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(54) Title: MINERAL-FILLED POLYPROPYLENE COMPOSITIONS FOR FOAMING

(57) Abstract: Mineral-filled polypropylene composition comprising: A) 15–70 wt% of a first heterophasic polypropylene (HECO-1) having an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 10–50 g/10 min, B) 0–70 wt% of a second heterophasic polypropylene (HECO-2) having an MFR₂ (ISO 133; 230°C; 2.16kg) in the range of 5–30 g/10 min, C) 10–30 wt% of a high melt strength polypropylene (HMS-PP), D) 5 to 20 wt% of a copolymer of ethylene and propylene or a C4-C10 alpha-olefin with a density of 0.860–0.910 g/cm³, E) 5–25 wt% of a high-density polyethylene (HDPE), F) 5–20 wt% of a mineral-filler, and G) 0–15 wt% of additives; and its use for preparing foamed articles, as well as the articles themselves.



Mineral-filled polypropylene compositions for foaming

Description

The present invention relates to new mineral-filled polypropylene compositions suitable for the
5 production of foamed moulded articles, e.g. automotive parts.

Background

Polypropylene is a material used in a wide variety of technical fields and mineral-filled
polypropylenes have in particular gained relevance in fields previously exclusively relying on non-
10 polymeric materials, in particular metals.

One particular example of mineral-filled polypropylenes is a polypropylene composition comprising
talc as mineral filler.

15 One application field of such polypropylene compositions is the automobile industry. In the
automobile industry there is a constant ambition to find new solutions to reduce the weight of the
respective parts of the automobile.

Therefore, for gaining lighter weight at final application foaming via physical and also chemical
foaming becomes more and more important.

20 Due to legislation requirements in Carbon emission reduction and the need for economical
engines it is a special interest in automotive industry to validate all kinds of lightweight potential.
Potential fields of interest include substitution of "high-density materials" by replacing with lighter
sources or slimming down the relevant part weight. One approach hereby is the use of either
chemical or physical foaming. For successful foaming of relevant applications on top to the
25 foaming reactivity it is desired to have good flowability of the used plastics in order to match thin
walled pre-filling and having low stress levels in the part to allow proper and constant foam
building and filling the required wall-thicknesses.

EP 2669329 discloses talcum-filled polypropylene compositions with excellent free-flowing
30 properties comprising (A) a propylene homopolymer and/or propylene copolymer and/or
heterophasic propylene polymer, (B) a heterophasic propylene polymer, (C) an ethylene-based
plastomer, (D) talc, optionally (E) a high-density polyethylene and (F) an anti-scratch additive. The
compositions are suitable for integral foaming of moulded articles such as finished parts for the
automotive industry, e.g. instrument panels of cars.

So, although there are already some suggestions for using special mineral-filled polypropylene compositions for the production of foamed automotive parts, these solutions suffer from insufficient impact performance.

- 5 Thus there is still the need for alternative or improved mineral-filled propylene polymer compositions being suitable for preparing foamed articles, which have beside excellent flowability and stiffness, improved energy absorption, i.e. improved puncture resistance.

10 Surprisingly the inventors found, that the above problems can be solved with a mineral-filled propylene composition, which comprises inter alia a combination of a heterophasic polypropylene and specific amount of high melt strength polypropylene and specific amount of low density copolymer of ethylene and propylene or a C₄ - C₁₀ alpha-olefin.

Summary of the Invention

15 Accordingly, the present invention relates in a first aspect to a mineral-filled polypropylene composition comprising

(A) 15 – 70 wt% of a first heterophasic polypropylene (HECO-1) having an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 30 – 50 g/10 min, comprising

20 (A-1) 65 – 90 wt% of a propylene homopolymer matrix (M-PP-1) with an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 150 – 400 g/10 min and a molecular weight distribution (MWD) in the range of 3.5 – 5.5 and

(A-2) 10 – 35 wt% of a dispersed phase (D-1) being a copolymer of propylene and ethylene or C₄ - C₁₀ alpha-olefin with an intrinsic viscosity (measured in decaline according to DIN ISO 1628/1 at 135°C) in the range of 2.0 - 4.0 dl/g, and an C₂-content of 20 – 65 wt%
25 (measured with infrared spectroscopy)

(B) 0 – 70 wt% of a second heterophasic polypropylene (HECO-2) having an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 5 – 25 g/10 min, comprising

30 (B-1) 65 – 90 wt% of a propylene homopolymer matrix (M-PP-2) with an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 20 – 120 g/10 min and an MWD in the range of 3.5 – 5.5 and

(B-2) 10 – 35 wt% of a dispersed phase (D2) being a copolymer of propylene and ethylene or C₄ - C₁₀ alpha-olefin with an intrinsic viscosity (measured in decaline according to DIN ISO 1628/1 at 135°C) in the range of 2.0 - 4.0 dl/g, and an C₂-content of 20 – 65 wt% (measured with infrared spectroscopy)

35 (C) 10 – 30 wt% of a high melt strength polypropylene (HMS-PP) having

(i) an MFR₂ (ISO 1133; 230 °C; 2.16kg) in the range of 1.0 to 5.0 g/10 min

(ii) a F30 melt strength of at least 30 cN, determined in the Rheotens test at 200°C; and

(iii) a melt extensibility v30 of at least 200 mm/s, determined in the Rheotens test at 200°C and

(ix) xylene hot unsolubles (XHU) content of less than 1.25 wt%

(D) 5 to 20 wt% of an copolymer of ethylene and propylene or a C₄ - C₁₀ alpha-olefin with a density of 0.860 – 0.910 g/cm³ and an MFR₂ (ISO 1133; 190°C; 2.16kg) in the range of 0.5 – 50 g/10 min (PE-COPO)

(E) 5 – 25 wt% of a high-density polyethylene (HDPE)

(F) 5 – 20 wt% of a mineral-filler and

(G) 0 – 15 wt% of additives selected from antioxidants (AO), slip agents (SA), UV-stabilizers, anti-scratch additives, odour-scavengers and pigments.

The sum of the percentage amounts of the individual components of the composition is equal to 100 percent.

The special combination of especially Components (A), (C) and (D) gives rise to compositions having improved impact performance, especially improved puncture resistance.

In a further aspect the invention is related to the use of the composition for preparing foamed articles comprising the inventive mineral-filled polypropylene composition, especially for foamed articles for the automotive industry, like door claddings, instrument panel, centre consoles, pillars, bumpers, etc. and to the articles themselves.

Detailed description

In the following the individual components are defined in more detail.

Heterophasic polypropylene in general:

The term "heterophasic polypropylene (HECO)" as used in the present invention refers to a composition comprising (semi)crystalline polypropylene and an elastomer. There are two types of HECOs which essentially differ in their method of preparation. The first, which is commonly referred to as "compound grade HECO", is made by physically blending a (semi)crystalline polypropylene with an elastomer. The second, which is commonly referred to as "reactor grade HECO" is made by first polymerizing propylene to a (semi)crystalline polypropylene and then polymerizing elastomer components, such as propylene and ethylene or C₄ - C₁₀ alpha-olefin, in the presence of the (semi)crystalline polypropylene. In any case the heterophasic polypropylene (HECO) according to this invention comprises a propylene homopolymer (H-PP) as a polypropylene matrix (M-PP) and dispersed therein a copolymer of propylene and ethylene or C₄ - C₁₀ alpha-olefin as dispersed phase (D). Thus the matrix phase contains (finely) dispersed inclusions being not part of the matrix phase and said inclusions contain the copolymer of

propylene and ethylene or C₄ - C₁₀ alpha-olefin as dispersed phase (D). The term inclusion indicates that the matrix and the inclusion form different phases within the heterophasic polypropylene (HECO), said inclusions are for instance visible by high resolution microscopy, like electron microscopy or scanning force microscopy.

5

Heterophasic polypropylenes are generally featured by a xylene cold soluble (XCS) fraction and a xylene cold insoluble (XCI) fraction.

For the purpose of the present application the xylene cold soluble (XCS) fraction of the heterophasic polypropylenes (A) and (B) is essentially identical with Component (A-2) and (B-2) of
10 said heterophasic polypropylenes.

Accordingly when talking about the intrinsic viscosity and the ethylene content of (A-2) and (B-2) of the heterophasic polypropylenes the intrinsic viscosity and the ethylene content of the xylene cold soluble (XCS) fraction of said heterophasic polyolefin compositions is meant.

15 The expression propylene homopolymer used in the instant invention relates to polypropylene that consists substantially, i.e. of more than 99.7 wt%, still more preferably of at least 99.8 wt%, of propylene units. In a preferred embodiment only propylene units in the propylene homopolymer are detectable.

20 As will be explained in detail below the polypropylene matrix (M-PP) and the dispersed phase (D), can be unimodal or multimodal, like bimodal in view of the molecular weight distribution and/or the comonomer content distribution.

Thus expression "multimodal" or "bimodal" used herein refers to the modality of the polymer, i.e.

25 ▪ the form of its molecular weight distribution curve, which is the graph of the molecular weight fraction as a function of its molecular weight.

