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(71) Applicant: SOLVAY SPECIALTY POLYMERS USA, LLC [US/US]; 4500 McGinnis Ferry Road, Alpharetta, Georgia 30005-3914 (US).

(72) Inventors: AXELRAD, Shari W.; 3192 Lynwood Drive, Atlanta, Georgia 30319 (US). GAUTAM, Keshav; 2663 Winsley Place, Duluth, Georgia 30097 (US). KLESING, Armin; Finkenweg 2, 56589 Niederbreitbach (DE). EL-HIBRI, Mohammad Jamal; 6851 Roswell Road, No. M-18, Atlanta, Georgia 30328 (US). SCHELLES, Marc; 5 Kanaaldijk, B-2400 Geel (BE). KENKARE, Nirupama; 4985 Cinnabar Drive, Alpharetta, Georgia 30022 (US).

(74) Agents: BENVENUTI, Federica et al; Rue de Ransbeek, 310, B-1120 Bruxelles (BE).

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(54) Title: THERMOFORMED FOAM ARTICLES

(57) Abstract: A method for manufacturing a thermo formed poly(biphenyl ether sulfone) foam article which comprises following three steps : Step 1. preparing a poly(biphenyl ether sulfone) foamable composition [composition (FP)], foaming the composition (FP) to yield a foamed poly(biphenyl ether sulfone) material [foam (P) material], and Step 2. molding said foam (P) material under the effect of heat and pressure to provide a thermoformed foamed article. Step 3. molding said foam (P) material under the effect of heat and pressure to provide a thermoformed foamed article.



Thermoformed foam articles

This application claims priority to U.S. provisional application No. 61/5791 12 filed December 22, 201 1 and to European applications No. 12155762.3 filed on February 16, 2012 and No. 12188357.3 filed on October 12, 2012, the whole content of each of these applications being  
5 incorporated herein by reference for all purposes.

**Field of invention**

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

**10 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  
15 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  
20 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  
25 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.

30 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 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 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 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 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 poly(biphenyl ether sulfone) foam article which comprises following three steps :

Step 1. preparing a poly(biphenyl ether sulfone) foamable composition [composition (FP)],

Step 2. foaming the composition (FP) to yield a foamed 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.

Another aspect of the present invention is directed to a thermoformed poly(biphenyl ether sulfone) foam article.

#### **Detailed description of embodiments**

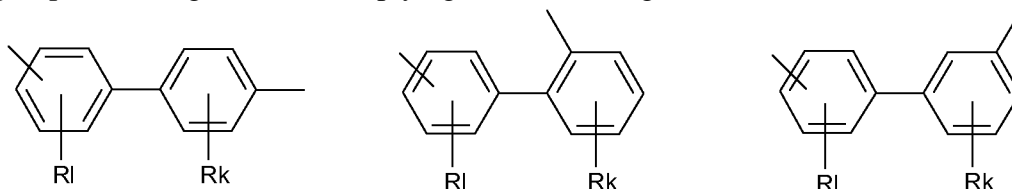
##### *Composition (FP)*

Generally, the composition (FP) prepared in the first step of the method of the present invention comprises a poly(biphenyl ether sulfone) (PI) polymer in an amount advantageously above 50 wt. % , preferably above 80 wt. % ; more preferably above 90 wt. % ; more preferably above 95 wt. % and more preferably above 99 wt. % , based on the total weight of the composition (FP).

If desired, the composition (FP) comprises no other polymer than the poly(biphenyl ether sulfone) (PI).

In the rest of the text, the expressions "poly(biphenyl ether sulfone)" is 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 poly(biphenyl ether sulfone) [poly(biphenyl ether sulfone) (PI)].

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

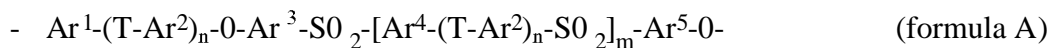


wherein R is selected from the group consisting of :

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

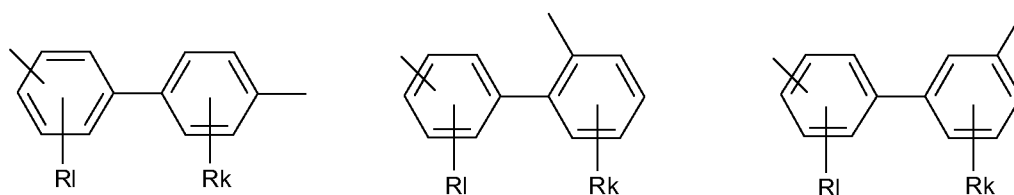
at least one ether group (-O-) and at least one sulfone group (-SO<sub>2</sub>-).

