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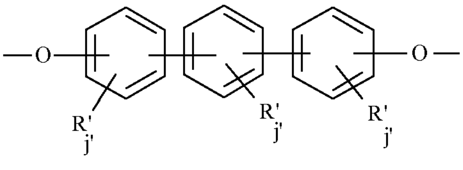
(54) Oil and gas recovery articles

(57) An oil and gas recovery article comprising at least one part made of a poly(arylether sulfone) polymeric material comprising at least one poly(arylether sulfone) polymer, wherein said (t-PAES) polymer comprising more than 50 % moles of recurring units (R_t) of formula (S_t): E-Ar^1-SO_2-[Ar^2-(T-Ar^3)$_n$-SO_2]$_m$-Ar^4 wherein n and m, equal to or different from each other, are independently zero or an integer of 1 to 5, each of Ar^1, Ar^2, Ar^3 and Ar^4 equal to or different from each other and at each occurrence, is an aromatic moiety, T is a bond or a divalent group and E is of formula (E_t) :



wherein each of R', equal to or different from each other, is selected from the group consisting of 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 ; j' is zero or is an integer from 1 to 4.

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Description

Field of invention

[0001] The present invention is related to an article suitable for use in oil/gas recovery industries comprising polyarylene ether sulfone (PAES) polymer based materials, wherein said (PAES) polymers comprise moieties derived from incorporation of 4,4"-terphenyl-p-diol. Said (PAES) polymer based material is characterized by having improved mechanical properties, in particular having an excellent balance of stiffness and ductility, good chemical resistance, high thermal resistance (e.g. Tg > 230°C), long term thermal stability, useful highest Tm between 360°C and 420°C.

Background of the invention

[0002] The Oil and Gas market currently represents about one third of the polyetheretherketone (PEEK) market worldwide. Polyetheretherketone (PEEK) polymers are semi-crystalline polymers used for a combination of properties including, primarily for its high temperature and chemical resistance.

[0003] Currently, the easy-to-reach oil fields become less and less productive; thus there is a need to start producing from harder-to-reach oil fields, which can be associated with the most challenging operating environments, such as much of which is deep under the ocean and under high pressure.

[0004] It is a critical challenge for the oil and gas market that articles suitable for use in oil and gas recovery application, for example as notably used in high pressure and high temperature [HP/HT, used herein after] deepwater oil and gas recovery applications, resist these extreme conditions of being exposed in a prolonged fashion to high pressure, e.g. pressures higher than 30,000 psi, high temperatures e.g. temperatures up to 260°C to 300°C and to harsh chemicals including acids, bases, superheated water/steam, and of course a wide variety of aliphatic and aromatic organics. For example, enhanced oil recovery techniques involve injecting of fluids such as notably water, steam, hydrogen sulfide (H_2S) or supercritical carbon dioxide (sCO_2) into the well. In particular, sCO_2 having a solvating effect similar to n-heptane, can cause swelling of materials in for instance seals, which affect consequently their performance.

[0005] Thus, oil and gas articles made from semi-crystalline PEEK polymers no longer resist pressures up to 30,000 psi and temperatures up to 300°C and have the drawbacks that said articles can not be used any more in the above mentioned HP/HT oil and gas recovery application.

[0006] As mentioned above, polymeric materials useful for providing articles suitable for use in said oil and gas recovery application should thus possess properties such as maintaining or improved mechanical rigidity and integrity (e.g. yield/tensile strength, hardness and impact toughness) at high pressure and temperatures of at least 300°C, good chemical resistance, in particular when exposed to CO_2, H_2S, amines and other chemicals at said high pressure and temperature, swelling and shrinking by gas and by liquid absorption, decompression resistance in high pressure oil/gas systems, gas and liquid diffusion and long term thermal stability.

[0007] Thus, there remains a continuous need for articles suitable for use in oil and gas recovery applications comprising at least one polymeric material that can overcome the drawbacks, mentioned above, and wherein said polymeric material features excellent mechanical properties (and in particular good combination of high stiffness and ductility), having an excellent balance of stiffness and ductility, good processability, high chemical resistance, high thermal resistance (e.g. Tg > 260°C) and long term thermal stability, and wherein said polymeric material provide final articles having all these improved properties, as mentioned above.

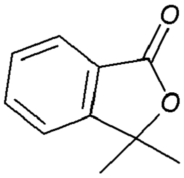
Summary of invention

[0008] The present invention addresses the above detailed needs and relates to an oil and gas recovery article comprising at least one part made of a poly(arylether sulfone) polymeric material [(t-PAES) polymeric material, herein after] comprising at least one poly(arylether sulfone) polymer [(t-PAES) polymer], wherein said (t-PAES) polymer comprising more than 50 % moles of recurring units (R_t) of formula (S_t) :

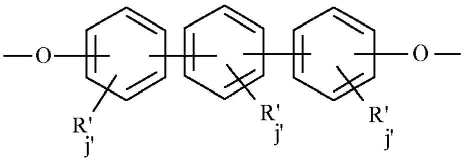
$$-E-Ar^1-SO_1-[Ar^1-(T-Ar^3)_n-SO_2]_m-Ar^4- \qquad \text{(formula } S_t\text{)}$$

wherein :

- n and m, equal to or different from each other, are independently zero or an integer of 1 to 5,
- each of Ar^1, Ar^2, Ar^3 and Ar^4 equal to or different from each other and at each occurrence, is an aromatic moiety,
- T is a bond or a divalent group optionally comprising one or more than one heteroatom ; preferably T is selected from the group consisting of a bond,- CH_2-, -C(O)-, -$C(CH_3)_2$-, -$C(CF_3)_2$-, -$C(=CCl_2)$-, -$C(CH_3)(CH_2CH_2COOH)$-, and a group of formula :



- E is of formula (E_t) :



wherein each of R', equal to or different from each other, is selected from the group consisting of 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 ; j' is zero or is an integer from 1 to 4.

The oil and gas recovery article

[0009] To the purposes of the invention, the term "oil and gas recovery article" is intended to denote any article that is designed to conveniently be used in oil and gas recovery applications, in particular in HP/HT conditions.

[0010] For the sake of clarity, the term "part of an oil and gas recovery article" is intended to denote a piece or portion which is combined with others to make up the whole oil and gas recovery article. The external coating of an oil and gas recovery article falls thus within this scope. Thus, the at least one part of the oil and gas recovery article according to the present invention, can be a coating.

[0011] Representative examples of oil and gas recovery applications, but not limited to, include (i) drilling and completion of deep, higher temperature, higher pressure oil and gas wells, as notably described in U.S. Pat. No. 5,662,170 the entire disclosure of those are incorporated herein by reference, (ii) an oil and gas recovery method as traditionally subdivided in three stages, namely a primary oil recovery stage, a secondary or assisted oil recovery and a tertiary or enhanced oil recovery stage (iii) gas and oil gathering treatment applications, (iv) complex transportation of gas and oil from said deep, higher temperature, higher pressure wells to refineries and the like.

[0012] All these applications as herein mentioned above, are well familiar to the skilled person, and should be understood under their common meaning.

[0013] As non limitative examples of oil and gas recovery articles useful in the present invention are drilling systems; as notably described in U.S. Pat. No. 2001/0214920 A1 the entire disclosure of which is incorporated herein by reference; drilling rigs; compressor systems, as notably described in U.S. Pat. No. 2010/0239441 A1, the entire disclosure of which is incorporated herein by reference; pumping systems; motor systems, sensors, such as reservoir sensors; control systems, such as temperature and/or pressure; stimulation and flow control systems; liner hanger systems, as notably described in U.S. Pat. No. 6,655,456 B1, the entire disclosure of which is incorporated herein by reference; packer systems, as notably described in U.S. Pat. No. 7,874,356 B2, the entire disclosure of which is incorporated herein by reference; pipe systems, valve systems, tubing systems, casing systems, and others.

[0014] All these systems as herein mentioned above, are well familiar to the skilled person, and should be understood under their common meaning.

[0015] By the term "drilling rig" is meant a structural housing equipment that is used to drill oil wells, or natural gas extraction wells, and may comprise a single article or comprise two or more components. Typically components of said drilling rig include, but not limited to, mud tanks, shale shakers, mud pumps, drill pipes, drill bits, drilling lines, electric cable trays.

[0016] As non limitative examples of pumping systems useful in the present invention are jet pump systems, submersible pumping systems, in particular electric submersible pumps, as notably described in U.S. Pat. No. 6,863,124 B2 the entire disclosure of which is incorporated herein by reference, beam pumps

[0017] As non limitative examples of motor systems useful in the present invention are mud motor assemblies, as notably described in U.S. Pat. No. 2012/0234603 A1, the entire disclosure of which is incorporated herein by reference.

[0018] As non limitative examples of pipe systems useful in the present invention, mention can be made of pipes including rigid pipes and flexible pipes, flexible risers, pipe-in-pipe, pipe liners, subsea jumpers, spools, umbilicals.

[0019] Typical flexible pipes have been described by way of example in WO 01/61232, U.S. Pat. No. 6,123,114 and U.S. Pat. No. 6,085,799; the entire disclosure of those are incorporated herein by reference. Such flexible pipes can notably be used for the transport of fluids where very high or very different water pressure prevails over the length of the pipe, and for example can take the form of flexible risers which run from the ocean floor up to equipment at or in the vicinity of the ocean surface, and they can also generally be used as pipes for the transport of liquids or gases between various items of equipment, or as pipes laid at great depth on the ocean floor, or as pipes between items of equipment close to the ocean surface, and the like.

