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(71) Applicants *(for all designated States except US)*: **COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION** [AU/AU]; Limestone Avenue, CAMPBELL, Australian Capital Territory 2612 (AU). **AORTECH BIOMATERIALS PTY LTD** [AU/AU]; 119 Evans Street, Rozelle, New South Wales 2039 (AU).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **GUNATILLAKE, Pathiraja, Arachchillage** [AU/AU]; 8 Katoomba Drive, Mulgrave, Victoria 3170 (AU). **PADSALGIKAR, Ajay, Devidas** [IN/AU]; 4 Donald Road, Wheelers Hill, Victoria 3150 (AU). **ADHIKAN, Raju** [AU/AU]; 9 Basil Crescent, Wheelers Hill, Victoria 3150 (AU). **GRIFFITHS, Ian, Michael** [GB/AU]; Unit 7, 135 Ormond Esplanade, Elwood, Victoria 3184 (AU). **BOWN, Mark** [AU/AU]; 6 Akuna Avenue, Notting Hill, Victoria 3168 (AU).

(74) Agent: GRIFFITH HACK; 509 St Kilda Road, MELBOURNE, Victoria 3004 (AU).

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(54) Title: POLYURETHANES

(57) Abstract: The present invention relates to cross-linked polyurethanes or polurethane-ureas and processes for their preparation. The polyurethane comprises a soft segment formed from (a) at least one polyether macrodiol and/or at least one polycarbonate macrodiol; and (b) at least one polysiloxane macrodiol, at least one polysiloxane macrodiamine and/or at least one silicon-based polycarbonate; and a hard segment formed from (c) a polyisocyanate and (d) at least one di-functional chain extender, wherein the segments are further formed from (e) at least one cross-linking agent. The Polyurethanes are biostable and creep resistant which makes them useful in the manufacture of biomaterials and medical devices, articles or implants, in particular orthopaedic implants such as spinal disc prostheses.

POLYURETHANES

The present invention relates to cross linked polyurethanes or polyurethane ureas and processes for their preparation. The polyurethanes are biostable and creep resistant which makes them useful in the manufacture of biomaterials and medical devices, articles or implants, in particular orthopaedic implants such as spinal disc prostheses.

BACKGROUND OF THE INVENTION

The development of methodology[1,2] to incorporate high proportions of siloxane segments as part of the polyurethane structure has resulted in the production of a range of thermoplastic siloxanepolyurethanes (Elast-Eon™) with biostability and mechanical properties suitable for a variety of medical implants. These thermoplastic polyurethanes are used in a range of cardiovascular, interventional cardiology and cardiac rhythm management applications. Materials that are used in medical implants subjected to cyclic strains or compressions such as orthopaedic implants require excellent flex-fatigue and creep resistance. Thermoplastic polymers generally exhibit a significant level of permanent deformation (creep) under tensile and compression loads. As a consequence, thermoplastic polyurethanes have limited use in load-bearing applications such as orthopaedic implants where dimensional stability is critical for optimum performance of the implant. There is a need for biostable polyurethanes which possess creep resistance.

SUMMARY OF THE INVENTION

According to the present invention there is provided a cross linked polyurethane or polyurethane urea which comprises a soft segment which is formed from:

(a) at least one polyether macrodiol and/or at least one polycarbonate macrodiol; and

(b) at least one polysiloxane macrodiol, at least one polysiloxane macrodiamine and/or at least one silicon-based polycarbonate; and/or

a hard segment which is formed from:

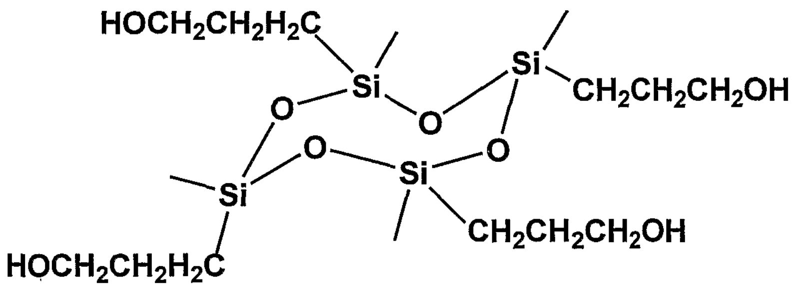
(c) a polyisocyanate; and

(d) at least one di-functional chain extender,

wherein the soft segment and/or the hard segment are further formed from:

(e) at least one cross linking agent.

Further according to the present invention there is provided a compound of formula (V):



(V)

which is a suitable silicon-containing cross linking agent for use in forming the polyurethanes of the present invention.

The present invention also provides a process for preparing the polyurethanes defined above which comprises the steps of:

(i) reacting components (a), (b) and (c) as defined above to form a prepolymer having terminally reactive polyisocyanate groups; and

(ii) reacting the prepolymer with components (d) and (e) defined above.

The present invention further provides a process for preparing the polyurethanes defined above which comprises the steps of:

(i) mixing components (a), (b), (d) and (e) defined above; and

(ii) reacting the mixture with component (c).

The polyurethanes of the present invention are biostable and creep resistant. These properties make the polyurethanes useful in the manufacture of biomaterials and medical devices, articles or implants.

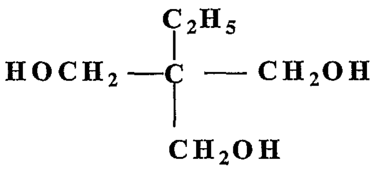
Thus, the present invention also provides a material, device, article or implant which is wholly or partly composed of the polyurethanes defined above.

DETAILED DESCRIPTION OF THE INVENTION

In the description of the invention, except where the context requires otherwise due to express language or necessary implication, the words "comprise" or variations such as "comprises" or "comprising" are used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

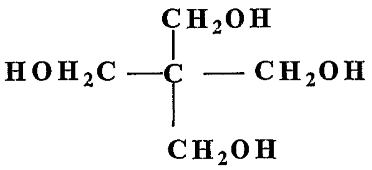
The cross linking agent (e) which forms part of the soft and/or hard segment preferably has 3 or more functional groups. The functional group may be any type of group which can react with isocyanate and is preferably selected from OH or NR'R'' in which R' and R'' are the same or different and selected from H, CO_2H and C_{1-6} alkyl, preferably H and C_{1-4} alkyl.

Examples of tri, tetra, hexa and octa-hydroxyl functional cross linking agents include trimethylol propane (TMP), trifunctional polyether polyol based on propoxylated glycerines such as Voranol 2770, pentaerythritol (PE), pentaerythritol tetrakis (2-mercapto acetate), dipentaerythritol (DPE) and tripentaerythritol (TPE).



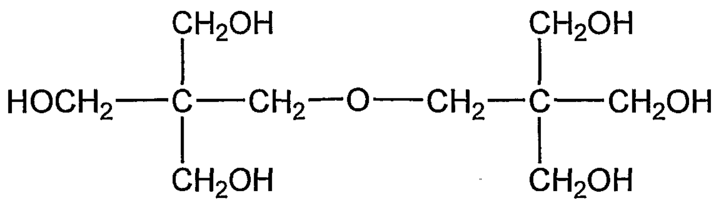
$HOCH_2-C(C_2H_5)(CH_2OH)-CH_2OH$

TMP



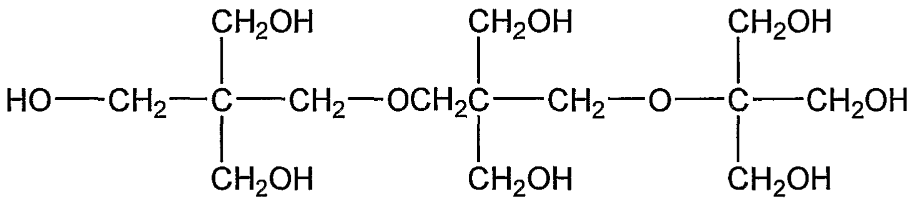
$HOH_2C-C(CH_2OH)(CH_2OH)-CH_2OH$

PE



$$HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2-O-CH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH$$

DPE

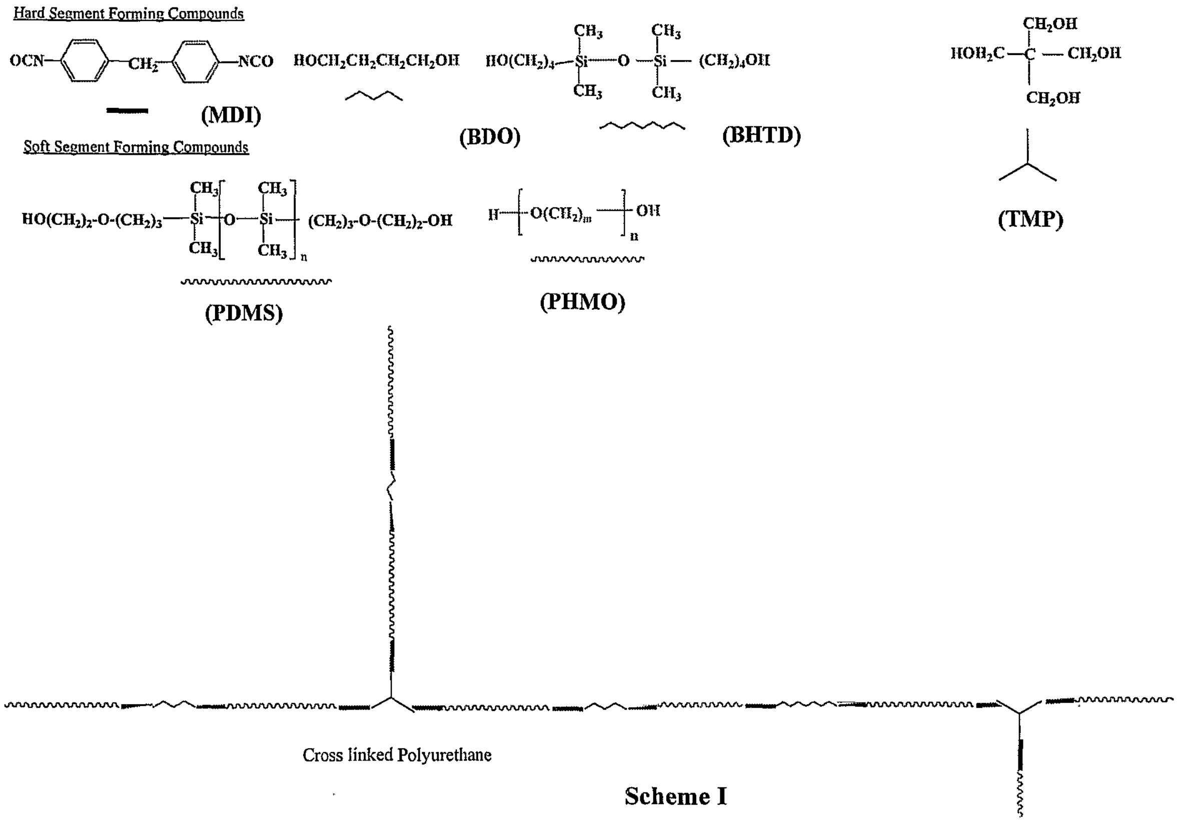


$$HO-CH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2-OCH_2\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2-O-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH$$

TPE

An example of an amine cross linker is triethanol amine.

