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(71) Applicant: THE CHEMOURS COMPANY FC, LLC
[US/US]; 1007 Market Street, Wilmington, DE 19801 (US).

(72) Inventors: WYSONG, Ernest, Byron; 30 Tall Oaks Drive, Hockessin, DE 19707 (US). CREAZZO, Joseph, Anthony; 5 Quail Court, Wilmington, DE 19810 (US). HITCHENS, Bruce, P; 336 Shagbark Ct., Bear, DE 19701 (US). KONTOMARIS, Konstantinos; 702 Abbey Road, Wilmington, DE 19808 (US).

(74) Agent: LEACH, Douglas, R.; 1007 Market Street, Patent Legal Group, 7028-1, Wilmington, DE 19801 (US).

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(54) Title: FOAMING OF STYRENE POLYMER

(57) Abstract: The present invention is a process for foaming thermoplastic polymer comprising polystyrene, said process comprising forming a molten foamable composition comprising said thermoplastic polymer, block copolymer, and blowing agent comprising at least one of Z-1,1,1,4,4,4 hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene and expanding said foamable composition to obtain as a result thereof foamed thermoplastic polymer, the process being preferably carried out by extruding the composition in molten form, whereupon the foaming of the thermoplastic polymer occurs.

TITLE**FOAMING OF STYRENE POLYMER****BACKGROUND INFORMATION****Field of the Disclosure**

5 This invention relates to the foaming of styrene polymer, wherein the blowing agent comprises HFO-Z-1336mzz.

Description of the Related Art

WO 2008/1118627 discloses the desire for hydrofluorocarbon blowing agents to have both low ODP (oxygen depletion potential) and GWP (global warming potential). This publication discloses a number of such blowing agents that have an ODP of zero and GWP of less than 50 and which have solubility in alkenyl aromatic polymers, especially polystyrene. HFO-1,1,1,4,4,4-hexafluoro-2-butene is one of the blowing agents disclosed that exhibits these ODP and GWP characteristics. It is known that HFO-1,1,1,4,4,4-hexafluoro-2-butene exists in two isomeric forms, the Z(cis)-isomer and the E(trans)-isomer.

WO 2007/084665 discloses a block copolymer compatibilizer having a first block that is functionally compatible with the thermoplastic resin being foamed, and a second block that is functionally compatible with the blowing agent. In the second full paragraph on p. 5 of this publication, these compatibility aspects are explained in terms of polystyrene being the resin to be foamed, i.e. the block copolymer containing polystyrene for compatibility with the resin and poly(butyl acrylate) for compatibility with HFC-134a blowing agent. Compatibility with the HFC-134a blowing agent is further explained in terms of acrylate polymers being soluble in HFC-134a.

SUMMARY

As part of the present invention, it has been discovered that both Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene are highly insoluble in molten polystyrene. It has also been discovered that block copolymer increases the solubility of these Z- and E-isomers in

molten polystyrene even though these isomers are highly insoluble in the block copolymer.

The insolubility of the Z- and E-isomers by themselves in molten polystyrene can be expressed as the absorption of the isomer in the

5 molten polystyrene. Any absorption of the isomer by the molten polystyrene is measured as weight gain by the polystyrene. Only a very small amount of the isomer is absorbed by the molten polystyrene as indicated by its weight gain being no greater than 8 wt% based on the original weight of the polystyrene by itself and much less as described

10 hereinafter.

These discoveries are embodied in the present invention, which can be described in one embodiment as a process for foaming thermoplastic polymer comprising polystyrene, said process comprising forming a molten foamable composition comprising said thermoplastic polymer,

15 block copolymer, and blowing agent comprising at least one of Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene, and expanding said foamable composition to obtain as a result thereof foamed thermoplastic polymer.

The molten foamable composition is preferably in an extruder and the

20 expanding of the molten foamable composition is the result of extruding said composition. Thus the process of the present invention can also be described by the preferred embodiment wherein the process comprises extruding the molten foamable composition comprising molten thermoplastic polymer comprising polystyrene, block copolymer, and

25 blowing agent comprising at least one of Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene to obtain as a result thereof foamed thermoplastic polymer.