When the matrix phase (M-PP) and the dispersed phase (D) are unimodal with respect to the molecular weight distribution, they may be prepared in a single stage process e.g. a slurry or gas
30 phase process in a slurry or gas phase reactor. Preferably, the unimodal matrix phase (M-PP) is polymerized as a slurry polymerization. Alternatively, the unimodal matrix may be produced in a multistage process using at each stage process conditions which result in similar polymer properties.

35 As will be explained below, the polypropylene matrix (M-PP) and the dispersed phase (D), if they are of multimodal or bimodal character, can be produced by blending different polymer types, i.e. of different molecular weight and/or comonomer content. However in such a case it is preferred

that the polymer components of the polypropylene matrix (M-PP) and the dispersed phase (D) are produced in a sequential step process, using reactors in serial configuration and operating at different reaction conditions. As a consequence, each fraction prepared in a specific reactor will have its own molecular weight distribution and/or comonomer content distribution.

5

When the distribution curves (molecular weight or comonomer content) from these fractions are superimposed to obtain the molecular weight distribution curve or the comonomer content distribution curve of the final polymer, these curves may show two or more maxima or at least be distinctly broadened when compared with curves for the individual fractions. Such a polymer,
10 produced in two or more serial steps, is called bimodal or multimodal, depending on the number of steps.

A) First heterophasic polypropylene (HECO-1)

The first heterophasic polypropylene (HECO-1) has an MFR₂ (ISO 1133; 230°C; 2.16kg) in the
15 range of 30 – 50 g/10 min, and comprises

(A-1) a propylene homopolymer matrix (M-PP-1) with an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 150 – 400 g/10 min and an MWD in the range of 3.5 – 5.5 and

(A-2) a dispersed phase (D-1) being a copolymer of propylene and ethylene or C₄ - C₁₀ alpha-olefin with an intrinsic viscosity (measured in decaline according to DIN ISO 1628/1 at
20 135°C) in the range of 2.0 - 4.0 dl/g, and an C₂-content of 20 – 65 wt% (measured with infrared spectroscopy)

(A-1) propylene homopolymer matrix (M-PP-1):

The propylene homopolymer matrix (M-PP-1) can be unimodal or multimodal, like bimodal, as
25 described above.

Preferably the propylene homopolymer matrix (M-PP-1) is multimodal, especially bimodal.

The propylene homopolymer matrix (M-PP-1) may be produced in a polymerization stage effected in one or more polymerization reactors. Desirably the propylene homopolymer matrix (M-PP-1) comprising two or more different propylene homopolymers may be produced by carrying out
30 polymerization in two or more different polymerization reactors (e.g. bulk and/or gas phase reactors; as bulk reactors, loop reactors are preferred) whereby to generate polymers of the different desired molecular weight distributions in the different polymerization reactors.

The propylene homopolymer matrix (M-PP-1) has a melt flow rate MFR₂ (ISO 1133; 230 °C; 2.16kg) in the range of 150 to 400 g/10 min, preferably in the range of 150 to 350 g/10 min and
35 more preferably in the range of 200 to 300 g/10 min.

The molecular weight distribution (MWD) of the propylene homopolymer matrix (M-PP-1) is in the range of 3.5 – 5.5, preferably in the range of 3.7 to 5.3 and more preferably in the range of 4.0 to 5.0.

- 5 Preferably the propylene homopolymer matrix (M-PP-1) is isotactic. Accordingly it is appreciated that the propylene homopolymer matrix (M-PP-1) has a rather high pentad concentration, i.e. higher than 80 mol%, more preferably higher than 85 mol%, still more preferably higher than 90 mol% and yet more preferably higher than 95 mol%.

10 *(A-2) dispersed phase (D-1)*

The dispersed phase (D-1) is a copolymer of propylene and ethylene or C₄ - C₁₀ alpha-olefin. Suitable C₄ - C₁₀ alpha-olefins are 1-butene, 1-pentene, 1-hexene, 1-heptene and 1-octene. Preferably the dispersed phase (D-1) is a copolymer of propylene and ethylene.

- 15 The amount of ethylene in the dispersed phase (D-1) is in the range of 20 – 65wt%, preferably in the range of 20 – 55wt% and more preferably from 20 to 45wt%.

The dispersed phase (D-1) has an intrinsic viscosity (IV) determined according to DIN ISO 1628/1 (in decaline at 135 °C) in the range of 2.0 to 4.0 dl/g, preferably in the range of 2.4 to 3.8 dl/g, and
20 more preferably in the range of 2.8 to 3.8 dl/.

In one embodiment, dispersed phase (D-1) is unimodal. More particularly, the dispersed phase (D-1) is preferably unimodal in view of the intrinsic viscosity and/or the comonomer distribution. Concerning the definition of unimodal and multimodal, like bimodal, it is referred to the definition
25 above.

Ad first heterophasic polypropylene (HECO-1)

The heterophasic polypropylene (HECO-1) comprises 65 – 90wt% of component (A-1) and 10 – 35wt% of (A-2), preferably 65 – 80wt% % of component (A-1) and 20 – 35wt% of (A-2) and more
30 preferably 65 – 75wt% % of component (A-1) and 25 – 35wt% of (A-2).

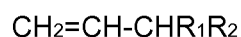
The first heterophasic polypropylene (HECO-1) has an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 30 – 50 g/10 min, preferably in the range of 30 – 45 g/10 min and more preferably in the range of 30 – 40 g/10 min.

Preferably the first heterophasic propylene copolymer (HECO-1) comprises a α -nucleating agent (A-3) selected from vinylcycloalkane polymer and vinylalkane polymer as discussed in more detail below.

It is especially preferred the first heterophasic propylene copolymer (HECO-1) contains a vinylcycloalkane, like vinylcyclohexane (VCH), polymer and/or vinylalkane polymer. In one specific embodiment the first heterophasic propylene copolymer (HECO-1) contains a vinylcycloalkane, like vinylcyclohexane (VCH), polymer and/or vinylalkane polymer. Preferably the vinylcycloalkane is vinylcyclohexane (VCH) polymer and is introduced into the first heterophasic propylene copolymer (HECO-1) by the BNT technology.

More preferably in this preferred embodiment, the amount of vinylcycloalkane, like vinylcyclohexane (VCH), polymer and/or vinylalkane polymer, more preferably of vinylcyclohexane (VCH) polymer, in the first heterophasic propylene copolymer (HECO-1) is less than 500 ppm, more preferably of 1 to 200 ppm, most preferably 5 to 100 ppm.

With regard to the BNT-technology reference is made to the international applications WO 99/24478, WO 99/24479 and particularly WO 00/68315. According to this technology a catalyst system, preferably a Ziegler-Natta procatalyst, can be modified by polymerizing a vinyl compound in the presence of the catalyst system, comprising in particular the special Ziegler-Natta procatalyst, an external donor and a cocatalyst, which vinyl compound has the formula:



wherein R_1 and R_2 together form a 5- or 6-membered saturated, unsaturated or aromatic ring or independently represent an alkyl group comprising 1 to 4 carbon atoms, and the modified catalyst is used for the preparation of the propylene copolymer according to this invention. The polymerized vinyl compound acts as an α -nucleating agent. The weight ratio of vinyl compound to solid catalyst component in the modification step of the catalyst is preferably of up to 5 (5:1), preferably up to 3 (3:1) most preferably from 0.5 (1:2) to 2 (2:1). The most preferred vinyl compound is vinylcyclohexane (VCH).

The first heterophasic polypropylene (HECO-1) as well its individual components (matrix (M-PP-1) and copolymer of dispersed phase (D-1)) can be produced by blending different polymer types, i.e. of different molecular weight and/or comonomer content, as is explained below for the blending of components (A) to (G).

However it is preferred that the first heterophasic polypropylene (HECO-1) are produced in a sequential step process.

The first heterophasic propylene copolymer (HECO-1) according to this invention is preferably produced in a sequential polymerization process, i.e. in a multistage process, known in the art, wherein the propylene homopolymer matrix (M-PP-1) is produced at least in one slurry reactor, preferably in a slurry reactor and optionally in a subsequent gas phase reactor, and subsequently
5 the dispersed phase (D-1) is produced at least in one, i.e. one or two, gas phase reactor(s).