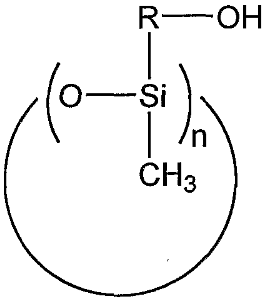
When cross linking agents such as TMP are incorporated into the hard segment of the polyurethane, the expected general structure is shown in Scheme I below:



Scheme I

The introduction of cross linking may cause some changes to polyurethane morphology. The effect may be minor if the desired improvement in creep resistance can be achieved by relatively lower level of cross linking, minimising the disruption to the hard segment ordering.

It will be appreciated that silicon-containing cross linking agents may also be used in the polyurethanes of the present invention. Examples include cyclic siloxanes of the formula (VII):



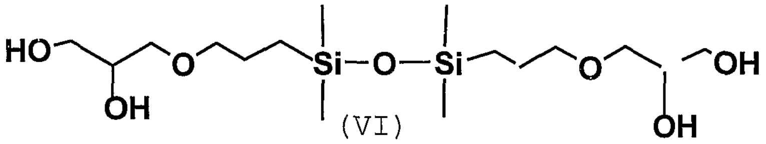
(VII)

wherein

n is an integer of 3 or greater; and

R is an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical having a backbone of at least 3 carbon atoms.

An example of a cyclic siloxane is tetramethyl tetrahydroxy propyl cyclotetrasiloxane of formula (V) shown above. Another suitable silicon-containing cross linking agent is 1,3(6,7-dihydroxy ethoxypropyl)tetramethyl disiloxane of formula (VI):



(VI)

The soft and hard segments of the polyurethanes typically phase separate and form separate domains. The hard segments organise to from ordered (crystalline) domains while the soft segments remain largely as amorphous domains and the two in combination is responsible for the excellent mechanical properties of polyurethanes. The introduction of cross links will affect this phase separation and the ordering of the hard and/or soft domains.

The soft segment which is formed from components (a) and (b) is preferably a combination of at least two macrodiols, at least two macrodiamines or at least one macrodiol and at least one macrodiamine.

Suitable polyether macrodiols include those represented by the formula (I)

$$HO-[(CH_2)_m-O]_n-H$$

(I)

wherein

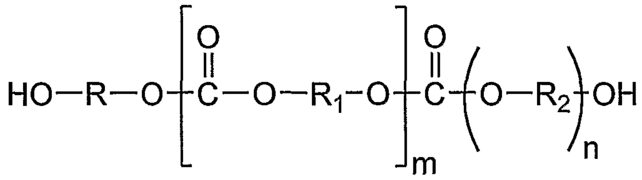
m is an integer of 4 or more, preferably 5 to 18; and

n is an integer of 2 to 50.

Polyether macrodiols of formula (I) wherein m is 5 or higher such as polyhexamethylene oxide (PHMO), polyheptamethylene oxide, polyoctamethylene oxide (POMO) and polydecamethylene oxide (PDMO) are preferred over the conventional polytetramethylene oxide (PTMO). The more preferred macrodiols and their preparation are described in Gunatillake *et al*[3] and US 5403912. Polyethers such as PHMO described in these references are particularly useful as they are more hydrophobic than PTMO and more compatible with polysiloxane macrodiols. The preferred molecular weight range of the polyether macrodiol is about 200 to about 5000, more preferably about 200 to about 1200. It will be understood that the molecular weight values referred to herein are "number average molecular weights".

Suitable polycarbonate macrodiols include poly(alkylene carbonates) such as poly(hexamethylene carbonate) and poly(decamethylene carbonate); polycarbonates prepared by reacting alkylene carbonate with alkanediol for example 1,4-butanediol, 1,10-decanediol (DD), 1,6-hexanediol (HD) and/or 2,2-diethyl 1,3-propanediol (DEPD); and silicon based polycarbonates prepared by reacting alkylene carbonate with 1,3-bis(4-hydroxybutyl)-1,1,3,3-tetramethyldisiloxane (BHTD) and/or alkanediols.

It will be appreciated when both the polyether and polycarbonate macrodiols are present, they may be in the form of a mixture or a copolymer. An example of a suitable copolymer is a copoly(ether carbonate) macrodiol represented by the formula (II)



$$HO-R-O\left[\overset{O}{\overset{\|}{C}}-O-R_1-O\right]_m\overset{O}{\overset{\|}{C}}\left(O-R_2\right)_n OH$$

(II)

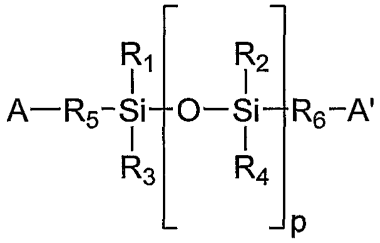
wherein

R_1 and R_2 are the same or different and selected from an optionally substituted straight chain, branched or cyclic alkylene, alkenylene, alkynylene or heterocyclic radical; and

m and n are integers of 1 to 20.

Although the compound of formula (II) above indicates blocks of carbonate and ether groups, it will be understood that they also could be distributed randomly in the main structure.

The polysiloxane macrodiol or macrodiamine may be represented by the formula (III):



$$A-R_5-\overset{R_1}{\underset{R_3}{Si}}-\left[O-\overset{R_2}{\underset{R_4}{Si}}\right]_p-R_6-A'$$

(III)

wherein

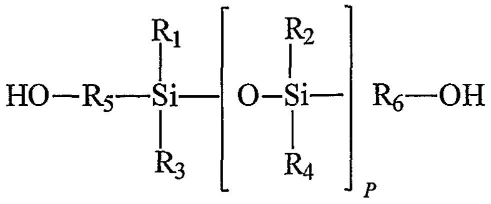
A and A' are OH or NHR wherein R is H or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical, preferably C_{1-6} alkyl, more preferably C_{1-4} alkyl;

R_1, R_2, R_3 and R_4 are the same or different and selected from hydrogen or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical;

R_5 and R_6 are the same or different and selected from an optionally substituted straight chain, branched or cyclic alkylene, alkenylene, alkynylene or heterocyclic radical; and

p is an integer of 1 or greater.

Preferred polysiloxanes are polysiloxane macrodiols which are polymers of the formula (III) wherein A and A' are hydroxy and include those represented by the formula (IIIa):



$$HO-R_5-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{Si}}-\left[O-\overset{\displaystyle R_2}{\underset{\displaystyle R_4}{Si}}-\right]_p R_6-OH$$

(IIIa)

wherein

R₁ to R₆ and p are as defined in formula (III) above.

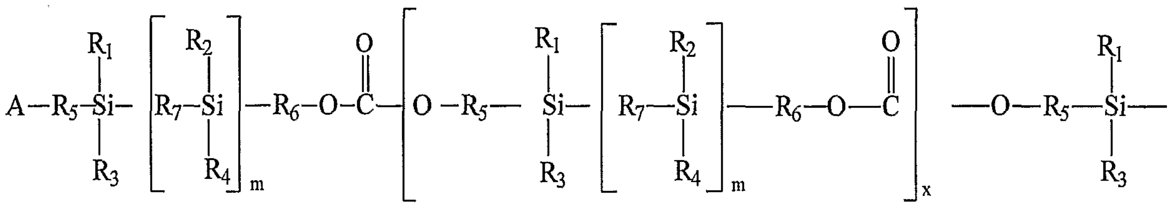
A preferred polysiloxane is PDMS which is a compound of formula (IIIa) wherein R_1 to R_4 are methyl and R_5 and R_6 are as defined above. Preferably R_5 and R_6 are the same or different and selected from propylene, butylene, pentylene, hexylene, ethoxypropyl ($-CH_2CH_2OCH_2CH_2CH_2-$), propoxypropyl and butoxypropyl.

The polysiloxane macrodiols may be obtained as commercially available products such as X-22-160AS from Shin Etsu in Japan or prepared according to known procedures. The preferred molecular weight range of the polysiloxane macrodiol is about 200 to about 6000, more preferably about 500 to about 2500.

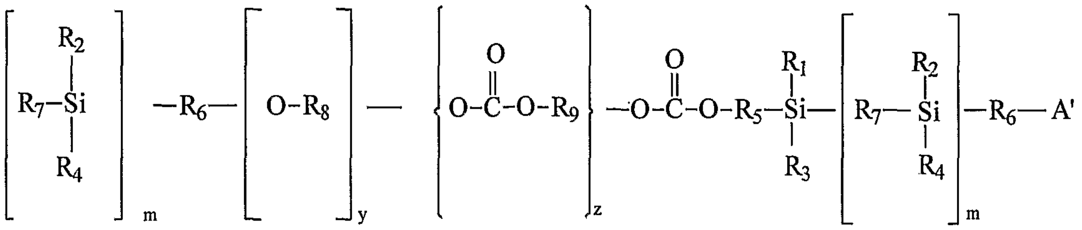
Other preferred polysiloxanes are polysiloxane macrodiamines which are polymers of the formula (III) wherein A is NH_2, such as, for example, amino-terminated PDMS.

Suitable silicon-based polycarbonates include those described in International Patent Publication No. WO 98/54242, the entire content of which is incorporated herein by reference.

