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(54) Heterophasic polymer composition of high stiffness

Heterophasenpolymerzusammensetzung mit hoher Festigkeit

Composition de polymère hétérophasique à grande rigidité

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(56) References cited:
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Description

[0001] The present invention relates to a heterophasic polymer composition of improved stiffness which is useful for the preparation of pipes, and to a process for the preparation of such a heterophasic polymer composition.

[0002] Pipes made of polymeric materials are frequently used for various purposes, such as fluid transport, i.e. transport of gases or liquids. The fluid may be pressurised such as when transporting natural gas or tap water, or non-pressurised such as when transporting sewage (wastewater), drainage (land and road drainage), for storm water applications or for indoor soil and waste. Moreover, the transported fluid may have varying temperatures, usually within the temperature range of from about 0°C to about 50°C. Pressureless (non-pressure) pipes may also be used for cable and pipe protection.

[0003] Such non-pressure pipes are herein also referred to as sewage pipes or non-pressure sewage pipes.

[0004] The term "pipe" as used herein is meant to comprise pipes in a broader sense, as well as supplementary parts like fittings, valves, chambers and all parts which are commonly necessary for e.g. a sewage piping system. It also comprises single or multilayer pipes, where for example one or more of the layers is a metal layer and which may include an adhesive layer. Structural-wall pipes, such as corrugated pipes, double-wall pipes with or without hollow sections, are also encompassed by the term "pipe".

[0005] Different requirements are imposed on pipes for the transport of pressurised fluids (so-called pressure pipes) and pipes for the transport of non-pressurised fluids such as sewage (so-called non-pressure pipes). While pressure pipes must be able to withstand an internal positive pressure, i.e. a pressure inside the pipe that is higher than the pressure outside the pipe, non-pressure pipes do not have to withstand any internal positive pressure, but are instead required to withstand an external positive pressure, i.e. the pressure outside the pipe is higher than the pressure inside the pipe. This higher outside pressure may be due to the earth load on the pipe when submerged in the soil, the groundwater pressure, traffic load, or clamping forces in indoor applications.

[0006] Non-pressure pipes such as sewage pipes are made in a variety of dimensions from about 0.1 to about 3 m diameter and of a variety of materials such as ceramics (vitrified clay mainly), concrete, polyvinyl chloride (PVC), polyethylene (PE), and polypropylene (PP). While ceramics and concrete are low-cost materials, they are unfortunately heavy and brittle. There has therefore been a trend during recent years to replace sewage pipes of ceramics or concrete with pipes of polymer materials such as PVC, PE or PP. While PVC costs less than PP per unit weight, PP has advantages over PVC in other respects by having a lower density and thus a lower weight per metre pipe, having superior high and low temperature properties, and being weldable.

[0007] Sewage pipes of PP must show sufficient stiffness to withstand the earth load without any help from internal pressure. The stiffness of the pipe is derived primarily from the pipe material and as a measure of stiffness, the tensile modulus of the pipe material may be taken. The higher the tensile modulus of the pipe material, the stiffer the pipe will be.

[0008] Furthermore, non-pressure pipes are often exposed to high as well as low temperatures. They must therefore be durable within a wide range of temperatures which means that they should display high impact strength, particularly at low temperature.

[0009] However, as stiffness and impact strength are conflicting properties, it remains difficult to increase tensile modulus of a PP pipe material while still keeping the impact strength on an acceptable level.

[0010] WO 99/24479 discloses a nucleated polypropylene composition containing a polymerized vinyl compound. The composition may comprise a propylene homopolymer matrix and an elastomeric ethylene/propylene copolymer dispersed therein. The ethylene content of the amorphous part can be in the range of 30 to 50 wt%. Furthermore, the amount of the dispersed rubber phase can vary in a wide range such as from 5 to 30 wt%, or 10 to 20 wt%. According to the examples, a tensile modulus of at least 2000 MPa could not be realised with heterophasic polymer compositions.

[0011] EP 1 026 184 A1 discloses a heterophasic polymer composition comprising a matrix made of a high molecular weight and a low molecular weight PP component, and a dispersed elastomeric phase made of an ethylene/alpha-olefin copolymer. The heterophasic polymer composition can have a xylene cold soluble fraction in an amount of 4 to 30 wt%. The amount of ethylene-derived monomer units in the elastomeric ethylene/alpha-olefin copolymer can be in the range of 22 to 38 wt%. According to the examples, all heterophasic polymer compositions have a flexural modulus of below 2000 MPa.

[0012] EP 1 632 529 A1 discloses a heterophasic polymer composition comprising a propylene homopolymer and an elastomeric propylene copolymer dispersed therein. The heterophasic polymer composition has a total amount of comonomer units, e.g. ethylene-derived comonomer units, of at least 2 wt%.

[0013] Considering the statements provided above, it is an object of the present invention to provide a polymer composition which is useful for the preparation of a pipe of high stiffness while simultaneously keeping low temperature impact strength on an acceptable level.

[0014] According to a first aspect of the present invention, the object outlined above is solved by providing a heterophasic polymer composition, comprising

- a matrix comprising a propylene homopolymer and/or a propylene copolymer having an amount of comonomer units

of less than 1.0 wt%,
- an elastomeric polypropylene which is dispersed within the matrix and comprises comonomer units derived from ethylene and/or a C4 to C12 alpha-olefin,

the heterophasic polymer composition having an amorphous fraction AM in an amount of 2.0 to 7.5 wt%, and the amorphous fraction AM having an amount of ethylene- and/or C4 to C 12 alpha-olefin-derived comonomer units of 20 to 45 wt%.

[0015] As a first approximation, it can be said that the amount of the amorphous fraction AM corresponds to the amount of elastomeric polymer(s) (i.e. rubber) being present in the heterophasic polymer composition. The amount of the amorphous fraction is easy to measure as described further below in the Examples under the headline "Measuring Methods" and is frequently used as a parameter indicating the amount of elastomeric components within heterophasic, impact-modified compositions. Another parameter frequently used to determine the amount of elastomeric and/or amorphous components within a polymer composition is the xylene cold soluble fraction XCS (sometimes also referred to as xylene solubles XS). The measuring method is described in further detail below under the headline "Measuring Methods". As a first approximation, the amount of the xylene cold soluble fraction XCS corresponds to the amount of rubber and the amount of those polymer chains of the matrix with low molecular weight and low stereoregularity. Thus, normally the XCS value is slightly higher than the AM value.