[0020] Preferred pipe systems are pipes, flexible risers and pipe liners.

[0021] By the term "valves" is meant any device for halting or controlling the flow of a liquid, gas, or any other material through a passage, pipe, inlet, outlet, and the like. As non limitative examples of valve systems useful in the present invention, mention can especially be made of choke valves, thermal expansion valves, check valves, ball valve, butterfly valve, diaphragm valve, gate valve, globe valve, knife valve, needle valve, pinch valve, piston valve, plug valve, poppet valve, spool valve, pressure reducing valve, sampling valves, safety valve.

[0022] The at least one part of the oil and gas recovery articles according to the present invention may be selected from a large list of articles such as fitting parts; such as seals, in particular sealing rings, preferably backup seal rings, fasteners and the like; snap fit parts; mutually moveable parts; functional elements, operating elements; tracking elements; adjustment elements; carrier elements; frame elements; films; switches; connectors; wires, cables; bearings, housings, compressor components such as compressor valves and compressor plates, any other structural part other than housings as used in an oil and gas recovery articles, such as for example shafts, shells, pistons.

[0023] In particular, the (t-PAES) polymeric material is very well suited for the production of seals, fasteners, cables, electrical connectors, housing parts of oil and gas recovery articles.

[0024] In one preferred embodiment, the at least one part of the oil and gas recovery article according to the present invention, is advantageously an oil and gas recovery housing, a seal, an electrical connector or a cable.

[0025] A cable can be notably wires electrically connecting the different parts within a oil and gas recovery article, for example connecting different electrical connectors, connecting tools to connectors, instruments or other tools, connecting instruments to connectors, other instruments or tools, connecting a power source to connectors, instruments or tools. A cable can also advantageously be used for carrying a signal to computer systems.

[0026] In a particularly aspect of this preferred embodiment, the cable is a coated wire or a wire coating.

[0027] By "oil and gas recovery housing" is meant one or more of the back cover, front cover, frame and/or backbone of an oil and gas recovery article. The housing may be a single article or comprise two or more components. By "backbone" is meant a structural component onto which other components of the oil and gas recovery article, are mounted. The backbone may be an interior component that is not visible or only partially visible from the exterior of the oil and gas recovery article.

[0028] Typical fasteners have been described by way of example in WO 2010/112435, the entire disclosure of those are incorporated herein by reference, and include, but not limited to, threaded fasteners such as bolts, nuts, screws, headless set screws, scrivets, threaded studs and threaded bushings, and unthreaded fastener, such as notably pins, retaining rings, rivets, brackets and fastening washers and the like.

[0029] Sealing of components of oil and gas recovery articles is important and it can be said that seals are used in all types of oil and gas recovery articles, as well as those used in parts of oil and gas recovery articles which remains in the well after completion, testing and production of the well. Thus the seals need to resist to these extreme conditions, as mentioned above, in substantially indefinite time. It is worthwhile mentioning that seals besides electronics can be considered as the most vulnerable parts of oil and gas recovery articles.

[0030] In one embodiment of the present invention, the at least part of an oil and gas recovery article is a seal wherein said seal is selected from a group consisting of a metal seal, an elastomeric seal, a metal-to-metal seal and an elastomeric and metal-to-metal seal.

[0031] Seals are typically used in drill bits, motor systems, in particular mud motors, reservoir sensors, stimulation and flow control systems, pump systems, in particular electric submersible pumps, packers, liner hangers, tubing's, casings and the like.

[0032] Representative examples of seals, but not limited to, include seal rings such as notably C-rings, E-rings, O-rings, U-rings, spring energized C-rings, backup rings and the like; fastener seals; piston seals, gask-O-seals; integral seals, labyrinth seals.

[0033] In a particularly preferred embodiment, the at least one part of the oil and gas recovery article according to the present invention, is a seal ring, preferably a backup seal ring.

[0034] The weight of the (t-PAES) polymeric material, based on the total weight of oil and gas recovery article, is usually above 1 %, above 5 %, above 10 %, preferably above 15 %, above 20 %, above 30 %, above 40 %, above 50 %, above 60 %, above 70 %, above 80 %, above 90 %, above 95 %, above 99 %.

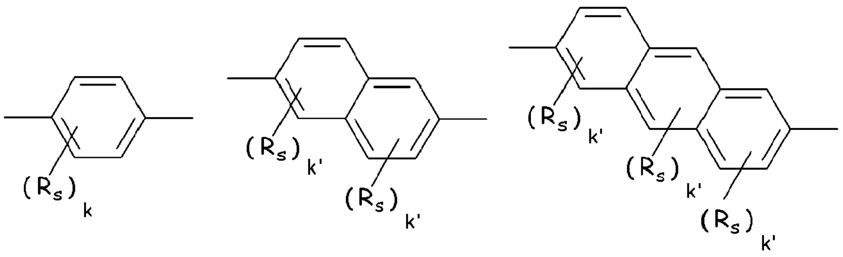
[0035] The oil and gas recovery article may consist of one part, i.e. it is a single-component article. Then, the single part preferably consists of the (t-PAES) polymeric material.

[0036] Alternatively, the oil and gas recovery article may consist of several parts. The case being, either one part or several parts of the oil and gas recovery article may consist of the (t-PAES) polymeric material. When several parts of the oil and gas recovery article consist of the (t-PAES) polymeric material, each of them may consist of the very same the (-PAES) polymeric material ; alternatively, at least two of them may consist of different the (t-PAES) polymeric material, in accordance with the invention.

[0037] As said above,

The (t-PAES) polymer

[0038] The aromatic moiety in each of Ar^1, Ar^2, Ar^3 and Ar^4 equal to or different from each other and at each occurrence is preferably complying with following formulae :



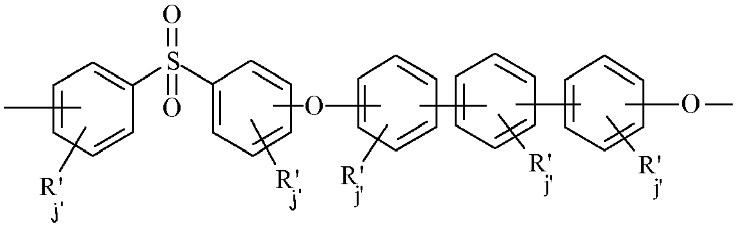
wherein :

- each R_s is independently selected from the group consisting of 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 is zero or an integer of 1 to 4 ; k' is zero or an integer of 1 to 3.

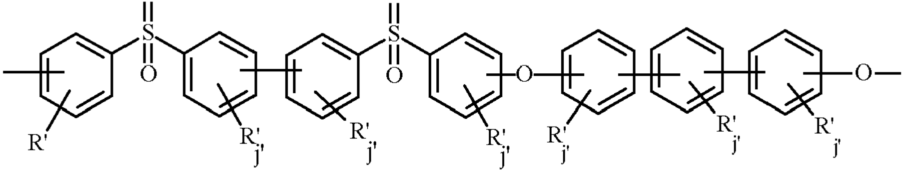
[0039] In recurring unit (R_t), the respective phenylene moieties may independently have 1,2-, 1,4- or 1,3 -linkages to the other moieties different from R or R' in the recurring unit. Preferably, said phenylene moieties have 1,3- or 1,4-linkages, more preferably they have 1,4-linkage.

[0040] Still, in recurring units (R_t), j', k' and k are at each occurrence zero, that is to say that the phenylene moieties have no other substituents than those enabling linkage in the main chain of the polymer.

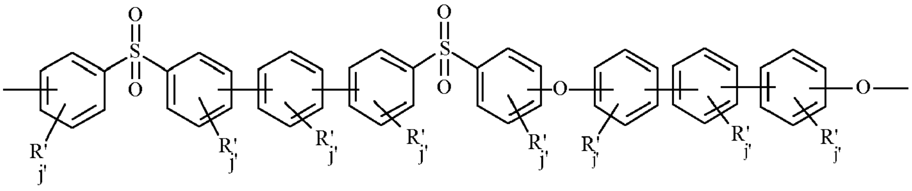
[0041] Preferred recurring units (R_t) are selected from the group consisting of those of formula $(S_t\text{-}1)$ to $(S_t\text{-}4)$ herein below :



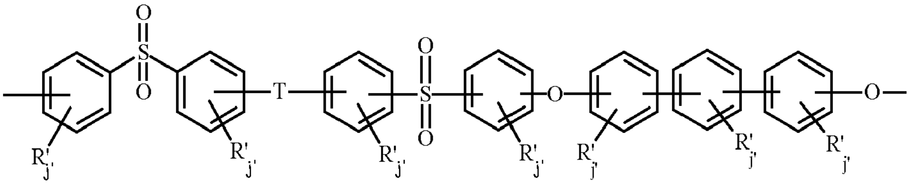
$(S_t\text{-}1)$



$(S_t\text{-}2)$



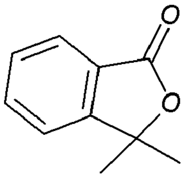
$(S_t\text{-}3)$



$(S_t\text{-}4)$

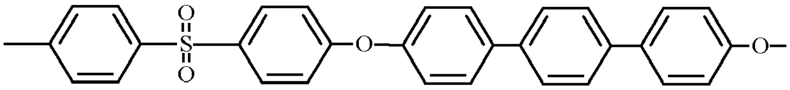
wherein

- each of R’, equal to or different from each other, is selected from the group consisting of 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 ;
- j’ is zero or is an integer from 1 to 4,
- T is a bond or a divalent group optionally comprising one or more than one heteroatom ; preferably T is selected from the group consisting of a bond, $-CH_2-$, -C(O)-, $-C(CH_3)_2-$, $-C(CF_3)_2-$, $-C(=CCl_2)-$, $-C(CH_3)(CH_2CH_2COOH)-$, and a group of formula :

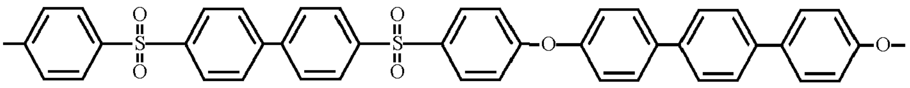


[0042] The above recurring units of preferred embodiments (R_t-1) to (R_t-4) can be each present alone or in admixture.

