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PATENT REQUEST AND NOTICE OF ENTITLEMENT

We HIMONT INCORPORATED

of 2801 Centerville Road, New Castle County, DELAWARE, U.S.A.

being the Applicant and Nominated Person, request the grant of a patent for an invention entitled POLYOLEFIN COMPOSITIONS AND PROCESS FOR THEIR PREPARATION which is described in the accompanying standard complete specification.

Convention priority is claimed from the following basic application:

Basic Applicant	Application Number	Application Date	Country	Country Code
Himont Incorporated	MI 91 A 002910	31 October 1991	Italy	IT

Decio Malucelli; Fausto Cocola and Francesco Forcucci are the actual inventors of the invention.

The inventors made the invention for and on behalf of the nominated person in the course of their duties as employees of the nominated person.

The basic application was the first application made in a Convention country in respect of the invention the subject of this request.

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DATED this 20th day of October 1992

HIMONT INCORPORATED
By their Patent Attorney

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POLYOLEFIN COMPOSITIONS AND PROCESS FOR THEIR PREPARATION

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(56) Prior Art Documents
US 4717743
US 4717742
US 4301047

(57) Claim

1. A polyolefin composition comprising one or more crystalline polymers of 1-olefins and copolymers of 1-olefins with other 1-olefins having a melt flow index at 230°C, 2.16 Kg, ASTM-D 1238, condition L of higher than 100 g/10 min, and, dispersed therein, a cellulosic material in particle or fiber form.

10. A process for the preparation of a polyolefin composition in the form of pellets comprising a polymer material and a cellulosic material in particle or fiber form dispersed in said polymer material, wherein said composite is obtained by extruding one or more crystalline polymers of 1-olefins and copolymers of 1-olefins with other 1-olefins having a melt flow index at 230°C, 2.16 Kg, ASTM-D 1238, condition L of higher than 100 g/10 min together with said cellulosic material at a temperature not higher than 200°C.

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Regulation 3.2

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ORIGINAL

COMPLETE SPECIFICATION

STANDARD PATENT

Invention Title: POLYOLEFIN COMPOSITIONS AND PROCESS FOR THEIR PREPARATION

The following statement is a full description of this invention, including the best method of performing it known to us:

GH&CO REF: P18765-AU:VNV:RK

FIELD OF THE INVENTION

The present invention concerns compositions comprising crystalline polymers of 1-olefins and copolymers of 1-olefins with other 1-olefins, of propylene in particular, and cellulosic materials, wood powders and fibers in particular, dispersed in the above mentioned polymers.

Moreover, the invention concerns the process for the preparation of compositions in the form of pellets, and of articles manufactured starting with the above mentioned pellets.

BACKGROUND OF THE INVENTION

Compositions based on olefin polymers, in particular crystalline polypropylene, filled with wood flour, are already known; because of their low cost and low specific weight (about 1 g/cm^3), these materials manufactured in the form of thermoformed sheets, found good application possibilities in the automotive, appliance, and building industries. However, some of the physical-mechanical properties of said materials are poor or barely satisfactory, such as in the case of dimensional stability at temperatures higher than ambient temperature, 40-70°C for example, which are usually required for the above mentioned applications, even for prolonged periods. Moreover, articles comprising said compositions can be obtained only by way of sheet thermoforming (previously obtained by using flat-die extruders) operating under very mild

conditions (in particular at temperatures lower than 200°C). With this technique, however, it is impossible to obtain articles with a complex form at fast molding cycles and without waste (scrap). For this purpose, one should resort to injection molding techniques with the proper molds, but said techniques would require, for the above mentioned composites, considerably more drastic operating conditions, in particular temperatures higher than 200°C, and generally ranging from 220 to 230°C, where the cellulosic phase would be subjected to significant thermodegradation, and consequently the articles would have an objectionable smell, poor appearance, and poor mechanical properties; moreover, the molding equipment and molds would be prone to damaging corrosion phenomena.

It has now been found that it is possible to eliminate the above mentioned drawbacks, i.e., adopt the injection molding technique but operating at temperatures which do not exceed 200°C, thus allowing the manufacture of articles with complex shapes with rapid cycles, if the composition utilizing a cellulosic material is obtained by using polyolefins having low molecular weight values corresponding to melt flow index values (MFI at 230°C, 2.16 Kg according to ASTM-D 1238, condition L) higher that 20, preferably within the 25-1000 g/10 min range, and more preferably within the 30-400 g/10 min range.