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



wherein :

- Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup>, Ar<sup>4</sup>, and Ar<sup>5</sup>, 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 Ar<sup>1</sup>through Ar<sup>5</sup>is an aromatic moiety containing at least one biphenylene group, selected from the group consisting of those complying with the following formulae :



- 4 -

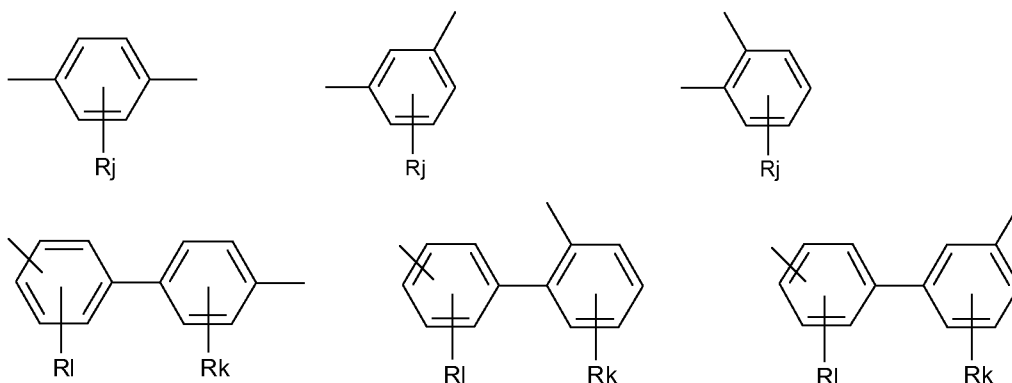
wherein R is selected from the group consisting of :

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 ;

Preferably, Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup>, Ar<sup>4</sup>, Ar<sup>5</sup> are equal or different from each other and are aromatic moieties preferably selected from the group consisting of those complying with following formulae :

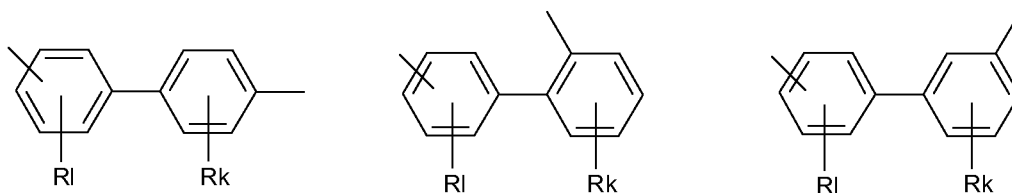


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wherein R is selected from the group consisting of :

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 with the proviso that at least one Ar<sup>1</sup> through Ar<sup>5</sup> is an aromatic moiety containing at least one biphenylene group, selected from the group consisting of those complying with following formulae :