[0016] Preferably, according to the first aspect of the present invention the heterophasic polymer composition has a xylene cold soluble fraction XCS_{total} in an amount of 3.0 to 8.5 wt%, and/or an amount of ethylene- and/or C4 to C 12 alpha-olefin-derived comonomer units of less than 2.0 wt%.

[0017] In the present invention, the term "matrix" is to be interpreted in its commonly accepted meaning, i.e. it refers to a continuous phase (in the present invention a continuous polymer phase) in which isolated or discrete particles such as rubber particles may be dispersed.

[0018] The matrix phase can be made of the propylene homo- and/or copolymer only but can also comprise additional polymers, in particular polymers which can be blended homogeneously with the propylene homo- or copolymer and together form a continuous phase which can act as a matrix. In a preferred embodiment, at least 80 wt% of the matrix, more preferably at least 90 wt%, even more preferably at least 95 wt% of the matrix are made of the propylene homo- and/or copolymer. Even further preferred, the matrix consists of the propylene homo- and/or copolymer.

[0019] In a preferred embodiment, the matrix only comprises the propylene homopolymer but does not comprise the propylene copolymer.

[0020] If present in the matrix, the propylene copolymer includes comonomer units derived from ethylene, C4 to C12 alpha-olefins, or any mixture thereof. As indicated above, the propylene copolymer has an amount of comonomer units of less than 1.0 wt%, preferably less than 0.75 wt%, more preferably less than 0.5 wt%.

[0021] Preferably, the propylene homopolymer and/or the propylene copolymer of the matrix has/have an MFR(230°C, 2.16 kg) within the range of 0.1 g/10 min to 1.5 g/10 min, more preferably 0.2 g/10 min to 1.0 g/10 min, even more preferably 0.2 g/10 min to 0.5 g/10 min.

[0022] As indicated above, in addition to the propylene homo- and/or copolymer the matrix may optionally comprise further polymer(s) which can be blended homogeneously with the propylene homo and/or copolymer. Preferably, the matrix, either consisting of the propylene homo- and/or copolymer or optionally comprising one or more additional polymers, has an MFR(2.16 kg, 230°C) within the range of 0.1 g/10 min to 1.5 g/10 min, more preferably 0.2 g/10 min to 1.0 g/10 min, even more preferably 0.2 g/10 min to 0.5 g/10 min.

[0023] Of course, if the matrix consists of the propylene homo- or copolymer, preferably of the propylene homopolymer, the MFR value of the matrix corresponds to the MFR value of the polymer.

[0024] The propylene homo- or copolymer constituting the matrix can be either unimodal or multimodal such as bimodal. As used herein, the term "multimodal" is intended to cover polymers having at least two differently centred maxima along the x-axis of their molecular weight distribution curve as determined by gel permeation chromatography. In such a curve d(log(MW)) is plotted as ordinate against log (MW), where MW is molecular weight.

[0025] Preferably, the high molecular weight fraction of the multimodal, preferably bimodal propylene homo- or copolymer of the matrix has an MFR(230°C, 10.0 kg) within the range of 0.1 g/10 min to 2.5 g/10 min, more preferably 0.5 g/10 min to 1.5 g/10 min, even more preferably 0.7 g/10 min to 1.5 g/10 min.

[0026] Preferably, the propylene homo- and/or copolymer of the matrix has/have a xylene cold soluble fraction $XCS_{PPmatrix}$ in an amount of less than 3.0 wt%, more preferably less than 2.0 wt%, even more preferably less than 1.5wt%.

[0027] As indicated above, in addition to the propylene homo- and/or copolymer the matrix may optionally comprise further polymer(s) which can be blended homogeneously with the propylene homo- and/or copolymer. Preferably, the matrix, either consisting of the propylene homo- and/or copolymer or optionally comprising one or more additional polymers, has a xylene cold soluble fraction XCS_{matrix} in an amount of less than 3.0 wt%, more preferably less than 2.0 wt%, even more preferably less than 1.5 wt%.

[0028] Of course, if the matrix consists of the propylene homo- or copolymer, preferably of the propylene homopolymer, as defined above, $XCS_{PPmatrix}$ and XCS_{matrix} are identical. In case the matrix includes one or more additional polymers, which are homogeneously blended with the propylene homo- or copolymer as defined above, $XCS_{PPmatrix}$ and XCS_{matrix} might slightly differ.

[0029] As indicated above, the heterophasic polymer composition further comprises an elastomeric polypropylene copolymer which is dispersed in the matrix and comprises comonomer units derived from ethylene and/or a C4 to C12 alpha-olefin.

[0030] Within the present invention, it is possible that, in addition to the elastomeric polypropylene as defined above and in further detail below, the heterophasic polymer composition may comprise further elastomeric polymer components. However, it is preferred that the elastomeric polypropylene represents at least 80 wt%, more preferably at least 90 wt%, even more preferably at least 95 wt% of the total rubber content in the heterophasic polymer composition. In a preferred embodiment, the elastomeric polypropylene is the only elastomeric polymer which is present in the heterophasic polymer composition.

[0031] Preferably, the elastomeric polypropylene copolymer comprises ethylene-derived and/or C4 to C12 alpha-olefin derived comonomer units, more preferably only ethylene-derived comonomer units. Preferably, these comonomer units are present in an amount of 20 wt% to 45 wt%, more preferably 22 wt% to 35 wt%, based on the weight of the elastomeric polypropylene.

[0032] In case the elastomeric polypropylene comprises comonomer units derived from a C4 to C12 alpha-olefin, these are preferably selected from 1-butene, 1-hexene, 1-octene, or any mixture thereof.

