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(57) Abstract: A method for manufacturing a thermoformed polyetherimide / poly(biphenyl ether sulfone) foam article which comprises following three steps: Step 1, preparing a polyetherimide (PEI) / poly(biphenyl ether sulfone) (P2) foamable composition [composition (FP)], wherein said composition (FP) comprises PEI in an amount ranging from 0.1 % weight (wt.) to 99.9 % wt., based on the total weight of the PEI and the poly(biphenyl ether sulfone) (P2), Step 2, foaming the composition (FP) to yield a foamed (PEI) / poly(biphenyl ether sulfone) material [foam (P) material], and Step 3, molding said foam (P) material under the effect of heat and pressure to provide a thermoformed foamed article.

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This application claims priority to U.S. provisional application No. 61/812482 filed on 16 April 2013 and to European application No. 13175832.8 filed on 9 July 2013, the whole content of each of these applications being incorporated herein by reference for all purposes.

5 Field of invention

The present invention relates to a method for manufacturing a thermoformed polyetherimide/ poly(biphenyl ether sulfone) foam article and said article made therefrom.

Background of the invention

In lightweight applications across multiple market segments such as transport, mobile electronics, building materials, household goods, food service trays and medical, the articles must meet certain requirements, including notably high strength-to-weight ratio, toughness, dimensional stability in use, thermal insulation, acoustic insulation, transparency to radio frequencies, resistance to aviation fluids such as hydraulic fluid, fuel, cleaning fluids, disinfectants, insecticides, adhesives, paints, and coatings.

In transport applications, notably aircraft, it is especially desirable to maximize weight reduction in a manner that does not compromise the strength and/or chemical properties of any component manufactured from a thermoplastic material. One way to reduce the weight of a particular aircraft component is to manufacture the component from a material having a relatively low density. By lowering the density of the materials used to make aircraft parts, improved weight/strength performance can be achieved. Of course, any reduction in weight may not come at the expense of a significant reduction in strength and/or chemical properties, such as notably their resistance to aircraft liquids.

Flammability characteristics are especially important in aircraft applications and any weight reductions must not result in poorer thermal oxidative degradation characteristics.

Thermoformed articles often suffer from drawbacks such as shrink and/or cracking especially upon thermoforming to steep part compound multiaxial bends, thus (i) increase of part density compared to unformed foam due to shrink, (ii) alternatively, weakening of mechanical performance compared to unformed foam, and (iii) difficulty to achieve and control part dimensions.
There is thus still a high need for methods for manufacturing thermoformed polyetherimide/ poly(biphenyl ether sulfone) foam articles which are characterized by dimensional stability in use, low degree of spring-back and shrink even at steep part angles, reliable performance at each point of the part and which can overcome all these drawbacks, mentioned above, and the thermoformed polyetherimide/ poly(biphenyl ether sulfone) foam articles made therefrom having excellent heat resistance, flame resistance, and environmental resistance, mechanical strength, and low-temperature impact resistance, and possesses excellent lightweight, thermal-insulating characteristics, soundproofing characteristics, vibration-proofing characteristics, chemical resistance, and recycling properties.

Summary of invention

The Applicant has now found surprisingly that a thermoformed polyetherimide/ poly(biphenyl ether sulfone) foam can be formed that combines contradicting properties such as high toughness in the application and low spring-back and shrink upon forming. Thus, the thermoformed polyetherimide/ poly(biphenyl ether sulfone) foam despite its strength and stiffness can be formed in well controlled circumstances into complex 3-dimensional thermoformed shapes.

The invention thus pertains to a method for manufacturing a thermoformed polyetherimide/ poly(biphenyl ether sulfone) foam article which comprises following three steps:

Step 1. preparing a polyetherimide [PEI, herein after]/ poly(biphenyl ether sulfone) (P2) foamable composition [composition (FP)], wherein said composition (FP) comprises PEI in an amount ranging from 0.1 % weight (% wt.) to 99.9 % wt., based on the total weight of the PEI and the poly(biphenyl ether sulfone) (P2)

Step 2. foaming the composition (FP) to yield a foamed PEI / poly(biphenyl ether sulfone) (P2) material [foam (P) material], and

Step 3. molding said foam (P) material under the effect of heat and pressure to provide a thermoformed foamed article.

Another aspect of the present invention is directed to a thermoformed PEI / poly(biphenyl ether sulfone) (P2) foam article.
Detailed description of embodiments

Composition (FP)

As said, the composition (FP) prepared in the first step of the method of the present invention comprises the PEI in an amount above 5 wt. %, preferably above 10 wt. %; more preferably above 20 wt. %; more preferably above 30 wt. % and even more preferably above 40 wt. %, based on the total weight of the polyetherimide and the poly(biphenyl ether sulfone) (P2). On the other hand, the weight of the PEI, based on the total weight of the PEI and the poly(biphenyl ether sulfone) (P2), is advantageously below 95 %, preferably below 90 %, more preferably below 85 % and still more preferably below 80 %.

The total weight of the PEI and the poly(biphenyl ether sulfone) (P2), based on the total weight of the composition (FP), is advantageously above 50 %, preferably above 80 %; more preferably above 90 %; more preferably above 95 % and more preferably above 99 %.

In the rest of the text, the expressions "PEI" and "poly(biphenyl ether sulfone) (P2)" are understood, for the purposes of the invention, both in the plural and the singular, that is to say that the composition (FP), foam (P) material and the thermoformed foam article may comprise one or more than one PEI and one or more than one poly(biphenyl ether sulfone).

For the purpose of the present invention, a polyetherimide is intended to denote any polymer of which more than 50 wt. % of the recurring units (R1) comprise at least one aromatic ring, at least one imide group, as such and/or in its amic acid form, and at least one ether group [recurring units (R1a)].

Recurring units (R1a) may optionally further comprise at least one amide group which is not included in the amic acid form of an imide group.

The recurring units (R1) are advantageously selected from the group consisting of following formulae (I), (II), (III), (IV) and (V), and mixtures thereof:
wherein

. Ar is a tetravalent aromatic moiety and is selected from the group consisting of a substituted or unsubstituted, saturated, unsaturated or aromatic monocyclic and polycyclic group having 5 to 50 carbon atoms;

. Ar'" is a trivalent aromatic moiety and is selected from the group consisting of a substituted or unsubstituted, saturated, unsaturated or aromatic monocyclic and polycyclic group having 5 to 50 carbon atoms and

. R is selected from the group consisting of substituted or unsubstituted divalent organic radicals, and more particularly consisting of (a) aromatic hydrocarbon radicals having 6 to 20 carbon atoms and halogenated derivatives thereof;
(b) straight or branched chain alkylene radicals having 2 to 20 carbon atoms;
(c) cycloalkylene radicals having 3 to 20 carbon atoms, and (d) divalent radicals of the general formula (VI):

\[ \text{(VI)} \]

wherein Y is selected from the group consisting of alkenyls of 1 to 6 carbon atoms, in particular \(-\text{C(CH}_3\text{)}_2\) and \(-\text{C}_n\text{H}_{2n}-\) (n being an integer from 1 to 6); perfluoroalkyls of 1 to 6 carbon atoms, in particular \(-\text{C(CF}_3\text{)}_2\) and \(-\text{C}_n\text{F}_{2n}-\) (n being an integer from 1 to 6); cycloalkylenes of 4 to 8 carbon atoms; alkylidenes of 1 to 6 carbon atoms; cycloalkylidenes of 4 to 8 carbon atoms; -O-; -S-; -C(O)-; -SO-; and R’ is selected from the group consisting of: hydrogen, halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium and i and j equal or different from each other, are independently 0, 1, 2, 3 or 4.
with the proviso that at least one of Ar, Ar' and R comprise at least one ether group.