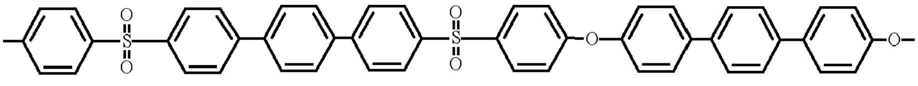
[0043] More preferred recurring units (R_t) are selected from the group consisting of those of formula (S'_t-1) to (S'_t-3) herein below :



$(S'_t\text{-}1)$



$(S'_t\text{-}2)$



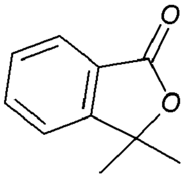
$(S'_t\text{-}3)$

[0044] Most preferred recurring unit (R_t) is of formula (S'_t-1), as shown above. According to certain embodiments, the (t-PAES) polymer, as detailed above, comprises in addition to recurring units (R_t), as detailed above, recurring units (R_a) of formula (K_a) :

$$-E-Ar^5-CO-[Ar^6-(T-Ar^7)_n-CO]_m-Ar^8- \qquad \text{(formula } K_a)$$

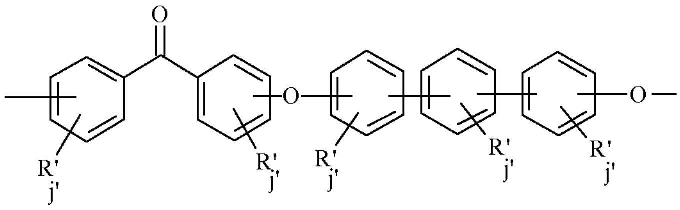
wherein :

- n and m, equal to or different from each other, are independently zero or an integer of 1 to 5,
- each of Ar^5, Ar^6, Ar^7 and Ar^8 equal to or different from each other and at each occurrence, is an aromatic moiety,
- T is a bond or a divalent group optionally comprising one or more than one heteroatom ; preferably T is selected from the group consisting of a bond, $-CH_2-$, $-C(O)-$, $-C(CH_3)_2-$, $-C(CF_3)_2-$, $-C(=CCl_2)-$, $-C(CH_3)(CH_2CH_2COOH)-$, and a group of formula :

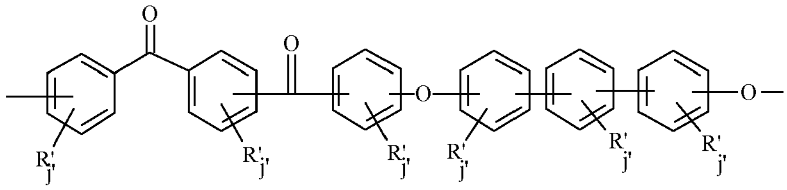


- E is of formula (E_t), as detailed above.

[0045] Recurring units (R_a) can notably be selected from the group consisting of those of formulae (K_a-1) or (K_a-2) herein below :



(K_a-1)

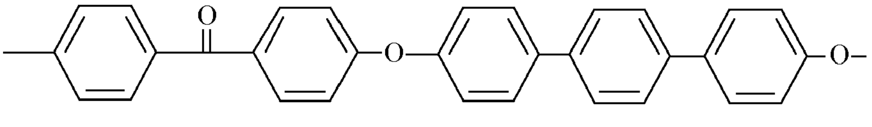


(K_a-2)

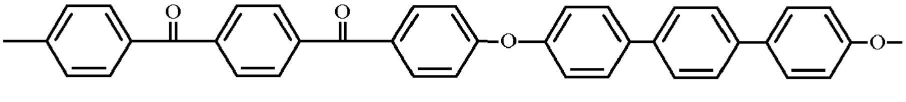
wherein

- each of R', equal to or different from each other, is selected from the group consisting of 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 ;
- j' is zero or is an integer from 1 to 4.

[0046] More preferred recurring units (R_a) are selected from the group consisting of those of formula (K'_a-1) or (K'_a-2) herein below :



(K'_a-1)



(K'_a-2)

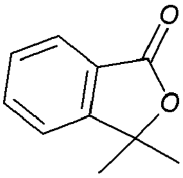
[0047] According to certain embodiments, the (t-PAES) polymer, as detailed above, comprises in addition to recurring units (R_t), as detailed above, recurring units (R_b) comprising a Ar-SO_2-Ar' group, with Ar and Ar', equal to or different from each other, being aromatic groups, said recurring units (R_b) generally complying with formulae (S1) :

(S1) : $-Ar^9-(T'-Ar^{10})_n-O-Ar^{11}-SO_2-[Ar^{12}-(T-Ar^{13})_n-SO_2]_m-Ar^{14}-O-$

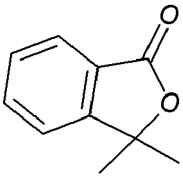
wherein :

Ar^9, Ar^{10}, Ar^{11}, Ar^{12}, Ar^{13} and Ar^{14}, equal to or different from each other and at each occurrence, are independently a aromatic mono- or polynuclear group ;

- T and T', equal to or different from each other and at each occurrence, is independently a bond or a divalent group optionally comprising one or more than one heteroatom ; preferably T' is selected from the group consisting of a bond, $-CH_2-$, -C(O)-, $-C(CH_3)_2-$, $-C(CF_3)_2-$, $-C(=CCl_2)-$, $-C(CH_3)(CH_2CH_2COOH)-$, $-SO_2-$, and a group of formula :

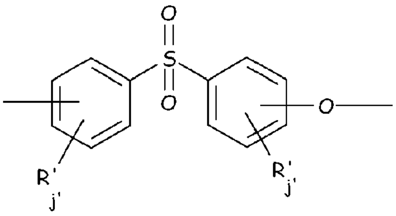


preferably T is selected from the group consisting of a bond, $-CH_2-$, -C(O)-, $-C(CH_3)_2-$, $-C(CF_3)_2-$, $-C(=CCl_2)-$, $-C(CH_3)(CH_2CH_2COOH)-$, and a group of formula :

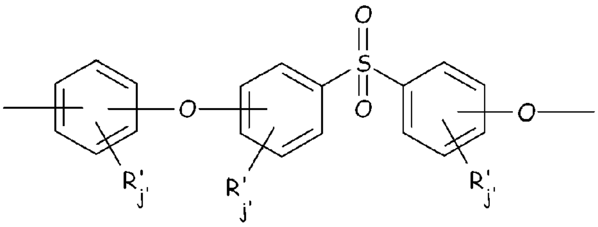


- n and m, equal to or different from each other, are independently zero or an integer of 1 to 5 ;

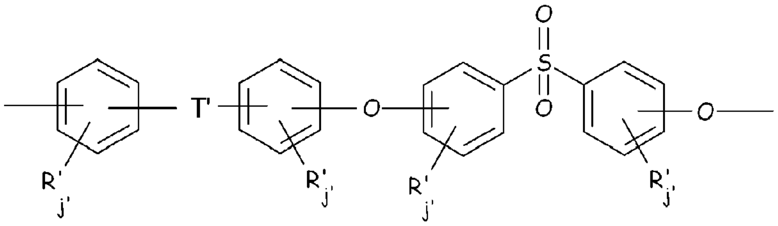
[0048] Recurring units (R_b) can be notably selected from the group consisting of those of formulae (S1-A) to (S1-D) herein below :



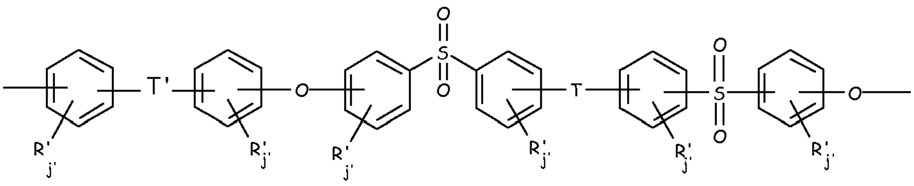
(S1-A)



(S1-B)



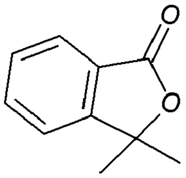
(S1-C)



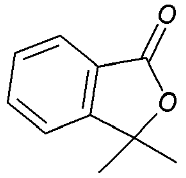
(S1-D)

wherein :

- each of R', equal to or different from each other, is selected from the group consisting of 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 ;
- j' is zero or is an integer from 0 to 4 ;
- T and T', equal to or different from each other are a bond or a divalent group optionally comprising one or more than one heteroatom ; preferably T' is selected from the group consisting of a bond, $-CH_2-$, -C(O)-, $-C(CH_3)_2-$, $-C(CF_3)_2-$, $-C(=CCl_2)-$, $-C(CH_3)(CH_2CH_2COOH)-$, $-SO_2-$, and a group of formula :



preferably T is selected from the group consisting of a bond, $-CH_2-$, -C(O)-, $-C(CH_3)_2-$, $-C(CF_3)_2-$, $-C(=CCl_2)-$, $-C(CH_3)(CH_2CH_2COOH)-$, and a group of formula :



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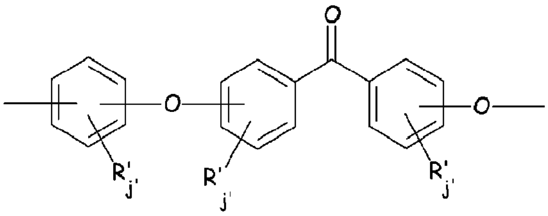
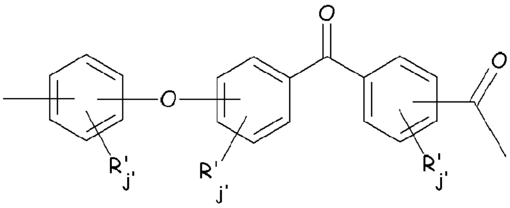
[0049] In recurring unit (R_b), the respective phenylene moieties may independently have 1,2-, 1,4- or 1,3 -linkages to the other moieties different from R' in the recurring unit. Preferably, said phenylene moieties have 1,3-or 1,4- linkages, more preferably they have 1,4-linkage. Still, in recurring units (R_b), j' is at each occurrence zero, that is to say that the phenylene moieties have no other substituents than those enabling linkage in the main chain of the polymer.