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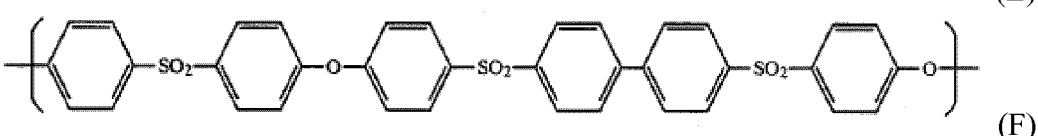
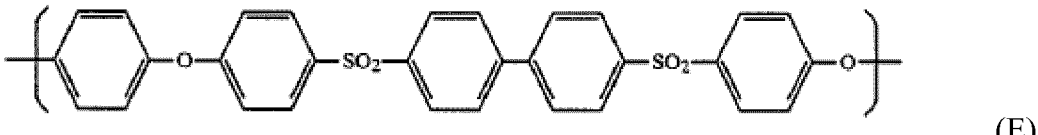
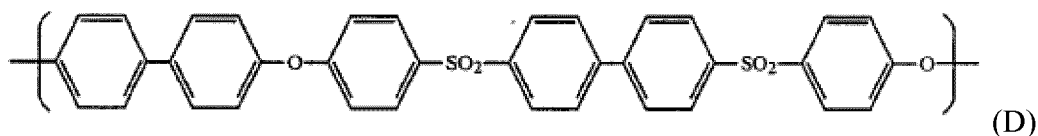
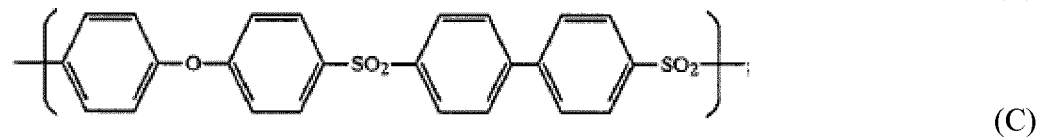
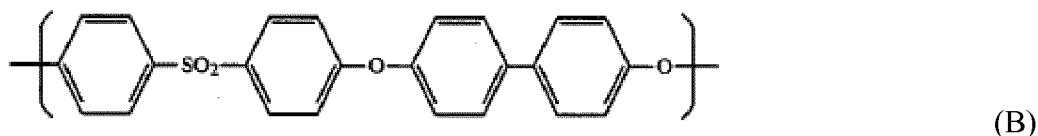
wherein R is selected from the group consisting of :

hydrogen, halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid,

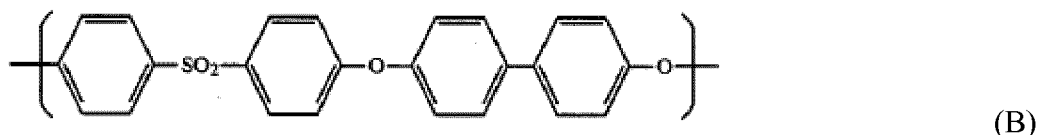
ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium and k and l equal or different from each other, are independently 0, 1, 2, 3 or 4.

- 5 Preferably, each of T, equal to or different from each other, is selected from the group consisting of a bond, -CH<sub>2</sub>- ; -O- ; -SO<sub>2</sub>- ; -S- ; -C(O)- ; -C(CH<sub>3</sub>)<sub>2</sub>- ; -C(CF<sub>3</sub>)<sub>2</sub>- ; -C(=CCl<sub>2</sub>)- ; -C(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>COOH)- ; -N=N- ; -R<sup>a</sup>C=CR<sup>b</sup>- ; where each R<sup>a</sup> and R<sup>b</sup> ; independently of one another, is a hydrogen or a Ci-Ci<sub>2</sub>-alkyl, Ci-Ci<sub>2</sub>-alkoxy, or C<sub>6</sub>-Ci<sub>8</sub>-aryl group ; -(CH<sub>2</sub>)<sub>n</sub>- and -(CF<sub>2</sub>)<sub>n</sub>-  
 10 with n = integer from 1 to 6, or an aliphatic divalent group, linear or branched, of up to 6 carbon atoms ; and mixtures thereof.

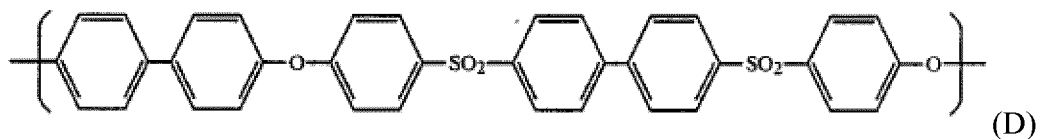
More preferably, recurring units (R2) are selected from the group consisting of formulae (B) to (F), as below detailed, and mixtures thereof :



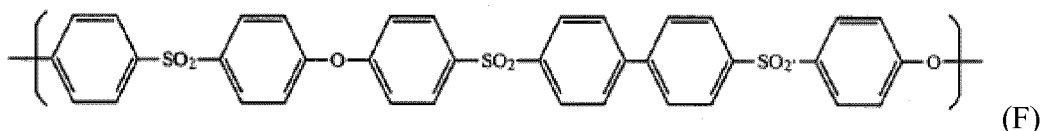
Still more preferably, recurring units (R2) are :