In both these embodiments, preferred aspects are as follows:

The block copolymer is non-polar. By non-polar is meant that the

30 polarity of the block copolymer is no greater than 1.0 D (Debye). This is in contrast to the poly(butylacrylate)-containing block copolymer of WO 2007/084665, which is polar. By polar is meant that the polarity of the block copolymer is at least 2.0 D. The blowing agent HFC-134a is also polar, in exhibiting a polarity of greater than 2.0 D. In contrast, for

example, E-1,1,1,4,4,4-hexafluoro-2-butene is non-polar, in exhibiting a polarity of less than 1.0 D.

The amount of the block copolymer present in the molten thermoplastic polymer composition is 5 to 15 wt%, based on the weight of 5 the foamable composition, which includes the weight of said thermoplastic polymer, Z-1,1,1,4,4,4-hexafluoro-2-butene and/or E-1,1,1,4,4,4-hexafluoro-2-butene blowing agent, and block copolymer and additives.

The insolubility of the Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene isomers in the molten thermoplastic 10 polymer is such that the absorption (weight gain) of these isomers in the molten thermoplastic polymer by itself is no greater than 6.0 wt% for the Z-isomer and no greater than 3 wt% for the E-isomer, based on the weight of the foamable composition.

The block copolymer is insoluble in the Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene. The Z- and E-isomers are 15 highly insoluble in the block copolymer as further described hereinafter.

The thermoplastic polymer comprises polymerized units, at least 60 mol% of which are derived from polymerizing styrene.

These preferred aspects may be used individually or in any 20 combination in the practice of the present invention.

DETAILED DESCRIPTION

The thermoplastic polymer being foamed according to the present invention comprises polystyrene. The polystyrene can be styrene homopolymer or can contain copolymerized monomer other than styrene. 25 The thermoplastic polymer can also be a blend of polystyrene with other thermoplastic polymer. The other thermoplastic polymer can also be a copolymer of styrene with monomer other than styrene. A preferred monomer other than styrene is acrylonitrile. Preferably any copolymer present in the thermoplastic polymer comprising polystyrene is a random 30 or alternating copolymer, not a block copolymer.

Whether the thermoplastic polymer being foamed is polystyrene or blends of polystyrene with other thermoplastic polymer, styrene is preferably the dominant polymerized monomer (unit) in the thermoplastic

polymer being foamed. More preferably, the polymerized units of styrene constitute at least 70 mol % or at least 80 mol% or at least 90 mol% or at least 100 mol% of the polymerized monomer units making up the thermoplastic polymer being foamed.

5 When the thermoplastic polymer contains styrene copolymer, the amount of other monomer copolymerized with the styrene, is such that the styrene content of the copolymer is at least 60 mol% of the copolymer, preferably at least 70 mol%, or at least 80 mol% or at least 90 mol% of the copolymer, based on the total mols (100%) making up the copolymer. This
10 applies whether the styrene copolymer is the only styrene-containing polymer in the thermoplastic polymer or is a blend with other thermoplastic polymer, such as styrene homopolymer or other styrene copolymer.

Preferably, the thermoplastic polymer being foamed is entirely polystyrene homopolymer. When the thermoplastic polymer being foamed
15 is a blend of polystyrene and other thermoplastic polymer as described above, the polystyrene component of this blend is preferably styrene homopolymer constituting at least 80 wt% of the combined weight of polystyrene and other thermoplastic polymer.

The molecular weight of the thermoplastic polymer being foamed is
20 sufficiently high to provide the strength necessary for the requirements of the foam application. Preferably, the Young's modulus of this thermoplastic polymer is at least 15 MPa or this polymer exhibits a melt flow rate of 1 to 50 g/10 min as determined in accordance with ASTM D 1238 at 200°C and using a 5 kg weight on the molten polymer.

25 The block copolymer used in the present invention comprises a polymer chain formed from of two or more segments of different homopolymers in the polymer chain. The different homopolymers can be two different homopolymers (diblock), three different homopolymers (triblock) or more than three (multiblock) different homopolymer segments.
30 Preferably one of the homopolymer segments is polystyrene. Preferably the other homopolymer segments are at least one of butadiene, butylene, acrylonitrile, ethylene, and isoprene. To exhibit the characteristic of being non-polar, the block copolymer is preferably free of poly(butyl acrylate) segments.

