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(54) **Title:** HIGHLY FILLED SOFT POLYOLEFIN COMPOSITIONS

(57) **Abstract:** Flexible highly filled polyolefin compositions with improved balance of properties particularly for applications where softness and ductility at low temperature is requested comprising a soft heterophasic polyolefin composition the fraction soluble in xylene at 25°C of said polyolefin composition having IV_{gpc} lower than 2.5 dl/g. Mw/Mn (GPC) equal to or higher than 4. Mz/Mw (GPC) equal to or higher than 2.5. Said polyolefin composition further comprising an inorganic filler (II) selected from flame-retardant inorganic fillers and inorganic oxides or salts and a further elastomeric polymer or polymer composition component (c) having flexural modulus (ISO 178) lower than 60 MPa, Shore A (ISO 868) lower than 90 and T_g (DMTA) lower than - 20°C.



TITLE:**"HIGHLY FILLED SOFT POLYOLEFIN COMPOSITIONS"**

The present invention concerns soft polyolefin compositions comprising a high amount of inorganic fillers.

BACKGROUND OF THE INVENTION

Polyolefin compositions having elastic properties while maintaining a good thermoplastic behavior have been used in many application fields, due to the valued properties which are typical of polyolefins, such as chemical inertia, mechanical properties and nontoxicity. Moreover, they can be advantageously transformed into finished products with the same techniques used for thermoplastic polymers. In particular, flexible polymer materials are widely used in the medical field, as well as for packaging, extrusion coating and electrical wires and cables covering. In many of these applications, vinyl chloride polymers containing adequate plasticizers, which are necessary to give said polymers their desired flexibility characteristics, are presently used. Said polymer products, however, are subject to ever increasing criticism both for the suspected toxicity of the plasticizers they contain and because when incinerated, they can disperse into the atmosphere extremely toxic by-products, such as dioxin. It would be very useful, therefore, to substitute said materials with products which besides the desired flexibility characteristics and transparency, would have the chemical inertia and nontoxicity typical of olefin polymers. Elastic polypropylene compositions retaining good thermoplastic behavior have been obtained in the art by way of sequential copolymerization of propylene, optionally containing minor quantities of olefin comonomers, and then ethylene/propylene or ethylene/alpha-olefin copolymers mixtures. Catalysts based on halogenated titanium compounds supported on magnesium chloride are commonly used for this purpose. For instance, EP-A-472 946 describes flexible elastoplastic polyolefin compositions comprising, in parts by weight: A) 10-50 parts of an isotactic propylene homopolymer or copolymer; B) 5-20 parts of an ethylene copolymer, insoluble in xylene at room temperature; and C) 40-80 parts of an ethylene/propylene copolymer containing less than 40% by weight of ethylene and being soluble in xylene at room temperature; the intrinsic viscosity of said copolymer is preferably from 1.7 to 3 dl/g. Said compositions are relatively flexible and have good elastic properties, as demonstrated by flexural modulus lower than 150 MPa values, Shore D hardness from 20 to 35, and Shore A hardness of about 90, associated with good tension set values (of 20-50% at

75% elongation, and about 33-40% at 100% elongation); nevertheless, such values are not fully satisfactory for many applications. Mineral fillers, such as aluminum and magnesium hydroxides or calcium carbonate, are commonly used at high concentration levels in polyolefin compositions for several reasons, for instance to impart self-extinguishing properties or to improve application-related physical properties, such as soft touch and printability. The major disadvantage of these mineral fillers, in particular when used on functional grounds as in the case of flame retardants, is the very high loading needed. Depending on the class of fire-retardancy requested, up to 65-70% by weight of filler can be necessary in order to reach adequate effectiveness in polyolefins: A lower amount of filler around 40-60 % wt can be also sufficient for flame retardancy in certain applications. Normally, this has a highly negative influence on the processing of the polymer, with difficulties in adding and dispersing such high levels of filler, and on the physical-mechanical properties of compounds, namely lower elongation at break, lower tensile strength and higher brittleness. EP 1 043 733 describes self-extinguishing electrical cables having a coating layer based on a polymer material containing a flame-retardant inorganic filler; this polymer material comprises a heterophase copolymer having at least 45% by weight of an elastomeric phase based on ethylene copolymerized with an alpha-olefin, and a thermoplastic crystalline phase based on propylene. While these compositions incorporate large amounts of flame-retardant filler, the very high levels of filler negatively affect the physical-mechanical properties of the polymer material, and in particular lead to low elongation values. As a result, the final product is no longer apt to various applications, such as roofing, membranes and cables. In order to compete with plasticised PVC in the above applications, it would be necessary to provide flexible polyolefin compositions, having low flexural modulus and hardness values, capable of incorporating large amounts of filler without deterioration of physical and mechanical properties, and in particular elongation at break, stress at break, tension set and having improved behaviour at low temperature. More flexible elastoplastic polyolefin compositions have been described in the International Application *WO03/011962*, and comprise, by weight:

- A) 8 to 25% of a crystalline polymer fraction selected from propylene homopolymer and propylene copolymers with a C4-8 alpha-olefin;
- B) 75 to 92% of an elastomeric fraction comprising two different propylene elastomeric copolymers, and more specifically: (1) a first elastomeric copolymer of propylene with 15 to

32% of ethylene and/or a C4-8 alpha-olefin, and (2) a second elastomeric copolymer of propylene with more than 32% up to 45% of ethylene and/or a C4-8 alpha-olefin, the (1)/(2) weight ratio ranging from 1:5 to 5:1. These polyolefin compositions have flexural modulus lower than 60 MPa, Shore A lower than 90, and tension set at 100% elongation lower than 35%. The compositions described in this document do not contain relevant amounts of fillers.

In the International Application *W02004/026957* the flexible polyolefin compositions described in *W003/011962* are filled with 40 to 80% by weight of an inorganic filler, selected from flame-retardant inorganic fillers and inorganic oxides or salts, without losing their physical-mechanical properties, and in particular retaining low hardness and flexural modulus values, high elongation at break and low tension set values. The highly filled soft polyolefin compositions described in *W02004/026957* have preferably Shore A hardness lower than 90, elongation at break (ASTM D638) higher than 400%, tensile strength at break (ASTM D638) equal to or higher than 4 MPa.

SUMMARY OF THE INVENTION

It is still felt the need of polyolefin compositions that, when appropriately compounded with inorganic fillers, show improved balance of properties particularly in applications where softness and ductility at low temperature is requested without excessive deterioration of other mechanical properties such as particularly tensile properties.

Object of the present invention is a filled polyolefin composition preferably having MFR 230°C/2,16 Kg of from 0.5 to 2 gr/10min comprising:

- a) 15 to 40% by weight of a flexible heterophasic polyolefin composition (I), comprising the following fractions (wherein the total of A and B fractions is 100%):
 - A) from 20 to 40, preferably from 25 to 35 % by weight of a crystalline polymer fraction consisting of a propylene homopolymer, or a copolymer of propylene with one or more comonomers selected from ethylene and a CH₂=CHR alpha-olefin, where R is a C₂-C₈ alkyl radical, or mixtures thereof; said homopolymer or copolymer containing at least 85% by weight of units derived from propylene, said crystalline fraction having a fraction insoluble in xylene at 25°C of at least 90% by weight, preferably having intrinsic viscosity of the xylene insoluble fraction of from 1.2 to 1.9 dl/g and preferably MFR (230°C/2.16Kg) of from 2 to 70, more preferably of from 20 to 50 g/10min.

