United States Patent Office 3,544,662 Patented Dec. 1, 1970

3,544,662

HIGH-MELTING POLYMER COMPOSITIONS COMPRISING A 3-METHYL-1-BUTENE POLYMER AND ANOTHER POLYOLEFIN

Walter J. Polestak, Summit, and Herbert W. Keuchel, Long Valley, N.J., assignors to Celanese Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Nov. 2, 1966, Ser. No. 591,453
Int. Cl. C08f 29/12
U.S. Cl. 260—896 4 Claims

ABSTRACT OF THE DISCLOSURE

Compositions of matter comprising a major amount of a 3-methyl-1-butene polymer blended with a minor but plasticizing amount of a poly-1-olefin capable of reducing melt flow and extrusion temperature properties of the 3-methyl-1-butene polymer and of increasing the tensile strength retention value at an elevated temperature of fibers spun from the polymer blend as compared with similar fibers spun without the poly-1-olefin modifier.

This invention relates broadly to the art of producing high-melting, hydrocarbon polymer compositions; and, more particularly, to polymer blends that are extrudable, e.g., spinnable, and that have improved properties (including improved melt-flow behavior) as compared with that of the primary component thereof.

Still more particularly the invention is concerned with means for improving the spinning and other useful characteristics of fiber-forming (fiber-formable), high-melting, branched-chain poly-1-olefins, specifically homopolymers and copolymers of 3-methyl-1-butene (3MB), whereby there is obtained a material improvement in such properties as spinning behavior and fiber-strength retension at elevated temperatures, as well as other improvements in the useful properties of the polymer (i.e., both homopolymer and copolymers) in fiber, film, sheet, ribbon, tape, rod, bar, or other form.

In extruding, as in spinning, high-melting poly-1-olefins it has been found that fibers melt-spun from such poly-1-olefins as homopolymeric and copolymeric 3-methyl-1-butene and the like do not retain their tensile properties at elevated temperatures, even at such moderate temperatures as 50°–100° C. The usual experience with fibers of such polymers has been that, even though the filamentary material is characterized by initially high tensile-strength values at ambient temperature (20°–30° C.), its tensile strength decreases markedly (i.e., it shows poor tensile-strength retention) when subjected to elevated temperatures.

The present invention is based on our discovery that the aforementioned deterioration in strength values of fibers of homopolymers and copolymers of 3MB under heat can be obviated or minimized by blending a major amount by weight of the 3MB polymer with a minor amount by weight, more particularly a minor but plasticizing amount, of a poly-1-olefin modifier, specifically plasticizer. Such an olefinic modifier should be capable of reducing the melt flow or apparent melt viscosity of the 3MB polymer as evidenced by actual determinations or by the lower temperature at which the modified polymer can be extruded through an orifice such as a spinning orifice. It is also desirable that the olefinic modifier have an inherent viscosity (I.V.) in Decalin (decahydronaphthalene) at 135° C. of from about 1.0 to about 3.2, more particularly from 1.8 to 2.2, and still more particularly about 2. Examples of such poly-1-olefin modifiers are

polypropylene having, for instance, an I.V. of 1.96 in Decalin at 135° C. and poly-(4-methyl-1-pentene) having an I.V. of 2.04 in Decalin at 135° C. Other examples include polyethylene, isotactic polystyrene, polyvinylcyclohexane, and 3MB polymer having a high-melt index, e.g., above 80.

When such blended olefinic polymers are melt-spun, fibers are obtained that show an unexpectedly and unobviously improved retention of tenacity at elevated temperatures and which is far greater than might be expected from the known properties of the individual primary and modifying polymers. In other words, the poly-1-olefin modifier has the capability of increasing the tensile-strength retention value at an elevated temperature of fibers spun from the blend of polymers above that of fibers similarly spun from the unmodified 3MB homopolymer or copolymer. Additionally, the extrusion of the blended polymers to yield fibers can be effected at lower temperatures, e.g., at from 10° to 50° C. lower, than is normally required for spinning the unmodified 3MB polymer.