A preferred silicon-based polycarbonate has the formula (IV):



$$A-R_5-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{Si}}-\left[R_7-\overset{\displaystyle R_2}{\underset{\displaystyle R_4}{Si}}\right]_m-R_6-O-\overset{\displaystyle O}{\overset{\|}{C}}-\left[O-R_5-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{Si}}-\left[R_7-\overset{\displaystyle R_2}{\underset{\displaystyle R_4}{Si}}\right]_m-R_6-O-\overset{\displaystyle O}{\overset{\|}{C}}\right]_x-O-R_5-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{Si}}-$$



$$\left[\begin{array}{c} R_2 \\ | \\ R_7-\text{Si} \\ | \\ R_4 \end{array}\right]_m -R_6- \left[O-R_8\right]_y - \left\{O-\overset{\overset{O}{\|}}{C}-O-R_9\right\}_z -O-\overset{\overset{O}{\|}}{C}-O-R_5-\underset{R_3}{\overset{R_1}{\text{Si}}}- \left[R_7-\underset{R_4}{\overset{R_2}{\text{Si}}}\right]_m -R_6-A'$$

(IV)

wherein

R_1, R_2, R_3, R_4 and R_5 are as defined in formula (III) above;

R_6 is an optionally substituted straight chain, branched or cyclic alkylene, alkenylene, alkynylene or heterocyclic radical;

R_7 is a divalent linking group, preferably O, S or NR_8;

R_8 and R_9 are same or different and selected from hydrogen or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical;

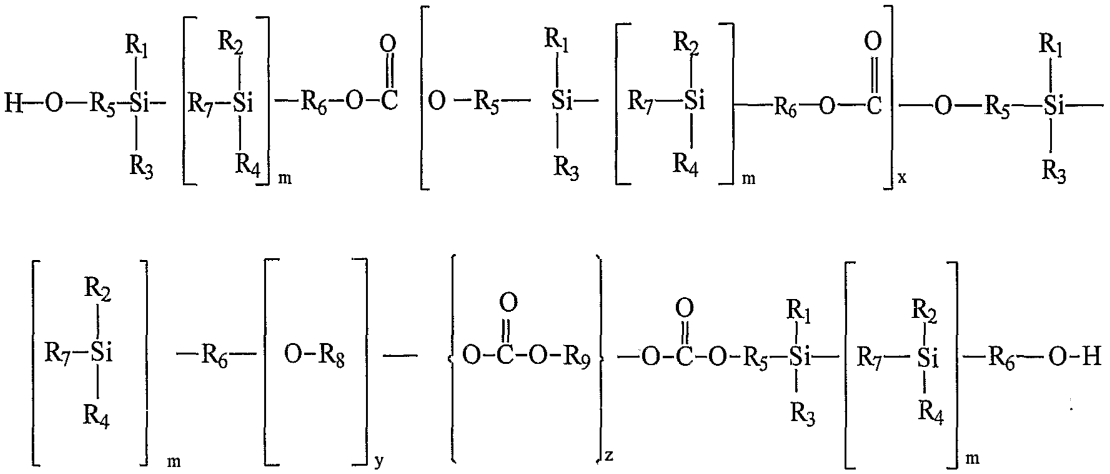
A and A' are as defined in formula (III) above;

m, y and z are integers of 0 or more; and

x is an integer of 0 or more.

Preferably z is an integer of 0 to about 50 and x is an integer of 1 to about 50. Suitable values for m include 0 to about 20, more preferably 0 to about 10. Preferred values for y are 0 to about 10, more preferably 0 to about 2.

A preferred polycarbonate is a compound of the formula (IV) wherein A and A' are hydroxy which is a polycarbonate macrodiol of the formula (IVa):



$$H{-}O{-}R_5{-}\underset{R_3}{\overset{R_1}{Si}}{-}\left[R_7{-}\underset{R_4}{\overset{R_2}{Si}}\right]_m{-}R_6{-}O{-}\overset{O}{\overset{\|}{C}}\left[O{-}R_5{-}\underset{R_3}{\overset{R_1}{Si}}{-}\left[R_7{-}\underset{R_4}{\overset{R_2}{Si}}\right]_m{-}R_6{-}O{-}\overset{O}{\overset{\|}{C}}\right]_x{-}O{-}R_5{-}\underset{R_3}{\overset{R_1}{Si}}{-}$$

$$\left[R_7{-}\underset{R_4}{\overset{R_2}{Si}}\right]_m{-}R_6{-}\left[O{-}R_8\right]_y{-}\left\{O{-}\overset{O}{\overset{\|}{C}}{-}O{-}R_9\right\}_z{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}R_5{-}\underset{R_3}{\overset{R_1}{Si}}{-}\left[R_7{-}\underset{R_4}{\overset{R_2}{Si}}\right]_m{-}R_6{-}O{-}H$$

(IVa)

wherein

R_1 to R_9, m, y, x and z are as defined in formula (IV) above.

Particularly preferred polycarbonate macrodiols are compounds of the formula (IVa) wherein R_1, R_2, R_3 and R_4 are methyl, R_8 is ethyl, R_9 is hexyl, R_5 and R_6 are propyl or R_4 butyl and R_7 is O or $-CH_2-CH_2-$,more preferably R_5 and R_6 are propyl when R_7 is O and R_5 and R_6 are butyl when R_7 is $-CH_2-CH_2-$. The preferred molecular weight range of the polycarbonate macrodiol is about 400 to about 5000, more preferably about 400 to about 2000.

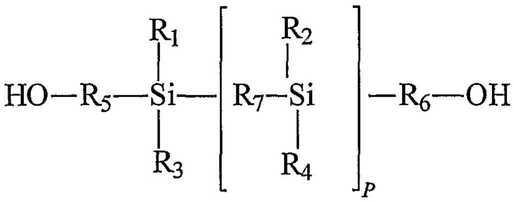
In a particularly preferred embodiment, the soft segment is a combination of PDMS or amino-terminated PDMS with a polyether of the formula (I) such as PHMO and/or a silicon-based polycarbonate such as siloxy carbonate.

The term "polyisocyanate" is used herein in its broadest sense and refers to di or higher isocyanates such as polymeric 4,4'-diphenylmethane diisocyanate (MDI). The polyisocyanate is preferably a diisocyanate which may be aliphatic or aromatic diisocyanates such as, for example MDI, methylene biscyclohexyl diisocyanate (H_{12}MDI), p-phenylene diisocyanate (p-PDI), trans-cyclohexane-1,4-diisocyanate (CHDI), 1,6-diisocyanatohexane (DICH), 1,5-diisocyanatonaphthalene (NDI), para-tetramethylxylenediisocyanate (p-TMXDI), meta-tetramethylxylene diisocyanate (m-TMXDI), 2,4-toluene diisocyanate (2,4-TDI) isomers or mixtures thereof or isophorone diisocyanate (IPDI). MDI is particularly preferred.

The term "di-functional chain extender" in the present context means any compound having two functional groups per molecule which are capable of reacting with the isocyanate group and generally have a molecular weight range of about 500 or less, preferably about 15 to about 500, more preferably about 60 to about 450.

The di-functional chain extender may be selected from diol or diamine chain extenders. Examples of diol chain extenders include 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,12-dodecanediol,1,4- cyclohexanediol, 1,4-cyclohexanedimethanol, p-xyleneglycol, 1,3-bis(4-hydroxybutyl) tetramethyldisiloxane, 1,3-bis(6-hydroxyethoxypropyl)tetramethyldisiloxane and 1,4-bis(2-hydroxyethoxy)benzene. Suitable diamine chain extenders include 1,2-ethylenediamine, 1,3-propanediamine,1,4-butanediamine, 1,3-bis(3-aminopropyl)tetramethyldisiloxane, 1,3-bis(4-aminobutyl)tetramethyldisiloxane and 1,6-hexanediamine.

The chain extender may also be a silicon-containing chain extender of the type described in International Patent Publication No. WO 99/03863, the entire contents of which are incorporated herein by reference. Such chain extenders include a silicon-containing diol of the formula (V):



$$HO-R_5-\underset{R_3}{\overset{R_1}{Si}}-\left[R_7-\underset{R_4}{\overset{R_2}{Si}}\right]_p-R_6-OH$$

(V)

wherein

R_1, R_2, R_3, R_4, R_5 and R_6 are as defined in formula (III) above;

R_7 is as defined in formula (IV) above, more preferably O; and

q is 0 or greater, preferably 2 or less.

Preferred silicon-containing diols of the formula (V) are 1,3-bis(4-hydroxybutyl)tetramethyl disiloxane (BHTD) (compound of formula (V) wherein R_1, R_2, R_3 and R_4 are methyl, R_5 and R_6 are butyl and R_7 is O), 1,4-bis(3-hydroxypropyl)tetramethyl disilylethylene (compound of formula (V) wherein R_1, R_2, R_3 and R_4 are methyl, R_5 and R_6 are propyl and R_7 is ethylene) and 1-4-bis(3-hydroxypropyl)tetramethyl disiloxane, more preferably BHTD.

The silicon-containing chain extender of formula (V) may be combined with the diol or diamine chain extenders described above. In a particularly preferred embodiment the chain extender of formula (V) is BHTD and the diol chain extender is BDO.

The silicon chain extender and diol or diamine chain extender can be used in a range of molar proportions with decreasing tensile properties as the molar percentage of the silicon chain extender increases in the mixture. A preferred molar percentage of silicon chain extender relative to the diol or diamine chain extender is about 1 to about 70%, more preferably about 60%. For example, when the chain extender is a combination of BHTD and BDO, then the relative proportions of these components is preferably 40% BHTD and 60% BDO.

Although the preferred chain extender contains one diol or diamine chain extender and one silicon-containing diol, it will be understood that combinations of more than one diol or diamine chain extender may be used in the polyurethanes of the present invention.

The "hydrocarbon radical" may include alkyl, alkenyl, alkynyl, aryl or heterocyclyl radicals.