Preferably, Ar is selected from the group consisting of those complying with the following formulae:

wherein X is a divalent moiety, having divalent bonds in the 3,3', 3,4', 4,3'' or the 4,4' positions and is selected from the group consisting of alkylenes of 1 to 6 carbon atoms, in particular -C(CH$_3$)$_2$ and -C$_n$H$_{2n}$- (n being an integer from 1 to 6); perfluoroalkylenes of 1 to 6 carbon atoms, in particular -C(F$_3$)$_2$ and -C$_n$F$_{2n}$- (n being an integer from 1 to 6); cycloalkylenes of 4 to 8 carbon atoms; alkylidenes of 1 to 6 carbon atoms; cycloalkylenes of 4 to 8 carbon atoms; -O-, -S-, -C(O)-, -SO$_2$-, -SO-, or X is a group of the formula 0-Ar"-0; and wherein Ar" is selected from the group consisting of those complying with following formulae (VII) to (XIII), and mixtures thereof:
wherein R and R’, equal or different from each other, are independently selected from the group consisting of: hydrogen, halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium and j, k, l, n and m equal or different from each other, are independently 0, 1, 2, 3 or 4, and W is selected from the group consisting of alkenyles of 1 to 6 carbon atoms, in particular -C(CH₃)₂ and -CₙH₂ₙ⁻ (with n being an integer from 1 to 6); perfluoroalkylenes of 1 to 6 carbon atoms, in particular -C(CF₃)₂ and -CₙF₂ₙ⁻ (with n being an integer from 1 to 6); cycloalkylenes of 4 to 8 carbon atoms; alkylidenes of 1 to 6 carbon atoms; cycloalkylidenes of 4 to 8 carbon atoms; -O−; -S−; -C(O)−; -SO⁻; and -SO−.

Preferably, Ar''' is selected from the group consisting of those complying with the following formulae:

\[ \text{formulae (XIV)} \]

wherein X has the same meaning as defined above.

In a preferred specific embodiment, the recurring units (Rla) are selected from the group consisting of units of formula (XIV) in imide form, of corresponding units in amic acid forms of formulae (XV) and (XVI), and of mixtures thereof:

\[ \text{formula (XIV)} \]
wherein:
- the $\rightarrow$ denotes isomerism so that in any recurring unit the groups to which the arrows point may exist as shown or in an interchanged position;
- $\text{Ar}''$ is selected from the group consisting of those complying with following formulae (VII) to (XIII)

wherein $R$ and $R'$, equal or different from each other, are independently selected from the group consisting of: hydrogen, halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium and $j, k, l, n$ and $m$ equal or different from each other, are independently 0, 1, 2, 3 or 4, and $W$ is selected
from the group consisting of alkylenes of 1 to 6 carbon atoms, in particular \(-\mathrm{C(CH}_3\mathrm{)}_2\) and \(-\mathrm{C}_n\mathrm{H}_{2n}\) (n being an integer from 1 to 6); perfluoroalkylenes of 1 to 6 carbon atoms, in particular \(-\mathrm{C(CF}_3\mathrm{)}_2\) and \(-\mathrm{C}_n\mathrm{F}_{2n}\) (n being an integer from 1 to 6); cycloalkylenes of 4 to 8 carbon atoms; alkyldienes of 1 to 6 carbon atoms; cycloalkyldienes of 4 to 8 carbon atoms; \(-\mathrm{O}-; -\mathrm{S}-; -\mathrm{C(O)}-; -\mathrm{SO}_2-; \) and \(-\mathrm{SO}-\); 

- E is selected from the group consisting of \(-\mathrm{C}_n\mathrm{H}_{2n}\) (n being an integer from 1 to 6), divalent radicals of the general formula (VI), as defined above, and those complying with formulae (XVII) to (XXII)

\[
\begin{align*}
\text{(XVII)} & \quad \text{(XVIII)} & \quad \text{(XIX)} \\
\text{(XX)} & \quad \text{(XXI)} & \quad \text{(XXII)} \\
\end{align*}
\]

wherein \(\text{R}'\) is selected from the group consisting of: hydrogen, halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium and \(\text{o, p}\), and \(\text{q}\) equal or different from each other, are independently 0, 1, 2, 3 or 4,

Preferably, E is selected from the group consisting of those complying with formulae (XVII) to (XIX), as defined above, more preferably, E is selected from the group consisting of unsubstituted m-phenylene and unsubstituted p-phenylene, and mixtures thereof.

Preferably, \(\text{Ar}''\) is of the general formula (XIII), as detailed above; more preferably, \(\text{Ar}''\) is
The polyetherimides wherein the recurring units (Rl) are recurring units of formula (XIV) as such, in imide form, and/or in amic acid forms [formulae (XV) and (XVI)], as defined above, may be prepared by any of the methods well-known to those skilled in the art including the reaction of any aromatic bis(ether anhydride)s of the formula

\[
\text{O} \quad \text{O} \quad \text{E} \quad \text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{O}
\]  

(XXIII)

where E is as defined hereinbefore, with a diamino compound of the formula

\[
\text{H}_2\text{N-Ar''-NH}_2
\]  

(XXIV)

where Ar'' is as defined hereinbefore. In general, the reactions can be advantageously carried out employing well-known solvents, e.g., o-dichlorobenzene, m-cresol/toluene, N,N-dimethylacetamide, etc., in which to effect interaction between the dianhydrides and diamines, at temperatures of from about 20°C to about 250°C.

Alternatively, these polyetherimides can be prepared by melt polymerization of any dianhydrides of formula (XXIII) with any diamino compound of formula (XXIV) while heating the mixture of the ingredients at elevated temperatures with concurrent intermixing.

The aromatic bis(ether anhydride)s of formula (XXIII) include, for example:

- 2,2-bis[4-(2,3-dicarboxyphenoxy)phenyl]propane dianhydride;
- 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl ether dianhydride;
- 1,3-bis(2,3-dicarboxyphenoxy)benzene dianhydride;
- 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfide dianhydride;
- 1,4-bis(2,3-dicarboxyphenoxy)benzene dianhydride;
- 4,4'-bis(2,3-dicarboxyphenoxy)benzophenone dianhydride;
- 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfone dianhydride;
- 2,2-bis[4(3,4-dicarboxyphenoxy)phenyl]propane dianhydride;
- 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl ether dianhydride;
- 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride;
- 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride;
1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride;
4,4'-bis(3,4-dicarboxyphenoxy)benzophenone dianhydride;
4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl-2,2-propane dianhydride; etc. and mixtures of such dianhydrides.

The organic diamines of formula (XX) include, for example, m-phenylenediamine, p-phenylenediamine, 2,2-bis(p-aminophenyl)propane, 4,4'-diaminodiphenyl-methane, 4,4'-diaminodiphenyl sulfide, 4,4'-diamino diphenyl sulfone, 4,4'-diaminodiphenyl ether, 1,5-diaminonaphthalene, 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine, and mixtures thereof.

In a preferred embodiment, the organic diamines of formula (XX) is chosen from a group selected from m-phenylenediamine and p-phenylenediamine and mixture thereof.

In a most preferred embodiment, the recurring units (Rla) are recurring units selected from the group consisting of those of formula (XXV) in imide form, their corresponding amic acid forms of formulae (XXVI) and (XXVII), and mixtures thereof:

![Molecular structure](XXV)

![Molecular structure](XXVI)

![Molecular structure](XXVII)

wherein in formulae (XXVI) and (XXVII) the → denotes isomerism so that in any recurring unit the groups to which the arrows point may exist as shown or in an interchanged position.

In another most preferred embodiment, the recurring units (Rla-4) are recurring units selected from the group consisting of those of formula (XXVIII) in imide form, their corresponding amic acid forms of formulae (XXIX) and (XXX), and mixtures thereof:

![Molecular structure](XXVIII)

![Molecular structure](XXIX)

![Molecular structure](XXX)
wherein in formulae (XXIX) and (XXX) the \( \rightarrow \) denotes isomerism so that in any recurring unit the groups to which the arrows point may exist as shown or in an interchanged position.

Preferably more than 75 wt. % and more preferably more than 90 wt. % of the recurring units of the PEI are recurring units (Rl). Still more preferably, essentially all, if not all, the recurring units of the PEI are recurring units (Rl).

In a preferred embodiment of the present invention, more than 75 wt. % more preferably more than 90 wt. %, more preferably more than 99 wt. %, even more preferably all the recurring units of the PEI are recurring units selected from the group consisting of those in imide form of formula (XXV), their corresponding amic acid forms of formulae (XXVI) and (XXVII), and mixtures thereof.