[0033] As indicated above, the heterophasic polymer composition according to the first aspect of the present invention has an amorphous fraction AM in an amount of 2.0 to 7.5 wt%, and the amorphous fraction AM has an amount of ethylene- and/or C4 to C12 alpha-olefin-derived comonomer units of 20-45 wt%

[0034] Preferably, the heterophasic polymer composition has an amorphous fraction AM in an amount of 3.0 wt% to 7.5 wt%, more preferably 3.0 wt% to 6.0 wt%.

[0035] Preferably, the amount of the ethylene- and/or C4 to C12 alpha-olefin-derived comonomer units, more preferably the amount of ethylene-derived comonomer units in the amorphous fraction AM of the heterophasic polymer composition is from 22 wt% to 35 wt%, more preferably from 23 wt% to 32 wt%.

[0036] Preferably, the elastomeric polypropylene represents at least 60 wt%, more preferably at least 65 wt%, even more preferably at least 70 wt% of the amorphous fraction AM of the heterophasic polymer composition.

[0037] Preferably, the heterophasic polymer composition has a xylene cold soluble fraction XCS_{total} in an amount of 3.0 to 7.0 wt%, more preferably 4.0 to 7.0 wt%.

[0038] Preferably, the heterophasic polymer composition has an amount of ethylene- and/or C4 to C12 alpha-olefin-derived comonomer units of less than 1.8 wt%, With respect to the lower limit, it is preferred that the heterophasic polymer composition has an amount of ethylene- and/or C4 to C12 alpha-olefin-derived comonomer units of at least 0.8 wt%, more preferably at least 1.0 wt%.

[0039] Preferably, the elastomeric polypropylene represents at least 60 wt%, more preferably at least 65 wt% of the xylene cold soluble fraction XCS_{total} of the heterophasic polymer composition.

[0040] Preferably, the amorphous fraction AM of the heterophasic polymer composition has an intrinsic viscosity within the range of 2.0 dl/g to 5.0 dUg, more preferably 2.5 dl/g to 5.0 dl/g, even more preferably 3.0 dl/g to 4.5 dl/g.

[0041] The polymer composition may include 0.05-3 wt% of one or more nucleating agents, such as talc, polymerized vinyl compounds such as polyvinyl cyclohexane (poly-VCH), dibenzylidene sorbitol (DBS), sodium benzoate, and di (alkylbenzylidene)sorbitol. Except for talc, the nucleating agents are usually added in small amounts of 0.0001-1 % by weight, preferably 0.001-0.7 % by weight. Talc is a specific case as it may be added both as a nucleating agent and as a filler. When added as a nucleating agent talc is added in an amount of 0.05-3 % by weight, preferably 0.1-2 % by weight.

[0042] Preferably, the heterophasic polymer composition has a tensile modulus, measured according to ISO 527-2/1B at 1 mm/min and 23°C, of more than 1800 MPa.

[0043] According to another aspect, the present invention provides a pipe, comprising the heterophasic polymer composition as defined above.

[0044] Preferably, the pipe is a non-pressure pipe such as a non-pressure sewage pipe. In other words, the pipe of the present invention is preferably used for the transport of non-pressurized fluids such as sewage.

[0045] Preferably, the pipe has a tensile modulus of more than 1900 MPa, more preferably more than 2000, even more preferably more than 2100 MPa, wherein the tensile modulus is determined by the following formula:

$$\text{tensile modulus} = RS \times 12 \times [(D - t)/t]^3$$

wherein
RS is ring stiffness, determined according to EN ISO 9969,

D is the outer diameter of the pipe in mm, and
t is the wall thickness of the pipe in mm.

[0046] Impact strength of a pipe can be determined by the so-called resistance to external blows which is measured according to EN 1411. The measurement provides a H50 value for a pipe, which is the height where 50% of the samples fail.

[0047] Preferably, the pipe of the present invention has an H50 value of at least 1100 mm, more preferably at least 1500 mm, even more preferably at least 2000 mm.

[0048] In general, the pipe can be manufactured by extrusion or injection moulding. Preferably, it is prepared by extrusion. A conventional plant for screw extrusion of polymer pipes comprises a single or double screw extruder, a nozzle, a calibrating device, cooling equipment, a pulling device, and a device for cutting or for coiling-up the pipe. The polymer is extruded into a pipe from the extruder.

[0049] According to a further aspect, the present invention provides a process for the preparation of the heterophasic polymer composition as defined above, comprising the following steps:

(i) preparing the propylene homo- or copolymer as defined above in at least one loop reactor and optionally in at least one gas phase reactor, and
(ii) transferring the propylene homo- or copolymer to at least one gas phase reactor and preparing the elastomeric polypropylene as defined above in the presence of the propylene homo- or copolymer.

[0050] Preferably, the temperature of the loop reactor is at least 80°C and the pressure is at least 4600-10000 kPa.

[0051] In a preferred embodiment, step (i) comprises a loop and a gas-phase reactor in a cascade. Preferably, the loop reactor operates in liquid propylene and at a high polymerization temperature of at least 80°C, most preferably at supercritical temperature and pressure conditions.

[0052] The term "supercritical" conditions means that both the temperature and the pressure in the reactor are above the corresponding supercritical temperature and pressure of the reaction medium. For a reaction medium of propylene this means a temperature of at least 92°C and a pressure of at least 4600 kPa. Preferred temperatures are in the range of 92-110 °C. Preferred pressures are in the range 4600-10000 kPa, more preferably 5000-7000 kPa.

[0053] If step (i) comprises a gas-phase reactor, it is preferably operated at a temperature of 50-115°C, more preferably 60-110°C, even more preferably 80-105°C and a pressure of 500-5000 kPa, more preferably 1500-3500 kPa. Preferably, when the loop polymerization step of step (i) is carried out at surpercritical conditions, the temperature of the gas-phase reactor is 85-95°C and the pressure is 2000-3000 kPa.

[0054] The production ratio by weight (the so-called "split") between the loop reactor and the gas-phase reactor of step (i) may be from 20:80 to 80:20, more preferably 30:70 to 70:30, even more preferably 40:60 to 60:40.

[0055] The gas-phase reactor(s) of step (i), if used, may be any ordinary fluidised bed reactor, although other types of gas-phase reactors can be used.