In one embodiment, the amount of block copolymer present in the composition is 6 to 14 wt%. In another embodiment, the amount of block copolymer in the composition is from 7 to 14 wt%. In yet another embodiment, the amount of block copolymer in the compositions is from 7 to 13 wt%. As the amount of block copolymer increases from 13 wt%, the properties of the foamed composition begins to suffer, which is the reason for not exceeding 15 wt% block copolymer in the foamable composition. These amounts of block copolymer are based on the total weight of the foamable composition.

10 The blowing agent comprising at least one of Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene can also contain additional ingredients, such as foam cell nucleating agent such as talc and/or co-blowing agent, that are often used in blowing agents for foaming polystyrene. When co-blowing agent is present, the Z-isomer and/or E-isomer content of the blowing agent is preferably at least 50 wt%, more preferably at least 60 wt% or at least 70 wt%, or 80 wt% or at least 90 wt% or at least 100 wt% of the total weight of the blowing agent. The use of co-blowing agent along with E-isomer blowing agent is preferred because of the low solubility of the E-isomer in molten polystyrene. The co-blowing agent should have greater solubility in the molten polystyrene. Examples of co-blowing agent include dimethyl ether and dichloroethylene.

20 The amount of the Z-isomer, E-isomer, or the combination of Z-and E-isomers in the foamable composition will depend on the density desired upon foaming. Preferably, the amount is effective to obtain a foamed density of at least 30 kg/m³. Generally the amount of blowing agent, preferably being the Z-isomer, the E-isomer, or the combination thereof, will be from 10 to 25 wt% based on the weight of the foamable composition.

25 The process of the present invention is preferably carried out using an extruder to form the molten foamable composition and to extrude it to form the foamed product. The thermoplastic polymer comprising polystyrene forms the feed to the extruder. The blowing agent is preferably fed into the extruder at a location intermediate the feed and extrusion ends of the extruder, typically into the molten foamable composition that is created as 30 the extrusion screw advances the feeds to the extruder along its length.

The other additives to the molten composition are added where convenient and as may be dictated by the state of the additive. For example, solid additives can be conveniently be added to the feed end of the extruder, possibly as a mixture with the polymer feed in particulate form to the extruder. The molten composition within the extruder is extruded through a die, thereby allowing the foamable composition to expand into a foamed product. The foamed product, which can be in such forms as sheet, plank, rod or tube, is then cooled.

As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus.

15 The transitional phrase "consisting of" excludes any element, step, or ingredient not specified. If in the claim, such would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase "consists of" appears in a clause of the body of a claim, rather than immediately following the

20 preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole. The transitional phrase "consisting essentially of" is used to define a composition, method that includes materials, steps, features, components, or elements, in addition to those literally disclosed provided that these additional included

25 materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention, especially the mode of action to achieve the desired result of any of the processes of the present invention. The term 'consisting essentially of' occupies a middle ground between "comprising" and 'consisting of'.

30 Where applicants have defined an invention or a portion thereof with an open-ended term such as "comprising," it should be readily understood that (unless otherwise stated) the description should be interpreted to also include such an invention using the terms "consisting essentially of "or "consisting of."

EXAMPLES

Solubility of Z-1,1,1,4,4,4-hexafluoro-2-butene (Z-1336mzz) and E-1,1,1,4,4,4-hexafluoro-2-butene (E-1336mzz) in molten polystyrene is determined by the following procedure: 78 grams of polystyrene is loaded into a 125 cc stainless steel Parr® reactor. The reactor is weighed, mounted to inlet/outlet piping and immersed in an oil bath. An HIP pressure generator (made by High Pressure Equipment Company) is used to load an excess amount of blowing agent into the reactor after it is evacuated. The oil bath is heated to the final temperature (179 °C), at which temperature the polystyrene becomes molten, in about 90 minutes and is kept at the temperature for 30 minutes. The final pressure is recorded, this pressure being analogous to the pressure encountered in an extruder when used in the foaming process. The Parr® reactor is removed from the oil bath and cooled down to room temperature. The reactor (with re-solidified polystyrene inside) is weighed after excess (non-dissolved in the polystyrene) blowing agent is vented (E-isomer)/drained (Z-isomer). The weight gain is recorded as solubility according to the following equation:

$$\text{Solubility (wt\%)} = (\text{weight gain} \div 78) \times 100$$

Solubility of the combination of Z-1,1,1,4,4,4-hexafluoro-2-butene and/or E-1,1,1,4,4,4-hexafluoro-2-butene in molten polystyrene plus block copolymer is determined by the same procedure, except the block copolymer is present.