Accordingly it is preferred that the first heterophasic propylene copolymer (HECO-1) is produced in a sequential polymerization process comprising the steps of

(a) polymerizing propylene in a first reactor (R1) obtaining the first polypropylene fraction of the polypropylene (M-PP-1),
10

(b) transferring the first polypropylene fraction into a second reactor (R2),

(c) polymerizing in the second reactor (R2) in the presence of said first polypropylene fraction propylene obtaining thereby the second polypropylene fraction, preferably said second polypropylene fraction is a second propylene homopolymer, wherein said first polypropylene fraction and said second polypropylene fraction form the polypropylene (M-PP-1), i.e. the matrix of the heterophasic propylene copolymer (HECO-1),
15

(d) transferring the polypropylene (M-PP-1) of step (c) into a third reactor (R3),

(e) polymerizing in the third reactor (R3) and in the presence of the polypropylene (M-PP-1) obtained in step (c) propylene and at least one ethylene and/or C₄ to C₁₀ alpha-olefin obtaining thereby a first propylene copolymer fraction, the first propylene copolymer fraction is dispersed in the polypropylene (M-PP-1),
20

(f) transferring the polypropylene (M-PP-1) in which the first propylene copolymer fraction is dispersed in a fourth reactor (R4), and

(g) polymerizing in the fourth reactor (R4) and in the presence of the mixture obtained in step (e) propylene and at least one ethylene and/or C₄ to C₁₀ alpha-olefin obtaining thereby the second propylene copolymer fraction,
25

the propylene homopolymer matrix (M-PP-1), the first propylene copolymer fraction, and the second propylene copolymer fraction form the heterophasic propylene copolymer (HECO-1).

The term "sequential polymerization process" indicates that the first heterophasic propylene copolymer (HECO1) is produced in at least two, like three or four reactors connected in series. Accordingly the present process comprises at least a first reactor (R1) and a second reactor (R2), more preferably a first reactor (R1), a second reactor (R2), a third reactor (R3) and a fourth reactor (R4). The term "polymerization reactor" shall indicate that the main polymerization takes place. Thus in case the process consists of four polymerization reactors, this definition does not
35 exclude the option that the overall process comprises for instance a pre-polymerization step in a

pre-polymerization reactor. The term "consist of" is only a closing formulation in view of the main polymerization reactors.

The first reactor (R1) is preferably a slurry reactor (SR) and can be any continuous or simple stirred batch tank reactor or loop reactor operating in bulk or slurry. Bulk means a polymerization in a reaction medium that comprises of at least 60 % (w/w) monomer. According to the present invention the slurry reactor (SR) is preferably a (bulk) loop reactor (LR).

The second reactor (R2) can be a slurry reactor, like a loop reactor, as the first reactor or alternatively a gas phase reactor (GPR).

The third reactor (R3) and the fourth reactor (R4) are preferably gas phase reactors (GPR).

Such gas phase reactors (GPR) can be any mechanically mixed or fluid bed reactors. Preferably the gas phase reactors (GPR) comprise a mechanically agitated fluid bed reactor with gas velocities of at least 0.2 m/sec. Thus it is appreciated that the gas phase reactor is a fluidized bed type reactor preferably with a mechanical stirrer.

Thus in a preferred embodiment the first reactor (R1) is a slurry reactor (SR), like a loop reactor (LR), whereas the second reactor (R2), the third reactor (R3) and the fourth reactor (R4) are gas phase reactors (GPR). Accordingly for the instant process at least four, preferably four polymerization reactors, namely a slurry reactor (SR), like a loop reactor (LR), a first gas phase reactor (GPR-1), a second gas phase reactor (GPR-2) and a third gas phase reactor (GPR-3) connected in series are used.

Preferably prior to the slurry reactor (SR) a pre-polymerization reactor is placed.

In another preferred embodiment the first reactor (R1) and second reactor (R2) are slurry reactors (SR), like a loop reactors (LR), whereas the third reactor (R3) and the fourth reactor (R4) are gas phase reactors (GPR). Accordingly for the instant process at least four, preferably four polymerization reactors, namely two slurry reactors (SR), like two loop reactors (LR), first gas phase reactor (GPR-1) and a second gas phase reactor (GPR-2) connected in series are used.

Preferably prior to the first slurry reactor (SR) a pre-polymerization reactor is placed.

A preferred multistage process is a "loop-gas phase"-process, such as developed by Borealis (known as BORSTAR® technology) described e.g. in patent literature, such as in EP 0 887 379, WO 92/12182 WO 2004/000899, WO 2004/111095, WO 99/24478, WO 99/24479 or in WO 00/68315.

A further suitable slurry-gas phase process is the Spheripol® process of Basell.

The catalyst components are preferably all introduced to the prepolymerization step. However, where the solid catalyst component (i) and the cocatalyst (ii) can be fed separately it is possible that only a part of the cocatalyst is introduced into the prepolymerization stage and the remaining part into subsequent polymerization stages. Also in such cases it is necessary to introduce so much cocatalyst into the prepolymerization stage that a sufficient polymerization reaction is obtained therein.

It is possible to add other components also to the prepolymerization stage. Thus, hydrogen may be added into the prepolymerization stage to control the molecular weight of the prepolymer as is known in the art. Further, antistatic additive may be used to prevent the particles from adhering to each other or to the walls of the reactor.

The precise control of the prepolymerization conditions and reaction parameters is within the skill of the art.

Preferably the above described polymerization is performed in the presence of using Ziegler-Natta catalyst, in particular a high yield Ziegler-Natta catalyst (so called fourth and fifth generation type to differentiate from low yield, so called second generation Ziegler-Natta catalysts), which comprises a catalyst component, a co-catalyst component and an internal donor based on either phthalate-compositions or phthalate-free compositions. Optionally also an external donor can be added.

B) Second heterophasic polypropylene (HECO-2)

The second heterophasic polypropylene (HECO-2) has an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 5 – 25 g/10 min, and comprises

(B-1) a propylene homopolymer matrix (M-PP-2) with an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 20 – 120 g/10 min and an MWD in the range of 3.5 – 5.5 and

(B-2) a dispersed phase (D2) being a copolymer of propylene and ethylene or C₄ - C₁₀ alpha-olefin with an intrinsic viscosity (measured in decaline according to DIN ISO 1628/1 at 135°C) in the range of 2.0 - 4.0 dl/g, and an C₂-content of 20 – 65 wt% (measured with infrared spectroscopy)

(B-1) propylene homopolymer matrix (M-PP-2):

The propylene homopolymer matrix phase (M-PP-2) can be unimodal or multimodal, like bimodal. However, it is preferred that the propylene homopolymer matrix phase (M-PP-2) is unimodal.

When the matrix phase (M-PP-2) is unimodal with respect to the molecular weight distribution, it may be prepared in a single stage process e.g. a slurry or gas phase process in a slurry or gas

phase reactor. Preferably, the unimodal matrix phase (M-PP-2) is polymerized as a slurry polymerization. Alternatively, the unimodal matrix may be produced in a multistage process using at each stage process conditions which result in similar polymer properties.

- 5 The propylene homopolymer matrix (M-PP-2) has a melt flow rate MFR_2 (ISO 1133; 230 °C; 2.16kg) in the range of 20 to 120 g/10 min, preferably in the range of 50 to 120 g/10 min and more preferably in the range of 70 to 100 g/10 min.

10 The molecular weight distribution (MWD) of the propylene homopolymer matrix (M-PP-2) is in the range of 3.5 – 5.5, preferably in the range of 3.7 to 5.3 and more preferably in the range of 4.0 to 5.0.

Preferably the propylene homopolymer matrix (M-PP-2) is isotactic. Accordingly it is appreciated that the propylene homopolymer matrix (M-PP-2) has a rather high pentad concentration, i.e.
15 higher than 80 mol%, more preferably higher than 85 mol%, still more preferably higher than 90 mol% and yet more preferably higher than 95 mol%.

(B-2) dispersed phase (D-2)

The dispersed phase (D-2) is a copolymer of propylene and ethylene or C_4 - C_{10} alpha-olefin.
20 Suitable C_4 - C_{10} alpha-olefins are 1-butene, 1-pentene, 1-hexene, 1-heptene and 1-octene.
Preferably the dispersed phase (D-2) is a copolymer of propylene and ethylene.

The amount of ethylene in the dispersed phase (D-2) is in the range of 20 – 65wt%, preferably in the range of 25 – 60 wt% and more preferably from 30 to 55 wt%.

25 The dispersed phase (D-2) has an intrinsic viscosity (IV) determined according to DIN ISO 1628/1 (in decaline at 135 °C) in the range of 2.0 to 4.0 dl/g, preferably in the range of 2.2 to 3.5 dl/g, and more preferably in the range of 2.2 to 3.0 dl/.

30 Preferably the dispersed phase (D-2) is multimodal.
More particularly, the dispersed phase (D-2) is preferably bimodal in view of the intrinsic viscosity and/or the comonomer distribution. Concerning the definition of multimodal, like bimodal, it is referred to the definition above.

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Ad second heterophasic polypropylene (HECO-2)

The heterophasic polypropylene (HECO-2) comprises 65 – 90wt% of component (B-1) and 10 – 35wt% of (B-2), preferably 65 – 80wt% % of component (B-1) and 20 – 35wt% of (B-2) and more preferably 65 – 75wt% % of component (B-1) and 25 – 35wt% of (B-2).

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The second heterophasic polypropylene (HECO-2) has an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 5 – 25 g/10 min, preferably in the range of 10 – 25 g/10 min and more preferably in the range of 15 – 20 g/10 min.

10 The second heterophasic polypropylene (HECO-2) as well its individual components (matrix (M-PP-2) and copolymer of dispersed phase (D-2)) can be produced by blending different polymer types, i.e. of different molecular weight and/or comonomer content, as described below for blending of components (A) to (G).