[0056] After having prepared in step (i) the propylene homo- or copolymer constituting the matrix, the product of step (i) is transferred to a gas phase reactor where the elastomeric polypropylene is prepared in the presence of the propylene homo- or copolymer and *in situ* dispersed therein (so-called "reactor blending"). Optionally, step (ii) may comprise one or more additional gas phase reactors provided in serial configuration.

[0057] As a catalyst for the polymerization in step (i) and/or step (ii), any stereospecific catalyst for propylene polymerization can be used, which is capable of catalysing polymerization and copolymerization of propylene and comonomers, preferably at a pressure of 500-10000 kPa, in particular 2500-8000 kPa, and at a temperature of 40-110°C, in particular 60-110°C. Preferably, the catalyst comprises a Ziegler-Natta-type catalyst which can be used at high polymerization temperatures of 80°C or more.

[0058] Generally, the Ziegler-Natta catalyst used in the present invention comprises a catalyst component, a cocatalyst component, an external donor, the catalyst component of the catalyst system primarily containing magnesium, titanium, halogen and an internal donor. Electron donors control the stereospecific properties and/or improve the activity of the catalyst system. A number of electron donors including ethers, esters, polysilanes, polysiloxanes, and alkoxysilanes are known in the art.

[0059] The catalyst preferably contains a transition metal compound as a procatalyst component. The transition metal compound is selected from the group consisting of titanium compounds having an oxidation degree of 3 or 4, vanadium compounds, zirconium compounds, cobalt compounds, nickel compounds, tungsten compounds and rare earth metal compounds, titanium trichloride and titanium tetrachloride being particularly preferred.

[0060] It is preferred to use catalysts which can withstand the high temperatures prevailing in the loop reactor. The conventional Ziegler-Natta catalysts for isotactic polymerization of propylene generally have an operating temperature limit of around 80°C, above which they either become deactivated or lose their stereoselectivity. This low polymerization temperature may put a practical limit on the heat removal efficiency of the loop reactor.

[0061] One preferred catalyst to be used according to the invention is disclosed in EP 0 591 224 which discloses a method for preparing a procatalyst composition from magnesium dichloride, a titanium compound, a lower alcohol and an ester of phthalic acid containing at least five carbon atoms. According to EP 0 591 224, a transesterification reaction is carried out at an elevated temperature between the lower alcohol and the phthalic acid ester, whereby the ester groups from the lower alcohol and the phthalic ester change places.

[0062] Magnesium dichloride can be used as such or it can be combined with silica, e.g. by absorbing the silica with a solution or slurry containing magnesium dichloride. The lower alcohol used may preferably be methanol or ethanol, particularly ethanol.

[0063] The titanium compound used in the preparation of the procatalyst is preferably an organic or inorganic titanium compound, which is at the oxidation state of 3 or 4. Also other transition metal compounds, such as vanadium, zirconium, chromium, molybdenum and tungsten compounds can be mixed with the titanium compound. The titanium compound usually is a halide or oxyhalide, an organic metal halide, or a purely metal organic compound in which only organic ligands have been attached to the transition metal. Particularly preferred are the titanium halides, especially titanium tetrachloride.

[0064] The alkoxy group of the phthalic acid ester used comprises at least five carbon atoms, preferably at least eight carbon atoms. Propylhexyl phthalate, dioctyl phthalate, diisodecyl phthalate and ditridecyl phthalate may be used. The molar ratio of phthalic acid ester and magnesium halide is preferably about 0.2:1.

[0065] The transesterification can be carried out, e.g. by selecting a phthalic acid ester - a lower alcohol pair, which spontaneously or by the aid of a catalyst, which does not damage the procatalyst composition, transesterifies the catalyst at an elevated temperature. It is preferred to carry out the transesterification at a temperature which is 110-150°C, preferably 120-140°C.

[0066] The catalyst can also be modified as described in EP 1 028 985.

[0067] The catalyst prepared by the method above is used together with an organometallic cocatalyst and with an external donor. Generally, the external donor has the formula

$$R_nR'_mSi(R''O)_{4-n-m}$$

wherein

R and R' can be the same or different and represent a linear, branched or cyclic aliphatic, or aromatic group; R" is methyl or ethyl;

n is an integer of 0 to 3;

M is an integer of 0 to 3; and

n+m is 1 to 3.

[0068] In particular, the external donor is selected from the group consisting of cyclohexyl methylmethoxysilane (CHMMS), dicyclopentyl dimethoxysilane (DCPDMS), diisopropyl dimethoxysilane, di-isobutyl dimethoxysilane, and di-t-butyl dimethoxysilane.

[0069] An organoaluminium compound is used as a cocatalyst. The organoaluminium compound is preferably selected from the group consisting of trialkyl aluminium, dialkyl aluminium chloride and alkyl aluminium sesquichloride.

[0070] In a preferred embodiment, step (ii) is carried out in the presence of a compound selected from a glycerol ester, an ethoxylated amine, an ethoxylated amide, carbon monoxide, or any combination thereof.

[0071] As these compounds may decrease catalyst activity, they can be used to lower the amount of rubber produced in step (ii).

[0072] As an example, reference can be made to Grindsted PS 432 from Danisco, which is a glycerol ester compound.

[0073] The present invention will now be described in further detail by making reference to the examples provided below.

Examples

I. Measuring methods

1. Melt flow rate MFR

[0074] Melt flow rate was measured according to ISO 1133, either at 230°C and 2.16 kg (MFR2.16kg/230°C) or at 230°C and 10 kg (MFR10kg/230°C).

2. Intrinsic viscosity IV

[0075] The intrinsic viscosity of the amorphous fraction was measured according to ISO 1628 in decahydronaphtalene (decalin) at 135°C .

3. Tensile modulus

3.1 Tensile modulus measured on injection moulded samples

[0076] Tensile modulus was determined according to ISO 527-2/1 B at 1 mm/min. and 23°C. To determine stress at yield and strain at yield, a speed of 50 mm/min. was used. Tensile modulus was determined on 4 mm thick test specimens according to ISO 527-2/1 B. The injection moulded test specimens are made in a positive mould according to ISO 1873-2, multipurpose specimen.

