixer zone.

8. The process of claim 7, wherein said mixer zone comprises a plurality of static mixing elements.
9. The process of claim 1, wherein said reactor temperature is from about 220°C to about 260°C.
10. The process of claim 1, wherein said reactor is essentially free of oxygen and free radical initiators.
11. The process of claim 1, wherein said mean residence time is from about 15 minutes to about 30 minutes.
12. The process of claim 1, wherein said 90 weight percent of reactor throughput has a residence time between about 85 and about 135 percent of the mean residence time.
13. The process of claim 1, wherein said recovered polyolefin is grafted to an enophile level of from about 0.01 to about 5 mole percent of the grafted polyolefin.
14. A polymer grafting process, comprising the steps of:
    (a) heating a polyolefin to a temperature at which it is molten, said polyolefin having at least about 30 weight percent crystallinity and comprising a copolymer of (i) an α-olefin selected from ethylene and propylene and (ii) a diene which incorporates from about 0.01 to about 5 mole percent unsaturation into said copolymer;
    (b) contacting said copolymer with an α,β-ethylenically unsaturated dicarboxylic acid or anhydride in a distributively mixed reactor essentially free of oxygen and free radical initiators comprising an extruder zone which feeds said copolymer to a distributive mixing zone having a plurality of static mixing

elements, said reactor having a temperature of from about 220°C to about 260°, a mean residence time of from about 15 to about 30 minutes, and a residence time distribution such that 90 weight percent of reactor throughput has a residence time between about 85 and about 135 percent of the mean residence time; and

(c) recovering from said reactor the copolymer grafted with said dicarboxylic acid or anhydride to a level of from about 0.01 to about 5 mole percent of said copolymer.

15. The process of claim 14, wherein said polyolefin comprises from about 30 to about 70 weight percent crystallinity.

16. The process of claim 14, wherein said copolymer further comprises ethylene or a C_3 to C_{12} α-olefin as a termonomer.

17. The process of claim 16, wherein said termonomer is selected from butene-1, hexene-1, octene-1 and decene-1.

18. The process of claim 14, wherein said diene has from about 5 to about 24 carbon atoms.

19. The process of claim 14, wherein said diene is selected from 1,4-pentadiene, 1,4-hexadiene, 4-methyl-1,4-hexadiene,5-methyl-1,4-hexadiene, 4,5-dimethyl-1,4-hexadiene, 2-methyl-1,7-octadiene, 7-methyl-1,6-octadiene, 1,9-decadiene, 1,13-tetradecadiene, norbornadiene, dicyclopentadiene and ethylidenenorbornene.

20. The process of claim 14, wherein said diene is selected from 1,4-hexadiene, 4,5-dimethyl-1,4-hexadiene and 7-methyl-1,6-octadiene.

21. The process of claim 14, wherein said copolymer comprises from about 0.1 to about 2 mole percent unsaturation.

22. The process of claim 14, wherein said copolymer comprises polyethylene having a density from about 0.86 to about 0.96 g/cm^3.

23. The process of claim 14, wherein said copolymer comprises polypropylene having a density of from about 0.86 to about 0.91 g/cm^3.

24. The process of claim 14, wherein said dicarboxylic acid or anhydride is selected from maleic acid, fumaric acid, itaconic acid, maleic anhydride, itaconic anhydride, himic anhydride, chloromaleic acid, chloromaleic anhydride, dichloromaleic anhydride, sulfomaleic anhydride, trimethyl silyl sulfomaleic anhydride, and ethoxymaleic anhydride.

25. The process of claim 14, wherein said dicarboxylic acid or anhydride comprises maleic acid, maleic anhydride or fumaric acid.

26. The process of claim 14, wherein said heated copolymer includes an antioxidant additive at from about 100 ppm to about 5000 ppm.

27. The process of claim 14, wherein said distributive mixing zone has a residence time distribution such that 90 percent of the mixing zone throughput has a residence time within 80 and 150 percent of the mean residence time of the mixing zone.

28. The process of claim 27, wherein said 90 percent of the mixing zone throughput has a residence time within 85 to 135 percent of said mixing zone mean residence time.

29. The process of claim 27, wherein said residence time of said 90 percent of the mixing zone throughput is within 90 to 125 percent of said mixing zone mean residence time.

30. The process of claim 14, wherein said mixing zone has an L/D of at least about 15:1.

31. The process of claim 14, wherein said mixing zone has an L/D of at least about 30:1.

32. The process of claim 14, wherein said residence time of said 90 percent of the reactor throughput is within 90 to 125 percent of said reactor mean residence time.