15 However it is preferred that the second heterophasic polypropylene (HECO-2) is produced in a sequential step process.

The second heterophasic propylene copolymer (HECO-2) according to this invention is preferably produced in a sequential polymerization process, i.e. in a multistage process, known in the art,
20 wherein the propylene homopolymer matrix (M-PP-2) is produced at least in one slurry reactor, preferably in a slurry reactor and optionally in a subsequent gas phase reactor, and subsequently the dispersed phase (D-2) is produced at least in one, i.e. one or two, gas phase reactor(s).

Accordingly it is preferred that the second heterophasic propylene copolymer (HECO-2) is
25 produced in a sequential polymerization process comprising the steps of

- (a) polymerizing propylene in a first reactor (R1) obtaining the propylene homopolymer (M-PP-2), i.e. the matrix of the heterophasic propylene copolymer (HECO-2),
- (b) transferring the propylene homopolymer (M-PP-2) of step (a) into a second reactor (R2),
- (c) polymerizing in the second reactor (R2) in the presence of the propylene homopolymer (M-PP-2) obtained in step (a) propylene and at least one ethylene and/or C₄ to C₁₀ alpha-olefin obtaining thereby a first propylene copolymer fraction, the first propylene copolymer fraction is dispersed in the propylene homopolymer (M-PP-2),
- (d) transferring the propylene homopolymer (M-PP-2) in which the first propylene copolymer fraction is dispersed in a third reactor (R3), and
- 35 (e) polymerizing in the third reactor (R3) and in the presence of the mixture obtained in step (c) propylene and at least one ethylene and/or C₄ to C₁₀ alpha-olefin obtaining thereby the second propylene copolymer fraction,

the propylene homopolymer matrix (M-PP-2), the first propylene copolymer fraction, and the second propylene copolymer fraction form the heterophasic propylene copolymer (HECO-2).

The term "sequential polymerization process" indicates that the second heterophasic propylene copolymer (HECO-2) is produced in at least two, like three or four reactors connected in series. Accordingly the present process comprises at least a first reactor (R1) and a second reactor (R2), more preferably a first reactor (R1), a second reactor (R2) and a third reactor (R3). The term "polymerization reactor" shall indicate that the main polymerization takes place. Thus in case the process consists of four polymerization reactors, this definition does not exclude the option that the overall process comprises for instance a pre-polymerization step in a pre-polymerization reactor. The term "consist of" is only a closing formulation in view of the main polymerization reactors.

The first reactor (R1) is preferably a slurry reactor (SR) and can be any continuous or simple stirred batch tank reactor or loop reactor operating in bulk or slurry. Bulk means a polymerization in a reaction medium that comprises of at least 60 % (w/w) monomer. According to the present invention the slurry reactor (SR) is preferably a (bulk) loop reactor (LR).

The second reactor (R2) can be a slurry reactor, like a loop reactor, as the first reactor or alternatively a gas phase reactor (GPR).

The third reactor (R3) and the optional fourth reactor (R4) are preferably gas phase reactors (GPR).

Such gas phase reactors (GPR) can be any mechanically mixed or fluid bed reactors. Preferably the gas phase reactors (GPR) comprise a mechanically agitated fluid bed reactor with gas velocities of at least 0.2 m/sec. Thus it is appreciated that the gas phase reactor is a fluidized bed type reactor preferably with a mechanical stirrer.

Thus in a preferred embodiment the first reactor (R1) is a slurry reactor (SR), like a loop reactor (LR), whereas the second reactor (R2), the third reactor (R3) and the optional fourth reactor (R4) are gas phase reactors (GPR). Accordingly for the instant process at least three, preferably three polymerization reactors, namely a slurry reactor (SR), like a loop reactor (LR), a first gas phase reactor (GPR-1) and a second gas phase reactor (GPR-2) connected in series are used.

If needed prior to the slurry reactor (SR) a pre-polymerization reactor is placed.

In another preferred embodiment the first reactor (R1) and second reactor (R2) are slurry reactors (SR), like a loop reactors (LR), whereas the third reactor (R3) and the optional fourth reactor (R4) are gas phase reactors (GPR). Accordingly for the instant process at least three, preferably three

polymerization reactors, namely two slurry reactors (SR), like two loop reactors (LR), first gas phase reactor (GPR-1) and a second gas phase reactor (GPR-2) connected in series are used.

If needed prior to the first slurry reactor (SR) a pre-polymerization reactor is placed.

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A preferred multistage process is a "loop-gas phase"-process, such as developed by Borealis (known as BORSTAR® technology) described e.g. in patent literature, such as in EP 0 887 379, WO 92/12182 WO 2004/000899, WO 2004/111095, WO 99/24478, WO 99/24479 or in WO 00/68315.

10 A further suitable slurry-gas phase process is the Spheripol® process of Basell.

The catalyst components are preferably all introduced to the prepolymerization step. However, where the solid catalyst component (i) and the cocatalyst (ii) can be fed separately it is possible that only a part of the cocatalyst is introduced into the prepolymerization stage and the remaining
15 part into subsequent polymerization stages. Also in such cases it is necessary to introduce so much cocatalyst into the prepolymerization stage that a sufficient polymerization reaction is obtained therein.

It is possible to add other components also to the prepolymerization stage. Thus, hydrogen may
20 be added into the prepolymerization stage to control the molecular weight of the prepolymer as is known in the art. Further, antistatic additive may be used to prevent the particles from adhering to each other or to the walls of the reactor.

The precise control of the prepolymerization conditions and reaction parameters is within the skill of the art.

25

Preferably the above described polymerization is performed in the presence of using Ziegler-Natta catalyst, in particular a high yield Ziegler-Natta catalyst (so called fourth and fifth generation type to differentiate from low yield, so called second generation Ziegler-Natta catalysts), which comprises a catalyst component, a co-catalyst component and an internal donor based on either
30 phthalate-compositions or phthalate-free compositions. Optionally also an external donor can be added.

C) High melt strength polypropylene (HMS-PP)

Component (C) is a high melt strength polypropylene with an MFR₂ (ISO 1133; 230 °C; 2.16kg) in the range of 1.0 to 5.0 g/10 min, preferably in the range of 1.2 to 4.0 g/10 min, and more preferably in the range of 1.5 to 3.5 g/10 min.

The high melt strength polypropylene is further characterized by a xylene hot unsolubles (XHU) content of less than 1.25 wt%, preferably of less than 1.00 wt%, more preferably of less than 0.80 wt% and most preferably of less than 0.50 wt%.

The XHU content is determined as described in the experimental part.

Suitable high melt strength polypropylenes are further characterized by a F30 melt strength of at least 30 cN, preferably in the range of 30 to 60 cN, more preferably 31 to 55 cN, even more preferably 32 to 50 cN and most preferably 33 to 45 cN.

The melt extensibility v30 of the high melt strength suitable according to the present invention is at least 200 mm/s, preferably in the range of 200 to 350 mm/s, more preferably in the range of 215 to 320 mm/s, even more preferably in the range of 220 to 300 mm/s and most preferably in the range of 230 to 275 mm/s.

Both quantities, F30 melt strength and melt extensibility v30, are determined at 200°C in the Rheotens melt strength test as described in the experimental part.

The polypropylene composition according to the present invention is characterized by a polymer structure being mainly responsible for the benefits of the present invention, particularly by the nature of long chain branching which may be expressed by the strain hardening factor being defined as

$$SHF = \frac{\eta_E^+(t, \dot{\epsilon})}{\eta_{LVE}^+(t)} = \frac{\eta_E^+(t, \dot{\epsilon})}{3\eta^+(t)}$$

wherein

$$\eta_E^+(t, \dot{\epsilon})$$

is the uniaxial extensional viscosity; and

$$\eta_{LVE}^+(t)$$

is three times the time dependent shear viscosity

$$\eta^+(t)$$

in the linear range of deformation.

The determination of the linear viscoelastic envelop in extension

$$\eta_{LVE}^+(t)$$

is based on IRIS Rheo Hub 2008 requiring the calculation of the discrete relaxation time spectrum from the storage and loss modulus data (G' , $G''(\omega)$). Details about the method can be found in the experimental part. The strain hardening factor mainly reflects the degree of "dispersion" (heterogeneity) of the branches relative to the polymer backbone. Secondly the strain hardening factor also provides information about the branching degree.

The high melt strength polypropylene suitable according to the present invention preferably has a strain hardening factor (SHF) of 6.0 to 12.0, preferably 6.3 to 11.0, more preferably 6.4 to 10.5 and most preferably 6.5 to 10.0 when measured at a strain rate of 3.0 s⁻¹ and a Hencky strain of 2.5.

Moreover, the high melt strength polypropylene suitable according to the present invention preferably has a strain hardening factor (SHF) of 3.6 to 8.0, preferably of 3.7 to 7.5, more preferably of 3.8 to 7.0, and most preferably 3.9 to 6.5 when measured at a strain rate of 1.0 s⁻¹ and a Hencky strain of 2.0.