3.2 Tensile modulus measured on an extruded pipe

[0077] The tensile modulus was determined by using the following formula:

$$\text{tensile modulus} = RS \times 12 \times [(D - t)/t]^3$$

wherein
RS is ring stiffness, determined according to EN ISO 9969,
D is the outer diameter of the pipe in mm, and
t is the wall thickness of the pipe in mm.

4. Ring stiffness

[0078] Ring stiffness is determined according to EN 9969 on pipes having a diameter of 110 mm and a wall thickness of about 4 mm (exact values in the table) at 23°C.

5. Resistance to external blows by stair case method, H50 value

[0079] The so-called resistance to external blows was determined according to EN 1411. The H50 value for a pipe is the height where 50% of the samples fail. The outer diameter for the pipes was 110 mm and the wall thickness 4 mm. The striker was 8 kg, type D 90, and the tests were made at -10°C.

6. Charpy notched impact strength

[0080] Charpy impact strength was determined according to ISO 179/1eA on injection molded test specimens made according to ISO 1873. The dimension of the test specimen was 80x10x4 mm.

7. Xylene cold soluble fraction XCS, amorphous fraction AM

[0081] XCS and AM were determined as follows:

> 2.0 g of polymer was dissolved in 250 ml p-xylene at 135°C under agitation. After 30±2 minutes the solution was allowed to cool for 15 minutes at ambient temperature and then allowed to settle for 30 minutes at 25±0.5°C. The solution was filtered with filter paper into two 100 ml flasks.

[0082] The solution from the first 100 ml vessel was evaporated in nitrogen flow and the residue dried under vacuum at 90°C until constant weight is reached.

$$XS\% = (100 \times m1 \times v0) / (m0 \times v1),$$

wherein
m0= initial polymer amount (g)
m1= weight of residue (g)
v0= initial volume (ml)
v1= volume of analyzed sample (ml)

[0083] The amorphous content (AM) is measured by separating the above xylene cold soluble fraction and precipitating the amorphous part with acetone. The precipitate was filtered and dried in a vacuum oven at 90°C.

$$AM\% = (100 \times m1 \times v0) / (m0 \times v1),$$

wherein
m0= initial polymer amount (g)
m1= weight of precipitate (g)
v0= initial volume (ml)
v1= volume of analyzed sample (ml)

8. Comonomer content

[0084] Measurement of the comonomer content (wt%) was based on Fourier transform infrared spectroscopy (FTIR) determination calibrated with ^{13}C-NMR.

II. Examples E1-E2 and CE1-CE2

[0085] E1 and E2 are inventive examples whereas CE1 and CE2 are comparative examples.

[0086] In all examples, the propylene polymers were prepared in the presence of a Ziegler-Natta catalyst which had been prepared according to Example 2 of WO 00/68315.

[0087] In Examples E1-E2 and CE1-CE2, the matrix is made of a propylene homopolymer which was prepared in a loop reactor and a gas phase reactor (GPR1). Further information about the propylene homopolymer constituting the matrix is shown in Table 1.

[0088] Subsequently, the propylene homopolymer was transferred to a second gas phase reactor (GPR2) where the elastomeric polypropylene was prepared. In E1 and E2, Grindsted PS 432 (a glycerol ester compound) was added to the second gas phase reactor at a feed rate of 3.3 g/h.

[0089] Further information about the process parameters is provided in Table 1.

[0090] In all examples, the final polymer composition also included phenolic antioxidants, process stabilisers, and talc.

[0091] Further information about the properties of the final heterophasic polymer composition is provided in Table 2.

[0092] The polymers were extruded into solid wall non-pressure sewage pipes in the following way:

External diameter: 110 mm
Wall thickness: 3.9 mm (examples E1 and E2), 4.4 mm (comparative examples CE1 and CE2)
Extruder: Conventional screw extruder, diameter 60 mm, length 36D Temperature profile: 200° C /210° C /210° C /210° C / 210° C Line speed: 1 m/min
Calibration and cooling: conventional methods

[0093] Table 2 also shows tensile modulus and H50 values as measured on the extruded pipe.

Table 1: Process parameters

	E1	E2	CE1	CE2
Catalyst feed (g/h)	5,0	5,2		
Ti content %	1,9	1,9		
Donor feed (g/t propylene)	80	80		
Al/Ti ratio (mol/mol)	127	122		
Al/donor ratio (mol/mol)	5,0	5,0		
Prepolymerisation				
Temperature (°C)	40	40	30	30
Hydrogen feed (g/h)	0,5	0,5		

(continued)

Loop reactor				
Temperature (°C)	85	85	85	85
Pressure (kPa)	5462	5471	5500	5500
H2/C3 ratio (mol/kmol)	0,07	0,08		
MFR10 (g/10 min)	1,1	1,3	0,8	0,8
Gas phase reactor 1				
Temperature (°C)	95	95	90	90
Pressure (kPa)	2301	2300	2500	2500
H2/C3 ratio (mol/kmol)	214	214		
MFR2 (g/10 min)	0,33	0,29	0,3	0,3
Gas phase reactor 2				
Temperature (°C)	60	60	70	80
Pressure (kPa)	2000	2000	2000	2000
C2/C3 ratio (mol/kmol)	700	700	550	550
H2/C2 ratio (mol/kmol)	14	22		
Additive feed (g/h) catalyst posion	3,3	3,3		

Table 2: Properties of the materials according to E1-E2 and CE1-CE2

	E1	E2	CE1	CE2
MFR2 (g/10 min)	0.31	0.3	0.25	0.25
Intrinsic Viscosity(dl/g))	4.12	4.06	3.5	3.5
XS (w%)	5.2	5.6	9	11
Ethene content (%)	1.6	1.7	3.7	5.1
AM (w%)	4.2	4.5	8	12
Ethene of AM (%)	29	26	34	33
Intrinsic Viscosity of AM (dl/g)	4.3	3.9	3.6	3.5
Stress at yield (MPa)	38.3	37.4	33.1	31.9
Strain at yield (%)	6.5	6.6	7.7	8.5
Strain at break (%)	130	150	58	58
Tensile modulus (MPa)	2040	2010	1778	1685
Charpy notched, 0°C (kJ/m2)	4.1	5.3	6.7	14
Pipe properties				
Ringstiffness (N/m2)	9169	9197	11260	10590
Tensile modulus (MPa)	2228	2156	1812	1707
Mean wall thickness, mm	3.9	3.95	4.4	4.4
Resistance to external blows, H50 (mm), -10°C	1625	2393	>4000	>4000

[0094] As can be seen from the Table, samples E1 and E2 have an amorphous fraction AM and an ethylene content within the amorphous fraction AM in amounts which are within the ranges as defined above and in the claims. Furthermore, E1 and E2 have an XCS fraction and a total ethylene content within the ranges as defined above and in the claims. As a consequence, a tensile modulus clearly exceeding 2000 MPa could be realized. Furthermore, impact strength of the extruded pipe, expressed as H50 value, could still be maintained on an acceptable level.