33. The process of claim 14, further comprising the step of devolatilizing unreacted dicarboxylic acid or anhydride from said recovered copolymer.

34. The process of claim 33, further comprising the step of processing said devolatilized copolymer in a finishing extruder.

35. A polyolefin grafted with an enophile produced according to the ene reaction process of claim 1 wherein the grafted polyolefin has a substantially intact molecular structure.

36. Apparatus for preparing grafted polyolefins, comprising:

    (a) means for continuously supplying molten, pressurized polyolefin containing unsaturation sites and an enophile graft reactant;

    (b) a distributively mixed reactor for receiving said molten polyolefin and reactant from said supplying means, for maintaining said polyolefin and reactant at a temperature of from about 180°C to about 265°C, and for producing a grafted polyolefin product with a mean residence time for melt-phase ene grafting of from about 12 to about 40 minutes with a residence time distribution such that 90 weight percent of said product has a residence time between about 75 and about 175 percent of said mean residence time.

37. The apparatus of claim 36, wherein said supplying means comprises an extruder.

38. The apparatus of claim 36, wherein said reactor comprises a tubular member equipped with a plurality of static mixing elements.

39. The apparatus of claim 36, further comprising means for devolatilizing unreacted enophile from said grafted polyolefin product.

40. The apparatus of claim 36, wherein said mean residence time is from about 15 to about 30 minutes.

41. The apparatus of claim 36, wherein said 90 weight percent of said product has a residence time between about 85 and about 135 percent of said mean residence time.

42. Apparatus for preparing graft copolymers, comprising:

    (a) a first extruder for continuously melting polyolefin containing unsaturation sites with an enophile graft reactant and producing a pressurized polyolefin/reactant mixture;

    (b) a tubular mixer-reactor for receiving said mixture from said first extruder and maintaining said mixture at ene reaction conditions to produce a grafted polyolefin product, said mixer-reactor comprising a plurality of static mixing elements sized and arranged for maintaining a minimum flow velocity of said mixture to avoid flow stagnation and loss of mixing;

    (c) a finishing extruder for receiving said grafted polyolefin product from said mixer-reactor, said finishing extruder including at least one zone for removing unreacted enophile from said product;

(d) wherein said first extruder, said mixer-reactor and said finishing extruder are operable so that said polyolefin-enophile mixture has a mean residence time at ene reaction conditions between about 12 and about 40 minutes and 90 percent of said mixture has a residence time between 75 and 175 percent of said mean residence time.

43. The apparatus of claim 42, further comprising means for injecting liquid enophile into a mixing zone of said first extruder.

44. The apparatus of claim 42, wherein said first extruder is a single screw extruder with an L/D of from 18:1 to 36:1.

45. The apparatus of claim 42, further comprising a connecting piece between said first extruder and said mixer-reactor for maintaining back pressure in said first extruder and for introducing said mixture into said mixer-reactor at a reduced pressure without substantial broadening of residence time distribution.

46. The apparatus of claim 42, wherein said mixer-reactor has a L/D of at least about 15:1.

47. The apparatus of claim 42, wherein said mixer-reactor has a L/D of at least about 30:1.

48. The apparatus of claim 42, wherein said mixer-reactor has a residence time distribution wherein 90 percent of said mixture has a residence time therein within 85 and 135 percent of the mean residence time in said mixer-reactor.

49. The apparatus of claim 48, wherein said mixer-reactor residence time for said 90 percent of said mixture is within 90 and 125 percent of said mixer-reactor mean residence time.

50. The apparatus of claim 42, wherein said mixer-reactor obtains a variation coefficient less than 0.05.

51. The apparatus of claim 42, further comprising a transition piece disposed between said mixer-reactor and said finishing extruder, said transition piece comprising an inert gas-inlet, an inert gas-polyolefin contacting zone and a gas vent for stripping unreacted enophile from said polyolefin.

52. The apparatus of claim 42, wherein said finishing extruder is a twin-screw extruder.

53. The apparatus of claim 42, wherein said twin screw extruder is a vented compounding extruder.

54. The apparatus of claim 42, wherein said mean residence time at ene reaction conditions is between about 15 and about 30 minutes.

55. The apparatus of claim 42, wherein said residence time of said 90 percent of said mixture at ene reaction conditions is within from about 85 to about 135 percent of said mean residence time.

56. The apparatus of claim 42, wherein said residence time of said 90 percent of said mixture at ene reaction conditions is within from about 90 to about 125 percent of said mean residence time.

57. The apparatus of claim 42, further comprising means for excluding oxygen from said mixer-reactor.

58. The apparatus of claim 57, wherein said oxygen excluding means comprises means in said first and second extruders for forming polymer seals.