In another preferred embodiment of the present invention, more than 75 wt. % more preferably more than 90 wt. %, more preferably more than 99 wt. %, even more preferably all the recurring units of the PEI are recurring units selected from the group consisting of those in imide form of formula (XXVIII), their corresponding amic acid forms of formulae (XXIX) and (XXX), and mixtures thereof.

Such aromatic polyimides are notably commercially available from Sabic Innovative Plastics as ULTEM® polyetherimides.

The compositions can comprise one and only one PEI. Alternatively, they can comprise two, three, or even more than three PEI.
Generally, PEI polymers useful in the present invention have a melt index of 0.1 to 10 grams per minute (g/min), as measured according to ASTM D1238 at 295°C, using a 6.6 kilogram (kg) weight.

In a specific embodiment, the PEI polymer has a weight average molecular weight (Mw) of 10,000 to 150,000 grams per mole (g/mole), as measured by gel permeation chromatography, using a polystyrene standard. Such PEI polymers typically have an intrinsic viscosity greater than 0.2 deciliters per gram (dl/g), beneficially 0.35 to 0.7 dl/g measured in m-cresol at 25°C.

The PEI polymers have been found particularly suitable for the thermoplastic compositions comprised in the foam material of the present invention in view of their advantageous high modulus of about 450 kpsi, a remarkable elevated thermal resistance, high dielectric strength, a broad chemical resistance profile, and its good melt processability.

For the purpose of the present invention, the poly(biphenyl ether sulfone) (P2) is intended to denote a polycondensation polymer of which more than 50 wt. % of the recurring units are recurring units (R2) of one or more formulae containing at least one biphenylene group preferably selected from the group consisting of those complying with following formulae:

\[
\text{R}_{i} \quad \text{R}_{j} \quad \text{R}_{k}
\]

wherein R is selected from the group consisting of:
hydrogen, halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium and j, k and l equal or different from each other, are independently 0, 1, 2, 3 or 4; and
at least one ether group (-O-) and at least one sulfone group (-SO_2^-).

The recurring units (R2) are advantageously recurring units of formula (A) as shown below:

\[
- \text{Ar}^n \text{T-Ar}^2 \text{O-Ar}^3 \text{SO}_2 ^{-}\text{[Ar}^d \text{T-Ar}^2 \text{SO}_2 ^{-}]_{n} \text{-A}^\wedge \text{O-}
\]
(formula A)

wherein:
- \text{Ar}^1, \text{Ar}^2, \text{Ar}^3, \text{Ar}^4, and \text{Ar}^5, equal to or different from each other and at each occurrence, are independently an aromatic mono- or polynuclear group; with the proviso that at least one \text{Ar}^1 through \text{Ar}^5 is an aromatic moiety containing
at least one biphenylene group, selected from the group consisting of those complying with the following formulae:

\[
\begin{align*}
\text{hydrogen, halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium and k and l equal or different from each other, are independently 0, 1, 2, 3 or 4, and} \\
\text{each of T, equal to or different from each other, is a bond or a divalent group optionally comprising one or more than one heteroatom;} \\
\text{n and m, equal to or different from each other, are independently zero or an integer of 1 to 5;} \\
\text{Preferably, Ar}^1, \text{Ar}^2, \text{Ar}^3, \text{Ar}^4, \text{Ar}^5 \text{ are equal or different from each other and are aromatic moieties preferably selected from the group consisting of those complying with following formulae:}
\end{align*}
\]

\[
\begin{align*}
\text{hydrogen, halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium and j, k and l equal or different from each other, are independently 0, 1, 2, 3 or 4, and with the proviso that at least one Ar}^1 \text{ through Ar}^5 \text{ is an aromatic moiety containing at least one biphenylene group, selected from the group consisting of those complying with following formulae:}
\end{align*}
\]
wherein R is selected from the group consisting of:
hydrogen, halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid,
ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali
or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary
ammonium and k and l equal or different from each other, are independently 0, 1,
2, 3 or 4.

Preferably, each of T, equal to or different from each other, is selected
from the group consisting of a bond, -CH₂⁻; -O⁻; -S0₂⁻; -S⁻; -C(0)⁻;
-C(CH₃)₂⁻; -C(CF₃)₂⁻; -C(=CC1₂)⁻; -C(CH₃)(CH₂CH₂COOH)⁻; -N=N⁻;
-R'C=CR'B⁻; where each R'A and R'B independently of one another, is a hydrogen
or a C₁₂⁻-alkyl, C₁₂⁻-alkoxy, or C₆-C₈-aryl group; -(CH₂)ₙ⁻ and -(CF₂)ₙ⁻
with n = integer from 1 to 6, or an aliphatic divalent group, linear or branched, of
up to 6 carbon atoms; and mixtures thereof.

More preferably, recurring units (R²) are selected from the group
consisting of formulae (B) to (F), as below detailed, and mixtures thereof:

Still more preferably, recurring units (R²) are:
In another preferred embodiment, recurring units (R2) are of formula (D), shown below:

In yet another preferred embodiment, recurring units (R2) are of formula (F), shown below:

The poly(biphenyl ether sulfone) (P2) may be notably a homopolymer, a random, alternate or block copolymer. When the poly(biphenyl ether sulfone) (P2) is a copolymer, its recurring units may notably be composed of (i) recurring units (R2) of at least two different formulae selected from formulae (B) to (F), or (ii) recurring units (R2) of one or more formulae (B) to (F) and recurring units (R2*), different from recurring units (R2), such as:

Preferably more than 75 wt. %, preferably more than 85 wt. %, preferably more than 95 wt. %, preferably more than 99 wt. % of the recurring units of the poly(biphenyl ether sulfone) (P2) are recurring units (R2).

Still, it is generally preferred that substantially all recurring units of the poly(biphenyl ether sulfone) (P2) are recurring units (R2), as detailed above; chain defects, or very minor amounts of other units might be present, being understood that these latter do not substantially modify the properties of (R2).
The poly(biphenyl ether sulfone) (P2) is then preferably a polyphenylsulfone (PPSU).

For the purpose of the present invention, a polyphenylsulfone (PPSU) polymer is intended to denote any polymer of which more than 50 wt. % of the recurring units are recurring units (R2) of formula (B).

In a preferred embodiment of the present invention, more than 75 wt. % more preferably more than 90 wt. %, more preferably more than 99 wt. %, even more preferably all the recurring units of the poly(biphenyl ether sulfone) (P2) are of formula (B).

RADEL® R polyphenylsulfone from Solvay Specialty Polymers USA, L.L.C. is an example of a commercially available PPSU homopolymer.

In another preferred embodiment of the present invention, more than 50 wt. %, more than 75 wt. %, more preferably more than 90 wt. %, more preferably more than 99 wt. %, even more preferably all the recurring units of the poly(biphenyl ether sulfone) (P2) are of formula (D).

SUPRADEL™ HTS high-temperature sulfone polymer from Solvay Specialty Polymers USA, L.L.C. is an example of a commercially available poly(biphenyl ether sulfone) (P2) comprising more than 50 wt. % of the recurring units of formula (D).

In another preferred embodiment of the present invention, more than 50 wt. %, more than 75 wt. %, more preferably more than 90 wt. %, more preferably more than 99 wt. %, even more preferably all the recurring units of the poly(biphenyl ether sulfone) (P2) are of formula (F).

As mentioned above, the thermoformed foam article may comprise one or more than one poly(biphenyl ether sulfone) [poly(biphenyl ether sulfone) (P2)].

In a specific embodiment of the present invention, poly(biphenyl ether sulfone) (P2) may also be a blend composed of at least two poly(biphenyl ether sulfone) (P2) chosen from a group consisting of a (PPSU) polymer, as detailed above and a SUPRADEL™ HTS high-temperature sulfone polymer, as detailed above.