[0095] The samples according to comparative examples CE1 and CE2 did not comply with these ranges and had tensile modulus values clearly below 2000 MPa.

Claims

1. A heterophasic polymer composition, comprising

- a matrix comprising a propylene homopolymer and/or a propylene copolymer having an amount of comonomer units of less than 1.0 wt%,
- an elastomeric polypropylene which is dispersed within the matrix and comprises comonomer units derived from ethylene and/or a C4 to C12 alpha-olefin,

the heterophasic polymer composition having an amorphous fraction AM in an amount of 2.0 to 7.5 wt%, and the amorphous fraction AM having an amount of ethylene- and/or C4 to C12 alpha-olefin-derived comonomer units of 20 to 45 wt%.

2. The heterophasic polymer composition according to claim 1, having a xylene cold soluble fraction XCS_{total} in an amount of 3.0 to 8.5 wt%, and/or an amount of ethylene- and/or C4 to C12 alpha-olefin-derived comonomer units of less than 2.0 wt%.

3. The heterophasic polymer composition according to one of the preceding claims, wherein at least 80 wt%, more preferably at least 90 wt% of the matrix are made of the propylene homopolymer.

4. The heterophasic polymer composition according to one of the preceding claims, wherein the matrix has an MFR (230°C, 2.16 kg) within the range of 0.1 g/10 min to 1.5 g/10 min.

5. The heterophasic polymer composition according to one of the preceding claims, wherein the matrix has a xylene cold soluble fraction XCS_{matrix} in an amount of less than 3.0 wt%, more preferably less than 2.0 wt%, even more preferably less than 1.5 wt%.

6. The heterophasic polymer composition according to one of the preceding claims, wherein the amount of the amorphous fraction AM in the heterophasic polymer composition is from 3.0 wt% to 7.5 wt%, more preferably 3.0 wt% to 6.0 wt%.

7. The heterophasic polymer composition according to one of the preceding claims, wherein the amount of ethylene-derived comonomer units in the amorphous fraction AM of the heterophasic polymer composition is from 22 wt% to 35 wt%, more preferably from 23 wt% to 32 wt%.

8. The heterophasic polymer composition according to one of the preceding claims, wherein the elastomeric polypropylene represents at least 60 wt%,

9. The heterophasic polymer composition according to one of the preceding claims, wherein the amount of the xylene cold soluble fraction XCS_{total} in the heterophasic polymer composition is from 3.0 wt% to 7.0 wt%, more preferably 4.0 wt% to 7.0 wt%.

10. The heterophasic polymer composition according to one of the preceding claims, wherein the elastomeric polypropylene represents at least 60 wt%, more preferably at least 65 wt% of the xylene cold soluble fraction XCS_{total} of the heterophasic polymer composition.

11. The heterophasic polymer composition according to one of the preceding claims, wherein the amount of ethylene-derived comonomer units in the heterophasic polymer composition is from 0.8 wt% to less than 2.0 wt%, more preferably from 1.0 wt% to 1.8 wt%.

12. The heterophasic polymer composition according to one of the preceding claims, wherein the amorphous fraction AM of the heterophasic polymer composition has an intrinsic viscosity within the range of 2.0 dl/g to 5.0 dl/g, more preferably 2.5 dl/g to 5.0 dl/g, even more preferably 3.0 dl/g to 4.5 dl/g.

13. A pipe, comprising the heterophasic polymer composition according to one of the claims 1 to 12.

14. The pipe according to claim 13, having a tensile modulus of more than 1900 MPa, more preferably more than 2000 MPa, the tensile modulus being determined by the following formula:

$$\text{tensile modulus} = RS \times 12 \times [(D - t)/t]^3$$

wherein
RS is ring stiffness, determined according to EN ISO 9969,
D is the outer diameter of the pipe in mm, and
t is the wall thickness of the pipe in mm.

15. The pipe according to claim 13 or 14, having a H50 value, determined according to EN 1411 at -10°C, of at least 1100 mm, more preferably at least 1500 mm, even more preferably at least 2000 mm.

16. A process for the preparation of the heterophasic polymer composition according to one of the claims 1 to 12, comprising the following steps:

(i) preparing the propylene homo- or copolymer in at least one loop reactor and optionally in at least one gas phase reactor,
(ii) transferring the propylene homo- or copolymer to at least one gas phase reactor and preparing the elastomeric polypropylene in the presence of the propylene homo- or copolymer.

17. The process according to claim 16, wherein steps (i) and (ii) are carried out in the presence of a Ziegler-Natta catalyst.

18. The process according to claim 16 or 17, wherein step (ii) is carried out in the presence of a compound selected from a glycerol ester, an ethoxylated amine, an ethoxylated amide, carbon monoxide, or any combination thereof.

Patentansprüche

1. Eine heterophasische Polymerzusammensetzung, umfassend

- eine Matrix, umfassend ein Propylenhomopolymer und/oder ein Propylencopolymer, welches weniger als 1,0 Gew.-% Comonomereinheiten aufweist,
- ein elastomeres Polypropylen, welches in der Matrix dispergiert ist und Comonomereinheiten umfasst, welche sich aus Ethylen und/oder einem C4-C12-alpha-Olefin ableiten,

wobei die heterophasische Polymerzusammensetzung einen amorphen Anteil AM von 2,0 bis 7,5 Gew.-% aufweist und der amorphe Anteil AM 20 bis 45 Gew.-% an Comonomereinheiten, die sich aus Ethylen und/oder einem C4-C12-alpha-Olefin ableiten, aufweist.