B) from 60 to 80%, preferably from 65 to 75% by weight of an elastomeric fraction consisting of a copolymer or blend of copolymers of ethylene with one or more comonomers selected from propylene and $\text{CH}_2=\text{CHR}$ alpha-olefins, where R is a $\text{C}_2\text{-C}_8$ alkyl radical, and optionally with minor quantities of a diene; said copolymer or blend containing units (i.e. polymer chain segments) derived from ethylene in a quantity lower than 40% by weight, said elastomeric fraction preferably having solubility in xylene at room temperature (25°C) greater than 50% by weight, and preferably intrinsic viscosity of the soluble fraction η of equal to or less than 2.3 dl/g. the fraction soluble in xylene at 25°C of said polyolefin composition having

- IVgpc lower than 2.5 dl/g, preferably of from 1.7 to 2.2 dl/g; and a broad molecular weight distribution Mw/Mn (GPC) equal to or higher than 4, preferably of from 4.2 to 6, Mz/Mw (GPC) equal to or higher than 2.5; and even more preferably MFR at 230°C/2,16 Kg of from 3 to 8 gr/10min;;
- b) 40 to 80% by weight of an inorganic filler (II) selected from flame-retardant inorganic fillers and inorganic oxides or salts; and
- c) 5 to 25 % by weight of an elastomeric polymer or polymer composition having flexural modulus (ISO 178) lower than 60 MPa, preferably lower than 20 MPa, Shore A (ISO 868) lower than 90 preferably lower than 80 and T_g (DMTA) lower than -20°C. Even more preferably tension set at 100% elongation (ISO 2285) lower than 45%, preferably lower than 35%.

Wherein the sum of a), b) and c) is 100%.

Preferably component c) is

i) an elastoplastic polypropylene composition consisting of:

- A) 8 to 25% of a crystalline polymer fraction selected from propylene homopolymer and propylene copolymers with a C4-8 alpha-olefin preferably having solubility in xylene at 25°C lower than 10% by weight;
- B) 75 to 92% an elastomeric fraction comprising two different propylene elastomeric copolymers, and more specifically: (1) a first elastomeric copolymer of propylene with 15 to 32% of ethylene and/or a C4-8 alpha-olefin preferably having solubility in xylene at 25°C greater than 50% by weight, and (2) a second elastomeric copolymer of propylene with more than 32% up to 45% of ethylene and/or a C4-8 alpha-olefin

preferably having solubility in xylene at 25°C greater than 80% by weight, the (1)/(2) weight ratio ranging from 1:5 to 5:1;

or

ii) a butene-1 copolymer having:

- a content of butene-1 derived units of 80wt% or more, preferably of 84wt% or more
- a flexural elastic modulus preferably of 40 MPa or less, even more preferably 30 MPa or less
- a melting temperature DSC (TmI) lower than 110°C, preferably equal to or lower than 50°C

The highly filled polyolefin compositions of the invention exhibit Shore Hardness D is lower than 50, preferably lower than 45; elongation at break (ISO 527-3, technically equivalent to the ASTM D638 norm) higher than 250% and tensile strength at break (ISO 527-3) equal to or higher than 10, preferably higher than 15 MPa. Furthermore an improved balance of flexibility, ductility and impact at low temperature is obtained.

The filled composition of the present invention are particularly suitable in application for roofing and geo-membrane where softness, elasticity and ductility of the material is essential. Particularly advantageously they will find use in sites with very rigid climate or broad seasonal or daily variations of temperature.

DETAILED DESCRIPTION OF THE INVENTION

The heterophasic polyolefin composition of the invention are able to incorporate and retain high amount of inorganic filler, maintaining very low flexural modulus values and flexible behavior and, at the same time exerting the property imparted by the filler, such as self-extinguishing properties in case of flame-retardant fillers, which is essential for most cable applications, roofing applications and soft sheeting. Moreover, the compositions of the invention, at comparable values of tensile strength, show elongation at break values equal to or higher than the ones shown by the filled compositions known in the art. Finally, the compositions of the invention are endowed with good low temperature behaviour in terms of lower glass transition temperature (DSC-Tg) and improved ductility at puncture impact behaviour test.

The component (a) according to the invention is an heterophasic polyolefin composition (I) comprising the following fractions:

- A) from 20 to 40, preferably 25 to 35% by weight of a crystalline polymer fraction consisting of a propylene homopolymer, or a copolymer of propylene with one or more comonomers selected from ethylene and a $\text{CH}_2=\text{CHR}$ alpha-olefin, where R is a $\text{C}_2\text{-C}_8$ alkyl radical, or mixtures thereof; said homopolymer or copolymer containing at least 85% by weight of units derived from propylene, said crystalline fraction having a fraction insoluble in xylene at 25°C of at least 90% by weight, preferably having intrinsic viscosity of the xylene insoluble fraction (XinsIV) of from 1.2 to 1.8 dl/g and preferably MFR ($230^\circ\text{C}/2.16\text{ Kg}$) of from 2 to 70, more preferably of from 20 to 50 g/10min;
- B) from 60 to 80%, preferably from 65 to 75% by weight of an elastomeric fraction consisting of a copolymer or blend of copolymers of ethylene with one or more comonomers selected from propylene and $\text{CH}_2=\text{CHR}$ alpha-olefins, where R is a $\text{C}_2\text{-C}_8$ alkyl radical, and optionally with minor quantities of a diene; said copolymers or blend containing units derived from ethylene in a quantity equal to or less than 40% by weight;
- wherein the total of A and B fractions is 100%,

the fraction soluble in xylene at 25°C of said polyolefin composition (I) having

the Intrinsic Viscosity of the fraction soluble in xylene at 25°C (IVgpc), measured by gel permeation chromatography (GPC), equal to or less than 2.5 dl/g, preferably of from 1.7 to 2.2 dl/g;

the ratio Mw/Mn of weight average molecular weight (Mw) to number average molecular weight (Mn) measured by gel permeation chromatography (GPC) equal to or more than 4, preferably of from 4.2 to 6,

the ratio Mz/Mw of Z-average molecular weight (Mz) to weight average molecular weight (Mw) measured by gel permeation chromatography (GPC) equal to or more than 2.5

By “elastomeric” is meant herein a polymer having low crystallinity or amorphous, preferably having solubility in xylene at room temperature (25°C) greater than 50%, preferably greater than 60% by weight. More preferably the intrinsic viscosity of the soluble fraction η of the compositions according to the invention is of equal to or less than 2.3 dl/g, preferably equal to or less than 2.1.