In this specific embodiment, the (PPSU) polymer is generally present in an amount of at least 5 wt. %, preferably of at least 10 wt. %, more preferably of at least 20 wt. %, more preferably of at least 30 wt. %, more preferably of at least 40 wt. %, based on the total weight of the (PPSU) polymer and SUPRADEL™ HTS high-temperature sulfone polymer. It is further understood that the weight percent of the (PPSU) polymer will generally be of at
most 95 wt. %, more preferably of at most 90 wt. %, more preferably of at
most 80 wt. %, more preferably of at most 70 wt. %, more preferably of at
most 60 wt. %, based on the total weight of the (PPSU) polymer and
SUPRADEL™ HTS high-temperature sulfone polymer.

Good results were obtained when the (PPSU) polymer is present in an
amount of 40-60 wt. % based on the total weight of the (PPSU) polymer and
SUPRADEL™ HTS high-temperature sulfone polymer. Excellent results were
obtained when the (PPSU) polymer is present in an amount of about 50 wt. %
based on the total weight of the (PPSU) polymer and SUPRADEL™ HTS high-
temperature sulfone polymer.

The poly(biphenyl ether sulfone) (P2) can be prepared by any method. The
molecular weight of the poly(biphenyl ether sulfone) (P2), when determined as
reduced viscosity in an appropriate solvent such as methylene chloride,
chloroform, N-methylpyrrolidone, or the like, can be greater than or equal
to 0.3 dl/g, or, more specifically, greater than or equal to 0.4 dl/g and, typically,
will not exceed 1.5 dl/g.

The poly(biphenyl ether sulfone) (P2) weight average molecular weight
can be 10,000 to 100,000 grams per mole (g/mol) as determined by gel
permeation chromatography following ASTM D5296 standard, using
polystyrene calibration curve. In some embodiments, the poly(biphenyl ether
sulfone) (P2) weight average molecular weight can be 20,000
to 70,000 grams per mole (g/mol).

The poly(biphenyl ether sulfone) (P2) may have glass transition
temperatures of 180 to 250°C, when determined according to ASTM D 3418.

Poly(biphenyl ether sulfone) (P2) polymers have been found particularly
suitable in the method for manufacturing of the thermoformed foam article of the
present invention because of their advantageous high toughness and impact
strength, high impact resistance, high chemical resistance, exceptional hydrolytic
stability, and very good inherent flame resistance.

In one preferred embodiment of the present invention, the foam material
made from a composition [composition (FP)] comprising a polyetherimide (PEI),
wherein more than 75 wt. % of the recurring units of the PEI are recurring
units (RI) selected from the group consisting of those of formula (XXV) in
imide form, corresponding amic acid forms of formulae (XXVI) and (XXVII),
and mixtures thereof:
and a poly(biphenyl ether sulfone) (P2), wherein more than 75 wt. % of the recurring units of the poly(biphenyl ether sulfone) (P2) are recurring units (R2) of formula (B).

\[
(XXIV)
\]

In another preferred embodiment of the present invention, the foam material made from a composition [composition (FP)] comprising a polyetherimide (PEI), wherein more than 75 wt. % of the recurring units of the PEI are recurring units (R1) selected from the group consisting of those in imide form of formula (XXVIII), their corresponding amic acid forms of formulae (XXIX) and (XXX), and mixtures thereof:

\[
(XXVIII)
\]

and a poly(biphenyl ether sulfone) (P2), wherein more than 75 wt. % of the recurring units of the poly(biphenyl ether sulfone) (P2) are recurring units (R2) of formula (B).

According to one embodiment of the present invention, the composition (FP) prepared in the first step of the method of the invention, can further contain one or more ingredients other than the polyetherimide (PEI) and the poly(biphenyl ether sulfone) (P2).

The composition (FP) may further contain conventional ingredients such as notably, additives such as UV absorbers; stabilizers such as light stabilizers and others; lubricants; plasticizers; pigments; dyes; colorants; anti-static agents; nucleating agents; foaming agents; blowing agents; metal deactivators; flame
retardants and combinations comprising one or more of the foregoing additives. Antioxidants can be compounds such as phosphites, phosphorates, hindered phenols or mixtures thereof. Surfactants may also be added to help nucleate bubbles and stabilize them during the bubble growth phase of the foaming process.

The weight of said conventional ingredients, based on the total weight of polymer composition (FP) ranges advantageously from 0 to 15 %, preferably from 0 to 10 % and more preferably from 0 to 5 %.

If desired, the composition (FP) comprises no other organic polymer components than the PEI, as defined below and the poly(biphenyl ether sulfone) (P2), as defined below.

For the purpose of the present invention, the expression "organic polymer components" refers to compounds characterized by repeated linked units, having typically a molecular weight of 2 000 or more and said repeated linked units have primarily carbon atoms, but may also include heteroatoms, such as notably oxygen, sulfur or nitrogen.

In a specific embodiment of the present invention, the composition (FP) comprises more than 85 wt. % of the polyetherimide and the poly(biphenyl ether sulfone) (P2) with the proviso that the polyetherimide and the poly(biphenyl ether sulfone) (P2) are the only organic polymeric components in composition (FP) and the remainder to make up to 100 % weight is one or more optional ingredients such as additives; stabilizers; lubricants; plasticizers; pigments; dyes; colorants; anti-static agents; nucleating agents, foaming agents; blowing agents; metal deactivators; antioxidants and surfactants might be present therein, without these components dramatically affecting relevant mechanical and toughness properties of composition (FP).

If desired, the composition (FP) comprises more than 85 wt. % of the polyetherimide and a blend composed of at least two poly(biphenyl ether sulfone) (P2) chosen from a group consisting of a (PPSU) polymer, as detailed above and a SUPRADEL™ HTS high-temperature sulfone polymer, as detailed above, with the proviso that the polyetherimide and the blend composed of at least two poly(biphenyl ether sulfone) (P2) chosen from a group consisting of a (PPSU) polymer, as detailed above and a SUPRADEL™ HTS high-temperature sulfone polymer, as detailed above, are the only organic polymeric components in composition (FP) and the remainder to make up to 100 % weight is one or more optional ingredients such as additives; stabilizers; lubricants;
plasticizers; pigments; dyes; colorants; anti-static agents; nucleating agents, foaming agents; blowing agents; metal deactivators; antioxidants and surfactants might be present therein, without these components dramatically affecting relevant mechanical and toughness properties of composition (FP).

If desired, the composition (FP) comprises more than 85 wt. % of the polyetherimide and the (PPSU) polymer with the proviso that the polyetherimide and the (PPSU) polymer are the only organic polymeric components in composition (FP) and the remainder to make up to 100 % weight is one or more optional ingredients such as additives; stabilizers; lubricants; plasticizers; pigments; dyes; colorants; anti-static agents; nucleating agents, foaming agents; blowing agents; metal deactivators; antioxidants and surfactants might be present therein, without these components dramatically affecting relevant mechanical and toughness properties of composition (FP).

In Step 1. of the method of the invention, a nucleating agent, or blends of nucleating agents, can advantageously be added to the composition (FP).

In general, the nucleating agent helps control the structure of the foam (P) material, formed in step 2 of the method of the invention, by providing a site for bubble formation, and the greater the number of sites, the greater the number of bubbles and the less dense the final product can be, depending on processing conditions.

Suitable nucleating agent that may be used in the present invention include, but are not limited to, metallic oxides such as titanium dioxide, clays, talc, silicates, silica, aluminates, barites, titanates, borates, nitrides, notably boron nitride, and even some finely divided, unreactive metals, carbon-based materials (such as diamonds, carbon black, nanotubes and graphenes) or combinations including at least one of the foregoing agents. In alternative embodiments, silicon and any crosslinked organic material that is rigid and insoluble at the processing temperature may also function as nucleating agents.

In alternative embodiments, other fillers may be used provided they have the same effect as a nucleating agent in terms of providing a site for bubble formation. This includes fibrous fillers such as aramid fibers, carbon fibers, glass fibers, mineral fibers, or combinations including at least one of the foregoing fibers. Some nano-fillers and nano-reinforcements can also be used as nucleating agents. These include such materials as nano-silicates, nano-clays, carbon nanofibers and carbon nanotubes as well as graphenes and multi-layered graphitic nano-platelets.
In a preferred embodiment, the nucleating agent is preferably used in the following amounts: advantageously from 0.1 to 5% by weight, preferably from 0.2 to 3% by weight based in each case on the total weight of the composition (FP).