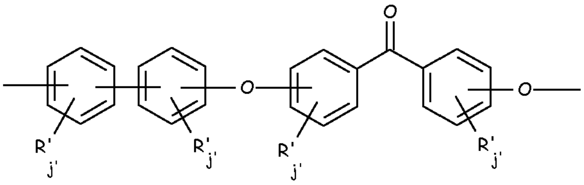
[0050] According to certain embodiments, the (t-PAES) polymer, as detailed above, comprises in addition to recurring units (R_t), as detailed above, recurring units (R_c) comprising a Ar-C(O)-Ar' group, with Ar and Ar', equal to or different from each other, being aromatic groups, said recurring units (R_c) being generally selected from the group consisting of formulae (J-A) to (J-L), herein below :



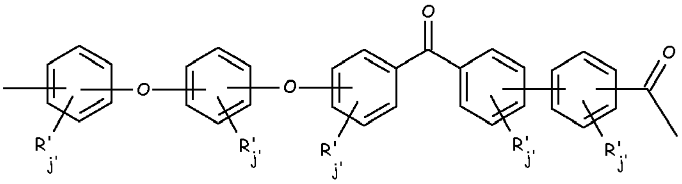
(J-A)



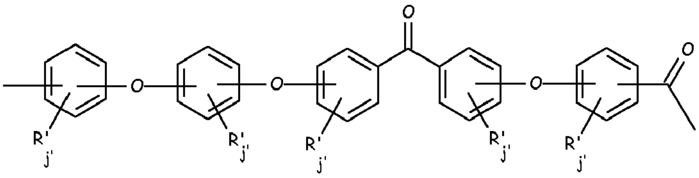
(J-B)



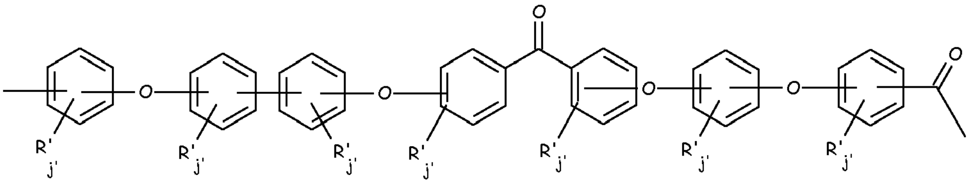
(J-C)



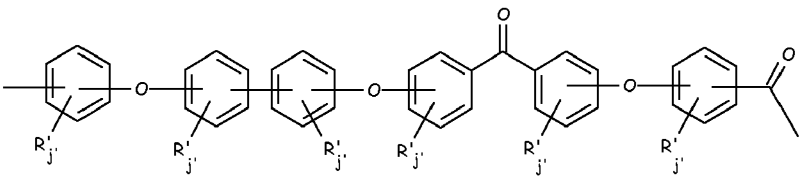
(J-D)



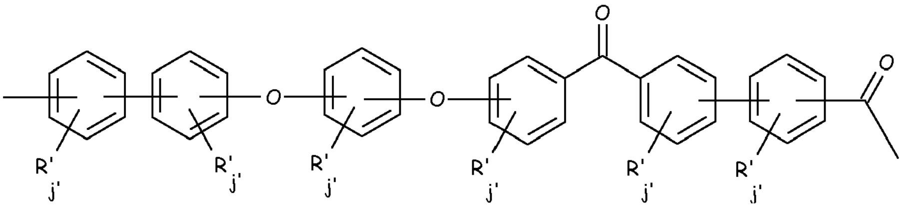
(J-E)



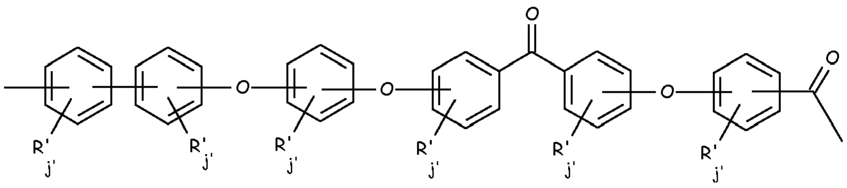
(J-F)



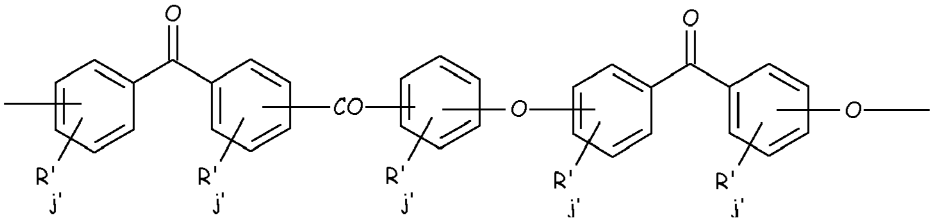
(J-G)



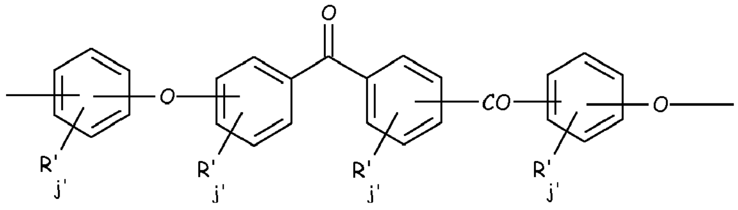
(J-H)



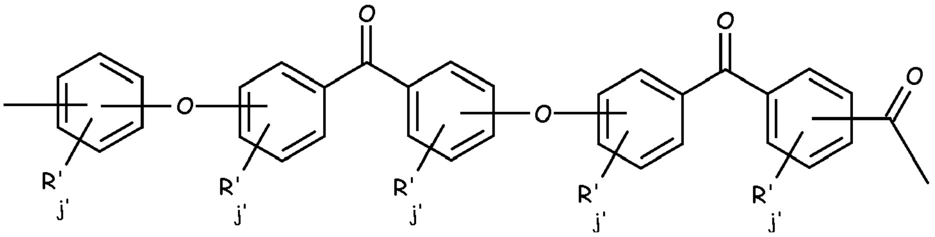
(J-I)



(J-J)



(J-K)



(J-L)

wherein :

- each of R', equal to or different from each other, is selected from the group consisting of 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 ;
- j' is zero or is an integer from 0 to 4.

[0051] In recurring unit (R_c), the respective phenylene moieties may independently have 1,2-, 1,4- or 1,3 -linkages to the other moieties different from R' in the recurring unit. Preferably, said phenylene moieties have 1,3-or 1,4- linkages, more preferably they have 1,4-linkage.

[0052] Still, in recurring units (R_c), j' is at each occurrence zero, that is to say that the phenylene moieties have no other substituents than those enabling linkage in the main chain of the polymer.

[0053] As said, the (t-PAES) polymer comprises recurring units (R_t) of formula (S_t) as above detailed in an amount of more than 50 % moles, preferably more than 60 % moles, more preferably more than 70 % moles, even more preferably more than 80 % moles, most preferably more than 90 % moles, the complement to 100 % moles being generally recurring units (R_a), as above detailed, and/or recurring units (R_b), and/or recurring units (R_c), as above detailed.

[0054] Still more preferably, essentially all the recurring units of the (t-PAES) polymer are recurring units (R_t), chain defects, or very minor amounts of other units might be present, being understood that these latter do not substantially modify the properties of the (t-PAES) polymer. Most preferably, all the recurring units of the (t-PAES) polymer are recurring units (R_t). Excellent results were obtained when the (t-PAES) polymer was a polymer of which all the recurring units are recurring units (R_t), as above detailed.

[0055] To the aim of providing polymers particularly suitable for being used in oil and gas recovery articles, the (t-PAES) polymer of the invention has advantageously a number average molecular weight (M_n) of at least 13 000, preferably at least 25 000, more preferably of at least 38 000.

[0056] Upper limit for the number average molecular weight (M_n) of the (t-PAES) polymer is not particularly critical and will be selected by the skilled in the art in view of final field of use.

[0057] In one embodiment of the present invention, the t-PAES polymer has advantageously a number average molecular weight (M_n) equal to or below 125 000, preferably equal to or below 95 000, preferably equal to or below 90 000, preferably equal to or below 80 000, preferably equal to or below 75 000, preferably equal to or below 70 000, preferably equal to or below 60 000, preferably equal to or below 56 000.