The term "alkyl" denotes straight chain, branched or mono- or poly-cyclic alkyl, preferably C_{1-12} alkyl or cycloalkyl, more preferably C_{1-6} alkyl, most preferably C_{1-4} alkyl. Examples of straight chain and branched alkyl include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, amyl, isoamyl, sec-amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, neopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, heptyl, 5-methylhexyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, octyl, 6-methylheptyl, 1-methylheptyl, 1,1,3,3-tetramethylbutyl, nonyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-methyloctyl, 1-, 2-, 3-, 4- or 5-ethylheptyl, 1-, 2- or 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- and 8-methylnonyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3- or 4-propylheptyl, undecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-methyldecyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-ethylnonyl, 1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl, 1-pentylhexyl, dodecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-methylundecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-ethyldecyl, 1-, 2-, 3-, 4-, 5- or 6-propylnonyl, 1-, 2-, 3- or 4-butyloctyl, 1,2-pentylheptyl and the like. Examples of cyclic alkyl include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl and the like.

The term "alkenyl" denotes groups formed from straight chain, branched or mono- or poly-cyclic hydrocarbon groups having at least one double bond, preferably C_{2-12} alkenyl, more preferably C_{2-6} alkenyl. The alkenyl group may have E or Z stereochemistry where applicable. Examples of alkenyl include vinyl, allyl, 1-methylvinyl, butenyl, iso-butenyl, 3-methyl-2-butenyl, 1-pentenyl, cyclopentenyl, 1-methyl-cyclopentenyl, 1-hexenyl, 3-hexenyl, cyclohexenyl, 1-heptenyl, 3-heptenyl, 1-octenyl, cyclooctenyl, 1-nonenyl, 2-nonenyl, 3-nonenyl, 1-decenyl, 3-decenyl, 1,3-butadienyl, 1,4-pentadienyl, 1,3- cyclopentadienyl, 1,3-hexadienyl, 1,4-hexadienyl, 1,3-cyclohexadienyl, 1,4-cyclohexadienyl, 1,3-cycloheptadienyl, 1,3,5-cycloheptatrienyl, 1,3,5,7-(cycloocta-tetraenyl) and the like.

The term "alkynyl" denotes groups formed from straight chain, branched, or mono- or poly-cyclic hydrocarbon groups having at least one triple bond. Examples of alkynyl include ethynyl, 1-propynyl, 1- and 2-butynyl, 2-methyl-2-propynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 10-undecynyl, 4-ethyl-1-octyn-3-yl, 7-dodecynyl, 9-dodecynyl, 10-dodecynyl, 3-methyl-1-dodecyn-3-yl, 2-tridecynyl, 11-tridecynyl, 3-tetradecynyl, 7-hexadecynyl, 3-octadecynyl and the like.

The term "aryl" denotes single, polynuclear, conjugated and fused residues of aromatic hydrocarbons. Examples of aryl include phenyl, biphenyl, terphenyl, quaterphenyl, phenoxyphenyl, naphthyl, tetrahydronaphthyl, anthracenyl, dihydroanthracenyl, benzanthracenyl, dibenzanthracenyl, phenanthrenyl and the like.

The term "heterocyclyl" denotes mono- or poly-cyclic heterocyclyl groups containing at least one heteroatom selected from nitrogen, sulphur and oxygen. Suitable heterocyclyl groups include N-containing heterocyclic groups, such as, unsaturated 3 to 6 membered heteromonocyclic groups containing 1 to 4 nitrogen atoms, for example, pyrrolyl, pyrrolinyl, imidazolyl, pyrazolyl, pyridyl, pyrimidinyl, pyrazinyl, pyridazinyl, triazolyl or tetrazolyl; saturated 3 to 6 membered heteromonocyclic groups containing 1 to 4 nitrogen atoms, such as pyrrolidinyl, imidazolidinyl, piperidino or piperazinyl; unsaturated condensed heterocyclic groups containing 1 to

5 nitrogen atoms, such as, indolyl, isoindolyl, indolizinyl, benzimidazolyl, quinolyl, isoquinolyl, indazolyl, benzotriazolyl or tetrazolopyridazinyl; unsaturated 3 to 6-membered heteromonocyclic group containing an oxygen atom, such as, pyranyl or furyl; unsaturated 3 to 6-membered heteromonocyclic group containing 1 to 2 sulphur atoms, such as, thienyl; unsaturated 3 to 6-membered heteromonocyclic group containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms, such as, oxazolyl, isoazolyl or oxadiazolyl; saturated 3 to 6-membered heteromonocyclic group containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms, such as, morpholinyl; unsaturated condensed heterocyclic group containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms, such as, benzoxazolyl or benzoxadiazolyl; unsaturated 3 to 6-membered heteromonocyclic group containing 1 to 2 sulphur atoms and 1 to 3 nitrogen atoms, such as thiazolyl or thiadiazolyl; saturated 3 to 6-membered heteromonocyclic group containing 1 to 2 sulphur atoms and 1 to 3 nitrogen atoms, such as, thiadiazolyl; and unsaturated condensed heterocyclic group containing 1 to 2 sulphur atoms and 1 to 3 nitrogen atoms, such as benzothiazolyl or benzothiadiazolyl.

In this specification, "optionally substituted" means that a group may or may not be further substituted with one or more groups selected from oxygen, nitrogen, sulphur, alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, alkynyloxy, aryloxy, carboxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloalkynyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, azido, amino, alkylamino, alkenylamino, alkynylamino, arylamino, benzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, acyloxy, aldehydo, alkylsulphonyl, arylsulphonyl, alkylsulphonylamino, arylsulphonylamino, alkylsulphonyloxy, arylsulphonyloxy, heterocyclyl, heterocycloxy, heterocyclylamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, arylthio, acylthio and the like.

Preferably, the amount of hard segment in the polyurethanes of the present invention is about 15 to about 100 wt%, more preferably about 20 to about 70 wt%, most preferably about 30 to about 60 wt%. However, it will be appreciated that this amount is dependent on the type of soft segment polymer used, in particular the molecular weight range of the soft segment which is generally about 300 to about 3000, more preferably about 300 to about 2500, most preferably about 500 to about 2000.

The soft segment preferably includes macrodiols derived from 40 to 98 wt%, more preferably 40 to 90%, of polysiloxane and 2 to 60 wt%, more preferably 10 to 60 wt% of a polyether and/or polycarbonate macrodiol.

The weight ratio of polysiloxane and/or silicon-based polycarbonate to polyether and/or polycarbonate in the preferred soft segment may be in the range of from 1:99 to 99:1. A particularly preferred ratio of polysiloxane to polyether and/or polycarbonate which provides increased degradation resistance, stability and clarity is 80:20. Another preferred ratio of polysiloxane and/or silicon-based polycarbonate to polyether and/or polycarbonate when the chain extender includes a silicon-containing chain extender such as BHTD is 40:60.

The polyurethanes of the present invention may be prepared by any technique familiar to those skilled in the manufacture of polyurethanes. These include one or two-step bulk or solution polymerisation procedures. The polymerisation can be carried out in conventional apparatus or within the confines of a reactive injection moulding or mixing machines.

In a one-step bulk polymerisation procedure the appropriate amount of components (a), (b) and (e) are mixed with the chain extender (d) first at temperatures in the range of about 45 to about 100°C, more preferably about 60 to about 80°C. If desired a catalyst such as stanneous octoate or dibutyltin dilaurate at a level of about 0.001 to about 0.5 wt % based on the weight of the total ingredients may be added to the initial mixture. Molten polyisocyanate (c) is then added and mixed thoroughly to give a homogeneous polymer liquid and cured by pouring the liquid polymer into Teflon-coated trays and heating in an oven to about 100°C.

The polyurethanes are preferably prepared by a two-step method where a prepolymer having terminally reactive polyisocyanate groups is prepared by reacting components (a) and (b) as defined above with a polyisocyanate component (c). The prepolymer is then reacted with the chain extender (d) and the cross linking agent (e).

The processes described above here do not generally cause premature phase separation and yield polyurethanes that are compositionally homogeneous and transparent having high molecular weights. These processes also have the advantage of not requiring the us of any solvent to ensure that the soft and hard segments are compatible during synthesis.

A further advantage of the incorporation of polysiloxane segments is the relative ease of processing of the polyurethane by conventional methods such as reactive injection moulding, rotational moulding, compression moulding and foaming without the need of added processing waxes. If desired, however, conventional polyurethane processing additives such as catalysts for example dibutyl tin dilaurate (DBTD), stannous oxide (SO), 1,8-diazabicyclo[5,4,0] undec-7-ene (DABU), 1,3-diacetoxy-1,1,3,3-tetrabutyldistannoxane (DTDS), 1,4-diaza-(2,2,2)-bicyclooctane (DABCO), N,N,N',N'-tetramethylbutanediamine (TMBD) and dimethyltin dilaurate (DMTD); antioxidants for example Irganox (Registered Trade Mark); radical inhibitors for example trisnonylphenyl phosphite (TNPP);

stabilisers; lubricants for example Irgawax (Registered Trade Mark); dyes; pigments; inorganic and/or organic fillers; and reinforcing materials can be incorporated into the polyurethane during preparation. Such additives are preferably added to the macrodiol mixture in step (i) of the processes of the present invention.

The polyurethanes of the present invention are particularly useful in preparing biomaterials and medical devices, articles or implants as a consequence of their biostability and creep resistance.

The term "biostable" is used herein in its broadest sense and refers to a stability when in contact with cells and/or bodily fluids of living animals or humans.

The term "biomaterial" is used herein in its broadest sense and refers to a material which is used in situations where it comes into contact with the cells and/or bodily fluids of living animals or humans.

The medical devices, articles or implants may include catheters; stylets; bone suture anchors; vascular, oesophageal and bilial stents; cochlear implants; reconstructive facial surgery; controlled drug release devices; components in key hole surgery; biosensors; membranes for cell encapsulations; medical guidewires; medical guidepins; cannularizations; pacemakers, defibrillators and neurostimulators and their respective electrode leads; ventricular assist devices; orthopaedic joints or parts thereof including spinal discs and small joints; cranioplasty plates; intraoccular lenses; urological stents and other urological devices; stent/graft devices; device joining/extending/repair sleeves; heart valves; vein grafts; vascular access ports; vascular shunts; blood purification devices; casts for broken limbs; vein valve, angioplasty, electrophysiology and cardiac output catheters; and tools and accessories for insertion of medical devices, infusion and flow control devices.

