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(54) Title: POLYMER BLEND HAVING IMPROVED MECHANICAL PROPERTIES

(57) Abstract: A polymer blend has improved mechanical properties and comprises polyethylene (HDPE) and an amorphous polymer. The polyethylene is present in an amount of from 90 to 99.5 weight-% having a density in the range of from 0.943 to 0.965 g/cm³ and the amorphous polymer is present in an amount of from 0.5 to 10 weight-%, based on total weight of the mix. Such polymer blend is suitable for the preparation of blow moulded parts having improved stiffness.



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Polymer blend having improved mechanical properties

The present invention pertains to a polymer blend comprising polyethylene and an amorphous polymer.

HDPE in general has excellent impact properties. However, HDPE has a relatively low stiffness. The stiffness of HDPE can be improved by increasing its crystallinity and thereby its density. But high tensile impact values are only obtained at sufficiently high molecular weights. Thus, the possibility of further increasing the stiffness is limited, because increase of the molecular weight decreases the density in parallel.

In that situation, another solution to increase the stiffness of HDPE was the creation of blends with other polymers. Whilst the volume production of completely new polymers having commercial viability has been small, the development of polymer blends has been highly significant. Of these the most important involve an amorphous resin in combination with a crystalline polymer. When suitably composed, it should be possible to approach rigid compounds with a high degree of toughness, particularly on impact, a combination of properties which tends to be lacking in most polymers.

In some cases the resulting blends are essentially physical mixtures, but often the situation is more complex and involves block or graft copolymers. In most cases, however, the crystalline component forms droplets within a continuous glassy, amorphous matrix resulting in a composition of enhanced toughness, hopefully.

Copolymers containing bicyclic olefins, especially those comprising ethylene-norbornene copolymers, are known in the art. They exhibit properties like high transparency, high heat distortion temperature, low warpage, high resistance towards polar solvents and high stiffness. The term warpage is understood as some curvature or dimensional distortion in the plastic after being processed, particularly when moulded. Warpage is related to material shrinkage and residual stress forced

upon it while being shaped in the mould in a viscous state. However, the copolymer's elongation at break and impact properties are poor.

In contrast to such cyclo-olefin copolymers, polyethylene, especially high density polyethylene (HDPE), has a relatively high impact strength combined with high warpage, but lower stiffness, expressed as E-modulus.

Blends or mixtures of polyethylene and copolymers made from cyclic olefins in order to generate resins with new property profiles are also known and described in literature.

DD 214 137 describes a polymer resin mainly based on a mixture of polyethylene and an ethylen-norbornen copolymer comprising a good balance of stiffness and impact properties.

DE 42 13 219 describes a polymer blend system consisting of at least one polyolefin, at least one copolymer containing cyclic olefins and a block-copolymer. The former copolymer was prepared by using metallocene catalysis.

JP1318052 describes a blend system consisting of 40 to 98 wt.-% of polyolefin being crystalline and 2 to 60 wt.-% copolymer containing cyclic olefins with a glass transition temperature T_g from 70 to 210 °C and a crystallinity of from 0 to 5 % having improved thermoforming behaviour and reduced shrinkage.

The combination of cyclo-olefin copolymers and polyethylene is well known in literature. [J. Kolařík, *Polymer engineering and science* 2005, p.817-826] described that cyclo-olefin copolymers may be used to be mixed with HDPE and improve the stiffness of polyethylene. However, mixing of cyclo-olefin copolymers with polyethylene reduces significantly the cold temperature impact properties in parallel. In addition, the blends described by that publication start with 10 weight-% COC and end up with 75 weight-% COC in the mix. A further disadvantage of blends

containing cyclo-olefin copolymers are the relatively high costs in comparison to the costs of polyethylene.

It was therefore the object of the present invention to increase the stiffness of thermoplastic HDPE, expressed as its E-modulus, especially that of high molecular weight HDPE, however, without reducing the HDPE's tensile impact properties too much.

Surprisingly, it has been found that a low amount of amorphous polymer (component B) in the range of up to 10 weight-% in maximum mixed with polyethylene (component A) is sufficient to obtain an excellent property balance, whereby polyethylene having a high density of more than $0,943 \text{ g/cm}^3$ is used as polyethylene component. The thus obtained blends show unique combination of cold temperature impact strength and high stiffness. Further the processability can be improved significantly by increased melt strength.

As an "amorphous polymer" the type of resin is addressed in which the molecular chains exist in random coil conformation. In the amorphous polymer no regularity of structure is to be observed, as it is with crystalline thermoplastic polymers. With other words, the structure of an amorphous polymer is characterized by the absence of a regular three-dimensional arrangement of molecules or subunits of molecules extending over distances that are large compared to atomic dimensions. The use of the term "amorphous polymer" implies that the plastic material is amorphous in the solid state, as long as all thermoplastic polymers are amorphous in solution or melt, as a matter of course.