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

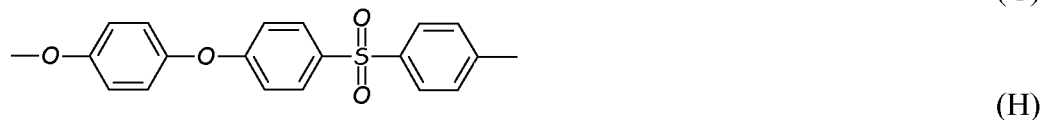


In yet another preferred embodiment, recurring units (R2) are of formula (F), shown below :

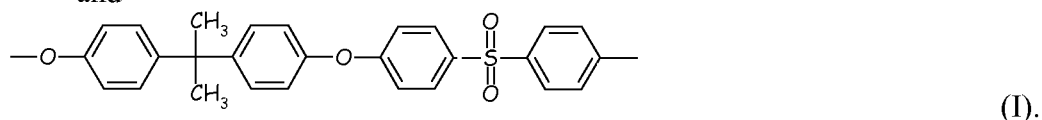


5 The poly(biphenyl ether sulfone) (PI) may be notably a homopolymer, a random, alternate or block copolymer. When the poly(biphenyl ether sulfone) (PI) is a copolymer, its recurring units may notably be composed of (i) recurring units (R2) of at least two different formulae selected from formulae (B)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

10 recurring units (R2\*), different from recurring units (R2), such as :



and



15 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) (PI) are recurring units (R2).

Still, it is generally preferred that substantially all recurring units of the poly(biphenyl ether sulfone) (PI) are recurring units (R2), as detailed above ;

20 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) (PI) is then preferably a polyphenylsulfone (PPSU).

For the purpose of the present invention, a polyphenylsulfone (PPSU)

25 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) (PI) are of formula (B).

5           PvADEL<sup>®</sup> R polyphenylsulfone from Solvay Specialty Polymers US, 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  
10 the poly(biphenyl ether sulfone) (PI) are of formula (D).

SUPPvADEL<sup>™</sup> HTS high-temperature sulfone polymer from Solvay Specialty Polymers US, L.L.C. is an example of a commercially available poly(biphenyl ether sulfone) (PI) comprising more than 50 wt. % of the recurring units of formula (D).

15           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) (PI) are of formula (F).

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

In a specific embodiment of the present invention, poly(biphenyl ether sulfone) (PI) may also be a blend composed of at least two poly(biphenyl ether sulfone) (PI) chosen from a group consisting of a (PPSU) polymer, as detailed above and a SUPRADEL<sup>™</sup> HTS high-temperature sulfone polymer, as detailed  
25 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  
30 SUPRADEL<sup>™</sup> 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  
35 SUPRADEL<sup>™</sup> 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) (PI) can be prepared by any method. The molecular weight of the poly(biphenyl ether sulfone) (PI), 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) (PI) 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) (PI) weight average molecular weight can be 20,000 to 70,000 grams per mole (g/mol).

The poly(biphenyl ether sulfone) (PI) may have glass transition temperatures of 180 to 250°C, when determined according to ASTM D 43 18.

Poly(biphenyl ether sulfone) (PI) 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.

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 poly(biphenyl ether sulfone) (PI).

The composition (FP) may further contain conventional ingredients of polymeric compositions such as miscible polymers, or polymers that can be compatibilized with PPSU, notably polymers as polyetherimides or polyetheretherketones, 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.

5           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 more than 85 wt. % of the poly(biphenyl ether sulfone) (PI) with the proviso that the poly(biphenyl ether  
10 sulfone) (PI) are the only polymeric components in the composition (FP) and one or more optional ingredients such as additives ; stabilizers ; lubricants ; plasticizers ; pigments ; dyes ; colorants ; anti-static agents ; nucleating agents ; blowing agents ; metal deactivators ; antioxidants and surfactants might be present therein, without these components dramatically affecting relevant  
15 mechanical and toughness properties of the composition (FP).

          In a preferred embodiment, the composition (FP) comprises more than 85 wt. % of the (PPSU) polymer, as detailed above, with the proviso that the (PPSU) polymer, is the only polymeric components in the composition (FP) and one or more optional ingredients such as additives ; stabilizers ; lubricants ;  
20 plasticizers ; pigments ; dyes ; colorants ; anti-static agents ; nucleating agents ; blowing agents ; metal deactivators ; antioxidants and surfactants might be present therein, without these components dramatically affecting relevant mechanical and toughness properties of the composition (FP).