59. The apparatus of claim 42, wherein said mixture has a flow velocity in said mixer-reactor of at least 4 inches per minute.

60. The apparatus of claim 42, wherein said mixture has a flow velocity in said mixer-reactor of at least 5 inches per minute.

61. The apparatus of claim 42, wherein said mixture has a flow velocity in said mixer-reactor of at least 6 inches per minute.

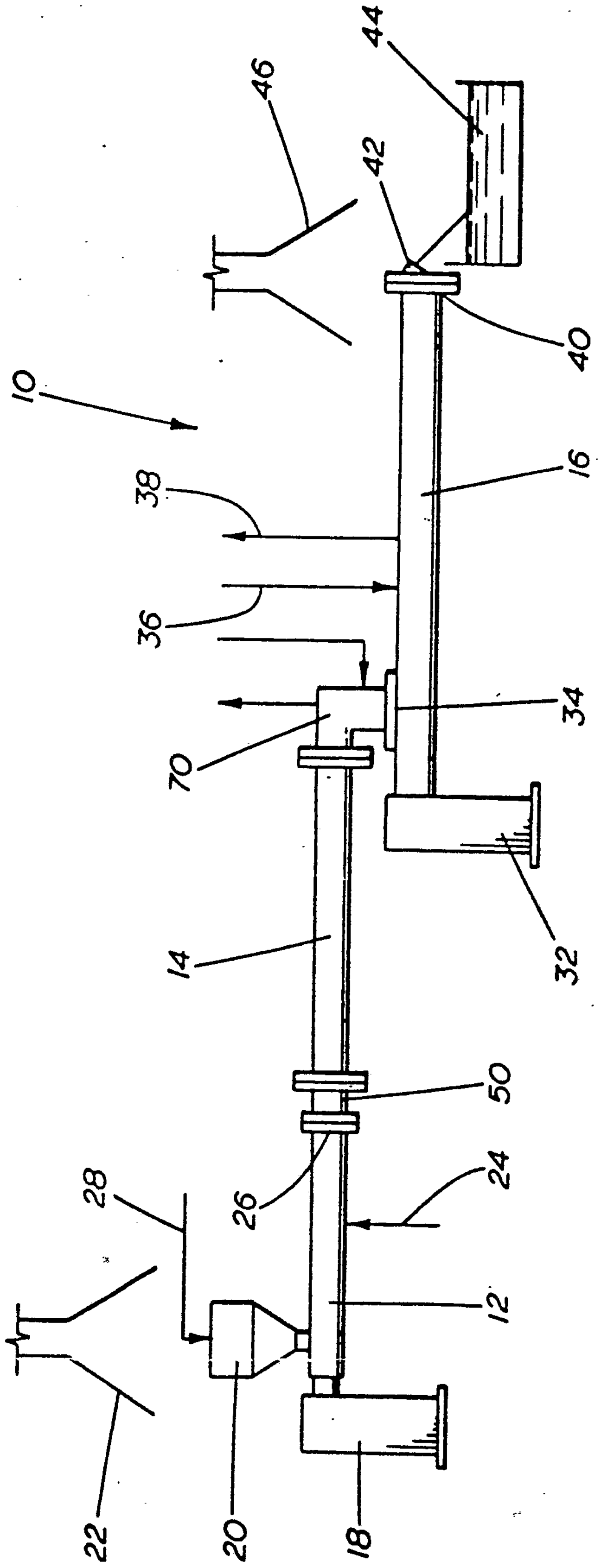

FIG. 1

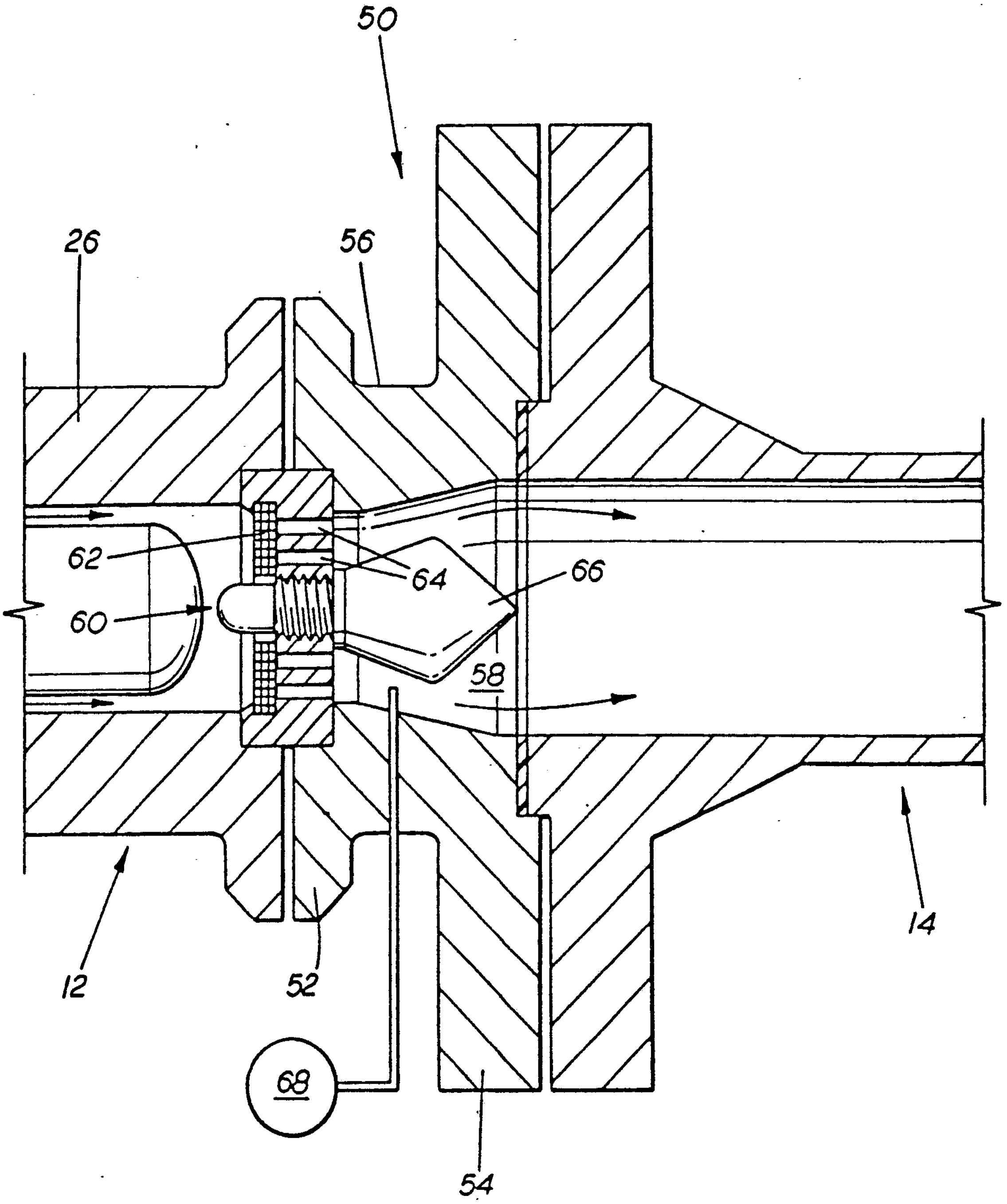

FIG.2

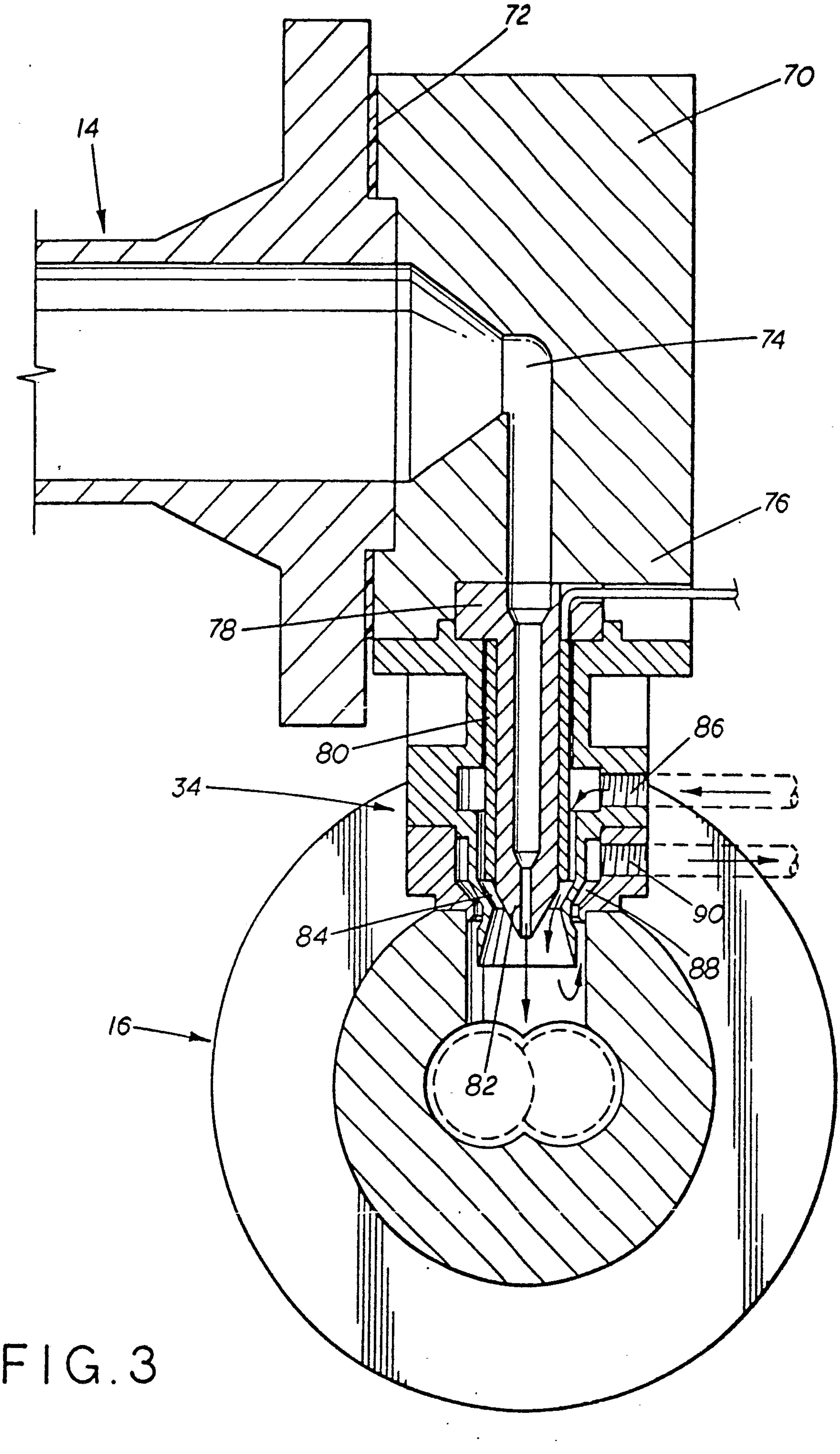

FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 9102480

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

B 29 C 47/10 B 29 C 47/50 B 29 C 47/64 C 08 F 255/06 //
B 29 K 23:00 B 29 K 96:02

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl.5	B 29 C C 08 F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
Y	US-A-4 814 130 (EIJI SHIROMATSU et al.) 21st March 1989, see abstract; figures 1,2; column 2, lines 43-64;; column 3, lines 32-44; column 4, lines 4-47; column 8, lines 37-56; table 2; column 13, lines 16-65; table 5; claims 1-13 ---	1-5,7-9,13,36-41