The invention is especially useful for blow moulding applications. However, also other applications like injection moulding, film blowing or pipe extrusion can be performed advantageously. Using the blow moulding technology, the preparation of fuel tanks for motor bicycles driven by combustion engines is one of the most preferred applications of the instant invention.

The polymer blend according to the instant invention comprises the following components A) and B):

Component A)

HDPE present in an amount of from 90 to 99.5 weight-%, preferably from 95 to 99.5 weight-%, having a density in the range of from 0.943 to 0.97 g/cm³, preferably from 0.95 to 0.965 g/cm³. The suitable HDPE has a HLMFR value (21.6 kg/190°C/ISO 11833) of from 0.5 to 40 g/10 min, preferably from 1 to 20 g/10 min.

Such HDPE is available usually by polymerization of ethylene or co-polymerization of ethylene together with other olefinic co-monomers in the presence of suitable catalysts like Ziegler or Phillips catalysts or metallocene catalysts in suspension or in gas phase and they are also addressed sometimes as low pressure PE. As co-monomers for the ethylene, other homologue olefins are suitable comprising from 3 to 10 carbon atoms, such as 1-propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene and 1-decene. The co-monomers may be present during the polymerization of the ethylene in an amount of from 1 to 8 % by weight, preferably from 2 to 7 % by weight, calculated on total weight of the monomers present in the reaction mix.

Component B)

Amorphous polymer such as atactic polystyrene (PS) having a glass transition temperature T_g in the range of from 70 to 110 °C, measured according to DIN EN ISO 11357-1 by means of DSC at a heating rate of 10 K/min, and a density of about 1.05 g/cm³ or polymethylstyrene (PMS) having a T_g of up to 115 °C or styrene-acrylonitrile copolymers (SAN) having a T_g of from 100 to 110 °C and a density of from 1.05 to 1.1 g/cm³ or grafted acrylonitrile-butadiene-styrene copolymer (ABS) having a T_g of from 85 to 105 °C and a density of from 1.03 to 1.08 g/cm³ or polymethylmethacrylate (PMMA) having a T_g of from 80 to 115 °C and a density of from 1.12 to 1.18 g/cm³ or cyclo-olefin copolymers (COC) containing preferably norbornene units as an essential ingredient having a T_g of above 50 °C and a density of from 0.95 to 1.15 g/cm³.

The amorphous polymers are present according to the instant invention in an amount of from 0.5 to 10 weight-%, preferably from 1.5 to 5 weight-%, based on total weight of the blend.

Preferred amorphous polymers of component B) are cyclo-olefin copolymers having a glass transition temperature T_g of above 60 °C. More preferred are cyclo-olefin copolymers comprising norbonene or tetracyclododecene or vinylnorbonene in combination with ethylene units. Also possible are ter-polymers comprised of ethylene/norbonene/vinylnorbonene or ethylene/tetracyclododecene/vinylnorbonene or ethylene/norbonene/dicyclopentadiene. Such coclo-olefin copolymers or terpolymers show viscosity numbers (VN) according to DIN 53 728 in the range of from 5 to 5000 ml/g, preferably from 5 to 2000 ml/g. The density of the coclo-olefin copolymers ranges from 0.96 to 1.1 g/cm³.

Optionally reinforcement fillers like inorganic particles based on calcium carbonate, silicon dioxide or barium sulfate or glass fibres and other additives such as heat stabilizers or UV-stabilizers or flame retardants can be added in respective suitable amounts.

Working Examples

The cyclo-olefin copolymer *TOPAS 9506F-04*[®] was received from *TOPAS Advanced Polymers* (Frankfurt/M.). Such *TOPAS 9506F-04*[®] has a density of 1.02 g/cm³ and a MFR-value of 1.0 (190°C/ 2,16 kg) according to ISO1183.

Used polyethylenes:

The properties of *Lupolen 5261Z H*, *Histif 5431I* and *Lupolen 4261A IM* all of them received from Basell Polyolefine GmbH, Germany, are indicated in Table 1, 2 and 3 respectively.

The blends were prepared by using a Berstorff ZE25 extruder having a screw diameter of 2 x 25 mm and a screw length of 2 x 825 mm (33 x D).

Cold temperature tensile impact strength (AZK) (Type 1, Method A, -30 °C) was measured according to ISO 8256.

The tensile (E) modulus at 23 °C was measured according to ISO527-1.

The density was measured according to ISO 1183, whereas the HLMFR (high load melt flow rate/ 21.6 kg/190°C) was determined according to ISO1133.