The olefinic polymers constituting the components of the blends of this invention are prepared by known stereospecific or coordination catalytic polymerization of the corresponding monomer or mixtures of monomers in making the olefinic homopolymer and copolymers, respectively. Such catalysts and their use in the production of copolymers (including some copolymers that are useful in practicing this invention) are given in the copending application of Charles L. Smart, Dagobert E. Stuetz and Manuel Slovinsky, Ser. No. 399,091, filed Sept. 24, 1964, assigned to the same assignee as the present invention and which, by this cross-reference, is made part of the disclosure of the instant application.

The major (more than 50 weight percent) component of the polymeric blend comprising the compositions of matter of this invention is a polymer of the group consisting of (a) homopolymeric 3-methyl-1-butene and (b) copolymers obtained by copolymerizing a major molar amount (more than 50 mole percent) of 3-methyl-1-butene and a minor molar amount of at least one other monoethylenically unsaturated hydrocarbon containing at least 2 carbon atoms. The latter is preferably a straight-chain 1-alkene containing from 2 through 26 carbon atoms, and still more preferably one that contains from 7 or 8 through 20 carbon atoms. To name specifically some monomers that are useful for copolymerization with 3-methyl-1-butene one may mention ethylene, propylene, 1-butene, 1-hexane, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicosene, especially the normal isomers. Other examples include 4-methyl-1-pentene and styrene. The normal or straight-chain 1-alkenes are preferred.

It is not essential that the 1-alkene comonomer be a single monomer having a definite number of carbon atoms within the specified ranges. For example, it may be commercial or pilot-plant fractions comprised of species containing a number of carbon atoms that is lower and/or higher than that which is within the specified ranges of carbon atoms so long as the average number of carbon atoms is within the prescribed range. Thus, the comonomer may be a commercial fraction of, for example, straight-chain 1-alkenes containing from 10 to 20 carbon atoms with an average of 15 carbon atoms. It is preferred to keep fractions of 1-alkenes of the kind just described within a relatively narrow range of minimum and maximum carbon contents of the individual species therein and which is economically consistent with the practical copolymerization results desired.

The 1-alkene or aryl-substituted 1-alkene (e.g., styrene) comonomer is used in a minor molar amount (less than

50 molar percent) with respect to the total molar amount of 3-methyl-1-butene and 1-alkene in the mixture of monomers. Generally the 1-alkene comonomer is employed in an amount ranging from 0.5 to about 20 mole percent, preferably from 0.5 to 10 mole percent, and still more preferably from 0.5 to 7 mole percent of the total monomers employed in making the copolymer. The final copolymer then may contain from 0.5 to about 20 mole percent (or 0.5–10 mole percent; or 0.5–7 mole percent) of copolymerized 1-alkene, more particularly straight-chain 1-alkene, based on the total copolymer. Numerous examples of such straight-chain 1-alkenes have previously been given.

As indicated hereinbefore, the 3MB homopolymer or copolymer (or mixtures thereof in any proportions as desired or as may be required) constitutes more than 50 weight percent of the blend of polymers and the poly-1-olefin modifier constitutes the remainder. Preferably the poly-1-olefin component constitutes from 2 to about 35, and still more preferably from about 5 to about 30, weight percent of the blended polymers. In most cases no particular advantage seems to accrue from using more than about 20 weight percent of the olefinic modifier, based on the total polymer content.

Any suitable method may be employed in blending the polymers together. For example, the polymers may be milled together on hot rolls to form sheets of homogeneous composition, which are then broken up and either powdered or pelletized as may be desired. For many applications, however, the components may be preblended shortly before they are fabricated. Another technique is to feed the individual polymers into the processing equipment thereby permitting mixing in the melt phase. This latter method is particularly advantageous in extrusion operations where a screw-type melt conveyor provides adequate mixing of the components. Still another method of blending the polymers is to dissolve the individual polymers in a common organic solvent, e.g., chlorinated hydrocarbons with boiling points above 200° C. including trichlorobenzene and Arochlor 1248, and separating the blend from the solution by any suitable means, e.g., by adding a liquid which is a non-solvent for the polymer but which is miscible with the mutual polymer solvent that is employed.