Generally, the composition (FP) can be prepared by a variety of methods involving intimate admixing of the polymer materials with any optional ingredient, as detailed above, desired in the formulation, for example by melt mixing or a combination of dry blending and melt mixing. Typically, the dry blending of the PEI polymer, poly(biphenyl melt sulfone) (P2) and all other optional ingredients, as above details, is carried out by using high intensity mixers, such as notably Henschel-type mixers and ribbon mixers.

So obtained powder mixture may be suitable for direct use in the second step of the method or can be a concentrated mixture to be used as masterbatch and diluted in further amounts of the PEI polymer, poly(biphenyl ether sulfone) (P2) in subsequent processing steps. Said masterbatches/concentrates can also be melt mixed prior to use in the second step of the method.

It is also possible to manufacture the composition (FP) of the invention by further melt compounding the powder mixture as above described. As said, melt compounding can be effected on the powder mixture as above detailed, or preferably directly on the PEI polymer, poly(biphenyl ether sulfone) (P2) and any other possible ingredient. Conventional melt compounding devices, such as co-rotating and counter-rotating extruders, single screw extruders, co-kneaders, disc-pack processors and various other types of extrusion equipment can be used. Preferably, extruders, more preferably twin screw extruders can be used.

In case blowing agent(s) is/are comprised in composition (FP), specially designed extruders, i.e. extruders specifically designed to effectively control temperature such that further processes such as foaming is not prematurely initiated and such that the composition may be melted, blended, extruded and pelletized without premature foaming of the composition, are particularly preferred. The design of the compounding screw, e.g. flight pitch and width, clearance, length as well as operating conditions will be advantageous chosen so that sufficient heat and mechanical energy is provided to advantageously fully melt the powder mixture or the ingredients as above detailed and advantageously obtain a homogeneous distribution of the different ingredients, but still mild enough to advantageously keep the processing temperature of the composition below that in which foaming may be prematurely initiated, in case optional
chemical foaming ingredients are comprised in the composition. Provided that the processing temperature is kept well above the softening point of the PEI polymer and poly(biphenyl ether sulfone) (P2) and, when chemical foaming agent(s) are comprised, below the decomposition temperature of any of said chemical foaming components possibly present, it is advantageously possible to obtain strand extrudates of the composition (FP) of the invention which have not undergone significant foaming. Such strand extrudates can be chopped by means e.g. of a rotating cutting knife aligned downwards the die plate, generally with an underwater device, which assures perfect cutting knife to die plate alignment, and collected under the form of pellets or beads. Alternatively, the strand extrudates may also be cooled using a water bath of conveyor belt and then cut using a pelletizer. Thus, for example composition (FP) which may be present in the form of pellets or beads can then be further used in the second step of the method of the present invention.

**Foam (P) material**

According to the method of the present invention, the composition (FP), as mentioned above, is foamed in Step 2. to yield the foam (P) material having high void content, low apparent density and substantially uniform cell sizes.

For the purpose of the present invention, the term "substantially uniform cell size" is intended to denote a foam material wherein the magnitude of one standard deviation of the cell size frequency distribution is at most 40% of the value of the estimated mean cell size, so as an example, a foam with an estimated mean cell size of 100 micrometers and a standard deviation of 35 micrometers in cell size distribution would fall within the scope of the above definition for "substantially uniform cell size".

It has been found that the foam (P) material prepared in the second step of the method of the present invention, endowed by having uniform cell size, has improved mechanical properties since larger cells act as a weak point in the foam, which may initiate a failure and, in addition, maintaining ability to be thermoformed, that is to say shaped into articles of possibly complex geometry by combined action of heat and pressure.

Foaming of polymer composition (FP) in Step 2. of the method of the present invention can be performed using any foaming technique, which is capable of yielding the foam (P) material. Suitable foaming techniques that may be used in the present invention include, but are not limited to, pressure cell
processes, autoclave processes, extrusion processes, direct (variotherm) injection processes and bead foaming.

The extrusion process is most preferred.

A pressure cell process, for example, is carried out batchwise; the composition (FP) is charged in a pressure cell with a gas under a pressure that is higher than atmospheric pressure and at a temperature that is below the glass transition temperature of the polymer/gas mixture. The temperature is then raised to a temperature that is above the glass transition temperature but below the critical temperature of the PEI polymer/poly(biphenyl ether sulfone) (P2)/gas mixture, by immersing in a heating bath, and then the gas is driven out of the mixture to produce the foam (P) material. Transfer from the pressure cell to the heating bath is generally carried out as fast as possible, considering that the dissolved gas can quickly diffuse out of the polymer at ambient pressure. After foaming, the foam (P) material is generally quenched in an ethanol/water mixture at about 20°C.

In an autoclave process, for example, the composition (FP) is charged with a gas in an autoclave at a temperature that is above the glass transition temperature of the PEI polymer/poly(biphenyl ether sulfone) (P2)/gas mixture and foaming is induced by spontaneous release of the pressure. In contrast to the pressure cell process, in which the gas-charged composition (FP) is normally transferred to a heating bath to raise the temperature to above the glass transition temperature but below the critical temperature of the polymer/gas mixture, the autoclave process does not need a heating stage as the polymer is already at the required temperature that is above the glass transition temperature on charging with the gas.

An extrusion process, in contrast to the two techniques described above, is a continuous process. In general, in the extrusion process, the foam (P) material is formed by melting the composition (FP) in the form of a pellet or a bead, mixing the so obtained molten mixture with at least one blowing agent under pressure. At the exit of the extruder, during depressurization, the blowing agent vaporizes and, by absorbing heat of evaporation, rapidly cools the molten mass thereby forming the foam (P) material.

Any suitable extrusion equipment capable of processing composition (FP) can be used for the extrusion. For example, single or multiple-screw extruders can be used, with a tandem extruder being preferred.
In a specific preferred embodiment, the composition (FP) is molten in a primary extruder. The blowing agent is then fed into the primary extruder and mixed into the molten blend under high pressure and temperature in the last sections of the primary extruder. The molten mass is then fed under pressure to a secondary extruder, which is used to cool the material to be foamed and transport it through a die to a calibrator to form the foam (P) material. The calibrator helps to control the cooling rate and expansion of the foam (P) material. Therefore, it is beneficial in helping to control the thickness, width and density of the foam (P) material. The die is operated at a specific temperature range and pressure range to provide the necessary melt strength and to suppress premature foaming in the die. In one embodiment, a single screw extruder is used for both the primary extruder and the secondary extruder. In an alternative embodiment, a twin-screw extruder is used for both the primary extruder and the secondary extruder. In yet another alternative embodiment, a single screw extruder is used for one of the primary extruder or the secondary extruder and a twin-screw extruder is used for the other.

In Step 2. of the method of the present invention, blowing agent, or blends of blowing agents, can advantageously be used in different amounts depending on the desired density of the foam (P) material. In one preferred embodiment of the present invention, the amount used of the blowing agent is from 0.5 to 15 percent by weight, preferably from 1 to 12 percent by weight, particularly preferably from 3 to 10 percent by weight, based in each case on the total weight of the composition (FP).

In general, a larger amount of blowing agent may be used for embodiments where lower density foams are to be formed.

In general, the blowing agent is selected to be sufficiently soluble to grow uniformly the voids into the bubbles that form a foam material having the selected density. As a result, if all of the parameters including solubility of the blowing agent with the PEI polymer/poly(biphenyl ether sulfone) (P2) melt (at pressure, temperature and shear rate) are balanced and the walls of the bubbles are sufficiently stable such that they do not rupture or coalesce until the viscosity/melt strength of the resin/ blowing agent is strong enough to form a stable foam (P) material as it cools, the result is a good, uniform, small celled foam (P) material having a selected density.

In general, the type of foam (P) material to be produced may also vary depending on other factors such as the presence of nucleating agent particles, the
loading and/or process conditions, and the type of equipment used to form the foam materials.