It will be appreciated that polyurethanes having properties optimised for use in the construction of various medical devices, articles or implants and possessing creep resistance will also have other non-medical applications. Such applications may include toys and toy components, shape memory films, pipe couplings, electrical connectors, zero-insertion force connectors, Robotics, Aerospace actuators, dynamic displays, flow control devices, sporting goods and components thereof, body-conforming devices, temperature control devices, safety release devices and heat shrink insulation.

BRIEF DESCRIPTION OF THE DRAWINGS

In the Examples, reference will be made to the accompanying drawings in which:

Fig. 1 is a graph showing the tensile creep resistance of the polyurethanes of Example 1.

Fig. 2 is a graph showing the creep loading (~1 MPa) and recovery in compression of the polyurethanes of Examples 2 to 6;

Fig. 3 is a graph showing the creep loading (~5 MPa) and recovery in tension for the polyurethanes of Examples 2 to 7;

Fig. 4 is a graph showing the creep loading (~5 MPa) and recovery in tension for the polyurethanes of Example 8; and

Fig. 5 is a graph showing the creep loading (~1 MPa) and recovery in compression of the polyurethanes of Example 8.

EXAMPLES

The invention will now be described with reference to the following non-limiting examples.

EXAMPLE 1

A series of four polyurethanes were prepared to illustrate the effect of incorporating the tri-functional cross linker trimethylol propane (TMP) on creep resistance and mechanical properties.

Raw Materials: Poly (hexamethylene oxide) (PHMO)was synthesised and purified according to previously reported method (Gunatillake PA, Meijs GF, Chatelier RC, McIntosh and Rizzardo E., Polymer Int. 27, 275 (1992). PHMO was degassed at 135°C under vacuum (0.01 torr) for 2h. α.ω-bis(6-hydroxy-ethoxypropyl)-polydimethylsiloxane (PDMS) was purchased from Shin-Etsu (Japan) and degassed at 105°C under vacuum (0.01 torr) for 4 h. 1,3-Bis(4-hydroxybutyl) 1,1,3,3-tertamethyldisiloxane (BHTD, Silar Laboratories) was degassed at ambient temperature under vacuum (0.01 torr) for several hours (~12 h). 1,4-butanediol (BDO, Aldrich) was degassed and dried at 105°C for 2h prior to use.

The moisture content of all reagents was determined using Columetric Karl-Fisher titration. The moisture level of all reagents remained below 150 ppm.

The hydroxy number of the polyols (PDMS and PHMO) and of BHTD was determined using ASTM 2628 method.

The following procedure illustrates the preparation of the prepolymer used to make all four polyurethanes.

A mixture of PDMS (200.00 g, MW 927.0) and PHMO (50.00 g, MW 710.0) was degassed at 105°C for 2h under vacuum (0.01 torr). Molten MDI (102.71 g) was weighed into a three-neck round bottom flask equipped with mechanical stirrer, dropping funnel and nitrogen inlet. The flask was heated in an oil bath at 70°C. The degassed macrodiol mixture (200.0 g) was then added through a dropping funnel over a period of 45 minutes. After the addition is over, the reaction mixture was heated for 2h with stirring under nitrogen at 80°C. The prepolymer mixture was then degassed at 80°C under vacuum (0.01 torr) for about 1h. The vacuum was released slowly under nitrogen atmosphere and 280.0 g of the degassed pre-polymer mixture was weighed into a tall dry polypropylene beaker and immediately placed in a nitrogen circulating oven at 80°C.

The un cross linked thermoplastic polyurethane PU-0 was prepared by reacting prepolymer (280.00 g) and a mixture of BDO (9.0769 g) and BHTD (19.2479 g). The chain extender mixture was weighed into a wet-tared 50 mL plastic syringe and added to the prepolymer with high speed stirring (4500 rpm) using a Silverson Mixer. The stirring continued for 2 min after addition of chain extender mixture. The polymer mixture was then poured into several Teflon-cloth lined aluminium moulds to produce 3mm and 10mm thick sheets. The polymer in moulds was first cured under 4 ton nominal pressure in a compression moulding press at 100°C for 2 hours followed by further curing for 15 h in a nitrogen circulating oven at 100°C.

The cross linked polyurethanes were prepared by incorporating various amounts of TMP as indicated in Table 1. Three different concentrations of TMP replacing 10, 20 and 40 mol-% of BDO used in the formulation of un cross linked polyurethane (PU-0) were used. This corresponds to cross link density of 1.4, 2.8 and 5.5 %, respectively for PU-10, PU-20 and PU-40, expressed as mol-% cross linker relative to the total number of moles of reagents used. The following procedure which illustrates the preparation PU-20 describes the general procedure used in making all cross linked polyurethanes.

BDO (7.2611g) and TMP cross linker (1.792) were mixed in a round bottom flask and stirred for about 2 min at 40°C temperature to obtain a homogenous solution. 19.2479g BHTD weighed separately was then added to this flask and stirred for about 30 minutes to obtain a homogenous solution. The chain extender mixture and cross linker (28.301 g) were then weighed into a wet-tarred syringe and added into the pre-polymer mixture (280.0 g) while high speed (4500 rpm) stirring using Silverson Mixer. Stirring was continued for about 2 min after addition. The polymer mixture was poured into Teflon-cloth lined aluminium moulds to produce 3 mm and 10 mm sheets. The polymer in moulds was first cured under 4 ton nominal pressure in a compression moulding press at 100°C for 2 hours followed by further curing for 15h in a nitrogen circulating oven at 100°C.

Table 1: Quantities of reagents used in making the polyurethanes of Example 1

Sample code	Prepolymer (g)	BDO (g)	BHTD (g)	TMP (g)
PU-0	280.0	9.0769	19.2479	-
PU-10	280.0	8.1697	19.2479	0.896
PU-20	280.0	7.2611	19.2479	1.792
PU-40	280.0	5.4467	19.2479	3.584

Mechanical Properties and Procedures for testing mechanical properties and tensile creep for the polyurethanes of Example 1

The material was conditioned at ambient conditions for 48 h before testing.

Specimen Type

- ISO Dumbbell
- Gauge length: 20mm
- Width: 40mm
- Thickness:~3mm

Equipment

- Instron 5866 with 5800 Console
- Merlin Software
- Load Cell:1000N
- Long Range, Contact Extensometer

Method for Tensile Modulus

- Number of Specimens: 2
- Speed: 1mm/min
- The specimen is strained to 1.3%
- Modulus is determined over the range 0.05% strain-0.95% strain. Nine points are taken in the range and

a line of best fit is determined by the software, the slope of the line is the material's Young's modulus.

Method for Tensile Strength and Tensile Strain at Break

- Number of Specimen: 2
- Speed: 200mm/min
- Load is applied until failure, ultimate tensile strength and the % tensile strain at break are recorded

Method for Tensile Creep

- Number of Specimen: 1
- The gauge length is measured using a microscope with magnification times 10, the microscope (Vision Engineering, with Acu-Rite) is connected to digital measuring device (Quadracheck 200). Points are selected manually and the instrument calculates the distance between those points, giving the gauge length
- Load of 60N applied within 10 seconds
- Specimen held at a load of 60N for 120 mins, the %strain is recorded at 0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 mins
- After 120 mins the specimen is released from the grips
- The gauge length is measured at 120, 122, 124, 126, 128, 130, 135, 140, 145, 150, 160, 170, 180, 190, 200, 210 and 220 minutes, using the microscope.
- The strain is calculated using the original gauge length.
- The Strain versus time is plotted in an excel spreadsheet.

The introduction of cross linking caused a reduction in tensile strength, elongation at break and modulus, however, the materials retained strengths over 20 MPa. It is surprising that such low modulus materials with high strength can be achieved with a relatively low level of cross linking.

Table 2: Mechanical Properties of Polyurethanes of Example 1

Sample Code	Cross Link Density (mol-%)	Modulus of Elasticity * (MPa)	Tensile strength (MPa)	% Strain at break	Durometer Hardness Shore A
PU-0	0	10.03	29.51	532	79
PU-10	1.4	8.62	23.36	525	81
PU-20	2.8	6.36	23.14	446	80
PU-40	5.5	4.82	20.33	370	74

Resistance to Tensile Creep

The resistance to tensile creep was measured on dumbbell shaped test specimens using an Instron Tester The test specimen was loaded to 60N (in about 10 sec), translating to a stress of approximately 5MPa, and held for 2 hours. After 2 hours the specimen was taken off the Instron and the gauge length was measured intermittently for 2 hours. The results are summarised in Fig. 1.

The results clearly demonstrate that the cross linked polyurethanes were significantly more resistant to creep compared to un cross linked polyurethane. Increasing cross link density increased the creep resistance and the material with the highest cross link density showed complete recovery after removing the load.

Effect of Cross Linking on Polymer Solubility

The polymers prepared in Example 1 were tested for their solubility/swelling in N,N-dimethylformamide (DMF), a good solvent for polyurethanes. A rectangular specimen of polymer (approximately 1 g) was placed in excess DMF (~30mL) at 50°C for 48h. The excess DMF was wiped off from the polymer surface by using Kimwipe and weighed again to calculate the swelling ratio, expressed as the % weight gain relative to the dry sample. The results shown in

Table 3 illustrate that the cross linked polymers swelled in DMF indicating the synthesis was successful and the presence of covalent cross linking.

Table 3: Effect of N,N-dimethylformamide on polymers in Example 1

Sample Code	Swelling Ratio
PU-0	**Dissolved**[a]
PU-10	**6.4**
PU-20	**3.91**
PU-40	**2.07**

[a]The GPC analysis of PU-0 showed a number average molecular weight of 106,00 and polydispersity of 2.7.

EXAMPLE 2

This example illustrates the preparation of a polyurethane using the tetra-functional cross linker pentaerythritol (PE). The amount of PE used corresponds to 20 mol% of the BDO chain extender resulting in an effective cross link density of 2.653, expressed as mol-% of all components.

A mixture of PDMS (200.00g, MW 927.0) and PHMO (50.00 g, MW 710.0) was degassed at 105°C for 2h under vacuum (0.01torr). Molten MDI (102.71 g) was weighed into a three-neck round bottom flask equipped with mechanical stirrer, dropping funnel and nitrogen inlet. The flask was heated in an oil bath at 70°C. The degassed macrodiol mixture (200.0 g) was then added through a dropping funnel over a period of 45 minutes. After the addition is over, the reaction mixture was heated for 2h with stirring under nitrogen at 80°C. The prepolymer mixture was then degassed at 80°C under vacuum (0.01 torr) for about 1h. The vacuum was released slowly under nitrogen atmosphere and 280.0 g of the degassed pre-polymer mixture was weighed into a tall dry polypropylene beaker and immediately placed in a nitrogen circulating oven at 80°C.