In order that those skilled in the art may better understand how the present invention can be carried into effect, the following examples are given by way of illustration and not by way of limitation. All parts and percentages are by weight unless otherwise stated.

The polymeric blends used in the examples were prepared by physically admixing powders of the individual polymers until a homogeneous admixture had been obtained. In the case of polypropylene (I.V.=1.96 in Decalin at 135° C.), which was commercially available in the form of pellets, the pellets were powdered by means of a Mikro pulverizer before admixture with the 3MB polymer.

In carrying out the spinning tests described in the examples the polymeric blend, formed into rods, was extruded on a micro-melt constant-pressure extruder activated by a hydraulic air cylinder. Samples of monofilament collected during an individual run represented changes in spinning temperature, pressure (throughput rates) and take-up speed (spin drawdown).

The term, "melt index," used in characterizing the 3MB polymer, is the weight in milligrams/minute of polymer extruded through an orifice of 0.1016 cm. diameter under a weight of 2160 grams at 330° C. The flow curve thus obtained, as a function of time, was extrapolated to zero time, and the value obtained is defined as the "melt index." A single-hole spinneret having a capillary diameter of 20 mils and an *L/D* ratio of 5 was used in all the individual runs. (The *"L/D"* ratio refers to the length and diameter of the capillary.) The countersink angle for the spinneret was 60°.

The high-temperature testing of the filaments was carried out in a water system at a temperature of 95° C. Data obtained from testing in hot water at 95° C. and in an oven at 100° C. indicated no significant difference between the two tests. The complete moisture insensitivity of these polyolefin fibers permitted more rapid testing in hot water without affecting the results.

EXAMPLE 1

This example illustrates the results obtained in melt-spinning (a) a copolymer (melt index=1.5) of 3-methyl-1-butene containing about 4.8 mole percent of 1-octene and with which copolymer there had been admixed, as a stabilizer, 0.3% by meight thereof of 1-phenyl-4-cyclohexylphenylenediamine; and (b) a blend of this copolymer with 5% by weight of polypropylene based on the weight of the blend.

The spinning data and characteristics of the filaments are summarized in Table 1.

TABLE I

Copolymer condition	Spinning temp., ° C.	Take-up speed, m./min.	Denier	Tensile properties: Elong., percent	Tensile properties: Ten., g./d.*	Tensile properties: 95° C. ten., g./d.*
Original powder	350	1,550	0.7	36	5.4	1.2
	350	1,325	0.5	38	5.7	1.9
	340	660	0.6	38	6.9	1.4
Powdered copolymer, blended with 5% by weight of the mixture, of polypropylene	330	520	2.9	36	8.1	2.9
	330	845	1.6	35	7.9	2.8
	330	450	2.1	34	6.4	3.2

* These are dry tenacity values at 23° C.

The data in Table I show the beneficial effects attained when a low-melt-index 3MB/1-octene copolymer is blended with 5% by weight thereof of polypropylene, and the resulting blend is then melt-spun to form a filament. It will be noted that improvements result both with respect to the lower temperature of extrusion of the blend and the 95° C. tenacity values as compared with the data for the unmodified copolymer.

EXAMPLE 2

This example illustrates the results obtained in melt-spinning a copolymer (melt index of the pelleted copolymer equals 1.6) of 3MB containing about 1.5 mole percent of 1-hexadecene and with which copolymer there had been admixed 0.5%, by weight thereof, of 9,10-dihydroanthracene as a stabilizer. Comparisons were made in melt-spinning this unmodified 3MB/1-hexadecene copolymer in both powder form and in pelleted form; and, also, the powder form and the pulverized pelleted form of the aforesaid copolymer each blended with 5%, by weight of the mixture, of polypropylene. The results are summarized in Table II.