Having regards to the nature of the blowing agent, the foaming process may be a chemical or a physical foaming process.

In one preferred embodiment, the foaming process is a physical foaming process.

In a physically foaming process, use is made of physical foaming ingredients, such as physical blowing agents and optionally nucleating agents.

Physical foaming agents generally refer to those compounds that are in the gaseous state in the foaming conditions (generally high temperature and pressure) because of their physical properties.

The physical foaming agents can be fed to the equipment, wherein foaming takes place, either in their gaseous form, or in any other form, from which a gas will be generated via a physical process (e.g. evaporation, desorption). Otherwise, physical foaming agent may be included in the pre-formed composition (FP), to be introduced in the foaming equipment.

In Step 2. of the method of the present invention, any conventional physical blowing agent can be used such as inert gases, e.g. C0₂, nitrogen, argon; hydrocarbons, such as propane, butane, pentane, hexane; aliphatic alcohols, such as methanol, ethanol, propanol, isopropanol, butanol; aliphatic ketones, such as acetone, methyl ethyl ketone; aliphatic esters, such as methyl and ethyl acetate; fluorinated hydrocarbons, such as 1,1,1,2-tetrafluoroethane (HFC 134a) and difluoroethane (HFC 152a); and mixtures thereof.

It is understood that as the physical blowing agent is supplied in fluid form to a melt, it advantageously generates bubbles, as the melt passes through the die and is de-pressurized. This may also be realized in extrusion devices.

In an alternative embodiment of the present invention, the foaming process is a chemical foaming process.

In a chemical foaming process, use is generally made of a chemical foaming agent, in particular a chemical blowing agent.

Chemical foaming agents generally refer to those compositions which decompose or react under the influence of heat in foaming conditions, to generate a foaming gas.

Chemical foaming agents can be comprised in the composition (FP) thereby generating in situ the foaming gas or can be added in present Step 2 of
the present invention. Chemical foaming may also be realized in extrusion devices.

Suitable chemical foaming agents include notably simple salts such as ammonium or sodium bicarbonate, nitrogen evolving foaming agents; notably aromatic, aliphatic-aromatic and aliphatic azo and diazo compounds, such as azodicarbonamide and sulphonhydrazides, such as benzene sulphonhydrazide and oxy-bis(benzenesulphonhydrazide). Said chemical foaming agents can optionally be mixed with suitable activators, such as for example amines and amides, urea, sulphonhydrazides (which may also act as secondary foaming agent) ; and the like.

While the foam (P) material is substantially free of the blowing agents, it is contemplated that residual amounts of the one or more blowing agents may remain in the foam material, although these residual amounts are not sufficient to adversely affect the foam characteristics of the foam (P) material.

In alternative embodiments, any of the residual blowing agent may be further reduced by exposing the foam (P) material further to a heat cycle.

In one embodiment of the present invention, the foam (P) material formed in Step 2 of the present invention has advantageously a density in the range from 10 to 170 kg/m³, preferably from 20 to 150 kg/m³; more preferably from 20 to 100 kg/m³, even more preferably from 20 to 55 kg/m³.

The foam (P) material of the present invention has advantageously an average cell size of less than 500 microns, preferably less than 100 microns, more preferably less than 50 microns.

The density can be measured according to ASTM D1622.

The cell size can be measured using optical or scanning electron microscopy.

The foam (P) material formed in Step 2 of the present invention may be in the form of a panel, a sheet or a film. It is also understood that the foam (P) material can be manufactured as a sheet or a panel either supported onto a supporting film or sandwiched between two supporting films. Such foam (P) material pre-forms are used in the Step 3 of the method of the present invention. More preferably, the foam (P) material is in the form of a foam panel or a foam film. Most preferably the foam (P) material is in the form of a foam panel.

In one specific embodiment of the method of the present invention, the foam panel formed in the Step 2 of the method of the present invention has...
advantageously a thickness in the range of from 1 mm to 30 mm, preferably from 3 mm to 10 mm, more preferably from 4 mm to 6 mm.

In another specific embodiment of the method of the present invention, the foam film formed in the Step 2 of the method of the present invention has advantageously a thickness in the range of from 0.1 mm to 3.0 mm, preferably from 0.2 mm to 1.0 mm, more preferably from 0.2 mm to 0.5 mm.

Thermoformed foam article

In the method of the present invention, the molding of the foam (P) material in Step 3, under the effect of heat and pressure to provide a thermoformed foamed article can be accomplished following various thermoforming processes known in the art.

Suitable thermoforming processes that may be used in the present invention include, but are not limited to vacuum forming, pressure forming, matched mold forming, twin sheet thermoforming processes. The vacuum forming process is particularly preferred.

Typically, a thermoforming process can be divided into four steps: (i) pre-forming the foam (P) material under the effect of heating (i.e. the pre-heating step), (ii) forming the thermoformed foamed article by holding the foam (P) material against a mold under pressure differential and heating (i.e. the forming step) (iii) cooling the thermoformed foamed article in the mold (i.e. the cooling step) (iv) trimming the thermoformed foamed article (i.e. the trimming step).

Any suitable thermoforming equipment capable of thermoforming the foam (P) material can be used in step 3 of the method of the present invention.

For example a vacuum table can be used with a temperature controlled vacuum table being preferred.

The pre-forming of the foam (P) material in step (i) is typically carried out by pre-heating the foam (P) material to its forming temperature by using for example conduction heaters such as notably contact heaters, convection heaters, such as notably gas fired heaters, hot air circulating ovens, induction headers or radiation heaters, such as notably, infrared-light- spectrum wavelengths heaters, radio-frequency heaters. Hot air circulating ovens are particularly preferred.

For the purpose of the present invention, the term "forming temperature" is intended to denote a temperature at which the polymer can be shaped under a controlled deformation rate but not so high as to cause excessive softening and collapse of the foam.
During the pre-heating step (i), the foam (P) material is generally pre-heated up to a temperature of at least 170°C, preferably at least 190°C and more preferably at least 200°C.

The foam (P) material is generally pre-heated up to a temperature of at least 10 min, preferably at least 30 min, more preferably at least 60 min.

The foam (P) material is generally pre-heated up to a temperature of at most 120 min, preferably at most 90 min, more preferably at most 70 min.

If desired, the forming step (ii) can be carried out without realizing the pre-heating step (i).

As said, during the forming step (ii), the foam (P) material is held against a temperature controlled mold under pressure differential.

The pressure in the forming step (ii) is advantageously at least 2 in. Hg, preferably at least 5 in. Hg, preferably at least 10 in. Hg.

The pressure in the forming step (ii) is advantageously at most 20 in. Hg, preferably at most 17 in. Hg, more preferably at most 15 in. Hg.

Said pressure differential can be suitably applied under the form of a vacuum, air pressure, mechanical aids such as plugs, rubber diaphragms, and combinations thereof.

Temperature in step (ii) is generally kept at the same temperature as in step (i).

In the vacuum forming process, as mentioned above, the pressure differential is applied under the form of a vacuum. Said vacuum can be applied using a variety of vacuum forming systems such as notably systems based on vacuum bagging techniques, heated vacuum forming tables.

A vacuum forming systems based on the vacuum bagging technique is particularly preferred.

It is understood that before applying vacuum, the pressure in the thermoforming equipment is equal to atmospheric pressure [(29.92 inches of mercury (in. Hg)].

In the forming step (ii), the vacuum can be applied in one stage or in two stages.

In a first embodiment in step (ii), the vacuum is applied in one stage.

In this embodiment, the vacuum is advantageously provided from atmospheric pressure to a maximum vacuum pressure level 1 [vacuum (1)] at a
vacuum rate of at least 2 in. Hg/min, preferably of at least 4 in. Hg/min, more preferably of at least 6 in. Hg/min.

Vacuum (1) is advantageously at least 5 in. Hg, preferably at least 7 in. Hg, preferably at least 10 in. Hg.

Vacuum (1) is advantageously at most 20 in. Hg, preferably at most 17 in. Hg, more preferably at most 15 in. Hg.