BDO (7.2611 g) and pentaerythritol cross linker (PE, 1.3706cg) was mixed in a round bottom flask and stirred for about 2 min at 40°C temperature to obtain a homogenous solution. The mixture (8.6317 g) was weighed into a plastic syringe. 1,3-Bis(4-hydroxybutyl)1,1,3,3-tetramethyldsiloxane (BHTD, 19.2479g) was weighed separately into a plastic syringe. BDO/PE and BHTD were added into the pre-polymer mixture (280.0 g) while stirring at high speed (4500 rpm) using Silverson Mixer and stirring continued for about 2 minutes. The polymer mixture was then poured into several Teflon-cloth lined aluminium moulds to produce 3mm, and 10mm thick sheets. The polymer in moulds was first cured under 4 ton nominal pressure in a compression moulding press at 100°C for 2 hours followed by further curing for 15 h in a nitrogen circulating oven at 100°C.

EXAMPLE 3

This example illustrates the preparation of a polyurethane using the hexa-functional cross linker dipentaerythritol (DPE). The amount of DPE used corresponds to 20 mol% of the BDO chain extender.

A mixture of PDMS (200.00g, MW 927.0) and PHMO (50.00 g, MW 710.0) was degassed at 105°C for 2h under vacuum (0.01torr). Molten MDI (102.71 g) was weighed into a three-neck round bottom flask equipped with mechanical stirrer, dropping funnel and nitrogen inlet. The flask was heated in an oil bath at 70°C. The degassed macrodiol mixture (200.0 g) was then added through a dropping funnel over a period of 45 minutes. After the addition was over, the reaction mixture was heated for 2h with stirring under nitrogen at 80°C. The prepolymer mixture was then degassed at 80°C under vacuum (0.01 torr) for about 1h. The vacuum was released slowly under nitrogen atmosphere and 280.0 g of the degassed prepolymer mixture was weighed into a tall dry polypropylene beaker and immediately placed in a nitrogen circulating oven at 80°C.

BDO (7.2611 g) and DPE cross linker (1.7073 g) were mixed in a round bottom flask separately whereas 1,3-Bis(4-hydroxybutyl)1,1,3,3-tetramethyldsiloxane (BHTD, 19.2479g) was weighed separately into a plastic syringe. The BDO/DPE mixture was heated until it was a clear solution and added into the prepolymer mixture along with BHTD (19.24 g) while stirring at high speed (5000 rpm) using Silverson Mixer and stirring continued for about 2 minutes. The polymer mixture was then poured into several Teflon-cloth lined aluminium moulds to produce 3mm, and 10mm thick sheets. The polymer in moulds was first cured under 4 ton nominal pressure in a compression moulding press at 100 °C for 2 hours followed by further curing for 15 h in a nitrogen circulating oven at 100C°.

EXAMPLE 4

This example illustrates the preparation of a polyurethane using the octa-functional cross linker tripentaerythritol (TPE). The amount of TPE used corresponds to 20 mol% of the BDO chain extender.

A mixture of PDMS (200.00g, MW 927.0) and PHMO (50.00 g, MW 710.0) was degassed at 105°C for 2h under vacuum (0.01torr). Molten MDI (102.71 g) was weighed into a three-neck round bottom flask equipped with mechanical stirrer, dropping funnel and nitrogen inlet. The flask was heated in an oil bath at 70°C. The degassed macrodiol mixture (200.0 g) was then added through a dropping funnel over a period of 45 minutes. After the addition was over, the reaction mixture was heated for 2h with stirring under nitrogen at 80°C. The prepolymer mixture was then degassed at 80°C under vacuum (0.01 torr) for about 1h. The vacuum was released slowly under nitrogen atmosphere and 280.0 g of the degassed prepolymer mixture was weighed into a tall dry polypropylene beaker and immediately placed in a nitrogen circulating oven at 80°C.

BDO (7.2611 g) and TPE cross linker (TPE, 1.88 g) were mixed in a round bottom flask separately whereas 1,3-

Bis(4-hydroxybutyl)1,1,3,3-tetramethyldsiloxane (BHTD, 19.2479g) was weighed separately into a plastic syringe. The BDO/TPE mixture was heated until it was a clear solution and added into the prepolymer mixture along with BHTD (19.24 g) while stirring at high speed (5000 rpm) using Silverson Mixer and stirring continued for about 2 minutes. The polymer mixture was then poured into several Teflon-cloth lined aluminium moulds to produce 3mm, and 10mm thick sheets. The polymer in moulds was first cured under 4 ton nominal pressure in a compression moulding press at 100 °C for 2 hours followed by further curing for 15 h in a nitrogen circulating oven at 100C°.

EXAMPLE 5

This example illustrates the addition of the tri-functional cross linker TMP of Example 1 to a polyurethane which does not include the silicon-containing chain extender BHTD.

A mixture of PDMS (200.00g, MW 927.0) and PHMO (50.00 g, MW 710.0) was degassed at 105°C for 2h under vacuum (0.01torr). Molten MDI (102.71 g) was weighed into a three-neck round bottom flask equipped with mechanical stirrer, dropping funnel and nitrogen inlet. The flask was heated in an oil bath at 70°C. The degassed macrodiol mixture (200.0 g) was then added through a dropping funnel over a period of 45 minutes. After the addition was over, the reaction mixture was heated for 2h with stirring under nitrogen at 80°C. The prepolymer mixture was then degassed at 80°C under vacuum (0.01 torr) for about 1h. The vacuum was released slowly under nitrogen atmosphere and 280.0 g of the degassed prepolymer mixture was weighed into a tall dry polypropylene beaker and immediately placed in a nitrogen circulating oven at 80°C.

BDO (8.079 g) and TMP cross linker (4.287 g) were mixed in a round bottom flask and heated to 40°C to obtain a clear solution. The BDO/TMP mixture was then added into the prepolymer mixture while stirring at high speed (5000 rpm) using Silverson Mixer and stirring continued for about 2 minutes. The polymer mixture was then poured into several Teflon-cloth lined aluminium moulds to produce 3mm, and 10mm thick sheets. The polymer in moulds was first cured under 4 ton nominal pressure in a compression moulding press at 100 °C for 2 hours followed by further curing for 15 h in a nitrogen circulating oven at 100C°.

EXAMPLE 6

This example illustrates the addition of the tri-functional cross linker TMP of Example 1 to the polyurethane of Examples 1 to 4 in which the amount of BHTD is reduced with constant BDO.

A mixture of PDMS (200.00g, MW 927.0) and PHMO (50.00 g, MW 710.0) was degassed at 105°C for 2h under vacuum (0.01torr). Molten MDI (102.71 g) was weighed into a three-neck round bottom flask equipped with mechanical stirrer, dropping funnel and nitrogen inlet. The flask was heated in an oil bath at 70°C. The degassed macrodiol mixture (200.0 g) was then added through a dropping funnel over a period of 45 minutes. After the addition was over, the reaction mixture was heated for 2h with stirring under nitrogen at 80°C. The prepolymer mixture was then degassed at 80°C under vacuum (0.01 torr) for about 1h. The vacuum was released slowly under nitrogen atmosphere and 280.0 g of the degassed prepolymer mixture was weighed into a tall dry polypropylene beaker and immediately placed in a nitrogen circulating oven at 80°C.

BDO (9.076 g) and TMP cross linker (3.603 g) were mixed in a round bottom flask separately whereas BHTD (7.7093 g) was weighed separately into a plastic syringe. The BDO/TMP mixture was added into the prepolymer mixture along with BHTD (19.24 g) while stirring at high speed (5000 rpm) using Silverson Mixer and stirring continued for about 2 minutes. The polymer mixture was then poured into several Teflon-cloth lined aluminium moulds to produce 3mm, and 10mm thick sheets. The polymer in moulds was first cured under 4 ton nominal pressure in a compression moulding press at 100 °C for 2 hours followed by further curing for 15 h in a nitrogen circulating oven at 100C°.

EXAMPLE 7

This example illustrates the addition of a silicon-containing cross linking agent of formula (VI) to the polyurethane of Examples 1 to 4 in which the amount of cross linking agent of formula (VI) used corresponds to 20 mol% of the BDO chain extender.

A mixture of PDMS (200.00g, MW 927.0) and PHMO (50.00 g, MW 710.0) was degassed at 105°C for 2h under vacuum (0.01 torr). Molten MDI (102.71 g) was weighed into a three-neck round bottom flask equipped with mechanical stirrer, dropping funnel and nitrogen inlet. The flask was heated in an oil bath at 70°C. The degassed macrodiol mixture (200.0 g) was then added through a dropping funnel over a period of 45 minutes. After the addition was over, the reaction mixture was heated for 2h with stirring under nitrogen at 80°C. The prepolymer mixture was then degassed at 80°C under vacuum (0.01 torr) for about 1h. The vacuum was released slowly under nitrogen atmosphere and 280.0 g of the degassed prepolymer mixture was weighed into a tall dry polypropylene beaker and immediately placed in a nitrogen circulating oven at 80°C.

BDO (7.2611 g) and 1,3(6,7-dihydroxy ethoxy propyl) tetramethyl disiloxane cross linker (SC) (4.762 g) was mixed in a round bottom flask separately whereas 1,3-bis(4-hydroxybutyl)1,1,3,3-tetramethyldisiloxane (BHTD, 19.2479g) was weighed separately into a plastic syringe. The BDO/SC mixture was added into the prepolymer mixture along with BHTD (19.24 g) while stirring at high speed (5000 rpm) using Silverson Mixer and stirring continued for about 2 minutes. The polymer mixture was then poured into several Teflon-cloth lined aluminium moulds to produce 3mm, and 10mm thick sheets. The polymer in moulds was first cured under 4 ton nominal pressure in a compression moulding press at 100°C for 2 hours followed by further curing for 15 h in a nitrogen circulating oven at 100°C.