The above said broad molecular weight distribution of the fraction soluble in xylene at room temperature of the elastomeric component B is preferably obtained by blending two or more

flexible heterophasic polyolefin compositions having different xylene soluble intrinsic viscosities (η_{SIV}), optionally and preferably obtainable by different degree of visbreaking. Particularly preferred is the blend of three heterophasic compositions as hereinbelow described in detail. Thus, the term “copolymer” as used herein means an elastomeric polymer component (a) (B) consisting of one or more copolymers.

According to a preferred embodiment, the elastomeric fraction (B) of the composition (I) comprises at least three components B1, B2 and B3. The intrinsic viscosity η of the fraction soluble in xylene at 25°C of B1, B2 and B3, measured as described in the experimental part, being respectively:

(η_{B1}) equal to or greater than 3, preferably from 3 to 10 dl/g;

(η_{B2}) from 2 to 3 dl/g;

(η_{B3}) equal to or less than 2, preferably from 1.5 to 2 dl/g.

Further preferably the intrinsic viscosities (η_{GPC}) of the fraction soluble in xylene at 25°C of B1, B2 and B3 measured via GPC, as described in the experimental part, are respectively:

η_{GPC} of B1 is equal to or greater than 2.5 dl/g,

η_{GPC} of B2 is of from 1.5 to 2.5 dl/g and

η_{GPC} of B3 is equal to or less than 1.5 dl/g

The composition (I) according to the invention preferably have MFR 230°C/2,16 Kg of from 3 to 8 gr/10min.

In the polyolefin composition (I), said alpha-olefin of formula $\text{H}_2\text{C}=\text{CHR}$ is preferably selected from, butene-1, pentene-1, 4-methylpentene, hexene-1, octene-1 and combinations thereof.

The copolymerization of propylene and ethylene or another alpha-olefin or combinations thereof, to form the elastomeric fraction (B), or the preferred copolymer components B1, B2 and B3 can occur in the presence of a diene, conjugated or not, such as butadiene, 1,4-hexadiene, 1,5-hexadiene and ethylidene-norbomene-1. The diene, when present, is contained in an amount of from 0.5 to 5% by weight, with respect to the weight of the fraction (B).

According to a preferred embodiment of the invention, the heterophasic polyolefin composition (I) is obtained in the form of spheroidal particles having an average diameter of 250 to 7,000 microns, a flowability of less than 30 seconds and a bulk density (compacted) greater than 0.4 g/ml. The heterophasic polyolefin composition (I) may be prepared by polymerization in sequential polymerization stages, with each subsequent polymerization being conducted in the

presence of the polymeric material formed in the immediately preceding polymerization reaction. The polymerization stages may be carried out in the presence of a Ziegler-Natta and/or a metallocene catalyst. According to a preferred embodiment, all the polymerization stages are carried out in the presence of a catalyst comprising a trialkylaluminum compound, optionally an electron donor, and a solid catalyst component comprising a halide or halogen-alcoholate of Ti and an electron donor compound supported on anhydrous magnesium chloride, said solid catalyst component having a surface area (measured by BET) of less than 200 m²/g, and a porosity (measured by BET) higher than 0.2 ml/g. Catalysts having the above mentioned characteristics are well known in the patent literature; particularly advantageous are the catalysts described in USP 4,399,054 and EP-A- 45 977. Other examples can be found in USP 4,472,524. The polymerization process is described in details in the International Application EP-A-472946, the content of which is incorporated herein by reference.

The polymerization stages may occur in liquid phase, in gas phase or liquid-gas phase. Preferably, the polymerization of the crystalline polymer fraction (A) is carried out in liquid monomer (e.g. using liquid propylene as diluent), while the copolymerization stages of the elastomeric copolymer(s) in fraction (B) are carried out in gas phase, without intermediate stages except for the partial degassing of the propylene. According to a most preferred embodiment, all the sequential polymerization stages are carried out in gas phase. The reaction temperature in the polymerization stage for the preparation of the crystalline polymer fraction (A) and in the preparation of the elastomeric copolymer(s) in fraction (B) can be the same or different, and is preferably from 40°C to 90°C; more preferably, the reaction temperature ranges from 50 to 80°C in the preparation of the fraction (A), and from 40 to 80°C for the preparation of components (B). The pressure of the polymerization stage to prepare the fraction (A), if carried out in liquid monomer, is the one which competes with the vapor pressure of the liquid propylene at the operating temperature used, and it may be modified by the vapor pressure of the small quantity of inert diluent used to feed the catalyst mixture, by the overpressure of optional monomers and by the hydrogen used as molecular weight regulator. The polymerization pressure preferably ranges from 33 to 43 bar, if done in liquid phase, and from 5 to 30 bar if done in gas phase. The residence times relative to the two stages depend on the desired ratio between the fractions (A) and (B), and can usually range from 15 minutes to 8 hours.

Conventional molecular weight regulators known in the art, such as chain transfer agents (e.g. hydrogen or ZnEt_2), may be used.

The preferred composition according to the present invention having component A and an elastomeric fraction made of components B1 B2 and B3 can be obtained with the above described process in four stages; one stage for the production of component (A) and three for the production of three elastomeric components B1 B2 and B3 having the required values of intrinsic viscosities.

Alternatively the composition according to the invention can be obtained by separate production of the components and subsequent blending e.g. melt blending in conventional extrusion or mixing equipments. Sequential polymerization and melt blending steps can be also used in mixed sequential and melt blending processes for the production of the composition according to the invention. Alternatively and even more preferably, an heterophasic composition according to the invention can be obtained producing an heterophasic composition HPO1, obtainable as a reactor blend by sequential polymerization as described in EP-A-472946, comprising:

- A) from 20 to 40, preferably from 25 to 35 % by weight of a crystalline polymer fraction consisting of a propylene homopolymer, or a copolymer of propylene with one or more comonomers selected from ethylene and a $\text{CH}_2=\text{CHR}$ alpha-olefin, where R is a $\text{C}_2\text{-C}_8$ alkyl radical, or mixtures thereof; said homopolymer or copolymers containing at least 85% by weight of units derived from propylene, said crystalline fraction having a fraction insoluble in xylene at 25°C of at least 90% by weight, preferably having intrinsic viscosity of the xylene insoluble fraction (XinsIV) of from 1.2 to 1.8 dl/g and preferably MFR ($230^\circ\text{C}/2.16 \text{ Kg}$) of from 2 to 70, more preferably of from 20 to 50 g/10min, even more preferably greater than 25 g/10 min.
- B) from 60 to 80%, preferably from 65 to 75% by weight of an elastomeric fraction consisting of a copolymer of ethylene with one or more comonomers selected from propylene and $\text{CH}_2=\text{CHR}$ alpha-olefins, where R is a $\text{C}_2\text{-C}_8$ alkyl radical, and optionally with minor quantities of a diene, or mixtures thereof; said copolymers containing units derived from ethylene in a quantity equal to or less than 40% by weight;

The said composition HPO1 having MFR1 ($290^\circ\text{C}/2.16 \text{ Kg}$) of equal to or less than 5, preferably of less than 1 gr/10min and Xylene Soluble Intrinsic Viscosity (XSIV η_1) of equal to or higher than 3. Suitable as composition HPO1 is an heterophasic polyolefin composition

commercialized by Basell under the commercial name *Hifax* Ca10A. The above said composition HPO1 can be subsequently visbroken via peroxide treatment producing further etherophasic compositions:

HPO2 having MFR2 values of from 5 to 10 g/10min and XSIV η_2 of from 2 to 3 dl/g, and

HPO3 having MFR3 values equal to or higher than 10 g/10min and XSIV η_3 of equal to or less than 2 dl/g. The said compositions HPO1 HPO2 and HPO3 are blended in proportion of

25 -50 %wt of HPO1, preferably 30-40 %wt

25 -50 %wt of HPO2, preferably 30-40 %wt and

25 -50 %wt of HPO3, preferably 30-40 %wt

wherein the total of HPO1, HPO2 and HPO3 is 100%, providing the composition (I) according to the invention. η_1 , η_2 , and η_3 substantially correspond to the values of η_{B1} , η_{B2} , and η_{B3} due to the low xylene solubility of component A.