2. Die heterophasische Polymerzusammensetzung gemäß Anspruch 1, welche einen Xylol kaltlöslichen Anteil XKL_{gesamt} von 3,0 bis 8,5 Gew.-% und/oder weniger als 2,0 Gew.-% an Comonomereinheiten, welche sich aus Ethylen und/oder einem C4-C12-alpha Olefin ableiten, aufweist.

3. Die heterophasische Polymerzusammensetzung gemäß einem der vorstehenden Ansprüche, wobei mindestens 80 Gew.-%, bevorzugter mindestens 90 Gew.-%, der Matrix durch das Propylenhomopolymer gebildet werden.

4. Die heterophasische Polymerzusammensetzung gemäß einem der vorstehenden Ansprüche, wobei die Matrix einen MFI(230°C, 2,16 kg) im Bereich von 0,1 g/10 min bis 1,5 g/10 min aufweist.

5. Die heterophasische Polymerzusammensetzung gemäß einem der vorstehenden Ansprüche, wobei die Matrix einen Xylol kaltlöslichen Anteil XKL_{Matrix} von weniger als 3,0 Gew.-%, bevorzugter weniger als 2,0 Gew.-%, noch bevorzugter weniger als 1,5 Gew.-% aufweist.

6. Die heterophasische Polymerzusammensetzung gemäß einem der vorstehenden Ansprüche, wobei der amorphe Anteil AM in der heterophasischen Polymerzusammensetzung 3,0 Gew.-% bis 7,5 Gew.-%, bevorzugter 3,0 Gew.-% bis 6,0 Gew.-% beträgt.

7. Die heterophasische Polymerzusammensetzung gemäß einem der vorstehenden Ansprüche, wobei der amorphe Anteil AM der heterophasischen Polymerzusammensetzung 22 Gew.-% bis 35 Gew.-%, bevorzugter 23 Gew.-% bis 32 Gew.-% an Comonomereinheiten, die sich von Ethylen ableiten, aufweist.

8. Die heterophasische Polymerzusammensetzung gemäß einem der vorstehenden Ansprüche, wobei das elastomere Polypropylen mindestens 60 Gew.-%, bevorzugter mindestens 65 Gew.-% des amorphen Anteils AM der heterophasischen Polymerzusammensetzung ausmacht.

9. Die heterophasische Polymerzusammensetzung gemäß einem der vorstehenden Ansprüche, wobei der Xylol kaltlösliche Anteil XKL_{gesamt} der heterophasischen Polymerzusammensetzung 3,0 Gew.-% bis 7,0 Gew.-%, bevorzugter 4,0 Gew.-% bis 7,0 Gew.-% beträgt.

10. Die heterophasische Polymerzusammensetzung gemäß einem der vorstehenden Ansprüche, wobei das elastomere Polypropylen mindestens 60 Gew.-%, bevorzugter mindestens 65 Gew.-% des Xylol kaltlöslichen Anteils XKL_{gesamt} der heterophasischen Polymerzusammensetzung ausmacht.

11. Die heterophasische Polymerzusammensetzung gemäß einem der vorstehenden Ansprüche, wobei die heterophasische Polymerzusammensetzung 0,8 Gew.-% bis weniger als 2,0 Gew.-%, bevorzugter 1,0 Gew.-% bis 1,8 Gew.-% an Comonomereinheiten, die sich aus Ethylen ableiten, aufweist.

12. Die heterophasische Polymerzusammensetzung gemäß einem der vorstehenden Ansprüche, wobei der amorphe Anteil AM der heterophasischen Polymerzusammensetzung eine intrinsische Viskosität im Bereich von 2,0 dl/g bis 5,0 dl/g, bevorzugter 2,5 dl/g bis 5,0 dl/g, noch bevorzugter 3,0 dl/g bis 4,5 dl/g aufweist.

13. Ein Rohr, umfassend die heterophasische Polymerzusammensetzung nach einem der Ansprüche 1 bis 12.

14. Das Rohr gemäß Anspruch 13, ein Zugmodul aufweisend von mehr als 1900 MPa, bevorzugter mehr als 2000 MPa, wobei das Zugmodul gemäß der folgenden Formel bestimmt wird:

$$\text{Zugmodul} = RS \text{ x } 12 \text{ x } [(D\text{-}t)/t]^3$$

wobei
RS die gemäß EN ISO 9969 bestimmte Ringsteifheit ist,
D der Aussendurchmesser des Rohrs in Millimeter ist, und
t die Wanddicke des Rohrs in Millimeter ist.

15. Das Rohr gemäß Anspruch 13 oder 14, einen H50-Wert, bestimmt gemäß EN 1411 bei -10°C, von mindestens 1100 mm, bevorzugter mindestens 1500 mm, noch bevorzugter mindestens 2000 mm aufweisend.

16. Ein Verfahren zur Herstellung der heterophasischen Polymerzusammensetzung gemäß einem der Ansprüche 1 bis 12, folgende Schritte umfassend:

(i) Herstellung des Propylenhomo- oder -copolymers in mindestens einem Schleifenreaktor und optional in mindestens einem Gasphasenreaktor,
(ii) Überführen des Propylenhomo- oder -copolymers in mindestens einen Gasphasenreaktor und Herstellung des elastomeren Polypropylens in der Anwesenheit des Propylenhomo- oder -copolymers.

17. Das Verfahren gemäß Anspruch 16, wobei die Schritte (i) und (ii) in der Anwesenheit eines Ziegler-Natta-Katalysators durchgeführt werden.

18. Das Verfahren gemäß Anspruch 16 oder 17, wobei Schritt (ii) in der Anwesenheit einer Verbindung, welche aus einem Glycerinester, einem ethoxylierten Amin, einem ethoxylierten Amid, Kohlenstoffmonoxid oder deren Kombinationen ausgewählt wird, durchgeführt wird.