Therefore, object of the present invention are

composition of polyolefins comprising one or more crystalline polymers of 1-olefins and copolymers of 1-olefins with other 1-olefins having a melt index higher than 20, preferably from 25 to 1000, and more preferably from 30 to 400 g/10 min, and, dispersed in said polymers or copolymers is a cellulosic material in particle or fiber form.

The present invention provides a polyolefin composition comprising one or more crystalline polymers of 1-olefins and copolymers of 1-olefin with other 1-olefins having a melt flow index at 230°C, 2.16 Kg, ASTM-D 1238, condition L of higher than 100 g/10 min, and, dispersed therein, a cellulosic material in particle or fiber form.

The polymers used for the compositions of the present invention are preferably selected from crystalline polymers of 1-olefins and copolymers of 1-olefins with other 1-olefins in which the 1-olefins are linear or branched olefins containing 2-10 carbon atoms; particularly preferred is polypropylene, and more particularly essentially isotactic polypropylene having an isotactic index ≥ 90% (% insoluble fraction in boiling n-heptane).

The above polyolefins are typically prepared with well known polymerization techniques using coordination catalysts, in particular the Ziegler-Natta catalysts.

Olefin polymers with high melt index values such as the ones required by the present invention, can be obtained, as it is known, by adequately reducing the molecular weight of the polyolefins by means of controlled thermodegradation processes, e.g. by way of thermomechanic treatments, optionally in the presence of radical initiators, such as organic peroxides. However, alternatively, it is possible to obtain polymers with a high melt index without resorting to degradation processes, by adequately increasing the quantity of molecular regulator generally

used in the Ziegler-Natta catalyst processes (particularly hydrogen).

The cellulosic material is preferably made up of wood powders or fibers, with a wide range of average dimensions (diameter or length), but generally from 0.01 to 5 mm, and having a bulk density of 0.05-0.3 g/cm^3.

The quantity of cellulosic material which can be incorporated in the compositions of the present invention can vary widely depending on the physical-mechanical performance desired from the finished products. For the above mentioned application, however, the preferred quantities are from 10 to 70% by weight with respect to the total weight of the composite material.

According to the present invention, by subjecting to extrusion mixtures of cellulosic material with a polyolefin, in particular polypropylene, having the characteristics specified above, one obtain pellets that can be converted, by way of known injection molding techniques and apparatuses, into articles with a very complex shape and having physical-mechanical characteristics superior to those of the equivalent commercial articles which are presently obtained only by sheet thermoforming (as mentioned above). In particular, the articles of the present invention have better rigidity and dimensional stability, both at ambient temperature and higher temperatures ($\geq 100^{\circ}C$), as clearly shown by higher flexural

modulus and HDT (Heat Distortion Temperature) values.

Moreover, during the molding phase of the articles of the present invention, the degradation phenomena of the cellulosic component are negligible or extremely contained, even when the content of said component is very high (40-70% by weight); consequently, the articles obtained possess considerably improved organoleptic characteristics (odor and color).

Finally, compared to the polypropylene/wood flour compositions presently on the market, the materials of the present invention are less sensitive to water absorption or humidity, with the consequent advantages related to storing the pellets, and the appearance of the manufactured articles.

As a whole, the good organoleptic , physical and mechanical properties, as well as the low cost of the products which are the object of the present invention favor their use in various application sectors, such as the automotive appliance and building industries, substituting not only the polypropylene/wood flour compositions available up to now, but also other materials, such as for example: acrylonitrile-butadiene- styrene polymers (ABS) or polypropylene reinforced with glass fiber, and talcum-filled polypropylene.

Moreover, it has been found, and this constitutes another object of the invention, that further improvements in the physical-mechanical and organoleptic characteristics can be obtained if the compositions contains substances which act as

compatibilizing agents for the two phases, i.e., the polyolefin and the cellulosic material. Said substances can be selected from already known and available compatibilizing agents used for polyolefin and organic or inorganic fillers composites, such as for example the titanium alcoholates; esters of phosphoric, phosphorous, phosphonic and silicic acid; metallic salts and esters of aliphatic, aromatic and cycloaliphatic acids; ethylene/acrylic or methacrylic acid, ethylene/esters of acrylic or methacrylic acid, ethylene/vinyl acetate, styrene/maleic anhydride or esters, ABS, methacrylate/butadiene/styrene (MBS), styrene/acrylonitrile (SAN), butadiene/acrylonitrile copolymers; polyolefins, in particular polyethylene or polypropylene, modified by grafting with polar monomers such as for example maleic anhydride or esters, acrylic or methacrylic acids or esters, vinyl acetate, acrylonitrile, and styrene. The above compatibilizers can be added in quantities ranging from 0.1 to 10%, preferably from 0.5 to 5% by weight, with respect to the total weight of the composition.