The highly filled soft polyolefin composition according to the invention is comprising from 15 to 40% by weight, preferably from 20 to 40% of the composition **(I)**, **component (a)** as above described; from 40 to 80% by weight, preferably from 45 to 75% of an inorganic filler **(II)**, **component (b)**, selected from flame-retardant inorganic fillers and inorganic oxides or salts; and from 5 to 25% by weight, preferably from 5 to 20 % of the elastomeric polymer or polymer composition **component (c)**; wherein the total of a, b and c is 100%.

In applications where self-extinguishing properties are required, preferred component (b) flame-retardant inorganic fillers are hydroxides, hydrated oxides, salts or hydrated salts of metals, in particular of Ca, Al or Mg, such as, for example: magnesium hydroxide $Mg(OH)_2$, aluminum hydroxide $Al(OH)_3$, alumina trihydrate $Al_2O_3 \cdot 3H_2O$, magnesium carbonate hydrate, magnesium carbonate $MgCO_3$, magnesium calcium carbonate hydrate, magnesium calcium carbonate, or mixtures thereof. $Mg(OH)_2$, $Al(OH)_3$, $Al_2O_3 \cdot 3H_2O$ and mixtures thereof are particularly preferred. The metal hydroxides, in particular the magnesium and aluminium hydroxides, are preferably used in the form of particles with sizes which can range between 0.1 and 100 μm , preferably between 0.5 and 10 μm . One inorganic filler which is particularly preferred according to the present invention is a precipitated magnesium hydroxide, having specific surface area of from 1 to 20 m^2/g , preferably from 3 to 10 m^2/g , an average particle diameter ranging from 0.5 to 15 μm , preferably from 0.6 to 1 μm . and the Precipitated magnesium hydroxide generally contains very low amounts of impurities deriving from salts, oxides and/or hydroxides of other

metals, such as Fe, Mn, Ca, Si, V, etc. The amount and nature of such impurities depend on the origin of the starting material. The degree of purity is generally between 90 and 99% by weight. The filler can be advantageously used in the form of coated particles. Coating materials preferably used are saturated or unsaturated fatty acids containing from 8 to 24 carbon atoms, and metal salts thereof, such as, oleic acid, palmitic acid, stearic acid, isostearic acid, lauric acid, and magnesium or zinc stearate or oleate. Inorganic oxides or salts are preferably selected from CaO, TiO₂, Sb₂O₃, ZnO, Fe₂O₃, CaCO₃, BaSO₄ and mixtures thereof.

The component (c) according to the present invention is a very soft elastoplastic material that can be preferably, as above said:

i) an elastoplastic polypropylene heterophasic composition consisting of:

- A) 8 to 25% of a crystalline polymer fraction selected from propylene homopolymer and propylene copolymers with a C4-8 alpha-olefin preferably having solubility in xylene at 25°C lower than 10% by weight;
- B) 75 to 92% of an elastomeric fraction comprising two different propylene elastomeric copolymers, and more specifically: (1) a first elastomeric copolymer of propylene with 15 to 32% of ethylene and/or a C4-8 alpha-olefin preferably having solubility in xylene at 25°C greater than 50% by weight, and (2) a second elastomeric copolymer of propylene with more than 32% up to 45% of ethylene and/or a C4-8 alpha-olefin preferably having solubility in xylene at 25°C greater than 90% by weight, the (1)/(2) weight ratio ranging from 1:5 to 5:1;

or

ii) a butene-1 copolymer having:

- a content of butene-1 derived units of 80wt% or more, preferably of 84wt% or more
- a flexural elastic modulus (MEF) preferably of 40 MPa or less, even more preferably 30 MPa or less
- a melting temperature DSC (TmI) lower than 110°C, preferably equal to or lower than 50°C

Component (c) (i) can be prepared according to the process described in WO0311962 herein incorporated by reference. It is explained that the expression “a copolymer of propylene with <...> ethylene and/or a C4-8 alpha-olefin” means a copolymer of propylene with one or more

comonomers selected from ethylene and a $\text{CH}_2=\text{CHR}$ alpha-olefin, where R is a $\text{C}_2\text{-C}_8$ alkyl radical, or mixtures thereof.

Component (c) (ii) can be prepared in presence of a metallocene catalyst according to WO2009/000637 herein incorporated by reference.

Said butene-1 copolymer component (c) (ii) further preferably is a 1-butene/ethylene copolymer having a content of copolymerized ethylene of from 5 % by mol to 18.00 % by mol preferably from 15.50% by mol to 17% by mol; one or more of the following preferred properties:

- a) distribution of molecular weight M_w/M_n lower than 3;
- b) hardness shore A (measured according to ISO 868) lower than 65; preferably lower than 60;
- c) tension set lower than 30% at 100% of deformation (ISO 2285) preferably lower than 20%;
- d) no melting point detectable at the DSC, measured cancelling the thermal history of the copolymer according to the methods described in this document;
- e) Melting enthalpy, measured after 10 days of aging at room temperature measured according to the methods described in this document, comprised between 4 and 15 J/g; preferably between 5 and 10 J/g.
- f) Content of 1-butene units in form of isotactic pentads (mmmm) higher than 90%; preferably higher than 98%

Said butene-1 copolymer component (c) (ii) can be further advantageously a composition consisting of:

- i) 80 wt% or more, preferably from 85 to 95 wt%, more preferably, 93-90% of said butene-1 copolymer, and
- ii) up to 20 wt%, preferably from 5 to 15wt%, more preferably from 7 to 10 wt% of a crystalline propylene polymer; provided that the total content of copolymerized ethylene and propylene is equal to or less than 16 wt% of the composition (i) + (ii).

The crystalline propylene polymer (ii) is preferably a propylene copolymer, more preferably a propylene terpolymer, even more preferably a copolymer of propylene with ethylene and a $\text{C}_4\text{-C}_8$ alpha-olefin or blends thereof. The overall handability of the butene-1 copolymer component (c) (ii) can be advantageously improved by in line compounding up to 20 wt% of the said

crystalline propylene polymer component (ii); without substantial deterioration of other mechanical properties. The crystalline propylene polymer (ii) has typically a value of melt flow rate (MFR) at 230 °C, 2.16 kg of from 0.6 to 10 g/10 min, preferably of from 2 to 10 g/10 min, melting temperature DSC of from 130°C to 160°C.