In this embodiment, the vacuum is further kept constant at vacuum (1) advantageously for a period of at least 20 min, preferably of at least 30 min.

In a second more preferred embodiment in step (ii), the vacuum is applied in two stages.

In a first stage of the second embodiment, the vacuum is advantageously provided from atmospheric pressure to a vacuum pressure level 2 [vacuum (2)] at a vacuum rate of at least 0.2 in. Hg/min, preferably of at least 0.4 in. Hg/min, more preferably of at least 1.0 in. Hg/min.

In said first stage, the vacuum is advantageously provided from atmospheric pressure to vacuum (2) at a vacuum rate of at most 6.0 in. Hg/min, preferably of at most 4.0 in. Hg/min, more preferably of at most 2.0 in. Hg/min. Vacuum (2) is advantageously at least 1 in. Hg, preferably at least 3 in. Hg, more preferably at least 5 in. Hg.

Vacuum (2) is advantageously at most 20 in. Hg, preferably at most 17 in. Hg, more preferably at most 15 in. Hg.

In a second stage of the second embodiment, the vacuum is further kept constant at vacuum (2), or is continuously increased until a maximum vacuum level 3 [vacuum (3)] or is increased in a stepwise manner until vacuum (3).

Vacuum (3) is advantageously at least 5 in. Hg, preferably at least 7 in. Hg, more preferably at least 10 in. Hg.

Vacuum (3) is advantageously at most 20 in. Hg, preferably at most 17 in. Hg, more preferably at most 15 in. Hg.

In one embodiment of the method of the invention, the vacuum in the second stage is continuously increased until vacuum (3) at a vacuum rate of at least 0.2 in. Hg/min, preferably of at least 0.4 in. Hg/min, more preferably of at least 1.0 in. Hg/min.

In said second stage, the vacuum is advantageously provided from atmospheric pressure to vacuum (3) at a vacuum rate of at most 6.0 in. Hg/min, preferably of at most 4.0 in. Hg/min, more preferably of at most 2.0 in. Hg/min.
In another embodiment of the method of the invention, the vacuum in the second stage is increased periodically in a stepwise manner until vacuum (3) whereby the vacuum in each step is advantageously increased at an amount ranging from 0.2 in. Hg to 10 in. Hg, preferably from 0.5 in. Hg to 5 in. Hg, even more preferably from 0.8 in. Hg to 1.5 in. Hg in corresponding periods varying from 0.1 to 20 min, preferably from 1 to 10 min, more preferably from 3 to 6 min. Good results were obtained when the vacuum was increased stepwise with increments of 1 in. Hg about every 5 minutes.

The cooling step (iii) and the trimming step (iv) in step 3. of the method of the present invention are typically carried out according to standard methods known in the art.

An aspect of the present invention also provides a thermoformed foamed article comprising at least one component comprising the foam (P) material, as detailed above, which provides various advantages over prior art parts and articles, in particular improved spring back, minimized shrinkage. Preferably, the thermoformed foamed article consists of the foam (P) material as detailed above.

In one embodiment of the present invention, the article is an aircraft structural component such as notably ceiling panels, sidewall panels, floor panels, privacy panels, stow bins, hand rails for stow bins, tablets, wet cell panels, ducts and plenums, passenger service units, galleys and galley doors, dado panels, cargo panels, seat shells.

In another embodiment of the present invention, the article is a mobile electronic device such as notably a laptop, a mobile phone, a GPS, a tablet, personal digital assistants, portable recording devices, portable reproducing devices and portable radio receives.

In yet another embodiment of the present invention, the article is a medical device such as notably medical trays, sterilization-resistant articles.

In yet another embodiment of the present invention, the article is a building material, a household good such as notably food service trays and the like.

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.
EXAMPLES

The invention will now be described in more details with reference to the following examples, whose purpose is merely illustrative and not intended to limit the scope of the invention.

5 Raw materials

Titanium Dioxide : -Tipure® R-105 titanium dioxide, a rutile TiO₂ manufactured by the chloride process, treated with silica and alumina.
RADEL® R PPSU from Solvay Specialty Polymers USA, L.L.C.
RADEL® R 5100 PPSU from Solvay Specialty Polymers USA, L.L.C.

10 Ultem™ 1000 PEI (from Sabic Innovative Plastics)

General procedure for the preparation of the foam material (P)

A polymer or polymer mixture was compounded with appropriate amounts of TiO₂ (see Table 1 below). Compounding into pellets was performed on a Berstorff 25 mm twin screw extruder having an L/D ratio of 40:1 and eight barrel sections, of which sections 2-8 are equipped with heating and cooling. In each case, the base polymer pellets and the TiO₂ were first tumble-blended for twenty minutes and then the mix was fed to the throat of the extruder. The extruder was set at a barrel temperature of 330°C for barrel sections 2-8. The die temperature was set at 340°C and a screw speed of 200 rpm was used along with a throughput rate of 25 lb/hr for each of the four formulations. Vacuum venting of the melt was performed at barrel section 7. The extrudate from the extruder in each case was cooled in a water trough and then pelletized. The pellets produced from the formulation are dried at temperatures between 130 and 180°C for 8 hours and are next fed to the foaming set up which consisted of a 4:l mm diameter Reifenhauser twin screw extruders that is set in series with a 50 mm Reifenhauser single screw extruder. The first extruder (A extruder) output fed via a melt pipe directly into the second (B extruder) in a T-configuration. The A extruder had an L/D ratio of 43 while the B extruder had an L/D of 30. The B extruder was equipped with a 1 mm slit die. The pellets produced from the formulation was fed to the A extruder where it was melted. The injection point for the blowing agent was located at two thirds of the way down the axial length of the A extruder. Ethanol was metered and injected into the polymer melt at pressures of 60-300 bar depending on the present melt pressure in the extruder. The homogenized polymer melt and ethanol mixture was then fed into the B extruder where the mixture was cooled down to temperatures between 180
and 230°C. The mixture is then extruded through the slit die and into the calibrator to form a foam panel.

Example 1

A foamed panel of 13 mm thickness was produced from a 75/25 blend of PPSU homopolymer from Solvay Specialty Polymers USA, L.L.C. and PEI polymer from Sabic Industries according to the general procedure, as described above. Said foamed panel was further sliced to between 6-7 mm using a horizontal band saw and used for thermoforming according to the general procedure described below, yielding a thermoformed foam article.

Scanning electron microscopy (SEM) analysis on the cross section of the sheet showed that the boards were of essentially uniform cell morphology throughout. The results are summarized in Table 1, see below.

Example 2

A foamed panel of 13 mm thickness was produced from a 50/50 blend of PPSU homopolymer from Solvay Specialty Polymers USA, L.L.C. and PEI polymer from Sabic Industries according to the general procedure, as described above. Said foamed panel was further sliced to a thickness between 6-7 mm using a horizontal band saw and used for thermoforming according to the general procedure described below, yielding a thermoformed foam article.

Scanning electron microscopy (SEM) analysis on the cross section of the sheet showed that the boards were of essentially uniform cell morphology throughout. The results are summarized in Table 1, see below.

General procedure for thermoforming of the foam material (P)

The sliced foam panel was placed in a hot air circulating oven, and preheated to 200°C for 30 min. Meanwhile, an assembly consisting of a metal mold placed on a ¼" thick aluminum plate which was covered by a nylon breather cloth was put together. A nylon bagging film was then placed over the plate and components and pinned down on 3 sides using tacky tape to form a bagging system. The sliced foam panel was taken from the oven and placed over the mold in the assembly, and the 4th side of the bag was then pinned down using the tacky tape. The entire assembly was then placed in the hot air circulating oven, and a quick release valve was inserted into the bagging system to allow the application of vacuum. The whole bagging system was then placed in the hot air circulating oven maintained at a temperature of 200°C. After 10 minutes of stabilization, a vacuum of 8 in. Hg was applied for a time period of 5 minutes. At this stage the foam was formed over the mold without cracking. The vacuum
was increased to 15 in. Hg for an additional 20 min. The hot air circulating oven was then cooled down to room temperature under vacuum. At that point, the vacuum was released and the thermoformed part was removed.