Solubility of the combination of E-1,1,1,4,4,4-hexafluoro-2-butene and co-blowing agent is determined by the same procedure except the co-blowing agent is present in the reactor.

Low weight gain is indicative of the insolubility of the isomer in the molten polystyrene. The weight (wt%) gains by the molten polystyrene reported herein are based on the original weight of the polystyrene.

Solubility of the Z- or E-isomer in the block copolymer is determined by measuring the absorption (weight gain) of the isomer by the block copolymer. The procedure for this measurement is as follows: 10.00 grams of the block copolymer are added to a 100 cc glass bottle with lid. The bottle, lid and contents are weighed, and then 20.00g of blowing

agent (Z-isomer or E-isomer) are added, mixed thoroughly, and allowed to sit for 24 hours at under the conditions described below, wherein the blowing agent is in the liquid state. After this time, the copolymer solids are filtered and weighed after excess agent was vented (E-isomer)/drained (Z-isomer). The weight gain is recorded as solubility according to the following equation:

$$\text{Solubility (wt\%)} = (\text{weight gain} \div 10) \times 100.$$

Low weight gain is indicative of the insolubility of the isomer in the block copolymer.

10 For the Z-isomer, which boils at 33°C (one atm. pressure), the soaking is carried out at ambient temperature (15-25°C). For the E-isomer, which boils at 7.5°C (one atm. pressure), the soaking is conducted at 0°C.

15 The weight (wt%) gains (solubility in block copolymer) reported for the absorption of isomer by the block copolymer are also applicable to the thermoplastic polymer comprising polystyrene as described above.

Example 1 - Solubility of 1,1,1,4,4,4-hexafluoro-2-butene in Block Copolymer

The following block copolymers were tested:

1. polystyrene/ethylene ran-butylene available as SA 432431 from Sigma-Aldrich Co. LLC
2. polystyrene/isoprene/butylene (ps content 19 wt%) available as D1171 P from Kraton Polymers LLC
3. polystyrene/isoprene/butylene (ps content 30 wt%) available as FG 1901 from Kraton Polymers LLC

25 All of these copolymers are non-polar, exhibiting a polarity of less than 1.0 D.

These copolymers in powder form were soaked in liquid Z-1,1,1,4,4,4-hexafluoro-2-butene according to the procedure described above. After soaking, all of the copolymers exhibited a weight gain as reported in 30 Table 1.

Table 1- Copolymer Solubility

Copolymer	Weight Gain (g)
1	0.32
2	0.28
3	0.20

The largest weight gain was 3.2 wt% (calculation: (0.32/10) X 100).

The fact that there was no weight loss indicates completely insolubility of the block copolymer in the Z-isomer. The same was true for the E-isomer.

5 Preferably, in the practice of the present invention, the weight gain by either the E-isomer or the Z-isomer will be no greater than 5 wt% of the weight of the block copolymer by itself.

Example 2 – Solubility in Molten Styrene Polymer

10 The solubility of Z-1336mzz in molten polystyrene was determined according to the procedure described above and found to be 5.7 wt%.

The solubility of E-1336mzz in molten polystyrene was determined according to the procedure described above and found to be 2.4 wt%. No block copolymer is present in the solubility determinations. Solubility of these isomers in molten polystyrene is substantially insensitive to 15 pressure. For example, solubility in molten polystyrene increases from 2.1 wt% at 800 psig (5.5 MPa) to 2.6 wt% at 2600 psig (17.9 MPa).

20 Addition of 10 wt% of block copolymer 2 to the composition that is melted to form the molten polystyrene gives the solubility results reported in Table 2. This 10 w% addition is based on the weight of the foamable composition.

Table 2 – Improvement in Isomer Solubility

Isomer	Solubility (wt%)
Z	7.9
E	3.2

25 The presence of the block copolymer in the molten polystyrene increases the solubility of the Z- and E-isomers by at least 33%. The pressures existing during the heating of the composition range from 2576 psia (17.6 MPa) to 2770 psia (18.9 MPa)

When copolymer 2 is replaced by copolymer 1 in the same amount and the pressure is 2544 psia (17.4 MPa), the resultant solubility of the Z-isomer is 6.8 wt%.