The total content of ethylene in the crystalline propylene polymer (ii) being preferably of from 1% to 5% by weight and the total content of C4-C8 alpha -olefin in the component (ii) being 2.4% to 12% by weight.

The highly filled soft polyolefin compositions according to the present invention can be prepared by mixing the polymer components, the filler and optionally further additives according to methods known in the state of the art. For instance, the components may be mixed in an internal mixer having tangential rotors (such as Banbury mixers) or having interpenetrating rotors, or alternatively in continuous mixers (such as Buss mixers) or corotating or counter-rotating twin-screw mixers.

The polymeric component of the invention, are capable of incorporating large amounts of fillers, at the same time retaining the physical and mechanical properties of unfilled and less flexible compositions. More specifically, the highly filled polyolefin compositions of the invention are preferably endowed with Shore D Hardness lower than 50 (ISO 868), more preferably lower than 45; elongation at break (ISO 527-3) higher than 250%, more preferably higher than 280%; even more preferably higher than 290; tensile strength at break (ISO 527-3) equal to or higher than 10MPa, more preferably higher than 15 MPa. Moreover, the polyolefin compositions of the invention preferably have flexural modulus (ISO 178 on compression molded samples 1 mm thick) of lower than 600 MPa, more preferably from 300 to 600 MPa. A further characteristic of the highly filled polyolefin compositions of the instant invention is that they are capable of retaining ductile behavior at very low temperature having Tg-DSC values lower than -40°C. Particularly advantageously exhibit tensile elastic modulus measured via DMTA (MET-DMTA) equal to or lower than 550 MPa. The ratio MET-DMTA/Tg-DSC is equal to or more than -15, preferably equal to or more than -13. Thus, with the addition of the component (c) in combination with the component (a) according to the invention a valuable balance of properties is obtained. An increase in flexibility also is unexpectedly obtained with a low temperature behavior improved with respect to reference materials and also with respect to the addition of different elastomeric components available in the art (e.g. Versify).

The filled polyolefin compositions of the present invention find application as plasticized PVC replacement. In fields where self-extinguishing properties are required, the compositions of the invention may be used in lieu of plasticized PVC, in applications such as reinforced and nonreinforced roofing membranes, inner filling for industrial cables, cable sheathing and adhesive tapes. Where flame-retardancy is not requested, the compositions of the invention may be advantageously used in non flame-retardant soft membranes, coupled or non-coupled with a reinforcement (e.g. in publicity banners, liners, tarpaulin, sport-wear and safety clothing), and as synthetic leather. Moreover, the compositions may be used in packaging and extrusion coating. Therefore, the present invention is further directed to an article comprising the above described filled polyolefin composition. Specifically and preferably it is also directed to blown or cast film or sheets suitable for application in the field of roofing and geomembrane, requiring flexibility softness and ductility at low temperature.

Conventional additives commonly used in the state of the art may be added to the highly filled soft polyolefin compositions of the present invention. For instance, in order to enhance the compatibility between the inorganic filler and the heterophasic polymer composition, coupling agents may be used; said coupling agents may be saturated silane compounds or silane compounds containing at least one ethylenic unsaturation, epoxides containing an ethylenic unsaturation, organic titanates, mono- or dicarboxylic acids containing at least one ethylenic unsaturation, or derivatives thereof such as anhydrides or esters.

Mono- or dicarboxylic acids containing at least one ethylenic unsaturation, or derivatives thereof, which can be used as coupling agents are, for example, maleic acid, maleic anhydride, fumaric acid, citraconic acid, itaconic acid, acrylic acid, methacrylic acid and the like, and the anhydrides or esters derived therefrom, or mixtures thereof. Maleic anhydride is particularly preferred.

The coupling agents can be used as such or pre grafted onto a polyolefin, for example polyethylene or copolymers of ethylene with an alpha-olefin, by means of a radical reaction (as described for instance in EP-A-530 940). The amount of grafted coupling agent is generally comprised between 0.05 and 5 parts by weight, preferably from 0.1 to 2 parts by weight, relative to 100 parts by weight of polyolefin. Polyolefins grafted with maleic anhydride are commonly available as commercial products, such as Polybond 3200 produced by Chemtura or *Qestron* by Basell.

Alternatively, the coupling agents of carboxylic or epoxy type mentioned above (for example maleic anhydride) or silanes containing an ethylenic unsaturation (for example vinyltrimethoxysilane) can be added to the mixture in combination with a radical initiator so as to graft the compatibilizing agent directly onto the polymer material. Initiators which can be used are organic peroxides, such as tert-butyl perbenzoate, dicumyl peroxide, benzoyl peroxide, di-tert-butyl peroxide and the like. This technique is described, for example, in USP 4,317,765.

The amount of coupling agent to be added to the mixture may vary according to the nature of the coupling agent used and the amount of flame-retardant filler added, and preferably ranges from 0.01 to 10%, more preferably from 0.1 to 5%, and even more preferably from 1 to 3% by weight with respect to the total weight of the highly filled polyolefin composition. Conventional additives such as processing aids, lubricants, nucleating agents, extension oils, organic and inorganic pigments, anti-oxidants and UV-protectors, commonly used in olefin polymers, may also be added.

Processing aids usually added to the polymer material are, for example, calcium stearate, zinc stearate, stearic acid, paraffin wax, synthetic oil and silicone rubbers. Examples of suitable antioxidants are polymerized trimethyldihydroquinoline, 4,4'-thiobis(3-methyl-6-tert-butyl)phenol; pentaerythrityltetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] and 2,2'-thiodiethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate].

Other fillers which can be used are, for example, glass particles, glass fibers, calcinated kaolin and talc.

The following analytical methods have been used to determine the properties reported in the present application.

Property	Method
<u>Melt Flow Rate - MFR</u>	ISO1133, at 230°C, 2.16 kg where not differently specified.
<u>MWD and IV determination via GPC</u>	The molecular weight distribution and related parameters Mn, Mw and Mz and IV _{gpc} values were measured by way of gel permeation chromatography (GPC) at 150°C using a Alliance GPCV 2000 instrument (Waters) equipped with four mixed-bed columns PLgel Olexis Agilent having a particle size of 13 µm. The dimensions of the columns are 300 × 7.8 mm. The mobile phase used is vacuum distilled 1,2,4-Trichlorobenzene (TCB) and the flow rate is kept at 1.0 ml/min. The sample solution is prepared by heating the sample under stirring at 150°C in TCB

for about two hours. The concentration is 1 mg/ml. To prevent degradation, 0.1 g/l of 2,6- di-tert-butyl-p-cresol are added. 308.5 μL of solution are injected into the column set. A calibration curve is obtained using 10 polystyrene standard samples (EasiCal kit by Polymer Laboratories) with molecular weights in the range from 580 to 7500000. It is assumed that the K values of the Mark-Houwink relationship are:

$K = 1.21 \times 10^{-4} \text{ dL/g}$ and $\alpha = 0.706$ for the polystyrene standards;

$K = 2.46 \times 10^{-4} \text{ dL/g}$ and $\alpha = 0.725$ for the propylene copolymer samples.