[0058] In one embodiment of the present invention, the t-PAES polymer has advantageously a number average molecular weight (M_n) in the range from 13 000 to 125 000, preferably ranging from 25 000 to 80 000, and preferably ranging from 38 000 to 80 000.

[0059] The (t-PAES) polymer having such specific molecular weight (M_n) range have been found to possess an excellent ductility (i.e high tensile elongation), good thoughness while maintaining high Tg, and good crystallizability and good chemical resistance.

[0060] The expression "number average molecular weight (M_n)" is hereby used according to it usual meaning and mathematically expressed as :

$$M_n = \frac{\sum M_i \cdot N_i}{\sum N_i}$$

wherein M_i is the discrete value for the molecular weight of a polymer molecule, N_i is the number of polymer molecules with molecular weight M_i, then the weight of all polymer molecules is $\sum M_i N_i$ and the total number of polymer molecules is $\sum N_i$.

[0061] M_n can be suitably determined by gel-permeation chromatography (GPC), calibrated with polystyrene standards.

[0062] Other molecular parameters which can be notably determined by GPC are the weight average molecular weight (M_w) :

$$M_w = \frac{\sum M_i^2 \cdot N_i}{\sum M_i \cdot N_i},$$

wherein M_i is the discrete value for the molecular weight of a polymer molecule, N_i is the number of polymer molecules with molecular weight M_i, then the weight of polymer molecules having a molecular weight M_i is $M_i N_i$.

[0063] For the purpose of the present invention, the polydispersity index (PDI) is hereby expressed as the ratio of weight average molecular weight (M_w) to number average molecular weight (M_n).

[0064] The details of the GPC measurement are described in detail in the method description given in the experimental section and notably described in our copending U.S. Provisional Patent Application.

[0065] The (t-PAES) polymer of the present invention has advantageously a polydispersity index (PDI) of more than 1.90, preferably more than 1.95, more preferably more than 2.00.

[0066] The (t-PAES) polymer of the present invention generally has a polydispersity index of less than 4.0, preferably of less than 3.8, more preferably of less than 3.5.

[0067] In addition, some other analytical methods can be used as an indirect method for the determination of molecular weight including notably viscosity measurements.

[0068] In addition, some other analytical methods can be used as an indirect method for the determination of molecular weight including notably viscosity measurements.

[0069] In one embodiment of the present invention, the (t-PAES) polymer of the present invention has a melt viscosity of advantageously at least 0.7 kPa.s, preferably at least 1.25 kPa.s, more preferably at least 2.3 kPa.s at 410°C and at a shear rate of 10 rad/sec, as measured using a parallel plates viscometer (e.g. TA ARES RDA3 model) in accordance with ASTM D4440. The (t-PAES) polymer of the present invention has a melt viscosity of advantageously of at most 46 kPa.s, preferably of at most 34 kPa.s, more preferably of at most 25 kPa.s at 410°C and at a shear rate of 10 rad/sec, as measured using a parallel plates viscometer (e.g. TA ARES RDA3 model) in accordance with ASTM D4440.

[0070] In another embodiment of the present invention, the (t-PAES) polymer of the present invention has a melt viscosity of advantageously at least 2.2 kPa.s, preferably at least 4.1 kPa.s, more preferably at least 7.4 kPa.s at 410°C and at a shear rate of 1 rad/sec, as measured using a parallel plates viscometer e.g. (TA ARES RDA3 model) in accordance with ASTM D4440. The (t-PAES) polymer of the present invention has a melt viscosity of advantageously of at most 149 kPa.s, preferably of at most 111 kPa.s, more preferably of at most 82 kPa.s at 410°C and at a shear rate of 1 rad/sec, as measured using a parallel plates viscometer (e.g. TA ARES RDA3 model) in accordance with ASTM D4440.

[0071] The (t-PAES) polymer of the present invention advantageously possesses a glass transition temperature of at least 210°C, preferably 220°C, more preferably at least 230°C.

[0072] Glass transition temperature (Tg) is generally determined by DSC, according to ASTM D3418.

[0073] The (t-PAES) polymer of the present invention advantageously possesses a melting temperature of at least 330°C, preferably 340°C, more preferably at least 350°C. The (t-PAES) polymer of the present invention advantageously possesses a melting temperature below 430°C, preferably below 420°C and more preferably below 410°C.

[0074] The melting temperature (Tm) is generally determined by DSC, according to ASTM D3418.

[0075] It is known that the crystallinity of polymers is characterized by their degree of crystallinity.

[0076] The degree of crystallinity can be determined by different methods known in the art such as notably by Wide Angle X-Ray diffraction (WAXD) and Differential Scanning Calorimetry (DSC).

[0077] The Applicant has found that the (t-PAES) polymer, as detailed above, is especially well suited for providing oil and gas recovery articles having a very high crystallinity.

[0078] The degree of crystallinity can advantageously be measured by DSC on compression molded samples of the (t-PAES) polymers of the present invention.

[0079] According to the present invention, molded parts of the (t-PAES) polymer have advantageously a degree of crystallinity above 5 %, preferably above 7 % and more preferably above 8 %.

[0080] The manufacturing of the (t-PAES) polymer of the present invention is not particularly limited. The (t-PAES) polymer can be prepared as notably described in EP 0 383 600 A2 or as notably described in our copending U.S. Provisional

Patent Application.

[0081] The Applicant has found that the (t-PAES) polymer, as detailed above, is especially well suited for providing oil and gas recovery articles, having (1) high Tg and Tm for thermal performance, (2) high chemical resistance to chemicals important to the oil and gas fields including notably sulfuric acid, (3) resistance to rapid decompression and are of (4) thermoplastic nature.

t-(PAES) polymeric material

[0082] The (t-PAES) polymeric material may comprise (t-PAES) polymer in a weight amount of at least 10 %, at least 30 %, at least 40 % or at least 50 %, based on the total weight of the (t-PAES) polymeric material. Preferably, the (t-PAES) polymeric material comprises (t-PAES) polymer in a weight amount of at least 70 %, based on the total weight of the (t-PAES) polymeric material. More preferably, the (t-PAES) polymeric material comprises the (t-PAES) polymer in a weight amount of at least 90 %, if not at least 95 %, based on the total weight of the (t-PAES) polymeric material. Still more preferably, the (t-PAES) polymeric material consists essentially of the (t-PAES) polymer. The most preferably, it consists essentially of the (t-PAES) polymer.

[0083] For the purpose of the present invention, the expression "consisting essentially of" is to be understood to mean that any additional component different from the (t-PAES) polymer, as detailed above, is present in an amount of at most 1 % by weight, based on the total weight of the composition (C), so as not to substantially alter advantageous properties of the composition.

[0084] The (t-PAES) polymeric material may further optionally comprise one or more than one additional ingredient (I) different from the (t-PAES) polymer, generally selected from the group consisting of (i) colorants such as notably a dye (ii) pigments such as notably titanium dioxide, zinc sulfide and zinc oxide (iii) light stabilizers, e.g. UV stabilizers (iv) heat stabilizers (v) antioxidants such as notably organic phosphites and phosphonites, (vi) acid scavengers (vii) processing aids (viii) nucleating agents (ix) internal lubricants and/or external lubricants (x) flame retardants (xi) smoke-suppressing agents (x) anti-static agents (xi) anti-blocking agents (xii) conductivity additives such as notably carbon black and carbon nanofibrils (xiii) plasticizers (xiv) flow modifiers (xv) extenders (xvi) metal deactivators and combinations comprising one or more of the foregoing additives.

[0085] When one or more than one additional ingredient (I) are present, their total weight, based on the total weight of polymer composition (C), is usually below 20 %, preferably below 10 %, more preferably below 5 % and even more preferably below 2 %.

[0086] If desired, the (t-PAES) polymeric material comprises more than 80 wt. % of the (t-PAES) polymer with the proviso that the (t-PAES) polymer is the only polymeric component in the (t-PAES) polymeric material and one or more than one additional ingredient (I) might be present therein, without these components dramatically affecting relevant mechanical and toughness properties of (t-PAES) polymeric material.

[0087] 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.

[0088] The (t-PAES) polymeric material may further comprise at least one reinforcing filler. Reinforcing fillers are well known by the skilled in the art. They are preferably selected from fibrous and particulate fillers different from the pigment as defined above. More preferably, the reinforcing filler is selected from mineral fillers (such as talc, mica, kaolin, calcium carbonate, calcium silicate, magnesium carbonate), glass fiber, carbon fibers, synthetic polymeric fiber, aramid fiber, aluminum fiber, titanium fiber, magnesium fiber, boron carbide fibers, rock wool fiber, steel fiber, wollastonite etc. Still more preferably, it is selected from mica, kaolin, calcium silicate, magnesium carbonate, glass fiber, carbon fibers and wollastonite etc.

[0089] Preferably, the filler is chosen from fibrous fillers. A particular class of fibrous fillers consists of whiskers, i.e. single crystal fibers made from various raw materials, such as Al_2O_3, SiC, BC, Fe and Ni.

[0090] In one embodiment of the present invention the reinforcing filler is chosen from wollastonite and glass fiber. Among fibrous fillers, glass fibers are preferred ; they include chopped strand A-, E-, C-, D-, S-, T- and R-glass fibers, as described in chapter 5.2.3, p. 43-48 of Additives for Plastics Handbook, 2nd edition, John Murphy.