When copolymer 2 is replaced by copolymer 3 in the same amount
5 and the pressure is 2521 psia (17.2 MPa), the resultant solubility of the Z-isomer is 6.8 wt%.

Example 3 – Addition of Co-blown Agent

Dimethyl ether (DME) is the co-blown agent used in this Example. DME is 16.9 wt% soluble in molten polystyrene at 178°C and 1325 psia (9.1 MPa). The arithmetic mean of this solubility and the solubility (2.4 wt%) of E-1336mzz is 9.7 wt%. The actual solubility of a 50:50 weight mixture of the E-isomer and DME is 11.9 wt%, which is greater than expected from the mixture. The solubility of a 87.5:12.5 weight mixture of E-133mzz and DME at 1500 psia was 6.2 wt % compared to a weighted 15 average solubility of the pure components of 4.3 wt %.

The solubility of neat Z-1336mzz, neat dimethyl ether (DME) and of a Z-1336mzz/DME (87.5/12.5wt%) blend in polystyrene homopolymer (with Melt Flow Index of about 5.0) was measured at 179 °C at 1,500 psia according to the method described above. The solubilities of neat HFO-20 1336mzz(Z) and neat DME were, based on the measurements, 5.5 and 17.9 wt%, respectively. The HFO-1336mzz(Z)/DME (87.5/12.5wt%) blend solubility expected as a weight-fraction weighted average of the solubilities of its neat components would be 7.1 wt%. Surprisingly, the 25 measurements revealed that the HFO-1336mzz(Z)/DME (87.5/12.5wt%) blend solubility at 179 °C and 1,500 psia was 10.2 wt%, i.e. significantly higher than expected.

Example 4 – Solubility of Blends with block copolymers

The solubility of Z-1336mzz and a blend of Z-1336mzz and DME (87.5/12.5 wt %) was determined as described above, at a temperature of 30 179°C at 3000 psia in polystyrene homopolymer (MFI 5) and in polystyrene with 10 wt % (polystyrene/iosoprene/butylene) block copolymer (block copolymer 3). Results are summarized in Table 3, below.

Table 3

Blowing Agent	Polymer	Solubility (wt%)
HFO-1336mzz(Z) neat	Polystyrene Homopolymer (with a MFI of about 5)	5.9
HFO-1336mzz(Z)/DME (87.5/12.5 wt%)	Polystyrene Homopolymer (with a MFI of about 5)	12.8
HFO-1336mzz(Z)/DME (87.5/12.5 wt%)	Blend of 90 wt% Polystyrene Homopolymer (with a MFI of about 5) with 10 wt% {Polystyrene(19 wt%)/Isoprene/Butylene} block copolymer (D1171 P from Kraton Polymers)	14.9

Example 5 – Foaming of Polystyrene

The composition being foamed is formed in a twin screw extruder and the foaming occurs upon the composition being extruded.

5 The extruder is a 30 mm twin screw (ZSK-30) extruder equipped with heaters heating the extruder shell to 200°C through a melting zone, followed by the shell temperature decreasing stepwise from 200°C to 180°C, then from 180°C to 160°C, from 160°C to 140°C, then from 140°C to 120°C, then from 120°C to 110°C, and finally at the 5/16 in (0.79 cm)

10 diameter circular orifice, from 110°C to 100°C. The polystyrene used has a melt flow rate of 6 g/10 min (ASTM D 1238 at 200C and 5 kg weight) and is available as Styrosolution© 1600 from Nova Chemicals. The blowing agent is the described below and is fed into the zone within the extruder where the polystyrene is molten. The rate of feed corresponds to the

15 composition desired within the extruder, i.e. 15 wt% of blowing agent. The block copolymer is copolymer 2 described above and is fed as a mixture with the polystyrene to the extruder. The amount of block copolymer is 10 wt% based on the total weight of the composition within the extruder, including the weight of blowing agent. Included in the mixture is 0.5 wt%

20 talc as a nucleating agent for the foam, based on the total weight of the composition within the extruder, including blowing agent. The pressure within the extruder at the extrusion orifice is 1355 psia (9.3 MPa). The foaming of the composition occurs upon the release of the composition from the pressure within the extruder, as the composition exits the

25 extruder orifice. A smooth foamed extrudate is obtained having a density of 6.5 lb/ft³ (195 kg/m³).