TABLE II

Copolymer condition	Spinning temp., ° C.	Take-up speed, m./min.	Denier	Tensile properties: Elong., percent	Ten., g./d.*	95°C. ten., g/d.
Original powder (M.I.=1.0)	340	820	1.9	35	5.8	2.4
	350	1,430	1.0	36	3.8	1.9
Blended with 5% polypropylene	330	620	1.3	36	5.2	2.7
	330	770	2.0	36	5.8	3.8
	330	635	2.9	36	5.5	3.6
Pellets (M.I.=1.6)	340	345	0.7	34	5.7	3.2
	350	635	1.6	35	5.7	3.0
	350	1,050	0.7	36	6.5	3.1
Pulverized pellets blended with 5% polypropylene	320	760	2.2	35	6.8	3.8
	320	845	1.6	36	6.7	3.4

*These are dry tenacity values at 23° C.

The data in Table II show the beneficial action that results from incorporating a small amount of polypropylene in a 3MB/1-hexadecene copolymer in powder form originally and in pulverized pellet form. It will be noted that the reduction of the spinning temperature when spinning the modified copolymer was accompanied by an improvement in the elevated-temperature (95° C.) retention of fiber strength.

EXAMPLE 3

This example illustrates the results obtained in melt-spinning a copolymer (melt index equals 1.0) of 3MB containing about 1.5 mole percent of 1-hexadecene and with which copolymer there had been admixed 0.3%, by weight thereof, of 1-phenyl-4-cyclohexylphenylenediamine as a stabilizer. Comparisons were made in melt-spinning the unmodified copolymer with the same copolymer modified with (a) 5 weight percent polypropylene, (b) 25 weight percent polypropylene and (c) 5 weight percent poly-(4-methyl-1-pentene), each based on the weight of the mixture. The poly-(4-methyl-1-pentene) had an I.V. of 2.04 in Decalin at 135° C. The results are summarized in Table III.

TABLE III

Copolymer condition	Spinning temp., ° C.	Take-up speed, m./min.	Denier	Tensile properties: Elong., percent	Ten., g./d.*	95° C. ten., g./d.
Original powder	350	1,125	0.9	35	3.4	1.8
	360	1,450	0.7	35	3.8	2.3
Powdered copolymer blended with 5% by weight of polypropylene	320	445	2.3	36	5.6	3.0
	330	1,070	1.6	38	5.9	2.9
Powdered copolymer blended with 25% by weight of polypropylene	310	755	2.5	35	5.3	2.9
	310	1,178	2.3	32	4.8	3.3
Powdered copolymer blended with 5% by weight of poly-(4-methyl-1-pentane)	330	645	1.7	35	5.2	3.4
	330	920	1.2	36	6.4	4.0
	340	1,295	0.8	35	5.3	3.2
	340	1,190	1.3	36	6.5	4.0
	340	1,150	1.2	35	6.2	3.9

* These are dry tenacity values at 43° C.

The data in Table III show the beneficial effect of adding two different poly-1-olefin modifiers to a 3MB/1-hexadecene copolymer having a lower melt index (higher molecular weight) than that used in Example 2. More particularly, the addition of the polypropylene and poly-(4-methyl-1-pentene) modifiers to this copolymer also permitted melt-spinning to be carried out at a lower temperature than with the unmodified copolymer, and provided improved tensile-strength retention of the fiber when subjected to an elevated temperature. Increasing the polypropylene content of the blend from 5 to 25% by weight of the copolymer decreased that initial spinning temperature without providing 95° C. tenacity improvements sufficient to warrant the use of the additional amount of polypropylene.

The results are similar to those described in Examples 1, 2, and 3 when homopolymeric 3-methyl-1-butene is substituted for the particular 3-methyl-1-butene copolymers employed in these examples.

The polymeric blends of this invention may be melt-spun into filaments using a spinning temperature within the range of, for example, from about 290° C. to about 370° C., spinning orifices having diameters within the range of, for instance, from about 10 mls to about 80 mils and length/diameter ratios within the range of from about 1 to about 20; and take-up speeds within the range of, for example, from about 100 to about 3000 meters/minute.