A third order polynomial fit is used for interpolate the experimental data and obtain the calibration curve. Data acquisition and processing is done by using Empower 1.0 with GPCV option by Waters.

For butene-1 polymers the Mark-Houwink relationship was used to determine the molecular weight distribution and the relevant average molecular weights: the K values were $K_{PS} = 1.21 \times 10^{-4} \text{ dL/g}$ and $K_{PB} = 1.78 \times 10^{-4} \text{ dL/g}$ for PS and PB respectively, while the Mark-Houwink exponents $\alpha = 0.706$ for PS and $\alpha = 0.725$ for PB were used.

For butene/ethylene copolymers, as far as the data evaluation is concerned, it was assumed for each sample that the composition was constant in the whole range of molecular weight and the K value of the Mark-Houwink relationship was calculated using a linear combination as reported below:

$$K_{EB} = x_E K_{PE} + x_P K_{PB}$$

where K_{EB} is the constant of the copolymer, K_{PE} ($4.06 \times 10^{-4} \text{ dL/g}$) and K_{PB} ($1.78 \times 10^{-4} \text{ dL/g}$) are the constants of polyethylene and polybutene, x_E and x_B are the ethylene and the butene wt% content. The Mark-Houwink exponents $\alpha = 0.725$ was used for all the butene/ethylene copolymers independently on their composition.

For Butene/propene copolymers, as PP and PB have very similar K , no corrections were applied and the copolymer was integrated using the K and α values of PB.

Low temperature impact properties: The impact properties were measured according to the ISO 6603 (Puncture Impact Behavior of Rigid Plastics) on samples obtained from 1mm sheets extruded on a Brabender 30mm, 25 L/D single screw extruder with 1mm thick flat die, and cut in machine direction. The instrumental apparatus for the impact

measurement was a CEAST-Fractovis INSTRON instrumented unit that allows to distinguish between ductile and brittle failure modes according to ISO 6603 without need for subjective judgments.

The modes of failure are:

- Ductile (YD)
- Ductile/Brittle (YS)
- Brittle/Ductile (YU)
- Brittle (NY)

The fracture mode was recorded for 10 samples per each composition tested.

Tensile properties: Tensile Strength at Break and Elongation at Break, were measured following the ISO 527-3 (item 5A, 500mm/min), on samples obtained from 1mm sheets extruded on a Brabender 30mm, 25 L/D single screw extruder with 1mm thick flat die, and cut and tested in machine direction.

Shore A (Sh.A) and Shore D (Sh.D) Hardness measured on a compression moulded plaques (thickness of 4mm) following the ISO 868.

Tg -DSC the glass transition temperature (Tg) was measured via DSC performed at 10°C/min. The Tg was determined after cooling starting from -90°C.

Tensile Elastic Modulus (MET-DMTA) Tensile Elastic Modulus (storage modulus) determined at 23°C via DMA analysis according to the ISO 6721-4 on 1mm thick compression moulded plaque.

Flexural Elastic Modulus (MEF) ISO 178 on 1mm thick compression moulded plaque.

Comonomer content (%wt) IR. Spectroscopy

Intrinsic Viscosity Determined in tetrahydronaphthalene at 135°C Determined in tetrahydronaphthalene at 135°C for the insoluble fractions (XinsIV) and for the xylene soluble fractions (XSIV=η). XSIV=η of the compositions (I) according to the invention, are assumed to correspond substantially to the viscosity of the solubles of the elastomeric fraction component(s) B.

Xylene soluble and insoluble fractions (%wt): determined as follows:

2.5 g of polymer composition and 250 cm³ of O-xylene are introduced in a glass flask equipped with a refrigerator and a magnetical stirrer. The temperature is raised in 30 minutes up to the boiling point of the solvent. The so obtained clear solution is then kept

under reflux and stirring for further 30 minutes. The closed flask is then cooled to 100°C in air for 10 to 15 minute under stirring and then kept for 30 minutes in thermostatic water bath at 25 °C for 30 minutes as well . The so formed solid is filtered on quick filtering paper. 100 cm³ of the filtered liquid is poured in a previously weighed aluminum container which is heated on a heating plate under nitrogen flow, to remove the solvent by evaporation. The container is then kept in an oven at 80 °C under vacuum until constant weight is obtained. The weight percentage of polymer soluble in xylene (XS) at room temperature (25°C) is then calculated.

The thermal properties (melting temperatures and enthalpies) of the butene-1 polymers were determined by Differential Scanning Calorimetry (D.S.C.) on a Perkin Elmer DSC-7 instrument. The melting temperatures of 1-butene homo and co-polymers were determined according to the following method:

- T_{mII} (measured in second heating run): a weighted sample (5-10 mg) obtained from the polymerization was sealed into aluminum pans and heated at 200°C with a scanning speed corresponding to 20°C/minute. The sample was kept at 200°C for 5 minutes to allow a complete melting of all the crystallites thus cancelling the thermal history of the sample. Successively, after cooling to -20°C with a scanning speed corresponding to 10°C/minute, the peak temperature was taken as crystallization temperature (T_c). After standing 5 minutes at -20°C, the sample was heated for the second time at 200°C with a scanning speed corresponding to 10°C/min. In this second heating run, the peak temperature when present was taken as the melting temperature of the poly1-butene (PB) crystalline form II (T_{mII}) and the area as global melting enthalpy (ΔH_{fII}).
- T_{m I} The melting enthalpy after 10 days and the melting temperature of crystalline form I was measured as follows by using the Differential Scanning Calorimetry (D.S.C.) on an Perkin Elmer DSC-7 instrument: A weighted sample (5-10 mg) obtained from the polymerization was sealed into aluminum pans and heated at 200°C with a scanning speed corresponding to 20°C/minute. The sample was kept at 200°C for 5 minutes to allow a complete melting of all the crystallites. The sample was then stored for 10 days at room temperature. After 10 days the sample was subjected to DSC, it was cooled to -20°C, and then it was heated at 200°C with a scanning speed corresponding to 10°C/min. In this heating run, the first peak temperature coming from the lower

temperature side in the thermogram was taken as the melting temperature (T_{mI}), and the area as global melting enthalpy after 10 days (ΔH_f). Sometimes at least partially convoluted T_{mI} and T_{mII} temperatures peaks can be evidenced with this procedure.

(ΔH_f) is measured as the total enthalpy of the overall at least partially convoluted peak.

When a propylene crystallinity is present coming from addition of a polypropylene polymer component B), a further melting temperature peak (PP) can be detected at higher temperatures.

T_g determination via DMTA analysis

Molded specimen of 76mm by 13mm by 1 mm are fixed to the DMTA machine for tensile stress. The frequency of the tension and relies of the sample is fixed at 1 Hz. The DMTA translate the elastic response of the specimen starting from -100°C to 130°C. In this way it is possible to plot the elastic response versus temperature. The elastic modulus for a viscoelastic material is defined as $E = E' + iE''$. The DMTA can split the two components E' and E'' by their resonance and plot E' vs temperature and $E'/E'' = \tan(\delta)$ vs temperature.