          In another preferred embodiment, the composition (FP) comprises more  
25 than 85 wt. % of a blend composed of at least two poly(biphenyl ether sulfone) (PI) 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 (PPSU) polymer and the SUPRADEL™ HTS high-temperature sulfone polymer are the only polymeric components in the  
30 composition (FP) and one or more optional ingredients such as additives ; stabilizers ; lubricants ; plasticizers ; pigments ; dyes ; colorants ; anti-static agents ; nucleating agents ; blowing agents ; metal deactivators ; antioxidants and surfactants might be present therein, without these components dramatically affecting relevant mechanical and toughness properties of the composition (FP).

- 10 -

The expression 'polymeric components' is to be understood according to its usual meaning, i.e. encompassing compounds characterized by repeated linked units, having typically a molecular weight of 2 000 or more.

In Step 1. of the method of the invention, a nucleating agent, or blends of  
5 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  
10 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  
15 (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  
20 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,  
25 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  
30 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  
35 blending of the poly(biphenyl ether sulfone) (PI) 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 poly(biphenyl ether sulfone) (PI) in  
5 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  
10 compounding can be effected on the powder mixture as above detailed, or preferably directly on the poly(biphenyl ether sulfone) (PI) 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.  
15 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  
20 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 advantageously 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  
25 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  
30 poly(biphenyl ether sulfone) (PI) 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  
35 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 polymer (PI)/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  
5 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 polymer (PI)/gas mixture and foaming is induced by spontaneous release of the pressure. In contrast to the pressure cell process, in  
10 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  
15 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  
20 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  
25 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  
30 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  
35 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.

5           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  
10           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  
15           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 poly(biphenyl ether sulfone) (PI) melt (at pressure, temperature and shear rate) are balanced and the walls of the bubbles are  
20           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  
25           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  
30           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  
35           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. CO<sub>2</sub>, 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.

5 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/m<sup>3</sup>, preferably from 20 to 150 kg/m<sup>3</sup>, more preferably from 20 to 100 kg/m<sup>3</sup>, even more preferably from 20 to 55 kg/m<sup>3</sup>.

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.

15 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.

25 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.

30 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.

#### *Thermofoamed foamed article*

35 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 thermo forming 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.

5 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 thermo formed foamed article by holding the foam (P) material against a mold under pressure differential and heating (i.e. the forming step) (iii) cooling the thermo formed foamed article in the mold (i.e. the  
10 cooling step) (iv) trimming the thermo formed 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  
15 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 heaters or  
20 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  
25 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 200°C, preferably at least 205°C and more preferably at least 210°C.

The foam (P) material is generally pre-heated up in step (i) for an interval  
30 of time 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 in step (i) for an interval of time of at most 120 min, preferably at most 90 min, more preferably at most 70 min.

35 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.

5 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.

10 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.

15 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))].

20 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.

25 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.

30 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.

35 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.

5 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.

10 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).

15 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.

20 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.

25 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  
30 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.

35 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.

- 20 -

An aspect of the present invention also provides a thermofoamed 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 thermofoamed 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.

#### **Raw materials**

*Titanium Dioxide* : -Tipure<sup>®</sup> R-105 titanium dioxide, a rutile TiO<sub>2</sub> manufactured by the chloride process, treated with silica and alumina.

RADEL<sup>®</sup> R PPSU from Solvay Specialty Polymers USA, L.L.C.

SUPRADEL<sup>™</sup> HTS -2600NT from Solvay Specialty Polymers USA, L.L.C.

RADEL<sup>®</sup> R 5100 PPSU from Solvay Specialty Polymers USA, L.L.C.

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

A polymer or polymer mixture was compounded with 2 parts of TiO<sub>2</sub> per hundred parts of resin. 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 TiO<sub>2</sub> 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 41 mm diameter Reifenhauer twin screw extruders that is set in series with a 50 mm Reifenhauer 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. Isopropanol 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 isopropanol 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.

#### 25 **Example 1**

A foamed panel of 19.1 mm thickness was produced from RADEL®R PPSU from Solvay Specialty Polymers USA, L.L.C. according to the general procedure, as described above. Said foamed panel was further sliced to 5mm 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.