[0091] Glass fibers optionally comprised in polymer (t-PAES) polymeric material may have a circular cross-section or a non-circular cross-section (such as an oval or rectangular cross-section).

[0092] When the glass fibers used have a circular cross-section, they preferably have an average glass fiber diameter of 3 to 30 μm and particularly preferred of 5 to 12 μm. Different sorts of glass fibers with a circular cross-section are available on the market depending on the type of the glass they are made of. One may notably cite glass fibers made from E- or S-glass.

[0093] Good results were obtained with standard E-glass material with a non-circular cross section. Excellent results were obtained when the polymer composition with S-glass fibers with a round cross-section and, in particular, when using round cross-section with a 6 μm diameter (E-Glass or S-glass).

[0094] In another embodiment of the present invention the reinforcing filler is a carbon fiber.

[0095] As used herein, the term "carbon fiber" is intended to include graphitized, partially graphitized and ungraphitized carbon reinforcing fibers or a mixture thereof. Carbon fibers useful for the present invention can advantageously be obtained by heat treatment and pyrolysis of different polymer precursors such as, for example, rayon, polyacrylonitrile (PAN), aromatic polyamide or phenolic resin ; carbon fibers useful for the present invention may also be obtained from pitchy materials. The term "graphite fiber" intends to denote carbon fibers obtained by high temperature pyrolysis (over 2000°C) of carbon fibers, wherein the carbon atoms place in a way similar to the graphite structure. Carbon fibers useful for the present invention are preferably chosen from the group composed of PAN-based carbon fibers, pitch based carbon fibers, graphite fibers, and mixtures thereof.

[0096] The weight of said reinforcing filler is advantageously preferably below 60 % wt., more preferably below 50 % wt., even more preferably below 45 % wt., most preferably below 35 % wt., based on the total weight of the (t-PAES) polymeric material.

[0097] Preferably, the reinforcing filler is present in an amount ranging from 10 to 60 % wt., preferably from 20 to 50 % wt., preferably from 25 to 45 % wt., most preferably from 25 to 35 % wt., based on the total weight of the polymer (t-PAES) polymeric material.

[0098] The (t-PAES) polymeric material can be prepared by a variety of methods involving intimate admixing of the at least one (t-PAES) polymer, optionally the reinforcing filler and optionally additional ingredient (I) desired in the polymeric material, for example by dry blending, suspension or slurry mixing, solution mixing, melt mixing or a combination of dry blending and melt mixing.

[0099] Typically, the dry blending of (t-PAES) polymer, as detailed above, preferably in powder state, optionally the reinforcing filler and optionally additional ingredient (I) is carried out by using high intensity mixers, such as notably Henschel-type mixers and ribbon mixers so as to obtain a physical mixture, in particular a powder mixture of the at least one (t-PAES) polymer, optionally the reinforcing filler and optionally additional ingredient (I).

[0100] Alternatively, the intimate admixing of the at least one (t-PAES) polymer, optionally the reinforcing filler and optionally additional ingredient (I) desired in the polymeric material, is carried out by tumble blending based on a single axis or multi-axis rotating mechanism so as to obtain a physical mixture.

[0101] Alternatively, the slurry mixing of the (t-PAES) polymer, as detailed above optionally the reinforcing filler and optionally additional ingredient (I) is carried out by first slurrying said (t-PAES) polymer in powder form with optionally the polymers (T), optionally the reinforcing filler and optionally additional ingredient (I) using an agitator in an appropriate liquid such as for example methanol, followed by filtering the liquid away, so as to obtain a powder mixture of the at least one (t-PAES) polymer, optionally the reinforcing filler and optionally additional ingredient (I).

[0102] In another embodiment, the solution mixing of the (t-PAES) polymer, as detailed above, optionally the reinforcing filler and optionally additional ingredient (I) using an agitator in an appropriate solvent or solvent blends such as for example diphenyl sulfone, benzophenone, 4-chlorophenol, 2-chlorophenol, meta-cresol. Diphenyl sulfone and 4-chlorophenol are most preferred.

[0103] Following the physical mixing step by one of the aforementioned techniques, the physical mixture, in particular the obtained powder mixture, of the at least one (t-PAES) polymer, optionally the reinforcing filler and optionally additional ingredient (I) is typically melt fabricated by known methods in the art including notably melt fabrication processes such as compression molding, injection molding, extrusion and the like, to provide the above described part of an oil and gas recovery article or a finished oil and gas recovery article.

[0104] So obtained physical mixture, in particular the obtained powder mixture can comprise the (t-PAES) polymer, as detailed above, the reinforcing filler, as detailed above, and optionally, other ingredients (I) in the weight ratios as above detailed, or can be a concentrated mixture to be used as masterbatch and diluted in further amounts of the (t-PAES) polymer, as detailed above, the reinforcing filler, as detailed above, and optionally, other ingredients (I) in subsequent processing steps. For example, the obtained physical mixture can be extruded into a stock shape like a slab or rod from which a final part can be machined. Alternatively, the physical mixture can be compression molded into a finished part of the oil and gas recovery article or into a stock shape from which a finished part of the oil and gas recovery article can be machined.

[0105] It is also possible to manufacture the composition 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 directly on the (t-PAES) polymer, as detailed above, the reinforcing filler, as detailed above, and optionally, other ingredients (I). 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.

[0106] If desired, 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 obtain a homogeneous distribution of the different ingredients. Provided that optimum mixing is achieved between the bulk polymer and filler contents. It is advantageously possible to obtain strand extrudates which are not ductile of the (t-PAES) polymeric material of the invention. Such strand extrudates can be chopped by means e.g. of a rotating cutting knife after some cooling time on a conveyer with water spray. Thus, for example (t-PAES) polymeric material which may be present in the form of pellets or beads can then be further used for the manufacture of the above described part of the oil and gas recovery article.

[0107] Another objective of the present invention is to provide a method for the manufacture of the above described part of the oil and gas recovery article. Such method is not specifically limited. The (t-PAES) polymeric material may be generally processed by injection molding, extrusion, or other shaping technologies.

[0108] In one embodiment of the present invention, the method for the manufacture of the above described part of the oil and gas recovery article or oil and gas recovery article includes the step of injection molding and solidification of the (t-PAES) polymeric material.

[0109] In another embodiment, the method for the manufacture of the above described part of the oil and gas recovery article or oil and gas recovery article includes the step of coating.

[0110] For example, the (t-PAES) polymeric material can be applied to a wire as a coating by using any suitable coating method, preferably by extrusion coating around a wire to form a coated wire, such as notably disclosed in U.S. Pat. No. 4,588,546.

[0111] Techniques for manufacturing wire coatings are well known in the art.

[0112] In another embodiment of the present invention, the method for the manufacture of the above described part of the oil and gas recovery article or the oil and gas recovery article, as described above includes the machining of a standard shaped structural part in a part having any type of size and shape. Non limiting examples of said standard shaped structural part include notably a plate, a rod, a slab and the like. Said standard shaped structural parts can be obtained by extrusion or injection molding of the polymer (t-PAES) polymeric material.

[0113] The Applicant has now found that said oil and gas recovery article parts and finished oil and gas recovery article comprising the (t-PAES) polymeric material of the present invention have (1) high Tg and Tm for thermal performance, (2) high chemical resistance to chemicals important to the oilfield including sulfuric acid, (3) resistance to rapid decompression and (4) thermoplastic nature. Thus said articles can be employed successfully in the HPHT oil and gas environments while at the same time having a more cost effective article fabrication

[0114] The invention will be now 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

[0115] l,l':4',l"-terphenyl-4,4"-diol commercially available from Yonghi Chemicals, China, further purified by washing with ethanol/water (90/10) at reflux. The purity of the resulting material was shown to be higher than 94.0 % area as measured by Gas Chromatography, as detailed below.

4,4'-difluorodiphenylsulfone commercially available from Aldrich (99 % grade, 99.32 % measured) or from Marshallton (99.92 % pure by GC).

Diphenyl sulfone (polymer grade) commercially available from Proviron (99.8 % pure).

Potassium carbonate with a d_{90} < 45 μm commercially available from Armand products.

Lithium chloride (99+ %, ACS grade) commercially available from Acros.
KetaSpire® KT-820 NT, a PEEK (Polyetheretherketone) fine powder with a maximum particle size defined by 100 % passage through a 100 mesh screen and a melt viscosity at 400°C and 1000 s^{-1} using ASTM D3835 in the range 0.38 - 0.50 kPa-s; commercially available from SOLVAY SPECIALTY POLYMERS USA, LLC.

General procedure for the preparation of the t-PAES polymer - Examples 1 and 2

[0116] In a 500 mL 4-neck reaction flask fitted with a stirrer, a N_2 inlet tube, a Claisen adapter with a thermocouple plunging in the reaction medium, and a Dean-Stark trap with a condenser and a dry ice trap were introduced 89.25 g of diphenyl sulfone, 28.853 g of a specific type of 1,1':4',1"-terphenyl-4,4"-diol and 27.968 g of 4,4'-difluorodiphenylsulfone (corresponding to a total % monomers of 38,9 % and molar ratio dihalo (BB)/diol of 1.000). The flask content was evacuated under vacuum and then filled with high purity nitrogen (containing less than 10 ppm O_2). The reaction mixture was then placed under a constant nitrogen purge (60 mL/min). The reaction mixture was heated slowly to 220°C. At 220°C, 15.354 g of K_2CO_3 were added via a powder dispenser to the reaction mixture over 30 minutes. At the end of the addition, the reaction mixture was heated to 320°C at 1°C/minute. After 13 minutes at 320°C, 1.119 g of 4,4'-difluorodiphenylsulfone were added to the reaction mixture while keeping a nitrogen purge on the reactor. After 2 minutes, 4.663 g of lithium chloride were added to the reaction mixture. 2 minutes later, another 0.280 g of 4,4'-difluorodiphenylsulfone were added to the reactor and the reaction mixture was kept at temperature for 5 minutes. The reactor content was then poured from the reactor into a stainless steel pan and cooled. The solid was broken up and ground in an attrition mill through a 2 mm screen. Diphenyl sulfone and salts were extracted from the mixture with acetone then water at pH between 1 and 12 then with acetone. The powder was then removed from the reactor and dried at 120°C under vacuum for 12 hours yielding 44 g of a light brown powder. The powder was further ground subsequently in a lab-scale grinder to yield a fine powder with an average particle size of around 100 μm.