As stated above, the compositions of the present invention can be easily manufactured in pellet form by way of extrusion and operating at temperatures not exceeding 200°C, preferably from 170 to 200°C.

Any known apparatus and technology can be used for this purpose. Particularly preferred are twin-screw co-rotating

extruders, with high homogenization capability, and having strand die, and a cold-cutting device which reduces the strands to pellets.

By using known injection molding apparatuses and technologies, and operating at the above mentioned temperatures, one can obtain the desired articles utilizing the above pellets.

During the preparation of the pellets, besides the two main components (polyolefin and cellulosic material) and possibly some compatibilizing agents, one can feed into the extruder other additives, such as stabilizing agents (against heat, light, U.V.), plasticizers, pigments or dyes, antistatic and water repellant agents.

The following examples illustrate, but do not limit, the invention.

EXAMPLE 1

The apparatus used consists of a MARIS (Turin) TM 85 extruder mixer equipped with co-rotating screws, whose length is equal to 36 times the diameter of the screws.

46.5 parts by weight of polypropylene in pellet form having a MFI/L= 35 g/10 min, and isotactic index (% insoluble in boiling n-heptane)= 97%, and a mixture of 0.3 parts by weight of the antioxidant additive IRGANOX B 225 [1/1 mixture by weight of tris(2,4-di-tert-butylphenyl)phosphite and pentaerythrityl-tetrakis[-3-(3,5-di-tert-butyl-4-

hydroxyphenyl)propionate] in 3.2 parts by weight of the propylene, are introduced at the extruder feed throat; 50 parts by weight of type "50" wood flour marketed by Joko (Salorno) are introduced at about 1/3 down the length of the extruder in the molten polymer. The wood flour used has the following characteristics:

bulk density : about 0.15 g/cm^3

particle size distribution :

diameter mm	% weight
>0.500	3
0.500-0.355	20
0.355-0.250	30
0.250-0.180	23
0.180-0.090	17
<0.090	7

The internal temperature of the extruder is maintained at 180-190°C. At the output the material is pelletized by way of cold strand cutting.

The pellets are then used to produce samples by way of injection molding at 170°C, and on said samples one determines the following: specific weight (g/cm^3, ASTM D-1505), flexural modulus MEF (MPa, 23°C, ASTM D-790), and heat distortion temperature HDT (°C, 1.82 N/mm^2, ASTM D-648).

The relevant data are reported in the attached Table.

EXAMPLE 2

Example 1 is repeated, but in this case the polypropylene used is in the form of spherical particles having MFI/L= 90 g/10 min and an isotactic index = 93%.

The characteristics of the composition are reported in the attached Table.

EXAMPLE 3

Example 1 is repeated, but in this case the polypropylene used is in the form of spherical particles having MFI/L= 150 g/10 min, and an isotactic index = 96%.

The characteristics of the composition are reported in the attached Table.

EXAMPLE 4

The apparatus and methods of Example 1 are used, but in this case one introduces at the throat of the extruder 45.5 parts by weight of polypropylene in pellet form having MFI/L= 35 g/10 min, and isotactic index = 96%, 0.3 parts by weight of IRGANOX B 225 in a mixture with 3.2 parts by weight of polypropylene, and 1 part by weight of polypropylene modified by grafting, containing about 5% by weight of maleic anhydride (compatibilizing agent).

1/3 down the length of the extruder one then introduced 50 parts by weight of type "50" wood flour.

The characteristics of the composition obtained are reported in the attached Table; comparing them with the ones of Example 1, one can see a considerable improvement in the

Heat Distortion Temperature (HDT) due to the use of the compatibilizing agent.

EXAMPLE 5

Example 4 is repeated, but in this case one uses polypropylene in spherical form having a MFI/L= 400 g/10 min, and isotactic index = 97%.