#### **Example 2**

35 A foamed panel is produced from SUPRADEL™ HTS high-temperature sulfone polymer from Solvay Specialty Polymers US, L.L.C according to the

general procedure, as described above, by using now 2 parts per 100 by weight of  $\text{TiO}_2$ , and the homogenized polymer melt and isopropanol mixture is now cooled down to temperatures between 230°C and 280°C in extruder B.

5 Scanning electron microscopy (SEM) analysis on the cross section of the sheet shows that the boards are of essentially uniform cell morphology throughout.

Said foamed panel is further sliced to 5 mm using a horizontal band saw and is used for thermoforming. The thermoforming is carried out according to the general procedure as described below, but the preheating and thermoforming  
10 temperature is increased to 255°C.

### **Example 3**

Example 3 is carried out as described for example 2 by using a poly(biphenyl ether sulfone) (PI) having all recurring units of formula (F).

### **Foaming procedure for the preparation of examples 4 and 5**

15 Polymer pellets of SUPRADEL™ HTS or blends of SUPRADEL™ HTS and RADEL®R PPSU precompounded with the appropriate amount of  $\text{TiO}_2$  (see Table 1) were fed into a foaming setup which consisted of a Collins twin screw extruder with a screw diameter of 25 mm, set in series with a single screw extruder with a screw diameter of 45 mm. The output of the first  
20 extruder (A extruder) was fed directly into the second extruder (B extruder) set in a right angle configuration. The A extruder had a L/D ratio of 42 and the B extruder had a L/D ratio of 30. The B extruder was equipped with a 0.6 mm slit die. The pellets produced from the formulation were fed to the A extruder where they were melted (see Table 1, the melt temperature). The injection point for the  
25 blowing agent was located at two thirds of the way down the axial length of the A extruder. Isopropanol (9 % wt.) was metered and injected into the polymer melt at pressures of 60-150 bar depending on the present melt pressure in the extruder. The homogenized polymer melt and isopropanol mixture were then fed into the B extruder where the mixture was cooled down to temperatures between  
30 250 and 280°C. The mixture was then extruded through the slit die to form a foamed film. The results are summarized in Table 1.

**Table 1**

<b>Examples N°</b>	<b>4</b>	<b>5</b>
SUPRADELTM HTS -2600NT (% wt.) <sup>a</sup>	100.0	50.0
RADEL <sup>®</sup> R 5100 PPSU (% wt.) <sup>a</sup>	-	50.0
TiO <sub>2</sub> (% wt.) <sup>b</sup>	-	0.5
Isopropanol (% wt.) <sup>b</sup>	9.0	9.0
Melt temperature (°C)	274	257
<b>Foam properties</b>		
Density (kg/m <sup>3</sup> ) <sup>c</sup>	148	82
Thickness (mm)	3.4	4.9
Cell size (microns) <sup>d</sup>	99	96

(<sup>a</sup>) % wt. relative to total weight of SUPRADELTM HTS -2600NT and RADEL<sup>®</sup> R 5100 PPSU (<sup>b</sup>) % wt. relative to total weight of all components in the composition

5 (<sup>c</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.

10 (<sup>d</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.

### 15 **General procedure for thermoforming of the foam material (P)**

The clay mold and the foam material (P) were preheated in an hot air circulating oven to a temperature of 210°C and preheated for a short time. After preheating the mold to 210°C, said mold was removed from the hot air circulating oven, and placed on a 1/4" aluminum plate. Between the mold and the plate, a nylon breather cloth was placed. The foam was then placed on the mold, covered with another piece of breather cloth, and pinned down a nylon bagging film with tacky tape thereby forming a bagging system. A quick release valve was inserted into the bagging system to allow bringing said system under vacuum. The whole bagging system was placed in the hot air circulating oven maintained at a temperature of 210°C. After 6 minutes of stabilization at 210°C, a vacuum was applied to 5 in. Hg in a time period of 1 min. Every 5 minutes thereafter, the vacuum was stepwise increased by 1 in. Hg. After 30 more minutes, the thermoformed part had been formed against the mold without

cracking. The hot air circulating oven was cooled down the oven to room temperature and when the mold center temperature reached 120°C inside, the vacuum was released. The thermo formed part was removed.