Filaments spun from the blends of polymers of this invention are suitable for use in a wide variety of applications. For example, they can be used in the manufacture of woven and knitted fabrics employed in apparent and industrial products such as, for instance, filter cloths, cordage, fishing nets, covers for outdoor and other furniture, and many other applications, especially those where a high resistance to moisture is desirable.

Films and sheets extruded from the polymeric blends of the instant invention are suitable for various covering and wrapping applications, e.g., wrapping and packaging of foods (both fresh and frozen); protective coverings for outdoor equipment; wrappings for underground pipe, cables, and the like; various miscellaneous household uses, e.g., as shower curtains; and numerous other uses that will be apparent from the foregoing illustrative examples.

The method of the present invention is applicable to homopolymeric and copolymeric 3-methyl-1-butenes having an initial melt index (M.I.) level within the range of from 0.5 to 80, and which may or may not have been thermally degraded prior to extrusion. Thus it is applicable to low-melt-index (high-molecular-weight) homopolymeric and copolymeric 3-methyl-1-butenes that have been thermally degraded, prior to extrusion in fiber or other form, in order to improve their tensile properties, both at ambient and elevated temperatures, as compared with the same polymers that have not been given such a thermal degradation treatment. When such thermally degraded polymers are used in practicing this invention, they can be extruded at a lower temperature than when no polymeric modifier of the kind used in this invention has been incorporated therein.

It will be understood, of course, by those skilled in the art that the detailed description given hereinbefore

is merely by way of illustration, and that many variations may be made therein without departing from the spirit of our invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition of matter comprising a blend of a major amount by weight of

(A) a polymer of the group consisting of (a) homopolymeric 3-methyl-1-butene and (b) copolymers obtained by copolymerizing a major molar amount of 3-methyl-1-butene and a minor molar amount of at least one other monoethylenically unsaturated hydrocarbon containing at least 2 carbon atoms, said polymer having a melt index in the range of about 0.5 to 80;

and a minor but plasticizing amount by weight of

(B) a poly-(4-methyl-1-pentene) in an amount ranging from 2 to about 35 weight percent of the blend of polymers (A) and (B) capable of reducing the initial extrusion temperature and the melt flow of the polymer of (A) and of increasing the tensile strength retention value at an elevated temperature of fibers spun from the blend of polymers above that of fibers similarly spun from the polymer of (A) alone, said poly-(4-methyl-1-pentene) having an inherent viscosity in decahydronaphthalene at 135° C. in the range of about 1.0 to 3.2.

2. The composition of claim 1 wherein the polymer of (A) is a copolymer obtained by copolymerizing a major molar amount of 3-methyl-1-butene and a minor molar amount of a straight-chain 1-alkene containing from 2 through 26 carbon atoms, wherein the straight-chain 1-alkene of (A) constitutes from 0.5 to 10 mole percent of the total molar amount of the copolymer of (A) and the poly-1-olefin of (B) is poly-(4-methyl-1-pentene) in an amount ranging from about 5 to about 30 weight percent of the blend of polymers of (A) and (B).

3. A composition as in claim 2 wherein the straight-chain 1-alkene component of the copolymer of (A) is hexadecene, said hexadecene constituting from 0.5 to 10 mole percent of the total molar amount of the copolymer of (A), and the poly-1-ole of (B) is poly-(4-methyl-1-pentene) having an inherent viscosity in decahydronaphthalene at 135° C. within the range of from about 1.8 to about 2.2 and constitutes from about 5 to about 30 weight percent of the blend of polymers of (A) and (B).

4. The composition of claim 2 in the form of filamentary material.

References Cited

UNITED STATES PATENTS

3,121,070 2/1964 Coover et al. ..... 260—45.5

MURRAY TILLMAN, Primary Examiner

C. J. SECCURO, Assistant Examiner

U.S. Cl. X.R.

260—897; 264—211