[0117] Examples 1 and 2 were prepared according to this general procedure. Except for example 2, 1.119 g of 4,4'-difluorodiphenylsulfone were added to the reaction mixture while keeping a nitrogen purge on the reactor after 27 minutes at 320°C instead of after 13 minutes at 320°C.

[0118] The molecular weights of the final t-PAES polymer were measured by GPC, as detailed below and for example 1, M_n was found to be 39,000 g/mole and Mw was found to be 112,500 g/mole; for example 2, M_n was found to be 47,925 g/mole and Mw was found to be 97,036 g/mole, 29 % crystallinity.

General description of the molding process of a (t-PAES) polymeric material - Examples 1 and 2

[0119] The t-PAES polymer (example 1 or 2) or the PEEK fine powder polymer (comparative example 3) were compression molded into 4 in x 4 in x 0.125 in plaques using a Fontijne programmable compression molding press according to the compression molding protocols as shown in Table 1. The compression molded plaques of example 1 and comparative example 3 were next machined into Type V ASTM tensile specimens and 0.5 in wide flexural specimens and these specimens were subjected to tensile testing per ASTM method D638 and flexural testing by ASTM method D790 before and after exposure to oil field simulated conditions, i.e. rapid gas depressurization such as in oil field downhole environments as described in detail below, see in Table3.

[0120] The compression molded plaques of example 2 and were machined into 2 in x 0.5 in x 0.125 in specimens. Said specimens were immersed in conc. Sulfuric acid at room temperature and their weight and aspect was checked every 24 h. The results after 240 h of immersion are summarized in Table 2

Table 1

t-PAES polymer (example 1)				
Segment	**Pressure (lbf 10^2)**	**Time (hh.mm.ss)**	**Heat (°F)**	**Cooling Control Contacts)**
1	45	0:15:00	790	
2	60	0:02:00	790	
3	60	0:20:00	610	
4	60	1:30:00	610	
5	45	1:10:00	75	Set @00 00 00 00 1, Water

Table 2: swelling in conc. H_2SO_4

Examples	Example 2	Comparative Example 3
% weight gain after 240h	1.2	dissolved in < 24 h
Surface aspect after 240h	Surface smooth and shiny, not affected	N/A sample dissolved
N/A : not applicable		

[0121] The results in Table 2 clearly demonstrate the superior resistance of the t-PAES polymer of the invention to oxidizing acids.

The following characterizations carried out on the materials of the

Examples are indicated hereinafter :

*Molecular weight measurements by **a** GPC method*

GPC condition :

[0122] Pump : 515 HPLC pump manufactured by Waters
Detector : UV 1050 series manufactured by HP
Software : Empower Pro manufactured by Waters
Injector : Waters 717 Plus Auto sampler
Flow rate : 0.5 ml/min
UV detection : 270 nm
Column temperature : 40°C
Column : 2x PL Gel mixed D, 5 micron, 300 mm X 7.5 mm 5 micron manufactured by Agilent
Injection : 20 μ liter
Runtime : 60 minutes
Eluent: N-Methyl- 2-pyrrolidone (Sigma-Aldrich, Chromasolv Plus for
HPLC >99 %) with 0.1 mol Lithium bromide (Fisher make). Mobile phase should be store under nitrogen or inert environment
Calibration standard : Polystyrene standards part number PL2010-0300 manufactured by Agilent was used for calibration. Each vial contains a mixture of four narrow polydispersity polystyrene standards (a total 11 standard, 371100, 238700, 91800, 46500, 24600, 10110, 4910, 2590, 1570,780 used to establish calibration curve)
Concentration of standard : 1 milliliter of mobile phase added in to each vial before GPC injection for calibration
Calibration Curve : 1) Type: Relative, Narrow Standard Calibration 2) Fit : 3rd order regression
Integration and calculation : Empower Pro GPC software manufactured by Waters used to acquire data, calibration and molecular weight calculation. Peak integration start and end points are manually determined from significant difference on global baseline.
Sample Preparation : 25 mg of the (t-PAES) polymer was dissolved in 10 ml of 4-chlorophenol upon heating at 170 to 200°C. A small amount (0.2 to 0.4 ml) of said solution obtained was diluted with 4 ml of N-Methyl-2-pyrrolidone. The resulting solution was passed through to GPC column according to the GPC conditions mentioned above.

Oil field simulated conditions

Rapid Gas Decompression Test

[0123] A rapid gas decompression (RGD) test was first conducted on flexural bar samples of the example 1 and comparative example 3. This test evaluates the ability of plastic materials to withstand rapid gas depressurization in oil field downhole environments. To perform this test, flexural molded specimens from Example 1 and from comparative example 3 were first placed into a pressure vessel and the vessel was sealed and heated to 175°C. A 90/10 by weight methane/CO_2 mixture was then introduced to the pressure vessel boosting the pressure in the vessel to 1000 bar (14500 psi). After one week maintained at these test pressure and temperature, the pressure was released from the vessel automatically at a controlled rate of 70 bar/minute. The pressure and temperature profile curves for this test are shown in Figure 1. Following the exposure, the specimens of the example 1 and comparative example 3 were taken out of the pressure vessel and were subjected to weight and volume change measurements as well as to flexural property testing. The measurements were performed on five replicate specimens for each material and the results as shown in Table 3, are the average values for the five replicates. Appearance of the exposed specimens was observed visually and reported in Table 3.

Table 3

Mass and volume change and flexural properties upon exposure to the rapid gas decompression test		
Examples	**Example 1**	**Comparative Example 3**
Mass Change (%)	-0.3	-0.19
Volume Change (%)	1.8	0.2
Mechanical properties		
Flex Strength Not Exposed (psi)	14500	21000
Flex Strength (psi)	14600	22600
Flex Strength Change (%)	+0.7	+7.6
Flex Modulus Not Exposed (ksi)	372	559
Flex Modulus (ksi)	356	572
Flex Modulus Change (%)	-4.3	+2.3
surface properties		
Appearance of Flex Bars after Exposure	1 out of 5 bars has 3 very small blisters	2 out of of 5 bars are heavily blisters

Hot Oil Exposure Test

[0124] A hot oil exposure test was conducted using the ASTM tensile test specimens from the example 1 and comparative example 3, as described above. The hot oil exposure test was undertaken at the prevailing vapor pressure in a pressure cell equipped with an external heater band, thermocouple and calibrated pressure sensor. Pressure and temperature were logged by a PC running dedicated software. Specimens were exposed in the high pressure cell at a temperature of 270°C and vapor pressure for a duration of 3 days after which the specimens were taken out and measured for weight change and dimensional change and then returned for an additional exposure time of 3 days at the same conditions. At the conclusion of the second 3 days of exposure, the test specimens were taken out for the final time and weight and dimensional changes were measured and logged and additionally tensile testing was conducted on the exposed specimens to determine if there has been any downgrade in mechanical performance as a result of the high pressure and high temperature oil exposure. Weight and volume change results as well as tensile properties before and after exposure are reported in Table 4.

Table 4

Mass and volume change and tensile properties upon 6 days of exposure to the hot oil test		
Examples	**Example 1**	**Comparative Example 3**
Mass Change (%)	+3.0	+3.5
Volume Change (%)	+3.1	+3.7
Mechanical properties		
Tensile Strength Not Exposed (psi)	12000	13000
Tensile Strength Exposed (psi)	12600	13900
Tensile Strength Change (%)	+5.0	+6.9
Tensile Modulus Not Exposed (ksi)	414	551
Tensile Modulus Exposed (ksi)	458	639
Tensile Modulus Change (%)	+10.6	+16.0

(continued)

Mechanical properties		
Tensile Elong. at Break Not Exposed(%)	14.0	79
Tensile Elongation at Break Exposed (%)	9.8	37
Tensile Elongation at Break Change (%)	-30	-53
Surface properties		
Appearance of Flex Bars after Exposure	No Change	No Change

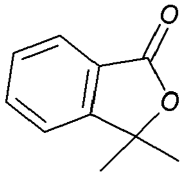
Claims

1. An oil and gas recovery article comprising at least one part made of a poly(arylether sulfone) polymeric material [(t-PAES) polymeric material, herein after] comprising at least one poly(arylether sulfone) polymer [(t-PAES) polymer], wherein said (t-PAES) polymer comprising more than 50 % moles of recurring units (R_t) of formula (S_t):

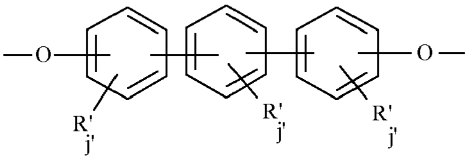
   $$-E-Ar^1-SO_1-[Ar^1-(T-Ar^3)_n-SO_2]_m-Ar^4- \qquad \text{(formula } S_t\text{)}$$

   wherein :