It should be understood that the preferred strain hardening factors (SHF) as mentioned above can be present individually but also can be present in combination.

Such high melt strength polypropylenes are known in the art and are commercially available for instance from Borealis (tradename Daploy, e.g. WB 140 HMS) or they can be prepared by known processes, as for example described in EP 879830, EP 1301343, EP 1440119 or EP 2520425, which are hereby incorporated by reference.

Preferably such high melt strength polypropylenes can be prepared by subjecting a polypropylene being made in the presence of a Ziegler-Natta catalyst or a metallocene catalyst to a post reactor peroxide treatment accompanied or followed by a treatment with of at least bi- or multifunctionally unsaturated monomers.

The starting polypropylene (i.e. the unmodified polypropylene) as used herein comprises propylene homopolymers, copolymers of propylene and ethylene and/or alpha-olefins with 4 to 18 carbon atoms and mixtures of the aforementioned polymers.

Thus the unmodified polypropylene is selected from any one or mixtures of

- a) conventional polypropylene polymers, preferably propylene homopolymers and/or copolymers of propylene, ethylene and/or alpha-olefins with 4 to 18 carbon atoms, obtainable by using Ziegler-Natta catalysts or metallocene catalysts, having a propylene content of 80.0 to 99.9 wt%, in the form of random copolymers, block copolymers and/or random block copolymers with melt indices of 0.1 to 40 g/10 min at 230 °C/2.16 kg and preferably 1 to 8 g/10 min at 230 °C/2.16 kg,
- b) a polyolefin mixture with an Mw/Mn ratio of 2 to 6 and a melt index of 1 to 40 g/10 min at 230 °C/2.16 kg, which comprises
- b1) 60 to 98 wt% of a crystalline copolymer of 85 to 99.5 wt% of propylene and 15 to 0.5 wt% of ethylene and/or an alpha-olefin of the general formula $\text{CH}_2=\text{CHR}$, in which R is a linear or branched alkyl group with 2 to 8 carbon atoms, and
- b2) 2 to 40 wt% of an elastic copolymer of 20 to 70 wt% of ethylene and 80 to 30 wt% of propylene and/or an alpha-olefin of the general formula $\text{CH}_2=\text{CHR}$, in which R is a linear or branched alkyl group with 2 to 8 carbon atoms, and
- c) essentially amorphous, non isotactic polymers of propylene with a melt index of 0.1 to 100 g/10 min at 230 °C/2.16 kg, the essentially amorphous polymers of propylene comprising homopolymers of propylene and/or copolymers of propylene comprising at least 85 wt% of propylene and not more than 15 wt% percent of one or more alpha-olefins of the general formula $\text{CH}_2=\text{CHR}$, in which R is a linear or branched alkyl group with 2 to 8 carbon atoms.

Preferably the unmodified polypropylene is either a polypropylene homopolymer or a polypropylene copolymer with a comonomer content of less than 5 mol% with respect to the total polypropylene copolymer.

A polypropylene copolymer with a comonomer content of less than 5 mol% is usually a polypropylene random copolymer.

More preferably the unmodified polypropylene is a homopolymer.

If however, the polypropylene base resin is a polypropylene copolymer the comonomer content preferably is below 4 mol%, more preferably below 2 mol% and most preferably below 1 mol%.

The comonomer(s), if present, preferably is/are selected from the group of ethylene and alpha olefins, more preferably ethylene and C4 to C12 alpha olefins, most preferably ethylene or butene.

The unmodified polypropylene may contain additives in an amount of up to 4 wt%.

Additives are preferably selected from the group of modifiers and stabilizers, antistatic agents, lubricants, nucleating agents, foam nucleators and pigments and combinations thereof. Specifically, such additives include primary antioxidants like sterically hindered

phenols and secondary antioxidants like phosphites, UV stabilizers like sterically hindered amines, acid scavengers, pigment, α -nucleating agents like sodium 2,2'-methylene-bis-(4,6-di-tert-butylphenyl) phosphate or β -nucleating agents like calcium pimelate, antistatic agents like glycerol monostearate, slip agents like oleamide and foam nucleators like talc.

The additives may be included during the polymerization process or after the polymerization by melt mixing. It is however preferred that the modifiers do not lower the melting temperature of the composition.

For modifying the unmodified polypropylene as described above, the unmodified polypropylene is pre-mixed with a suitable peroxide, like acyl peroxides, alkyl peroxides, hydroperoxides, etc., and a bifunctional unsaturated monomers, like C4 to C10 dienes and/or C7 to C10 divinyl compounds and further melt mixed in a melt mixing device at a barrel temperature in the range of 180 to 300 °C

Further details of the modification step are described in the above cited patent literatures.

D) Copolymer PE-COPO

As component D) a copolymer of ethylene and propylene or a C₄- C₁₀ alpha-olefin is used.

Suitable C₄ - C₁₀ alpha-olefin include 1-buten, 1-hexene and 1-octene, preferably butene or octene and more preferably octene.

Preferably copolymers of ethylene and 1-octene are used.

Suitable copolymers (PE-COPO) have a density in the range of 0.860 – 0.910 g/cm³, preferably in the range of 0.860 to 0.900 g/cm³, more preferably in the range of 0.860 – 890 g/cm³ and most preferably in the range of 0.860 – 880 g/cm³.

The MFR₂ (ISO 1133; 190°C; 2.16kg) of suitable copolymers (PE-COPO) is in the range of 0.5 – 50 g/10 min (PE-COPO), preferably in the range of 0.5 – 40 g/10 min and more preferably in the range of 0.5 – 35 g/min.

The melting points (measured with DSC according to ISO 11357-3:1999) of suitable copolymers (PE-COPO) are below 130°C, preferably below 120°C, more preferably below 110°C and most preferably below 100°C.

Furthermore suitable copolymers (PE-COPO) have a glass transition temperature T_g (measured with DMTA according to ISO 6721-7) of below -25°C, preferably below -30°C, more preferably below -35°C.

In case the copolymer (PE-COPO) is a copolymer of ethylene and propylene it has an ethylene content from 10 to 55 wt%, preferably from 15 to 50 wt% and more preferably from 18 to 48 wt%.

In case the copolymer (PE-COPO) is a copolymer of ethylene and a C₄ - C₁₀ alpha olefin it has an ethylene content from 50 to 95 wt%, preferably from 55 to 90 wt% and more preferably from 60 to 85 wt%.

Copolymers (PE-COPO) suitable as component D) can be any copolymer of ethylene and propylene or ethylene and C₄ - C₁₀ alpha olefin having the above defined properties, which are commercial available, i.a. from Borealis Plastomers (NL) under the tradename Queo, from DOW Chemical Corp (USA) under the tradename Engage, or from Mitsui under the tradename Tafmer.

Alternately these copolymers (PE-COPO) can be prepared by known processes, in a one stage or two stage polymerization process, comprising solution polymerization, slurry polymerization, gas phase polymerization or combinations therefrom, in the presence of suitable catalysts, like vanadium oxide catalysts or single-site catalysts, e.g. metallocene or constrained geometry catalysts, known to the art skilled persons.

Preferably these copolymers (PE-COPO) are prepared by a one stage or two stage solution polymerization process, especially by high temperature solution polymerization process at temperatures higher than 100°C.

Such process is essentially based on polymerizing the monomer and a suitable comonomer in a liquid hydrocarbon solvent in which the resulting polymer is soluble. The polymerization is carried out at a temperature above the melting point of the polymer, as a result of which a polymer solution is obtained. This solution is flashed in order to separate the polymer from the unreacted monomer and the solvent. The solvent is then recovered and recycled in the process.

Preferably the solution polymerization process is a high temperature solution polymerization process, using a polymerization temperature of higher than 100°C. Preferably the polymerization temperature is at least 110°, more preferably at least 150°C. The polymerization temperature can be up to 250°C.

The pressure in such a solution polymerization process is preferably in a range of 10 to 100 bar, preferably 15 to 100 bar and more preferably 20 to 100 bar.

The liquid hydrocarbon solvent used is preferably a C₅₋₁₂-hydrocarbon which may be unsubstituted or substituted by C₁₋₄ alkyl group such as pentane, methyl pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane and hydrogenated naphtha. More preferably unsubstituted C₆₋₁₀-hydrocarbon solvents are used.

A known solution technology suitable for the process according to the invention is the COMPACT technology.

E) High density polyethylene (HDPE)

The high density polyethylene (HDPE) suitable for the present invention has a melt flow rate MFR₂ (190 °C) in the range of 2 to 30 g/10 min, more preferably in the range of 3 to 20 g/10 min, still more preferably in the range of 5 to 15 g/10 min.

The high density polyethylene (HDPE) suitable for the present invention typically has a density (ISO 1183) of at least 0.920 g/cm³, preferably at least 0.940 g/cm³, more preferably 0.945 g/cm³, still more preferably in the range of 0.945 to 0.970 g/cm³.

In one embodiment, the HDPE is an ethylene homopolymer.

The HDPE may also be a copolymer, for example a copolymer of ethylene with one or more alpha-olefin monomers such as propylene, butene, hexene, etc.