**Example 6**

- 5           Foam material of example 4 is thermo formed according to the general procedure, as detailed above, instead now the hot air circulating oven was preheated to 220°C and the foam was placed on a metal mold. Said assembly was then placed on a 1/4" aluminum plate. The whole bagging system was now placed in the hot air circulating oven maintained at a temperature of 220°C.
- 10          After 5 minutes of stabilization, a vacuum of 7.5 in Hg was applied for a time period of an additional 5 minutes. Instead, at this stage the foam was now formed over the mold without cracking. The thermo formed part shows no springback and has a density of 145 kg/m<sup>3</sup>.

**Example 7**

- 15           Foam material of example 5 is thermo formed in the same way as described for example 6. The thermo formed part shows no springback and has a density of 81 kg/m<sup>3</sup>.

CLAIMS

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

5 Step 1. preparing a poly(biphenyl ether sulfone) foamable composition [composition (FP)],

Step 2. foaming the composition (FP) to yield a foamed 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.

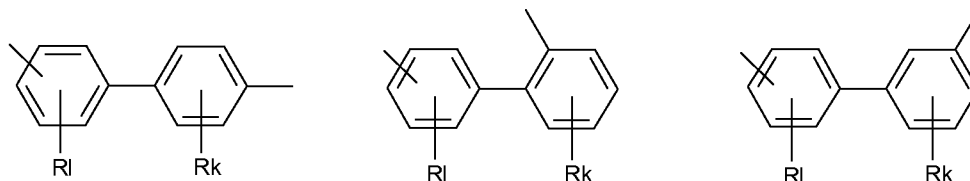
10 2. The method according to claim 1, wherein the composition (FP) comprises a poly(biphenyl ether sulfone) (PI) polymer in an amount above 50 wt. %, based on the total weight of the composition (FP).

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



wherein :

20 - Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup>, Ar<sup>4</sup>, and Ar<sup>5</sup>, 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 Ar<sup>1</sup> through Ar<sup>5</sup> is an aromatic moiety containing at least one biphenylene group, selected from the group consisting of those complying with the following formulae :



wherein R is selected from the group consisting of :

- 26 -

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 any one of claims 1 to 3, 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).

5. The method according to any one of claims 1 to 4, 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.

6. The method according to claim 5, wherein a blowing agent is used in Step 2. in an amount from 1 to 15 % 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 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.

8. The method according to claim 7, 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).

9. The method according to any one of claims 7 or 8, wherein the thermoforming process is a vacuum forming process.

10. The method according to any one of claims 8 or 9, 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.

11. The method according to any one of claims 8 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.

10 12. The method according to claim 11, 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.

15 13. The method according to claim 11, 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  
20 stepwise manner until vacuum (3).

14. A thermofoamed article prepared according to the method according to any one of claims 1 to 13.

25 15. The thermofoamed article according to claim 14, wherein said article is an aircraft structural component, a mobile electronic device, a medical device, a building material or a household good.

INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2012/076116

A. CLASSIFICATION OF SUBJECT MATTER  
**INV. C08J9/228 C08J9/36 C08J9/00**  
 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**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
**EPO-Internal , WPI Data**

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 710 522 A (HUGGARD MARK T [US] ) 1 December 1987 (1987-12-01) column 4, lines 8-12 ; claim 1 column 6, lines 3-5 column 8, lines 3-24 -----	1-15
X	US 2010/324171 A1 (MAUKOVIC NIKICA [US] ET AL) 23 December 2010 (2010-12-23) paragraphs [0237] , [0239] ; claims 1, 2, 4, 27, 41 -----	1-15
A	Wo 2010/112508 A1 (BASF SE [DE] ; WEBER MARTIN [DE] ; MALETZKO CHRISTIAN [DE] ; LANGE GERHAR) 7 October 2010 (2010-10-07) page 3, lines 5-9 ; claims 1, 12, 17 -----	1-15
A	US 8 017 699 B1 (SANNER MARK [US] ET AL) 13 September 2011 (2011-09-13) claims 1, 22, 26, 28 -----	1-15

Further documents are listed in the continuation of Box C.  See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search <b>19 April 2013</b>	Date of mailing of the international search report <b>26/04/2013</b>
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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 <b>Clement, Silvia</b>
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No <b>PCT/EP2012/076116</b>
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