Example 1 (inventive)

Table 1

<i>LP5261Z HI</i> [wt-%]	<i>TOPAS 9506F -04</i> [wt-%]	HLMFR [g/10 min]	Density [g/cm ³]	E-Modulus [MPa]	AZK(-30°C) [kJ/m ²]
100	0	1,7	0,954	1250	237
99	1	1,9	0,954	1374	220
95	5	1,9	0,957	1465	190
90	10	2,2	0,959	1465	163

Table 1 shows the results of blends of HDPE *Lupolen5261Z HI* and *TOPAS 9506F-04* in different amounts, whereas table 2 shows the results of blends of HDPE *Histif5431* and *TOPAS 9506F-04*.

The E-Modulus of HDPE blends containing only low amounts of up to 10 weight-% of cyclo-olefin copolymer were significantly increased while showing a still very high cold temperature tensile impact.

Example 2 (inventive)

Table 2

<i>Histif5431</i> [wt-%]	<i>TOPAS9506F -04</i> [wt-%]	HLMFR [g/10 min]	Density [g/cm ³]	E-Modulus [MPa]	AZK(-30°C) [kJ/m ²]
100	0	2,4	0,954	1250	285
97,5	2,5	2,3	0,956	1373	247

In contrast to the above described observations blends of *Topas 9506F-04* with *Lupolen 4261A IM* did not show a noteworthy increase of the E-modulus at low amounts of COC in the blend but only a decrease in cold temperature impact AZK (see example 3).

Example 3 (comparison)

Table 3

<i>LP4261A IM</i> [wt-%]	<i>TOPAS9506 -04</i> [wt-%]	HLMFR [g/10 min]	Density [g/cm ³]	E-Modulus [MPa]	AZK(-30°C) [kJ/m ²]
100	0	14	0,940	800	153
95	5	14	0,941	805	130

The comparison example shows that the density of the polyethylene employed for the blend with the cyclo-olefin copolymer should be preferably higher than 0.943 g/cm³ according to the instant invention.

* * * * *

Claims:

1. Polymer blend comprising polyethylene having a density in the range of from 0.943 to 0.97 g/cm³ and an amorphous polymer, wherein the polyethylene is present in an amount of from 90 to 99.5 weight-% and the amorphous polymer is present in an amount of from 0.5 to 10 weight-%, based on total weight of the mix.
2. Polymer blend according to claim 1, wherein the polyethylene having a density in the range of from 0.95 to 0.965 g/cm³ is present in an amount of from 95 to 99.5 weight-% and the amorphous polymer is present in an amount of from 0.5 to 5 weight-%, based on total weight of the mix.
3. Polymer blend according to claim 1 or 2, wherein the polyethylene has a HLMFR value (21.6 kg/190°C) of from 0.5 to 40 g/10 min, preferably from 1 to 20 g/10 min.
4. Polymer blend according to claim 1 or 2, wherein the amorphous polymer is selected from the group comprising polystyrene, polymethylstyrene, styrene-acrylonitrile copolymer, grafted acrylonitrile-butadiene-styrene copolymer, polymethylmethacrylate or cyclo-olefin copolymers.
5. Polymer blend according to claim 1 or 2, wherein the amorphous polymer is a cyclo-olefin copolymer comprising norbornene units and has a glass transition temperature T_g of above 50 °C, preferably of above 60 °C.
6. Polymer blend according to claim 1 or 2, wherein the amorphous polymer is a cyclo-olefin copolymer having a viscosity number (VN) in the range of from 5 to 5000 ml/g, preferably from 5 to 2000 ml/g.

7. Polymer blend according to claim 1 or 2, wherein the amorphous polymer is a cyclo-olefin copolymer having a density of from 0.96 to 1.1 g/cm³.
8. Polymer blend according to any of claims 1 to 7 showing increased E-Modulus of more than 1300 MPa, while showing still high cold temperature tensile impact strength of more than 150 kJ/m².
9. Use of a polymer blend according to any of claims 1 to 8 for the preparation of blow moulded articles.
10. Use according to claim 9, wherein the blow moulded articles are plastic fuel tanks for motor bicycles driven by combustion engine.

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/001923

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08L23/06

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	claims 1,4,7,10,11,12,19 paragraphs [0009], [0010], [0066]	1-10
Y	US 2006/173123 A1 (YANG HENRY W [US] ET AL) 3 August 2006 (2006-08-03) paragraphs [0002], [0004], [0005], [0007] claims 1,62	1-10
Y	US 5 460 818 A (PARK CHUNG P [US] ET AL) 24 October 1995 (1995-10-24) claims 1,7,19 column 1, line 18 - line 21 column 6, line 23 column 8, line 32 - line 38 -/-	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/001923

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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