Y	EP-A-0 088 541 (CELANESE CORP.) 14th September 1983, see page 7, lines 11-37; page 15, line 33 - page 16, line 29; claims 1-14; figures 1-7	1-5,7-9,13,36-41,14-34
X	---	42-61

-/-

° Special categories of cited documents : [10]

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

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"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

"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

IV. CERTIFICATION

Date of the Actual Completion of the International Search 25-07-1991	Date of Mailing of this International Search Report 12.09.91
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer Mme Dagmar FRANK

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP-A-0 033 220 (ROHM AND HAAS CO.) 5th August 1981, see abstract; page 3, line 5 - page 4, line 21; page 5, line 9 - page 10, line 25; claims 1-15; figure 1 ---	1-6,14-23,33-35
Y	US-A-4 476 283 (P.G. ANDERSEN) 9th October 1984, see figure 3; column 2, line 31 - column 3, line 65; specially lines 50-51; column 4, lines 4-62; column 5, line 34 - column 6, line 33; column 8, lines 35-68; claims 1-11 ---	14-34
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A	EP-A-0 280 454 (DU PONT CANADA INC.) 31st August 1988, see abstract; specially column 2, lines 28-31; column 2, line 43 - column 4, line 15; claims 1-11 ---	10,14-26
T	Journal of Polymer Science, vol. 5, part A-1, July 1967, New York, US; S. Porejko et al.: "Grafting of Maleic Anhydride on Polyethylene. II. Mechanism of Grafting in a Homogeneous Medium in the Presence of Radical Initiators", pages 1563-1571 see figure 2; specially page 1567, line 46 - page 1568, line 9; figures 4-5 -----	1,11,12,35

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9102480

SA 46969

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 06/09/91
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		JP-A- 63254118	20-10-88

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82