From the characteristics reported in the Table, one can see in this case as well, an improvement in the HDT value due to the compatibilizing agent in the composition.

EXAMPLE 6 (Comparative)

Example 4 is repeated, but in this case one uses pelletized polypropylene having a MFI/L= 1.8 g/10 min.

As one can see in the Table, the composition obtained possesses flexural modulus and HDT values clearly inferior to the ones obtained with polypropylene with MFI higher than 20 g/10 min, both with and without addition of compatibilizing agents. The organoleptic properties of the pellets and molded samples are also considerably worse.

EXAMPLE 7

The polypropylene used in Example 1 (MFI/L= 35 g/10 min) is subjected to thermomechanical degradation at 200°C in a MARIS TM 35 extruder, in the presence of 0.4% by weight of TRIGONOX 101 [bis(tert-butylperoxyisopropyl)benzene].

The polypropylene thus treated, having MFI/L= 400 g/10 min, is then used for the preparation of the composition with

wood flour, operating as described in Example 1.

The characteristics of said composition are reported in the attached Table.

TABLE

Example n.	Specific weight g/cm^3	MEF (MPa)	HDT (^oC)
1	1.09	4200	120
2	1.09	4420	118
3	1.08	4400	123
4	1.09	4290	133
5	1.09	4520	133
6 comp.	1.08	2770	96
7	1.09	4270	115

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A polyolefin composition comprising one or more crystalline polymers of 1-olefins and copolymers of 1-olefins with other 1-olefins having a melt flow index at 230°C, 2.16 Kg, ASTM-D 1238, condition L of higher than 100 g/10 min, and, dispersed therein, a cellulosic material in particle or fiber form.

2. A polyolefin composition of claim 1, wherein said cellulosic material is present in quantities ranging from 10 to 70% by weight with respect to the total weight.

3. A polyolefin composition of claim 1 or claim 2 wherein said cellulosic material is selected from the group consisting of wood powders or fibers.

4. A polyolefin composition of claim 3, wherein said cellulosic material has average dimensions of from 0.01 to 5 mm.

5. A polyolefin composition of any one of claims 1 to 4, wherein said crystalline polymers of 1-olefins and copolymers of 1-olefins with other 1-olefins are selected from the polymers and copolymers of 1-olefins, linear or branched, containing 2-10 carbon atoms.

6. A polyolefin composition of claim 5, wherein said olefin polymer is polypropylene.

7. A polyolefin composition of any one of claims 1 to 6 further comprising from 0.1 to 10% by weight, with respect to the total weight, of a compatibilizing agent.

8. A polyolefin composition of claim 7, wherein said compatibilizing agent is polypropylene grafted with maleic anhydride.

9. A polyolefin composition of claim 1 in the form of extruded pellets.

10. A process for the preparation of a polyolefin composition in the form of pellets comprising a polymer material and a cellulosic material in particle or fiber form dispersed in said polymer material, wherein said composite is obtained by extruding one or more crystalline polymers of 1-olefins and copolymers of 1-olefins with other 1-olefins having a melt flow index at 230°C, 2.16 Kg, ASTM-D 1238, condition L of higher than 100 g/10 min together with said cellulosic material at a temperature not higher than 200°C.

11. A process for manufacturing an article product comprising a polymer material and a cellulosic material in particle or fiber form dispersed in said polymer material, where said article is obtained by subjecting the polyolefin composition in the form of extruded pellets of claim 9, to injection molding at a temperature not higher than 200°C.

12. Articles obtained by using the process of claim 11.

13. A process for preparing a polyolefin composition in pelletized form according to claim 10 substantially as herein described with reference to any one or more of Examples 2 to 5 and 7.

Dated this 2nd day of August 1994

HIMONT INCORPORATED
By their Patent Attorney
GRIFFITH HACK & CO

"POLYOLEFIN COMPOSITIONS AND PROCESS FOR THEIR PREPARATION"

ABSTRACT:

Polyolefin compositions comprising one or more crystalline polymers or copolymers of 1-olefins having Melt Index values higher that 20 g/10 min, and, dispersed in the above mentioned polymers or copolymers, a cellulosic material in the form of particles or fiber, as well as the process for the preparation of the above mentioned composites in pelletized form and their conversion into products by way of injection molding.

(HM 9119 EST)