Mechanical properties and procedures for testing mechanical properties and tensile creep for the polyurethanes of Examples 2 to 7

Table 4: Mechanical Properties of Polyurethanes of Examples 2 to 7

Example	Modulus of Elasticity (MPa)	Tensile strength (MPa)	% Strain at break	Durometer Hardness Shore A
2	6.34	23.35	405	78
3	5.96	19.29	363	72
4	7.87	19.43	420	76
5	22.84	26.18	321	93
6	8.53	22.07	359	80
7	7.21	22.01	496	-

Method for testing films

Conditioning

The material is kept in the room in which it is to be tested for at least 48 hours prior to testing. The temperature of the room averages 23°C.

Specimen Type

- ISO Rectangle
- Gauge length: 100mm
- Width: 10mm
- Thickness:~0.2mm

Equipment

- Instron 5866 with 5800 Console

- Merlin Software
- Load Cell:1000N
- Long Range, Contact Extensometer

Method for Tensile Modulus

- Number of Specimens: 2
- Speed: 1mm/min
- The specimen is strained to 0.4%
- Modulus is determined over the range 0.05% strain-0.3% strain. Nine points are taken in the range and a line of best fit is determined by the software, the slope of the line is the material's Young's modulus.

Method for Tensile Strength and Tensile Strain at Break

- Number of Specimen: 2
- Speed: 500mm/min
- Load is applied until failure, ultimate tensile strength and the % tensile strain at break are recorded

Method for Tensile Creep

- Number of Specimen:1
- The gauge length is measured using a microscope with magnification times 10, the microscope (Vision Engineering, with Acu-Rite) is connected to digital measuring device (Quadracheck 200). Points are selected manually and the instrument calculates the distance between those points, giving the gauge length
- Load of 12N applied within 10 seconds (Stress applied is the same as for dumbbells, 5 MPa)
- Specimen held at a load of 12N for 120mins, the %strain is recorded at 0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120mins
- After 120mins the specimen is released from the grips

- The gauge length is measured at 120, 122, 124, 126, 128, 130, 135, 140, 145, 150, 160, 170, 180, 190, 200, 210 and 220 minutes, using the microscope.
- The strain is calculated using the original gauge length.
- The Strain versus time is plotted in an excel spreadsheet.

These results show that the higher functional cross linkers such as DPE improve the creep resistance significantly.

EXAMPLE 8

This example illustrates the preparation of a polyurethane using the trifunctional macrodiol,Voranol 2070, a trifunctional polyether polyol based on proproxylated glycerine having a number average molecular weight of 700 as a cross linking agent. This polyurethane does not contain any cross linker in the hard segment.

The prepolymer containing PDMS, PHMO AND MOI was prepared as described in Example 1.

The cross linked polyurethanes were prepared by incorporating two different amounts of Voranol 2070. The amounts of Voranol 2070 corresponded to 20 and 40 mole % of BDO used in the formulation of the un crosslinked polyurethane (PU-0).

BDO, BHTD and Voranol 2070 were mixed together in a round bottom flask for 30 min to obtain a homogeneous solution. The mixture was then weighed into a wet tared syringe and added into the prepolymer mixture while high speed (4500 rpm) stirring using the Silverson mixer. Stirring was continued for about 2 min after the addition. The polymer was poured into Teflon coated moulds to produce 3 mm thick sheets. The polymer was first cured under 4 ton nominal pressure in a compression moulding press at 100°C for 2 hours followed by further curing for 15h in a nitrogen circulating oven at 100°C.

Table 5: Quantities of reagents used in making the polyurethanes of Example 8

Sample code	Prepolymer (g)	BDO (g)	BHTD (g)	Voranol 2070 (g)
PU-20V	280	7.47	19.298	9.703
PU-40V	280	5.609	19.298	19.393

Mechanical properties for the polyurethanes of Example 8

The mechanical properties were tested using the procedures described in Example 1.

Table 6: Mechanical properties of polyurethanes of Example 8

Sample code	Modulus of Elasticity (MPa)	Tensile Strength (MPa)	% Strain at Break	Durometer Hardness Shore A
PU-20V	10.12	25.96	479	78
PU-40V	5.03	22.10	428	73

REFERENCES

1. Gunatillake PA, Meijs GF and Adhikari A, International Patent Application PCT/AU98/00546, US6,420,452 B1

2. Adhikari R., Gunatillake PA., Mejis GF., McCarthy SJ. J Appl Polym Sci (2002), 83, 736-746.

3. Gunatillake PA, Meijs GF, Chatelier RC, McIntosh DM and Rizzardo E, *Polym. Int.*, Vol. 27, pp 275-283 (1992).

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

CLAIMS:

1. A cross linked polyurethane or polyurethane urea which comprises a soft segment which is formed from:
    - (a) at least one polyether macrodiol and/or at least one polycarbonate macrodiol; and
    - (b) at least one polysiloxane macrodiol, at least one polysiloxane macrodiamine and/or at least one silicon-based polycarbonate; and/or

    a hard segment which is formed from:
    - (c) a polyisocyanate; and
    - (d) at least one di-functional chain extender,

    wherein the soft segment and/or the hard segment are further formed from:
    - (e) at least one cross linking agent.

2. A polyurethane or polyurethane urea according to claim 1 in which the cross linking agent (e) has 3 or more functional groups.

3. A polyurethane or polyurethane urea according to claim 2 in which the functional group is capable of reacting with isocyanate.

4. A polyurethane or polyurethane urea according to claim 2 or 3 in which the functional group is selected from OH and NR'R'' in which R' and R'' are the same or different and selected from H, CO_2H and C_{1-6} alkyl.

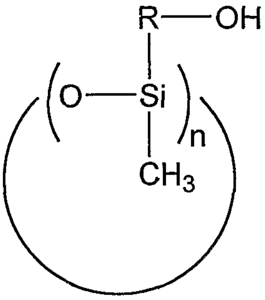
5. A polyurethane or polyurethane urea according to any one of claims 1 to 4 in which the cross linking agent (e) is a hydroxyl, amine or silicon-containing cross linking agent.

6. A polyurethane or polyurethane urea according to claim 5 in which the hydroxyl cross linking agent is selected from trimethylol propane (TMP), trifunctional polyether polyol based on polytetramethylene oxide

(Voranol 2070), pentaerythritol (PE), pentaerythritol tetrakis (2-mercapto acetate), dipentaerythritol (DPE) and tripentaerythritol (TPE).

7. A polyurethane or polyurethane urea according to claim 5 in which the amine cross linking agent is triethanol amine.

8. A polyurethane or polyurethane urea according to claim 5 in which the silicon-containing cross linking agent is a cyclic siloxane of the formula (VII):

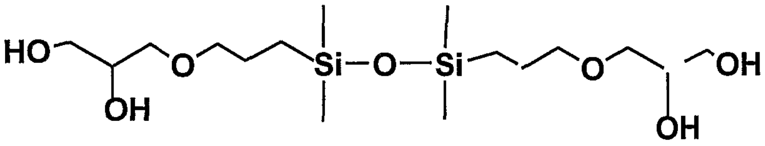


(VII)

wherein

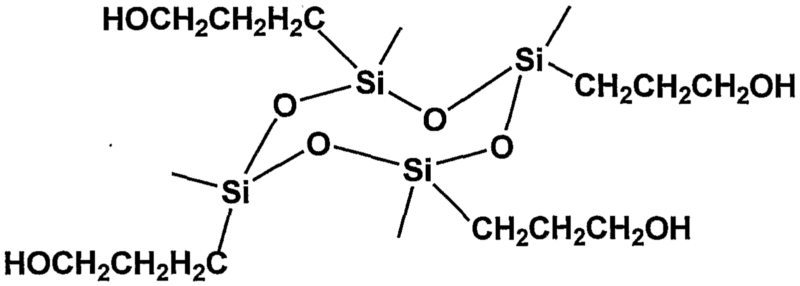
n is an integer of 3 or greater; and

R is an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical having a backbone of at least 3 carbon atoms; or 1,3(6,7-dihydroxy ethoxypropyl)tetramethyl disiloxane of formula (VI):



(VI)

9. A polyurethane or polyurethane urea according to claim 8 in which the cyclic siloxane is tetramethyl tetrahydroxy propyl cyclotetrasiloxane of formula (V):



(V)

10. A polyurethane or polyurethane urea according to any one of the preceding claims in which the soft segment which is formed from components (a) and (b) is a combination of at least two macrodiols, at least two macrodiamines or at least one macrodiol and at least one macrodiamine.

11. A polyurethane or polyurethane urea according to any one of the preceding claims in which the polyether macrodiol is represented by the formula (I)

$$HO-[(CH_2)_m-O]_n-H$$

(I)

wherein

m is an integer of 4 or more, preferably 5 to 18; and
n is an integer of 2 to 50.

12. A polyurethane or polyurethane urea according to claim 11 in which m is 5 or higher.

13. A polyurethane or polyurethane urea according to claim 12 in which the polyether macrodiol selected from polyhexamethylene oxide (PHMO), polyheptamethylene oxide, polyoctamethylene oxide (POMO) and polydecamethylene oxide (PDMO)

14. A polyurethane or polyurethane urea according to claims 11 to 13 in which the molecular weight range of the polyether macrodiol is about 200 to about 5000.

15. A polyurethane or polyurethane urea according to claim 14 in which the molecular weight range of the polyether macrodiol is about 200 to about 1200.

16. A polyurethane or polyurethane urea according to any preceding claims in which the polycarbonate macrodiol is selected from poly(alkylene carbonates), polycarbonates prepared by reacting alkylene carbonate with alkanediol and silicon based polycarbonates.

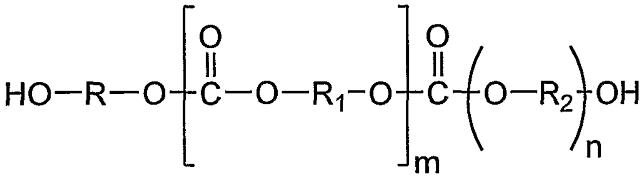
17. A polyurethane or polyurethane urea according to claim 16 in which the polyalkylene carbonate is selected from poly(hexamethylene carbonate) and poly(decamethylene carbonate).

18. A polyurethane or polyurethane urea according to claim 16 in which the polycarbonate prepared by reacting alkylene carbonate with alkanediol is selected from 1,4-butanediol, 1,10-decanediol (DD), 1,6-hexanediol (HD) and 2,2-diethyl 1,3-propanediol (DEPD).