In one embodiment the high density polyethylene (HDPE) is the commercial product MG9641 of Borealis AG.

F) Mineral-filler

In addition to the polymer components listed above, the polypropylene composition according to the present invention comprises also a mineral filler.

Preferably the mineral filler is a phyllosilicate, mica or wollastonite. More preferably the mineral filler is selected from the group of mica, wollastonite, kaolinite, smectite, montmorillonite and talc. The most preferred mineral filler is talc.

The mineral filler preferably has an average particle size d₅₀ in the range of 1 to 20 µm, more preferably in the range of 1 to 10 µm, still more preferably in the range of 1 to 5 µm.

Typically the mineral filler has a cutoff particle size d₉₅ [mass percent] of equal or below 20 µm, more preferably in the range of 2.5 to 10 µm, still more preferably in the range of 2.5 to 8 µm.

G) Additives

The polypropylene composition according to the present invention comprises furthermore optional additives useful for instance in the automobile sector.

Such additives are usually selected from antioxidants (AO), slip agents (SA), UV stabilizers, like hindered amine light stabilizers (HALS), anti-scratch additives, antistatic agents, nucleating agents and carbon black or other pigments and co-additives, which improve the thermal resistance, and reduce odour (odour-scavenger), like epoxy resins, in amounts usual in the art.

Polypropylene composition

As mentioned above, the polypropylene composition according to the present invention comprises components (A) to (G).

The individual components are present in the following amounts:

- (A) 15 – 70 wt%, preferably 20 – 60 wt% and more preferably 25 -50 wt% of the first heterophasic polypropylene (HECO-1),
 - (B) 0 – 70 wt%, preferably 0.2 – 40 wt% and more preferably 0.5 -10 wt% of the second heterophasic polypropylene (HECO-2),
 - (C) 10 – 30 wt%, preferably 15 – 30 wt% and more preferably 20 - 30 wt% of the high melt strength polypropylene (HMS-PP),
 - (D) 5 to 20 wt%, preferably 7 – 18 wt% and more preferably 10 -15 wt% of the copolymer of ethylene and propylene or a C₄ - C₁₀ alpha-olefin (PE-COPO),
 - (E) 5 – 25 wt%, preferably 5 – 20 wt% and more preferably 5 -15 wt% of the high-density polyethylene (HDPE),
 - (F) 5 – 20 wt%, preferably 7 – 20 wt% and more preferably 10 -20 wt% of the mineral-filler and
 - (G) 0 – 15 wt%, preferably 1 – 12 wt% and more preferably 2 -10 wt% of additives,
- whereby the sum of the percentage amounts of the individual components of the composition is equal to 100 percent .

The polypropylene composition according to the present invention has the following properties:

- (i) The MFR₂ (230°C) is preferably in the range of 5 – 30 g/10min, preferably in the range of 8 – 25 g/10 min and more preferably in the range of 10 – 20 g/10 min.

- (ii) Charpy notched impact strength (Charpy NIS) at 23°C according to ISO 179-15 1eA:2000 of at least 25.0 kJ/m², preferably of at least 30 kJ/m² and more preferably of at least 35 kJ/m².
- (iii) Puncture energy (23°C) determined in instrumented falling weight at 23°C according to ISO 6603-2 using injection moulded plaques of 60x60x3 mm and a test speed of 4.4 m/s of at least 30.0 J, preferably in the range of 30.0 to 50.0 J, like in the range of 35 to 45 J.
- (iv) Puncture energy (-30°C) determined in instrumented falling weight at -30°C according to ISO 6603-2 using injection moulded plaques of 60x60x3 mm and a test speed of 4.4 m/s of at least 30.0 J, preferably in the range of 30.0 to 60.0 J, like in the range of 40 to 55 J.

The polypropylene composition according to the present invention is prepared by mechanically mixing the individual components (A) to (G) in the desired amounts in conventional compounding or blending apparatus, e.g. a Banbury mixer, a 2-roll rubber mill, Buss-co-kneader or a twin screw extruder. Preferably, mixing is accomplished in a co-rotating twin screw extruder.

The polymer materials recovered from the extruder are usually in the form of pellets.

These pellets are then preferably further processed, e.g. by injection moulding or foaming, preferably by foaming, to generate articles and products of the inventive mineral-filled polypropylene composition.

Foaming can be accomplished by chemical and/or physical foaming agents.

For foaming the polypropylene composition according to the invention, any physical or chemical foaming agent may be used.

For examples, as a physical foaming agent (PBA), preferably carbon dioxide can be used. However, other foaming agents, such as, for example nitrogen, butane or pentane, may be used as well.

A chemical foaming agent is defined to be a chemical substance that decomposes or reacts by the influence of heat. In direct gas foaming processes the "chemical foaming agents" may also be used as "nucleating agents" to produce uniform and fine cell structures.

Typical chemical blowing agents are inert, volatile liquids, such as e.g. lower hydrocarbons, having a boiling point of higher than 80°C whose expansion is triggered by heating the mould. Other examples are hydrogen carbonates which release carbon dioxide under heat.

As chemical foaming agent (CBA) for the purpose of the present invention, for example commercially available Hydrocerol CF70, manufactured from Clariant, Germany may be used. Hydrocerol CF70 is a chemical foaming and nucleating agent masterbatch for foaming of thermoplastic resins, containing effective components in an amount of 70wt%. At polypropylene extrusion conditions it releases carbon dioxide which acts as foaming agent. However, any other chemical foaming agent may be used for that purpose as well.

Thus, in a suitable process for foaming of moulded articles the melt is injected into the mould, as in conventional injection moulding. Prior to injection however, during melting and extruding of the melt, a physical foaming agent and optionally a nucleating agent (for direct gas foaming process) or a chemical foaming agent (for indirect gas foaming process) is added.

Preferably the process is an integral foaming process, e.g. the so-called "breathing mould process", as describe for example in EP 2669329.

Typically, such integral foams have a sandwich structure, as essentially derived from expansion of a moulded sheet; both the parallel, large surfaces flanking, as in sandwich, the foam layer, retain their dense structure as in the original sheet. After injection in the mould of the melt, the mould volume filled with the melt polymer is caused to increase and the foam is thus formed.

Due to its excellent puncture resistance the polypropylene composition according to the invention is especially suitable for producing automotive parts, preferably foamed automotive parts/articles, like car interiors and exteriors, like bumpers, side trims, step assists, body panels, spoilers, dashboards, interior trims and centre consoles.

Thus, the present invention is also related to the use of the polypropylene composition for preparing foamed automotive articles and to foamed articles, comprising the polypropylene composition of the present invention.

The present invention will now be described in further detail by the examples provided below.

Experimental Part:**A) Methods:****Melt Flow Rate**

The melt flow rate (MFR) is determined according to ISO 1133 and is indicated in g/10 min. The MFR is an indication of the flowability, and hence the processability, of the polymer. The higher the melt flow rate, the lower the viscosity of the polymer. The MFR₂ of polypropylene is determined at a temperature of 230 °C and a load of 2.16 kg. It is also designated in this application as “MFR₂”

Comonomer content

Quantitative Fourier transform infrared (FTIR) spectroscopy was used to quantify the amount of comonomer. Calibration was achieved by correlation to comonomer contents determined by quantitative nuclear magnetic resonance (NMR) spectroscopy. 20

The calibration procedure based on results obtained from quantitative ¹³C-NMR spectroscopy was undertaken in the conventional manner well documented in the literature.

The amount of comonomer (N) was determined as weight percent (wt%) via: 25

$$N = k_1 (A / R) + k_2$$

wherein A is the maximum absorbance defined of the comonomer band, R the maximum absorbance defined as peak height of the reference peak and with k₁ and k₂ the linear constants obtained by calibration. The band used for ethylene content quantification is selected depending if the 30 ethylene content is random (730 cm⁻¹) or block-like (720 cm⁻¹). The absorbance at 4324 cm⁻¹ was used as a reference band.

XHU content

About 2 g of the polymer (m_p) are weighted and put in a mesh of metal which is weighted (m_p+m). The polymer in the mesh is extracted in a soxhlet apparatus with boiling xylene for 5 hours. The eluent is then replaced by fresh xylene and the boiling is continued for another hour. Subsequently, the mesh is dried and weighted again (m_{XHU+m}). The mass of the xylene hot unsolubles m_m - m_{XHU+m} = m_{XHU} is put in relation to the weight of the polymer to obtain the fraction of xylene insolubles m_{XHU}/m_p.

Rheotens test

The test described herein follows ISO 16790:2005.

The strain hardening behaviour is determined by the method as described in the article "Rheotens-Mastercurves and Drawability of Polymer Melts", M. H. Wagner, Polymer Engineering and Science, Vol. 36, pages 925 to 935. The content of the document is included by reference. The strain hardening behaviour of polymers is analysed by Rheotens apparatus (product of Göttfert, Siemensstr.2, 74711 Buchen, Germany) in which a melt strand is elongated by drawing down with a defined acceleration.