The glass transition temperature T_g is assumed to be the temperature at the maximum of the curve $E'/E'' = \tan(\delta)$ vs temperature.

Products Used in Working Examples

- HPO1: Heterophasic polyolefin composition having MFR 0.8 g/10min MEF 80 MPa, Shore D Hardness (Sh.D) 30, having η_{BI} 3.3 dl/g , M_w/M_n 5.8, M_z/M_w 2.4, IV_{gpc} 2.78 dl/g; and comprising
- 31 %wt. of a crystalline copolymer of propylene (A1) with 3.3 %wt. of units derived from ethylene, having MFR A1 25 g/10min, soluble fraction in xylene at 25°C of 6%wt, and XinsIV 1, 8 dl/g, and
- 69 %wt. of an elastomeric fraction of propylene with ethylene (B1) having 27 % by weight of units derived from ethylene, 89%wt of fraction soluble in xylene at 25°C.
- HPO2: Heterophasic polyolefin composition having MFR (230°C , 2.16 kg) of 8g/10min MEF 80 MPa, Shore D Hardness (Sh.D) 30; obtained by slight visbreaking HPO1 via peroxide treatment during pelletization, and further having

η_{B2} 2.8 dl/g, M_w/M_n 4.0, M_z/M_w 2.2, IV_{gpc} 1.90 dl/g. B2 being the elastomeric component after visbreaking.

- HPO3: Heterophasic polyolefin composition having MFR (230°C, 2.16 kg) of 14g/10min MEF 80 MPa, Shore D Hardness (Sh.D) 30, obtained by visbreaking HPO1 via peroxide treatment during pelletization, and having η_{B3} 1,75 dl/g, M_w/M_n 3.40, M_z/M_w 2.1, IV_{gpc} 1.48 dl/g. B3 being the elastomeric component after visbreaking.
- HPO4-(c)(i) Heterophasic polyolefin composition comprising 15 %wt. of a crystalline copolymer of propylene with 3.3 %wt, and 85 %wt. of elastomeric fraction of propylene with ethylene, prepared as in Example 3 of the International Application no. WO03/011962. The elastoplastic polymer was visbroken with peroxide (100 ppm Luperox 101) in a twin screw Berstoff extruder to a final melt index MFR (230°C/2,16kg) of 2.8 g/10min and η_{B4} (intrinsic viscosity of the fraction soluble in xylene) of 2 dl/g. Before visbreaking, the polymer of Example 3 showed MFR of 0.07 g/10min and η of 4.57 dl/g. HPO4 flexural modulus (ISO 178) is 35 MPa, Shore A (ISO 868) 75, Tg (DMTA) is -23°C.
- PB1 is a butene-1/ethylene copolymer produced according to the process described in WO2009/000637.
- PB2 was obtained from PB1 by in-line compounding a crystalline terpolymer (ii) added in amount of 7 wt% with respect to the weight of the copolymer composition (A)=(i)+(ii)=PB1+(ii). PB2 (component (c) (ii)) has a content ethylene copolymerized of 8,5%wt, a melt index MFR (190°C/2,16kg) 1 dl/g. Flexural modulus MEF (ISO 178) 12 MPa, Shore A (ISO 868) 64,5, Tg (DMTA) is -27°C and tension set at 100% elongation (ISO 2285) 18%. DSC temperatures were Tm II non detectable Tm I 40.3°C for the polybutene component.
- PB3 is a comparative butene-1 copolymer with propylene, produced with a Ziegler Natta catalyst in absence of external donor according to the process described in the International application WO2006/042815 A1. PB3 has melt index MFR (190°C/2,16kg) 0.49 dl/g. flexural modulus MEF (ISO 178) 31 MPa, Shore A (ISO 868) 74.5 and Tg (DMTA) -5.8°C. DSC temperatures were Tm II 100°C and Tm I 118°C.

Mg(OH)₂: Kisuma 5A-C by Kyowa Chemical Industry, precipitated magnesium hydroxide coated with fatty acid for compatibilization with polyolefins having average particle size of 0.94 μm , purity 97.65%.

Processing Aid: Propylene homopolymer grafted with maleic anhydride (MA), with MFR (190°C, 2,16 Kg) of 115 g/10 min and MA content of 1 % weight (Polybond 3200, sold by Chemtura).

Stabilizer: Irganox B215 commercialized by Ciba.

Reference Example 1

A polyolefin composition was obtained by blending in a Leistritz 27mm twin screw extruder the heterophasic polyolefin compositions HPO1, HPO2 and HPO3 and the mineral filler and additives as reported in Table 1. The mechanical and thermal properties of this composition is reported in Table 1.

Example 1 and 2

An highly filled polyolefin composition according to the invention was obtained by blending in a Leistritz 27mm twin screw extruder the heterophasic polyolefin compositions HPO1, HPO2 and HPO3 the soft elastoplastic heterophasic component HPO4 - (c) (i) and the mineral filler and additives as reported in Table 1. The mechanical and thermal properties of this composition is reported in Table 1.

Comparative Example 2

Polyolefin composition similar to the one prepared in Example 1 was obtained, with the exception that PB3 was used instead of HPO4. The mechanical and thermal properties of this compositions are reported in Table 1.

Example 3

Polyolefin composition similar to the one prepared in Example 1 was obtained, with the exception that the component (c) (ii) PB2 was used instead of HPO4. The mechanical and thermal properties of this compositions are reported in Table 1.

Comparative Example 6

Polyolefin composition was obtained, for comparative purposes, by blending a commercial crystalline propylene random copolymer with ethylene derived units in amount equal to 3%wt, insolubility in xylene at 25°C of 96% wt and MFR (230°C, 2,16 Kg) of 8 g/10min, with a

commercial elastomeric polymer *Versify 3401* produced by Dow Chemicals having the following properties:

Versify 3401 is a propylene ethylene octene copolymer with 24%wt of ethylene, 3-4 %wt octene, MFR (230°C, 2.16 kg) 8 g/10min, MEF 22 MPa, Sh.A 72, Sh.D 22 and Narrow Molecular Weight Distribution ($MWD=M_w/M_n$) 3, M_z/M_w 2, IV_{gpc} 1.90.

The mechanical and elastic properties of this composition are reported in Table 1.

All the highly filled compositions show similarly high stress at break (about 16 Mpa), Elongation at break is maintained sufficiently high, while surprisingly low T_g values are exhibited by the highly filled composition of the present invention in combination with ductility at low temperature. The same balance is not showed by the comparative compositions and reference composition 1.