   - n and m, equal to or different from each other, are independently zero or an integer of 1 to 5,
   - each of Ar^1, Ar^2, Ar^3 and Ar^4 equal to or different from each other and at each occurrence, is an aromatic moiety,
   - T is a bond or a divalent group optionally comprising one or more than one heteroatom ; preferably T is selected from the group consisting of a bond, $-CH_2-$, -C(O)-, $-C(CH_3)_2-$, $-C(CF_3)_2-$, $-C(=CCl_2)-$, $-C(CH_3)(CH_2CH_2COOH)-$, and a group of formula :

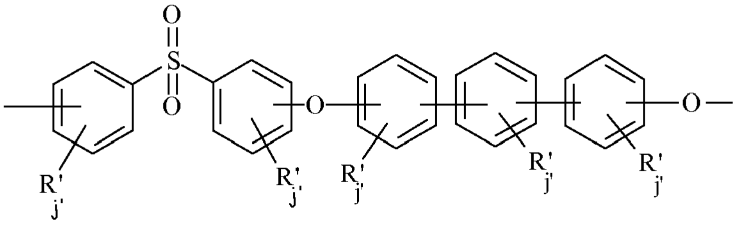


   - E is of formula (E_t) :

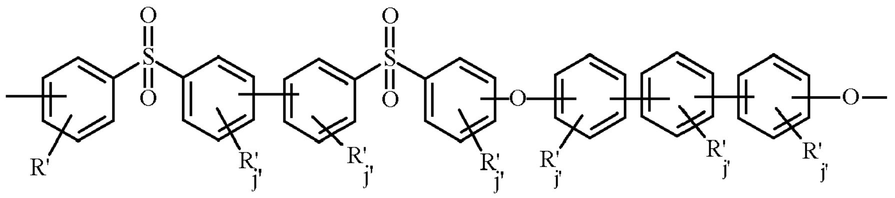


   wherein
   each of R', equal to or different from each other, is selected from the group consisting of halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium ; j' is zero or is an integer from 1 to 4.

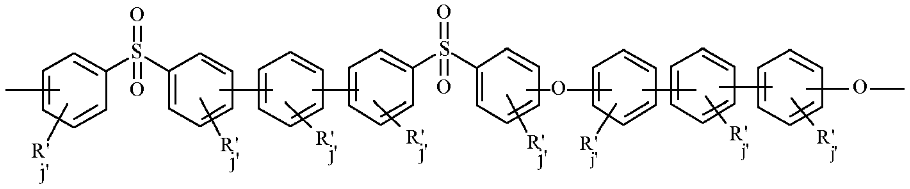
2. The oil and gas recovery article according to claim 1 wherein said recurring units (R_t) are selected from the group consisting of those of formula (S_t-1) to (S_t-4) herein below :



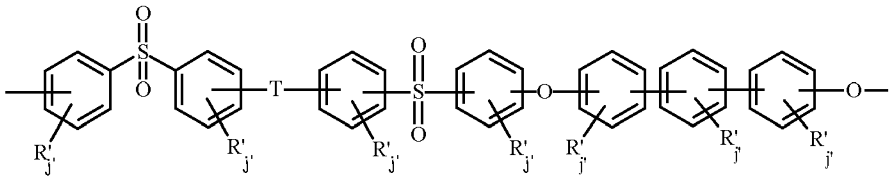
$(S_t\text{-}1)$



$(S_t\text{-}2)$



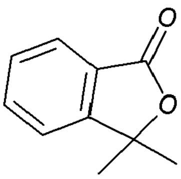
$(S_t\text{-}3)$



$(S_t\text{-}4)$

wherein

- each of R', equal to or different from each other, is selected from the group consisting of 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 ;
- j' is zero or is an integer from 1 to 4,
- T is a bond or a divalent group optionally comprising one or more than one heteroatom ; preferably T is selected from the group consisting of a bond, $-CH_2-$, $-C(O)-$, $-C(CH_3)_2-$, $-C(CF_3)_2-$, $-C(=CCl_2)-$, $-C(CH_3)(CH_2CH_2COOH)-$, and a group of formula :



3. The oil and gas recovery article according to any one of claims 1 to 2 wherein (t-PAES) polymeric material further comprise one or more than one additional ingredient (I) different from the (t-PAES) polymer.

4. The oil and gas recovery article according to any one of claims 1 to 3 wherein (t-PAES) polymeric material further comprise at least one reinforcing filler.

5. The oil and gas recovery article according to any one of claims 1 to 4 wherein said oil and gas recovery article is a drilling system, a drilling rig, a compressor system, a pumping system, a motor system, a sensor, a control system, a liner hanger a packer system, a pipe system, a valve system, a tubing system, or a casing system.

6. The oil and gas recovery article according to claim 6 wherein the pipe system is a pipe, a flexible riser, a pipe-in-pipe, a pipe liner, a subsea jumper, a spool or an umbilical, preferably a pipe, a flexible riser or pipe liner.

7. The oil and gas recovery article according to any one of claims 1 to 5, wherein said part is a seal, a fastener, a cable, an electrical connector or an oil and gas recovery housing.

8. The oil and gas recovery article according to claim 7, wherein said part is a seal wherein said seal is suitable for use in drill bits, motor systems, reservoir sensors, stimulation and flow control systems, pump systems, packers, liner hangers, tubing's, casings and the like.

9. The oil and gas recovery article according to claim 8, wherein the seal is a seal ring, preferably a backup seal ring.

10. The oil and gas recovery article according to any one of claims 1 to 5, wherein said part is a coating, preferably a wire coating.

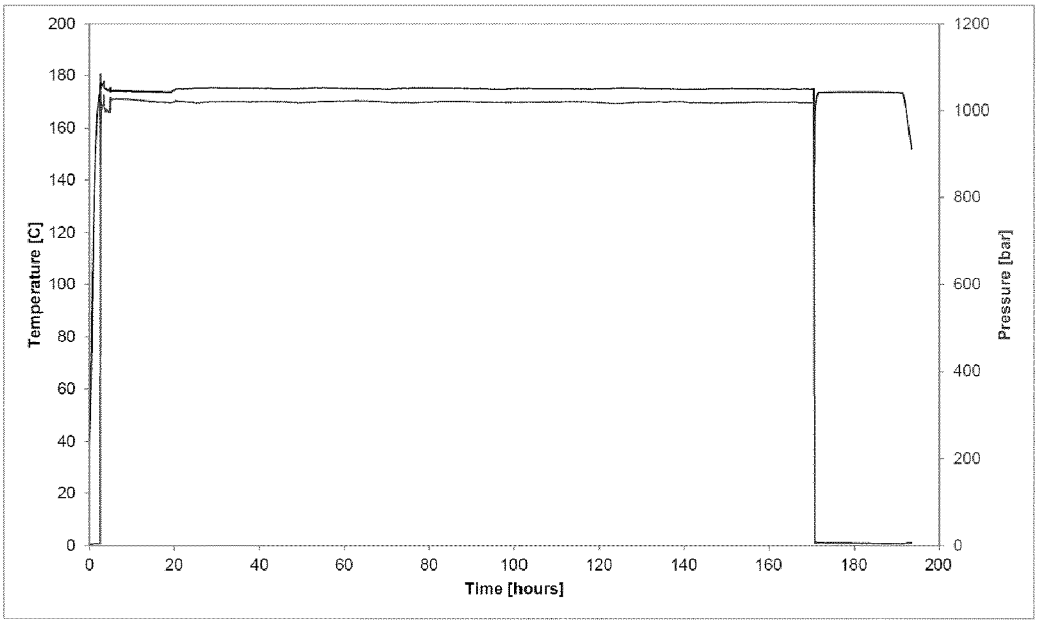
11. A method for the manufacture of a part of the oil and gas recovery article or the oil and gas recovery article according to anyone of the claims 1 to 10, comprising a step of injection molding, extrusion, or other shaping technologies.

12. The method for the manufacture of a part of the oil and gas recovery article or the oil and gas recovery article according to claim 11, comprising the step of injection molding and solidification of the (t-PAES) polymeric material.

13. A method for the manufacture of a part of the oil and gas recovery article or the oil and gas recovery article according to anyone of the claims 1 to 11, comprising a step of coating, preferably extrusion coating.

Figure 1

Pressure and temperature logs for rapid gas decompression test



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EUROPEAN SEARCH REPORT

Application Number
EP 13 18 5207

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X Y	EP 0 383 600 A2 (ICI PLC [GB]) 22 August 1990 (1990-08-22) * page 3, line 47 - page 4, line 1; claims 1,7; examples 1,2; table 2 * * page 4, lines 8-20 *	1-4, 10-13 1-13	INV. C08G75/23 E21B33/12 E21B34/00 E21B43/00 E21B1/00
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Y	US 2013/112409 A1 (BALENO BRIAN [US] ET AL) 9 May 2013 (2013-05-09) * paragraph [0012]; claims 1,2; table 1 *	1-13	
A	US 2012/279577 A1 (GOERING RAINER [DE] ET AL) 8 November 2012 (2012-11-08) * paragraphs [0017], [0028], [0034]; claims 1,2 *	1-13	
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A	EP 0 278 720 A2 (ICI PLC [GB] VICTREX MFG LTD [GB]) 17 August 1988 (1988-08-17) * page 1, lines 5-20; claims 1,7,8,11,12; example 7 * * page 1, lines 56-59 * * page 2, lines 14-36 *	1-13	C09K E21B C08G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	25 November 2013	Redecker, Michael

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 13 18 5207

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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