The Rheotens experiment simulates industrial spinning and extrusion processes. In principle a melt is pressed or extruded through a round die and the resulting strand is hauled off. The stress on the extrudate is recorded, as a function of melt properties and measuring parameters (especially the ratio between output and haul-off speed, practically a measure for the extension rate). For the results presented below, the materials were extruded with a lab extruder HAAKE Polylab system and a gear pump with cylindrical die ($L/D = 6.0/2.0$ mm). The gear pump was pre-adjusted to a strand extrusion rate of 5 mm/s, and the melt temperature was set to 200°C. The spinline length between die and Rheotens wheels was 80 mm. At the beginning of the experiment, the take-up speed of the Rheotens wheels was adjusted to the velocity of the extruded polymer strand (tensile force zero): Then the experiment was started by slowly increasing the take-up speed of the Rheotens wheels until the polymer filament breaks. The acceleration of the wheels was small enough so that the tensile force was measured under quasi-steady conditions. The acceleration of the melt strand (2) drawn down is 120 mm/sec². The Rheotens was operated in combination with the PC program EXTENS. This is a real-time data-acquisition program, which displays and stores the measured data of tensile force and drawdown speed. The end points of the Rheotens curve (force versus pulley rotary speed) is taken as the melt strength and drawability values.

Charpy notched impact Strength (NIS)

Charpy notched impact strength was determined according to ISO 179-15 1eA:2000 at 23 °C, and at -20 °C by using injection moulded test specimens (V-notched samples) as described in EN ISO 1873-2 (80 x 10 x 4 mm).

Instrumented falling weight test

Puncture energy, maximum force and puncture deflection was determined in the instrumented falling weight test according to ISO 6603-2 using injection moulded plaques of 60x60x3 mm and a test speed of 4.4 m/s. The reported puncture energy results from an integral of the failure energy curve measured at +23°C and -30°C.

B. Examples**Materials used**

Component (A): first heterophasic polypropylene (HECO-1)

EG001AE: nucleated heterophasic polypropylene commercially available from Borealis AG, Austria, having an MFR₂ (230°C) of 35.0 g/10min;
Having a PP-homopolymer matrix (M-PP-1) with an MFR₂ (230°C) of 250 g/10min and an MWD of 4.2
and 31% of dispersed phase (D-1) (respectively XCS) having 33 wt% of ethylene and an intrinsic viscosity of 3.2 dl/g

Component (B): second heterophasic polypropylene (HECO-2)

EF015AE: heterophasic polypropylene commercially available from Borealis AG, Austria, having an MFR₂ (230°C) of 18.0 g/10min
Having a PP-homopolymer matrix (M-PP-2) with an MFR₂ (230°C) of 85 g/10min and an MWD of 4.5
and 29% of dispersed phase (D-2) (respectively XCS) having 45 wt% of ethylene and an intrinsic viscosity of 2.6 dl/g

Component (C): high melt strength polypropylene (HMS-PP)

WB140HMS: high melt strength homo-polypropylene commercially available from Borealis AG, Austria, having an MFR₂ (230°C) of 2.1 g/10min, XCU of 0.3%, F30 melt strength of 36 cN and a melt extensibility v30 of 255 mm/s.

Component (D): copolymer (PE-COPO)

Engage 8200: ethylene-octene copolymer commercially available from DOW Chemical Company, having an MFR₂ (190°C) of 5.0 g/10min, density of 0.870 g/cm³, melting point T_m of 59°C, glass transition temperature of -53°C and an C₂-content of 62 wt%.

Component (E): high density polyethylene (HDPE)

MG9641: high density polyethylene commercially available from Borealis AG, Austria, having an MFR₂ (190°C) of 8.0 g/10min and density of 0.964 g/cm³

Component (F): mineral-filler

Talc: Jetfine 3CA (hydrated magnesium silicate)

Component (G): Additives

The following additives have been used:

Carbon Black Master Batch (*CB-MB*): MB 97-Black 7-PE-40: commercially available from Cabot Plasblak PE1639 containing 40% carbon black

HC001A-B1: propylene homopolymer (*HPP*), commercially available from Borealis AG, Austria, with a density of 0.905 g/cm³ and an MFR (2.16 kg, 230°C) of 3.2 g/10 min. (for additive dosing)

Slip Agents (SA-1 and SA-2)

SA150GRA (SA-1): Crodamide EBS-MB-(GD), provided by Croda, (N,N'-ethylene-bis-stearamide)

SA100GRA (SA-2): Crodamide ER beads; provided by Croda, (Erucamide (13-docosenamide)

OT700FLA: Polyfunctional epoxide compound (*Epoxide*); commercially available from Huntsman Advanced Materials (brand name Araldite®), i.e. Solid bisphenol A diglycidyl ether; ARALDITE GT 7072 (odour scavenger)

UV575PEL2: CYASORB UV-3808 PP5, UV stabilizer (*UV-Stab*), commercially available from Cytec Industries

Antioxidants: (AO-1 and AO-2)

Irganox 1010 FF (AO-1): Pentaerythrityl-tetrakis(3-(3',5'-di-tert. butyl-4-hydroxyphenyl)-propionate; commercially available from BASF

Irgafos 168 FF (AO-2): Tris (2,4-di-*t*-butylphenyl) phosphite; commercially available from BASF

(H) Foaming Agent:

Hydrocerol® CF40: commercially available from Clariant; sodium bicarbonate-citric acid nucleating agents (40 percent concentration of sodium bicarbonate and citric acid in a wax and polyethylene base in pellet form)

The following inventive example IE1 and comparative example CE1 and CE2 were prepared by melt blending of the components (A) to (G) with a twin-screw extruder ZSK 40, (Werner & Pfleiderer/ 1991), screw diameter: 2 x 40, 40D with a screw rotation speed of 400 rpm and a melt temperature of 210 °C.

Table 1: Composition of IE1, CE1 and CE2

Component	IE1	CE1	CE2
<i>HECO-1 [wt%]</i>	34	20	0
<i>HECO-2 [wt%]</i>	0.8	37.3	69.8
<i>HMS-PP [wt%]</i>	25	12.5	0
<i>PE-COPO [wt%]</i>	12	2	2
<i>HDPE [wt%]</i>	8	8	8
<i>Talc [wt%]</i>	15	15	15
<i>Additives</i>			
<i>CB-MB[wt%]</i>	3	3	3
<i>HPP [wt%]</i>	0.9	0.9	0.9
<i>SA-1</i>	0.3	0.3	0.3
<i>SA-2</i>	0.25	0.25	0.25
<i>Epoxide</i>	0.25	0.25	0.25
<i>UV-Stab</i>	0.2	0.2	0.2
<i>AO-1</i>	0.2	0.2	0.2
<i>AO-2</i>	0.1	0.1	0.1

The above polypropylene compositions have the following properties:

Table 2: Properties of compositions of IE1, CE1 and CE2

Property	unit	IE1	CE1	CE2
MFR ₂	[g/10min]	11.6	13.0	14.5
NIS 23°C	kJ/m ²	40.5	20.3	47.6
IPT 23°C*				
60x60x3mm				
Maximum Force	N	2777	2820	2477
Puncture Deflection	mm	21.2	20.8	21.4
Puncture Energy	J	39	39	36
IPT -30°C*				
60x60x3mm				
Maximum Force	N	4690	4400	4185
Puncture Deflection	mm	15	11.5	17
Puncture Energy	J	45	29	47

* IPT: Instrumented Puncture Test on non-foamed test specimens

From the above table it can be seen that with the inventive composition, comprising a special combination of Components (A), (C) and (D) the puncture energy and maximum force (parameters for puncture resistance) of the test specimens is in sum increased compared to other compositions, which do not comprise this special combination of Components (A), (C) and (D).

Patent claims**1. Mineral-filled polypropylene composition comprising**

- (A) 15 – 70 wt% of a first heterophasic polypropylene (HECO-1) having an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 30 – 50 g/10 min, comprising
- (A-1) 65 – 90 wt% of a propylene homopolymer matrix (M-PP-1) with an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 150 – 400 g/10 min and a molecular weight distribution (MWD) in the range of 3.5 – 5.5 and
- (A-2) 10 – 35 wt% of a dispersed phase (D-1) being a copolymer of propylene and ethylene or C₄ - C₁₀ alpha-olefin with an intrinsic viscosity (measured in decaline according to DIN ISO 1628/1 at 135°C) in the range of 2.0 - 4.0 dl/g, and an C₂-content of 20 – 65 wt% (measured with infrared spectroscopy)
- (B) 0 – 70 wt% of a second heterophasic polypropylene (HECO-2) having an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 5 – 25 g/10 min, comprising
- (B-1) 65 – 90 wt% of a propylene homopolymer matrix (M-PP-2) with an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 20 – 120 g/10 min and an MWD in the range of 3.5 – 5.5 and
- (B-2) 10 – 35 wt% of a dispersed phase (D2) being a copolymer of propylene and ethylene or C₄ - C₁₀ alpha-olefin with an intrinsic viscosity (measured in decaline according to DIN ISO 1628/1 at 135°C) in the range of 2.0 - 4.0 dl/g, and an C₂-content of 20 – 65 wt% (measured with infrared spectroscopy)
- (C) 10 – 30 wt% of a high melt strength polypropylene (HMS-PP) having
- (i) an MFR₂ (ISO 1133; 230 °C; 2.16kg) in the range of 1.0 to 5.0 g/10 min
- (ii) a F30 melt strength of at least 30 cN, determined in the Rheotens test at 200°C; and
- (iii) a melt extensibility v30 of at least 200 mm/s, determined in the Rheotens test at 200°C and
- (ix) xylene hot insolubles (XHU) content of less than 1.25 wt%
- (D) 5 to 20 wt% of a copolymer of ethylene and propylene or a C₄ - C₁₀ alpha-olefin with a density of 0.860 – 0.910 g/cm³ and an MFR₂ (ISO 1133; 190°C; 2.16kg) in the range of 0.5 – 50 g/10 min (PE-COPO)
- (E) 5 – 25 wt% of a high-density polyethylene (HDPE)
- (F) 5 – 20 wt% of a mineral-filler and
- (G) 0 – 15 wt% of additives selected from antioxidants (AO), slip agents (SA), UV-stabilizers, anti-scratch additives, odour-scavengers and pigments, whereby the sum of the percentage amounts of the individual components of the composition is equal to 100 percent .