Table 1

COMPONENTS (%WT)		REF. EX. 1	. EX. 1	EX. 2	COMP. EX.2	EX.3	COMP. EX. 6
Raco MIL 8 C2=3%	%wt				9.85	15	13
HPO1	%wt	14	11.5	9	11.5	11.5	
HPO3	%wt	17.85	13.85	9	13.85	13.85	
HPO2	%wt	14	11.5	9	11.5	11.5	
HPO4 (c) (i)	%wt		9	18.85			
Comparative C4C3 copo PB3	%wt				9		
C4C2C3 copo (c) (ii) PB2	%wt					9	
Versify3401	%wt						32.85
C - KISUMA 5A Mg(OH) ₂	%wt	50	50	50	50	50	50
IRGANOX B215	%wt	0.15	0.15	0.15	0.15	0.15	0.15
polybond 3200	%wt	4	4	4	4	4	4
Total composition	%wt	100	100	100	100	100	100
Properties							
MFR (MIL) 230°C/2.16kg	gr/10'	1.3	0.85	0.96	1.2	1.07	2.4
IV _{gpc} *	dl/g	2.02					
Mw/Mn *		4.5					
Mz/Mw*		2.6					
Mw*		293237					
Mz*		775710					
Mn*		65020					
Failure test ISO 6603							
Temperature	°C	-40	-40	-40	-40	-40	-40
B (YU)	Num	10	10	10	0	8	0
C (NY)	Num	0	0	0	10	2	10
Temperature	°C	-30	-30	-30	-30	-30	-30
B (YU)	Num	10	10	10	8	10	8
C (NY)	Num	0	0	0	2	0	2
Temperature	°C	-20	-20	-20	-20	-20	-20
D (YS)	Num	10	10	10	0	10	10
B (YU)	Num	0	0	0	10	0	0
C (NY)	Num	0	0	0	0	0	0
Tensile stress @ yield	MPa	12.3	11.5	10.6	10.9	11.2	10.8
Elongation @ yield	%	16	19.3	20.4	22.7	24	15.1
Tensile stress @ break	MPa	16.9	16.4	15.5	16.4	16.1	15
Elongation @ break	%	295	293	296	329	305	280
Shore D Hardness -		46.4	43.6	41.7	43.8	42.9	46.2
Tg - DSC Data	°C	-41.3	-42.4	-42.9	-39.1	-42.9	-38.5
MET -DMTA (23°C)	MPa	636	545	500	530	452	443

*GPC data measured on the fraction Xylene Soluble at 25°C of the polymer blend without additive and filler-Kisuma.

CLAIMS

1. A filled polyolefin composition comprising:

a) 15 to 40% by weight of a flexible heterophasic polyolefin composition (I), comprising the following fractions (wherein the total of A and B fractions is 100%):

A) from 20 to 40% by weight of a crystalline polymer fraction consisting of a propylene homopolymer, or a copolymer of propylene with one or more comonomers selected from ethylene and a $\text{CH}_2=\text{CHR}$ alpha-olefin, where R is a $\text{C}_2\text{-C}_8$ alkyl radical, or mixtures thereof; said homopolymer or copolymer containing at least 85% by weight of units derived from propylene, said crystalline fraction having a fraction insoluble in xylene at 25°C of at least 90% by weight;

B) from 60 to 80% by weight of an elastomeric fraction consisting of a copolymer or blend of copolymers of ethylene with one or more comonomers selected from propylene and $\text{CH}_2=\text{CHR}$ alpha-olefins, where R is a $\text{C}_2\text{-C}_8$ alkyl radical, and optionally with minor quantities of a diene, or mixtures thereof; said copolymer or blend containing units derived from ethylene in a quantity lower than 40% by weight; the fraction soluble in xylene at 25°C of said polyolefin composition having IV_{gpc} lower than 2.5 dl/g and a broad molecular weight distribution Mw/Mn (GPC) equal to or higher than 4, Mz/Mw (GPC) equal to or higher than 2.5;

b) 40 to 80% by weight of an inorganic filler (II) selected from flame-retardant inorganic fillers and inorganic oxides or salts; and

c) 5 to 25 % by weight of an elastomeric polymer or polymer composition having flexural modulus (ISO 178) lower than 60 MPa, Shore A (ISO 868) lower than 90 and T_g (DMTA) lower than -20°C;

wherein the sum of a), b) and c) is 100%.

2. A filled polyolefin composition according to claim 1 wherein the elastomeric fraction B of component (a) have solubility in xylene at room temperature greater than 50% by weight.

3. A filled polyolefin composition according to anyone of the previous claims, wherein the elastomeric fraction (B) of component (a) comprises at least three components B1, B2, and B3, the intrinsic viscosity η of the xylene soluble fraction of B1, B2 and B3 being respectively:

(η_{B1}) equal to or higher than 3 dl/g;

(η_{B2}) from 2 to 3 dl/g;

(η_{B3}) equal to or lower than 2 dl/g.

- 4 A filled polyolefin composition according to anyone of the previous claims having MFR 230°C/2.16 Kg of from 3 to 8 gr/10min.
5. A filled polyolefin composition according to anyone of the previous claims, wherein the inorganic filler (II) is a flame-retardant inorganic filler selected from hydroxides, hydrated oxides, salts and hydrated salts of metals.
6. The filled polyolefin composition according to claim 5, wherein the flame-retardant inorganic filler is selected from $Mg(OH)_2$, $Al(OH)_3$, $Al_2O_3 \cdot 3H_2O$, magnesium carbonate hydrate, $MgCO_3$, magnesium calcium carbonate hydrate, magnesium calcium carbonate, and mixtures thereof.
7. The filled polyolefin composition according to claim 5, wherein the inorganic filler (II) is an inorganic oxide or salt selected from CaO , TiO_2 , Sb_2O_3 , ZnO , Fe_2O_3 , $CaCO_3$, $BaSO_4$ and mixtures thereof.
8. A filled polyolefin composition according to anyone of the previous claims wherein component c) is
- i) an elastoplastic polypropylene composition consisting of:
- A) 8 to 25% of a crystalline polymer fraction selected from propylene homopolymer and propylene copolymers with a C4-8 alpha-olefin;
- B) 75 to 92% an elastomeric fraction comprising two different propylene elastomeric copolymers, and more specifically: (1) a first elastomeric copolymer of propylene with 15 to 32% of ethylene and/or a C4-8 alpha-olefin, and (2) a second elastomeric copolymer of propylene with more than 32% up to 45% of ethylene and/or a C4-8 alpha-olefin, the (1)/(2) weight ratio ranging from 1:5 to 5:1;
- or
- ii) a butene-1 copolymer having:
- a content of butene-1 derived units of 80wt% or more
 - a melting temperature DSC (T_m) lower than 110°C.
9. A filled polyolefin composition according to anyone of the previous claims having Shore D hardness lower than 50, elongation at break higher than 250 %, tensile strength at break equal to or higher than 10 MPa.
10. An article comprising a polyolefin composition according to anyone of claims 1 to 9.

11. Sheets or film for roofing comprising a polyolefin composition according to anyone of claims 1 to 9.
12. Inner filling for industrial cables or cable sheathing comprising a polyolefin composition according to anyone of claims 1 to 9.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/058477

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08L23/10 C08L23/16
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 043 733 A1 (PIRELLI CAVI E SISTEMI SPA [IT] PIRELLI & C SPA [IT]) 11 October 2000 (2000-10-11) cited in the application the whole document	1-12
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Further documents are listed in the continuation of Box C.



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