The results of extrusion foaming are as follows: A smooth foamed extrudate is obtained when the blowing agent is Z-isomer when the block

copolymer is present in the foamable composition. The same is true when the blowing agent is a 70:30 weight mixture of the E-isomer/trans-1,2-dichloro- ethylene. The smoothness of the foamed extrudate indicates improved solubility of the blowing agent provided by the presence of the 5 block copolymer in the foamable composition. In contrast when the block copolymer is not added to (present in) the foamable composition, the surface of the extruded foamed extrudate is rough. Similar results are obtained when block copolymers 1 and 3 are substituted for copolymer 2.

CLAIMS

What is claimed is:

1. Process for foaming thermoplastic polymer comprising polystyrene, said process comprising forming a molten foamable composition comprising said thermoplastic polymer, block copolymer, and blowing agent comprising at least one of Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene and expanding said foamable composition to obtain as a result thereof foamed thermoplastic polymer.
- 10 2. The process of claim 1 wherein said molten foamable composition is in an extruder and said expanding is the result of extruding said composition.
3. The process of claim 1 wherein said block copolymer is non-polar.
4. The process of claim 1 wherein the amount of said block copolymer present in said composition is 5 to 15 wt%, based on the weight of said foamable composition.
- 15 5. The process of claim 1 wherein said Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene are highly insoluble in said molten thermoplastic polymer as indicated by a weight gain of no greater than 8 wt%
- 20 6. The process of claim 1 wherein said block copolymer is insoluble in said Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene.
7. The process of claim 1 wherein said Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene are highly insoluble in said block copolymer as indicated by a weight gain of no greater than 5 wt%.
- 25 8. The process of claim 1 wherein said thermoplastic polymer comprises polymerized monomer units, at least 60 mol% of which are styrene.
- 30 9. The process of claim 1, wherein said blowing agent comprises at least one of Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-

hexafluoro-2-butene and a co-blowing agent selected from the group consisting of dimethyl ether and trans-1,2-dichloroethylene.

10. A foam product comprising: a polymer matrix comprising a thermoplastic material selected from the group consisting of 5 polystyrene, polystyrene copolymers, and blends of polystyrene with other thermoplastic polymers, a block copolymer, and a blowing agent comprising at least one of Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene, defining a plurality of cells having an average cell size, having a density of less than 50 kg/m².
- 10 11. The composition of claim 9, wherein the thermoplastic material is polystyrene.
12. The composition of claim 9, wherein the block copolymer is a non-polar block copolymer.
13. The composition of claim 12, wherein the block copolymer is a 15 diblock or triblock copolymer of styrene and at least one of butadiene, butylene, acrylonitrile, ethylene, and isoprene.
14. The composition of claim 9, wherein the amount of said block copolymer present in said composition is 5 to 15 wt%, based on the weight of said foam product composition.
- 20 15. The composition of claim 9, wherein the blowing agent is from 10% to 25% by weight of said foam product composition.
16. The composition of claim 15, where the blowing agent comprises Z-1,1,1,4,4,4-hexafluoro-2-butene.
17. The composition of claim 16, wherein the blowing agent comprises a 25 mixture of the Z- and the E- isomers and wherein the Z- isomer comprises more than 50% of said blowing agent.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/031052

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08J9/00 C08J9/14 C08L25/04 C08L53/00
 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)
C08J 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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/118627 A2 (DOW GLOBAL TECHNOLOGIES INC [US]) 2 October 2008 (2008-10-02) cited in the application page 3, line 21 - page 6, line 7 page 7, line 25 - page 9, line 26 page 15, line 13 - page 16, line 32 ----- X WO 2015/197152 A1 (CLARIANT INT LTD [CH]) 30 December 2015 (2015-12-30) page 2, line 4 - page 3, line 4 page 6, line 4 - line 22 page 7, line 9 - page 8, line 23 page 9, line 14 - page 11, line 33 page 12, line 18 - line 31 page 15, line 26 - page 16, line 29 page 16, line 31 - page 20, line 2 -----	1-17 1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
7 June 2017	20/06/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Lichau, Holger

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/031052

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