2. Mineral-filled polypropylene composition according to claim 1,
wherein the first heterophasic polypropylene (HECO-1) has an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 30 – 45 g/10 min, and comprises
- (A-1) 65 – 80 wt% of a propylene homopolymer matrix (M-PP-1) with an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 150 – 350 g/10 min and a molecular weight distribution (MWD) in the range of 3.7 – 5.3 and
 - (A-2) 20 – 35 wt% of a dispersed phase (D-1) being a copolymer of propylene and ethylene with an intrinsic viscosity (measured in decaline according to DIN ISO 1628/1 at 135°C) in the range of 2.0 - 4.0 dl/g, and an C₂-content of 20 – 55 wt% (measured with infrared spectroscopy) and
 - (A-3) less than 500 ppm of an α -nucleating agent selected from vinylcycloalkane polymer and vinylalkane polymer.
3. Mineral-filled polypropylene composition according to claim 1,
wherein the second heterophasic polypropylene (HECO-2) has an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 10 – 25 g/10 min, and comprises
- (B-1) 65 – 80 wt% of a propylene homopolymer matrix (M-PP-2) with an MFR₂ (ISO 1133; 230°C; 2.16kg) in the range of 50 – 120 g/10 min and an MWD in the range of 3.7 – 5.3 and
 - (B-2) 20 – 35 wt% of a dispersed phase (D2) being a copolymer of propylene and ethylene with an intrinsic viscosity (measured in decaline according to DIN ISO 1628/1 at 135°C) in the range of 2.0 - 4.0 dl/g, and an C₂-content of 25 – 60 wt% (measured with infrared spectroscopy).
4. Mineral-filled polypropylene composition according to claim 1,
wherein the high melt strength polypropylene (HMS-PP) has
- (i) an MFR₂ (ISO 1133; 230 °C; 2.16kg) in the range of 1.2 to 4.0 g/10 min
 - (ii) a F30 melt strength in the range of 30 cN to 60 cN, determined in the Rheotens test at 200°C; and
 - (iii) a melt extensibility v30 in the range of 200 mm/s to 350 mm/s, determined in the Rheotens test at 200°C and
 - (ix) xylene hot unsolubles (XHU) content of less than 1.00 wt%
5. Mineral-filled polypropylene composition according to claim 1,

wherein component (D) is a copolymer of ethylene and 1-octene with a density of 0.860 – 0.900 g/cm³ and an MFR₂ (ISO 1133; 190°C; 2.16kg) in the range of 0.5 – 40 g/10 min.

6. Mineral-filled polypropylene composition according to claim 1,
wherein component (E) is a high-density polyethylene with an MFR₂ (ISO 1133; 190°C; 2.16kg) in the range of 2 – 30 g/10 min and a density of at least 0.950 g/cm³.
7. Mineral-filled polypropylene composition according to claim 1,
wherein component (F) is selected from mica, wollastonite, kaolinite, smectite, montmorillonite and talc.
8. Mineral-filled polypropylene composition according to any of the preceding claims 1 - 7,
wherein the components (A) to (G) are present in specific amounts of
(A) 20 – 60 wt% of the first heterophasic polypropylene (HECO-1),
(B) 0.2 – 40 wt% of the second heterophasic polypropylene (HECO-2),
(C) 15 – 30 wt% of the high melt strength polypropylene (HMS-PP),
(D) 7 – 18 wt% of the copolymer of ethylene and propylene or a C₄ - C₁₀ alpha-olefin (PE-COPO),
(E) 5 – 20 wt% of the high-density polyethylene (HDPE),
(F) 7 – 20 wt% of the mineral-filler and
(G) 1 – 12 wt% 2 -10 wt% of additives,
whereby the sum of the percentage amounts of the individual components of the composition is equal to 100 percent .
9. Mineral-filled polypropylene composition according to any of the preceding claims 1 - 8,
having
 - (i) an MFR₂ (230°C) in the range of 5 – 30 g/10min,
 - (ii) a Charpy notched impact strength (Charpy NIS) at 23°C (according to ISO 179-15 1eA:2000) of at least 25.0 kJ/m²,
 - (iii) a Puncture energy (23°C) determined in instrumented falling weight at 23°C according to ISO 6603-2 using injection moulded plaques of 60x60x3 mm and a test speed of 4.4 m/s of at least 30.0 J,
 - (iv) a Puncture energy (-30°C) determined in instrumented falling weight at -30°C according to ISO 6603-2 using injection moulded plaques of 60x60x3 mm and a test speed of 4.4 m/s of at least 30.0 J.

10. Mineral-filled polypropylene composition according to claims 9, having
 - (i) an MFR₂ (230°C) in the range of 8 – 25g/10min,
 - (ii) a Charpy notched impact strength (Charpy NIS) at 23°C (according to ISO 179-15 1eA:2000) of at least 30.0 kJ/m²,
 - (iii) a Puncture energy (23°C) determined in instrumented falling weight at 23°C according to ISO 6603-2 using injection moulded plaques of 60x60x3 mm and a test speed of 4.4 m/s in the range of 30.0 J to 50.0 J,
 - (iv) a Puncture energy (-30°C) determined in instrumented falling weight at -30°C according to ISO 6603-2 using injection moulded plaques of 60x60x3 mm and a test speed of 4.4 m/s in the range of 30.0 J to 60.0 J.
11. Use of the mineral-filled polypropylene composition according to any of the preceding claims 1 - 10 for preparing foamed articles comprising the said mineral-filled polypropylene composition.
12. Use according to claim 11, wherein the prepared foamed articles are suitable for the automotive industry.
13. Foamed articles comprising the mineral-filled polypropylene composition according to any of the preceding claims 1 – 10.
14. Foamed articles according to claim 13, wherein the articles are suitable for the automotive industry.
15. Foamed articles according to claim 14, wherein the articles are door claddings, instrument panel, centre consoles, pillars and bumpers.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/065285

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L23/12
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 2 669 329 A1 (BASELL POLIOLEFINE SRL [IT]) 4 December 2013 (2013-12-04) cited in the application the whole document -----	1-15
A	EP 2 423 257 A1 (BOREALIS AG [AT]) 29 February 2012 (2012-02-29) claims 1-15; examples 1-3 -----	1-10
A	WO 2013/026864 A1 (BOREALIS AG [AT]; GREIN CHRISTELLE [AT]; KOCK CORNELIA [AT]; TRANNINGE) 28 February 2013 (2013-02-28) claims 1-16; examples 1,2 -----	1-10
A	WO 2013/041507 A1 (BOREALIS AG [AT]; KOCK CORNELIA [AT]; KNIESEL CLAUDIA [AT]; DOSHEV PET) 28 March 2013 (2013-03-28) claims 1-16; examples 1-3 -----	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/065285

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2669329	A1	04-12-2013	CN 104769033 A 08-07-2015
		EP 2669329 A1	04-12-2013
		EP 2855578 A1	08-04-2015
		JP 2015518078 A	25-06-2015
		US 2015148437 A1	28-05-2015
		WO 2013178509 A1	05-12-2013

EP 2423257	A1	29-02-2012	CN 103080212 A 01-05-2013
		EP 2423257 A1	29-02-2012
		ES 2397547 T3	07-03-2013
		US 2013203908 A1	08-08-2013
		WO 2012025584 A1	01-03-2012

WO 2013026864	A1	28-02-2013	CN 103748162 A 23-04-2014
		EP 2748250 A1	02-07-2014
		KR 20140041963 A	04-04-2014
		US 2014187708 A1	03-07-2014
		WO 2013026864 A1	28-02-2013

WO 2013041507	A1	28-03-2013	CN 103827200 A 28-05-2014
		EP 2758467 A1	30-07-2014
		WO 2013041507 A1	28-03-2013