Revendications

1. Composition polymère hétérophasique comprenant :

- une matrice qui comprend un homopolymère de propylène et/ou un copolymère de propylène présentant une quantité de motifs comonomères inférieure à 1,0 % en poids,
- un polypropylène élastomère qui est dispersé au sein de la matrice et comprend des motifs comonomères dérivés d'éthylène et/ou d'alpha- oléfine en C_4 à C_{12},

la composition polymère hétérophasique présentant une fraction amorphe AM dans une quantité comprise entre 2,0 et 7,5 % en poids, et la fraction amorphe AM présentant une quantité de motifs comonomères dérivés d'éthylène et/ou d'alpha-oléfine en C_4 à C_{12} comprise entre 20 et 45 % en poids.

2. Composition polymère hétérophasique selon la revendication 1, présentant une fraction de matières solubles à froid dans le xylène XCS_{total} dans une quantité comprise entre 3,0 et 8,5 % en poids, et/ou une quantité de motifs comonomères dérivés d'éthylène et/ou d'alpha-oléfine en C_4 à C_{12} inférieure à 2,0 % en poids.

3. Composition polymère hétérophasique selon l'une des revendications précédentes, dans laquelle au moins 80 % en poids, de façon plus préférentielle au moins 90 % en poids, de la matrice sont composés de l'homopolymère de propylène.

4. Composition polymère hétérophasique selon l'une des revendications précédentes, dans laquelle la matrice a un indice de fluidité (MFR) (230 °C, 2,16 kg) dans la gamme allant de 0,1 g/10 min à 1,5 g/10 min.

5. Composition polymère hétérophasique selon l'une des revendications précédentes, dans laquelle la matrice présente une fraction de matières solubles à froid dans le xylène $XCS_{matrice}$ dans une quantité inférieure à 3,0 % en poids, de façon plus préférentielle inférieure à 2,0 % en poids, et de façon encore plus préférentielle inférieure à 1,5 % en poids.

6. Composition polymère hétérophasique selon l'une des revendications précédentes, dans laquelle la quantité de fraction amorphe AM dans la composition polymère hétérophasique est comprise entre 3,0 % en poids et 7,5 % en poids, de façon plus préférentielle entre 3,0 % en poids et 6,0 % en poids.

7. Composition polymère hétérophasique selon l'une des revendications précédentes, dans laquelle la quantité de motifs comonomères dérivés d'éthylène dans la fraction amorphe AM de la composition polymère hétérophasique est comprise entre 22 % en poids et 35 % en poids, de façon plus préférentielle entre 23 % en poids et 32 % en poids.

8. Composition polymère hétérophasique selon l'une des revendications précédentes, dans laquelle le polypropylène élastomère représente au moins 60 % en poids, de façon plus préférentielle au moins 65 % en poids, de la fraction amorphe AM de la composition polymère hétérophasique.

9. Composition polymère hétérophasique selon l'une des revendications précédentes, dans laquelle la quantité de fraction soluble à froid dans le xylène XCS_{total} dans la composition polymère hétérophasique est comprise entre 3,0 % en poids et 7,0 % en poids, de façon plus préférentielle entre 4,0 % en poids et 7,0 % en poids.

10. Composition polymère hétérophasique selon l'une des revendications précédentes, dans laquelle le polypropylène élastomère représente au moins 60 % en poids, de façon plus préférentielle au moins 65 % en poids, de la fraction soluble à froid dans le xylène XCS_{total} de la composition polymère hétérophasique.

11. Composition polymère hétérophasique selon l'une des revendications précédentes, dans laquelle la quantité de motifs comonomères dérivés d'éthylène dans la composition polymère hétérophasique est comprise entre 0,8 %

en poids et moins de 2,0 % en poids, de façon plus préférentielle entre 1,0 % en poids et 1,8 % en poids.

12. Composition polymère hétérophasique selon l'une des revendications précédentes, dans laquelle la fraction amorphe AM de la composition polymère hétérophasique possède une viscosité intrinsèque dans la gamme de 2,0 dl/g à 5,0 dl/g, de façon plus préférentielle de 2,5 dl/g à 5,0 dl/g, et de façon encore plus préférentielle de 3,0 dl/g à 4,5 dl/g.

13. Tuyau, comprenant une composition polymère hétérophasique selon l'une des revendications 1 à 12.

14. Tuyau selon la revendication 13, présentant un module d'élasticité en traction supérieur à 1 900 MPa, de façon plus préférentielle supérieur à 2 000 MPa, le module d'élasticité en traction étant déterminé par la formule suivante :

$$\text{Module d'élasticité en traction} = RS \times 12 \times [(D - t)/t]^3$$

où
RS est la rigidité en anneau, déterminée conformément à EN ISO 9969,
D est le diamètre externe du tuyau, en mm, et
t est l'épaisseur de paroi du tuyau, en mm.

15. Tuyau selon la revendication 13 ou 14, présentant une valeur H50, déterminée conformément à EN 1411 à - 10 °C, au moins égale à 1 100 mm, de façon plus préférentielle au moins égale à 1 500 mm, de façon encore plus préférentielle au moins égale à 2 000 mm.

16. Procédé de préparation de la composition polymère hétérophasique selon l'une des revendications 1 à 12, comprenant les étapes suivantes :

(i) préparation de l'homopolymère ou du copolymère de propylène dans au moins un réacteur à boucle et en option dans au moins un réacteur en phase gazeuse,
(ii) transfert de l'homopolymère ou du copolymère de propylène vers au moins un réacteur en phase gazeuse et préparation du polypropylène élastomère en présence de l'homopolymère ou du copolymère de propylène.

17. Procédé selon la revendication 16, dans lequel les étapes (i) et (ii) sont conduites en présence d'un catalyseur Ziegler-Natta.

18. Procédé selon la revendication 16 ou 17, dans lequel l'étape (ii) est conduite en présence d'un composé sélectionné parmi un ester de glycérol, une amine éthoxylée, un amide éthoxylé, du monoxyde de carbone ou une combinaison quelconque de ceux-ci.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 9924479 A **[0010]**
- EP 1026184 A1 **[0011]**
- EP 1632529 A1 **[0012]**
- EP 0591224 A **[0061]**
- EP 1028985 A **[0066]**
- WO 0068315 A **[0086]**