**Example 3**

The sliced foam panel of example 1 having a thickness of 6.3 mm was thermoformed according to the general procedure, as detailed above. The thermoformed part shows negligible shrinkage and springback. The results are summarized in Table 1, see below.

**Example 4**

The sliced foam panel of example 2 having a thickness of 6.5 mm was thermoformed according to the general procedure, as detailed above. The thermoformed part shows negligible shrinkage and springback. The results are summarized in Table 1, see below.

**Table 1**

<table>
<thead>
<tr>
<th>Examples No.</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultem™ 1000 PEI</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>RADEL® R 5100 PPSU (% wt.)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>75</td>
<td>50</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt; (%) wt.&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Ethanol (% wt.)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Melt temperature (°C)</td>
<td>228</td>
<td>227</td>
</tr>
</tbody>
</table>

| Foam properties | Density (kg/m<sup>3</sup>)<sup>c</sup> | 48.8 | 64.0 |
|                | Thickness (mm) | 13 | 13  |
|                | Cell size (microns)<sup>d</sup> | 135±28 | 102±18 |

<table>
<thead>
<tr>
<th>Thermoformed Foam properties</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (mm)</td>
<td>6.3</td>
<td>6.5</td>
</tr>
<tr>
<td>Density (kg/m&lt;sup&gt;3&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt; before thermoforming</td>
<td>47.7</td>
<td>69.2</td>
</tr>
<tr>
<td>Density (kg/m&lt;sup&gt;3&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt; after thermoforming</td>
<td>48.4</td>
<td>68.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> % wt. relative to total weight of Ultem™ 1000 PEI and RADEL® R 5100 PPSU
<sup>b</sup> the density was determined according to the buoyancy method whereby the sample was immersed in water for about 1 minute and the displaced volume was measured (Archimedes principle). In said buoyancy technique weighing of the foam specimens was carried out in air and in water as in the procedure of ASTM method D792.

<sup>c</sup> cell size and cell size distribution in the foams obtained were characterized by scanning electron microscopy (SEM). Image analysis of the SEM images of foam cross sections was performed using the "ImageJ" image analysis software Version 1.44 which is publically available on the Internet.

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CLAIMS

1. A method for manufacturing a thermoformed polyetherimide/poly(biphenyl ether sulfone) foam article which comprises following three steps:

Step 1. preparing a polyetherimide (PEI)/poly(biphenyl ether sulfone) (P2) foamable composition [composition (FP)], wherein said composition (FP) comprises PEI in an amount ranging from 0.1 % weight (% wt.) to 99.9 % wt., based on the total weight of the PEI and the poly(biphenyl ether sulfone) (P2).

Step 2. foaming the composition (FP) to yield a foamed (PEI)/poly(biphenyl ether sulfone) material [foam (P) material], and

Step 3. molding said foam (P) material under the effect of heat and pressure to provide a thermoformed foamed article.

2. The method according to claim 1, wherein the composition (FP) comprises a (PEI)/poly(biphenyl ether sulfone) (P2) polymer in an amount above 50 wt. %, based on the total weight of the composition (FP).

3. The method according to claims 1 or 2, wherein more than 50 wt. % of the recurring units of the poly(biphenyl ether sulfone) (P2) polymer are recurring units (R2) of formula (A):

\[
\text{Ar}^1_-\text{Ar}^2_\text{Ar}^3_\text{Ar}^4_\text{Ar}^5_-\text{O}^\text{O}_{\text{Ar}}^-\text{SOa}-\text{Ar}^1_\text{Ar}^2_\text{Ar}^3_\text{Ar}^4_\text{Ar}^5_-\text{SOa}^-\text{O}-
\]  
(formula A)

wherein:

- \(\text{Ar}^1, \text{Ar}^2, \text{Ar}^3, \text{Ar}^4,\) and \(\text{Ar}^5\), equal to or different from each other and at each occurrence, are independently an aromatic mono- or polynuclear group; with the proviso that at least one \(\text{Ar}^1\) through \(\text{Ar}^5\) is an aromatic moiety containing at least one biphenylene group, selected from the group consisting of those complying with the following formulae:

\[
\text{Ar}^1, \text{Ar}^2, \text{Ar}^3, \text{Ar}^4, \text{Ar}^5
\]
wherein R is selected from the group consisting of:

hydrogen, halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium and k and l equal or different from each other, are independently 0, 1, 2, 3 or 4, and

each of T, equal to or different from each other, is a bond or a divalent group optionally comprising one or more than one heteroatom;

n and m, equal to or different from each other, are independently zero or an integer of 1 to 5;

4. The method according to claims 1 or 2, characterized in that in the polyetherimide (PEI) more than 50% of the recurring units (R1) are recurring units (Rla) selected from the group consisting of those of formula (XXV) in imide form, their corresponding amic acid forms of formulae (XXVI) and (XXVII), and mixtures thereof:

![Chemical Structures](XXV)

![Chemical Structures](XXVI)

![Chemical Structures](XXVII)
wherein in formulae (XXVI) and (XXVII) the \( \rightarrow \) denotes isomerism so that in any recurring unit the groups to which the arrows point may exist as shown or in an interchanged position.

5. The method according to claims 1 or 2, characterized in that in the polyetherimide (PEI) more than 50% of the recurring units (Rl) are recurring units (Rla-4) selected from the group consisting of those of formula (XXVIII) in imide form, their corresponding amic acid forms of formulae (XXIX) and (XXX), and mixtures thereof:

\[
\text{(XXVIII)}
\]

\[
\text{(XXIX)}
\]

\[
\text{(XXX)}
\]

wherein in formulae (XXIX) and (XXX) the \( \rightarrow \) denotes isomerism so that in any recurring unit the groups to which the arrows point may exist as shown or in an interchanged position.

6. The method according to any one of claims 1 to 5, wherein a nucleating agent is used in Step 1, in an amount from 0.1 to 5% by weight based on the total weight of the composition (FP).
7. The method according to any one of claims 1 to 6, wherein the foaming in Step 2 is performed by a foaming technique selected from a group consisting of pressure cell processes, autoclave processes, extrusion processes, direct (variotherm) injection processes and bead foaming.

8. The method according to any one of claims 1 to 7, wherein the molding of the foam (P) material in Step 3 is performed by a thermoforming process selected from a group consisting of vacuum forming, pressure forming, matched mold forming and twin sheet thermoforming processes.

9. The method according to claim 8, wherein the thermoforming process is performed in four steps: (i) pre-forming the foam (P) material under the effect of heating (i.e. the pre-heating step), (ii) forming the thermoformed foamed article by holding the foam (P) material against a mold under pressure differential and heating (i.e. the forming step) (iii) cooling the thermoformed foamed article in the mold (i.e. the cooling step) (iv) trimming the thermoformed foamed article (i.e. the trimming step).

10. The method according to any one of claims 8 or 9, wherein the thermoforming process is a vacuum forming process.

11. The method according to any one of claims 9 or 10, wherein the foam (P) material is pre-heated up in the pre-heating step (i) to a temperature of at least 200°C and for an interval of time of least 10 min.

12. The method according to any one of claims 9 to 10, wherein, the foam (P) material in the forming step (ii) is held against a temperature controlled mold under pressure differential wherein said pressure is at least 2 in. Hg, the pressure differential is preferably under the form of a vacuum.

13. The method according to claim 12, wherein the vacuum is applied in one stage and is provided from atmospheric pressure to a maximum vacuum pressure level 1 [vacuum (1)] of at least 5 in. Hg and a vacuum rate of at least 2 in. Hg/min.
14. The method according to claim 12, wherein the vacuum is applied in two stages, wherein in the first stage, the vacuum is provided from atmospheric pressure to a vacuum pressure level 2 [vacuum (2)] of at least 1 in. Hg and at a vacuum rate of at least 0.2 in. Hg/min and in a second stage, the vacuum is further kept constant at vacuum (2), or is continuously increased until a maximum vacuum level 3 [vacuum (3)] of at least 5 in. Hg or is increased in a stepwise manner until vacuum (3).

15. A thermoformed foamed article prepared according to the method according to any one of claims 1 to 14.