19. A polyurethane or polyurethane urea according to claim 16 in which the silicon based carbonate is prepared by reacting alkylene carbonate with 1,3-bis (4-hydroxybutyl)-1,1,3,3-tetramethyldisiloxane (BHTD) and/or alkanediols.

20. A polyurethane or polyurethane urea according to any one of the preceding claims in which the polyether and polycarbonate macrodiols are in the form of a mixture or a copolymer.

21. A polyurethane or polyurethane urea according to claim 20 in which the copolymer is a copoly(ether carbonate) macrodiol represented by the formula (II)



$$HO-R-O-\left[\overset{O}{\overset{\|}{C}}-O-R_1-O\right]_m-\overset{O}{\overset{\|}{C}}-\left(O-R_2\right)_n-OH$$

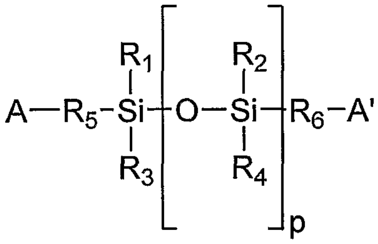
(II)

wherein

R$_1$ and R$_2$ are the same or different and selected from an optionally substituted straight chain, branched or cyclic alkylene, alkenylene, alkynylene or heterocyclic radical; and

m and n are integers of 1 to 20.

22. A polyurethane or polyurethane urea according to any preceding claims in which polysiloxane macrodiol or macrodiamine is represented by the formula (III):



$$A-R_5-\underset{R_3}{\overset{R_1}{Si}}-\left[O-\underset{R_4}{\overset{R_2}{Si}}\right]_p-R_6-A'$$

(III)

wherein

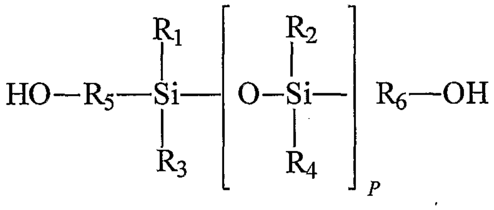
A and A' are OH or NHR wherein R is H or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical, preferably C_{1-6} alkyl, more preferably C_{1-4} alkyl;

R$_1$, R$_2$, R$_3$ and R$_4$ are the same or different and selected from hydrogen or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical;

R_5 and R_6 are the same or different and selected from an optionally substituted straight chain, branched or cyclic alkylene, alkenylene, alkynylene or heterocyclic radical; and

p is an integer of 1 or greater.

23. A polyurethane or polyurethane urea according to claim 22 in which the polysiloxane is a polysiloxane macrodiol of the formula (III) wherein A and A' are hydroxy and is represented by the formula (IIIa):



$$HO-R_5-\underset{R_3}{\overset{R_1}{Si}}-\left[O-\underset{R_4}{\overset{R_2}{Si}}-\right]_p R_6-OH$$

(IIIa)

wherein

R_1 to R_6 and p are as defined in claim 22.

24. A polyurethane or polyurethane urea according to claim 22 or claim 23 in which the polysiloxane is polydimethyl siloxane (PDMS) which is a compound of formula (IIIa) wherein R_1 to R_4 are methyl and R_5 and R_6 are as defined in claim 23.

25. A polyurethane or polyurethane urea according to claim 24 in which R_5 and R_6 are the same or different and selected from propylene, butylene, pentylene, hexylene, ethoxypropyl ($-CH_2CH_2OCH_2CH_2CH_2-$), propoxypropyl and butoxypropyl.

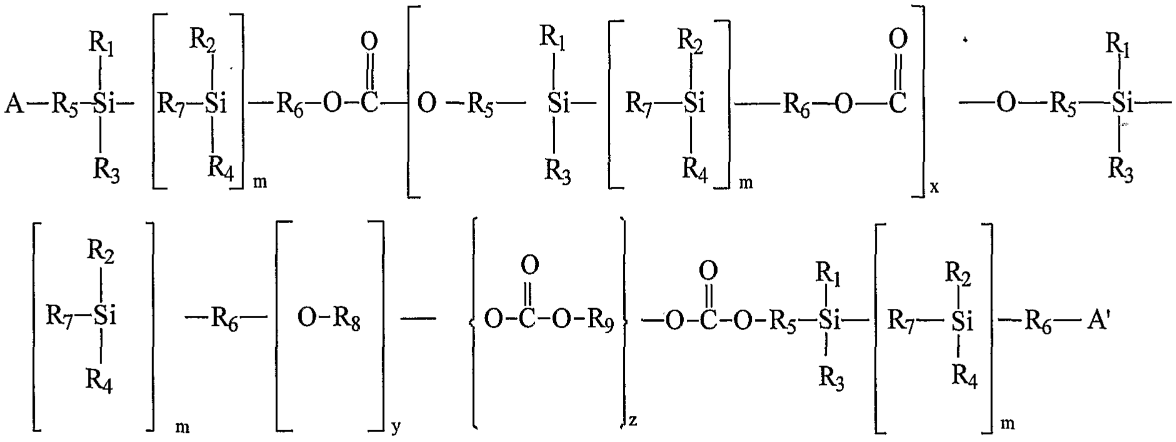
26. A polyurethane or polyurethane urea according to any one of claims 22 to 25 in which the molecular weight range of the polysiloxane macrodiol is about 200 to about 6000.

27. A polyurethane or polyurethane urea according to claim 26 in which the molecular wieght range of the polysiloxane macrodiol is about 500 to about 2500.

28. A polyurethane or polyurethane urea according to claim 22 in which the polysiloxane is a polysiloxane macrodiamine which has the formula (III) as defined in claim 22 wherein A is NH_2.

29. A polyurethane or polyurethane urea according to claim 28 in which the polysiloxane macrodiamine is amino-terminated PDMS.

30. A polyurethane or polyurethane urea according to any one of the preceding claims in which the silicon-based polycarbonate has the formula (IV):



$$A-R_5-\underset{R_3}{\overset{R_1}{Si}}-\left[R_7-\underset{R_4}{\overset{R_2}{Si}}\right]_m-R_6-O-\overset{O}{\overset{\|}{C}}-\left[O-R_5-\underset{R_3}{\overset{R_1}{Si}}-\left[R_7-\underset{R_4}{\overset{R_2}{Si}}\right]_m-R_6-O-\overset{O}{\overset{\|}{C}}\right]_x-O-R_5-\underset{R_3}{\overset{R_1}{Si}}-$$

$$\left[R_7-\underset{R_4}{\overset{R_2}{Si}}\right]_m-R_6-\left[O-R_8\right]_y-\left\{O-\overset{O}{\overset{\|}{C}}-O-R_9\right\}_z-O-\overset{O}{\overset{\|}{C}}-O-R_5-\underset{R_3}{\overset{R_1}{Si}}-\left[R_7-\underset{R_4}{\overset{R_2}{Si}}\right]_m-R_6-A'$$

(IV)

wherein

R_1, R_2, R_3, R_4 and R_5 are as defined in formula (III) above;

R_6 is an optionally substituted straight chain, branched or cyclic alkylene, alkenylene, alkynylene or heterocyclic radical;

R_7 is a divalent linking group, preferably O, S or

NR_8;

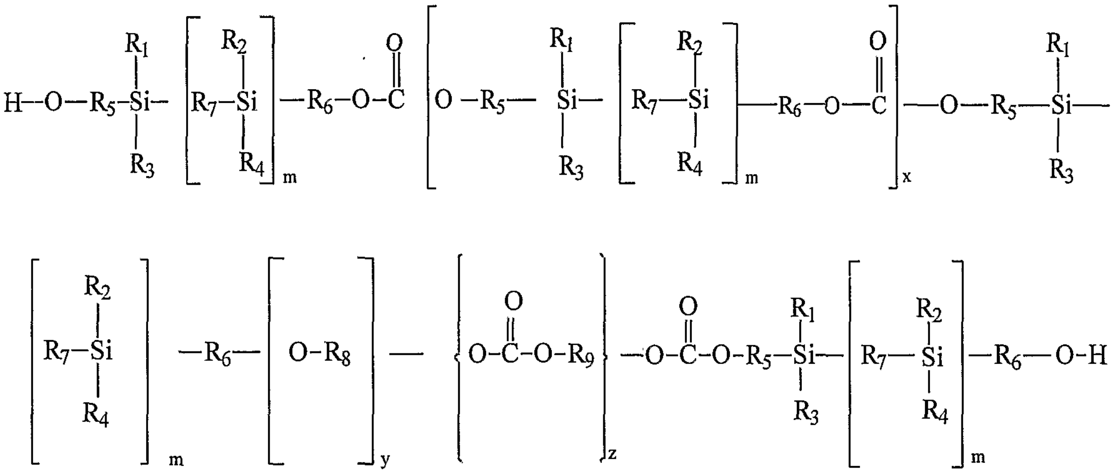
R_8 and R_9 are same or different and selected from hydrogen or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical;

A and A' are as defined in formula (III) above;

m, y and z are integers of 0 or more; and

x is an integer of 0 or more.

31. A polyurethane or polyurethane urea according to claim 30 in which polycarbonate is a compound of the formula (IV) wherein A and A' are hydroxy which is a polycarbonate macrodiol of the formula (IVa):



$$H-O-R_5-\underset{R_3}{\overset{R_1}{Si}}-\left[R_7-\underset{R_4}{\overset{R_2}{Si}}\right]_m-R_6-O-\overset{O}{\overset{\|}{C}}\left[O-R_5-\underset{R_3}{\overset{R_1}{Si}}-\left[R_7-\underset{R_4}{\overset{R_2}{Si}}\right]_m-R_6-O-\overset{O}{\overset{\|}{C}}\right]_x-O-R_5-\underset{R_3}{\overset{R_1}{Si}}-\left[R_7-\underset{R_4}{\overset{R_2}{Si}}\right]_m-R_6-\left[O-R_8\right]_y-\left\{O-\overset{O}{\overset{\|}{C}}-O-R_9\right\}_z-O-\overset{O}{\overset{\|}{C}}-O-R_5-\underset{R_3}{\overset{R_1}{Si}}-\left[R_7-\underset{R_4}{\overset{R_2}{Si}}\right]_m-R_6-O-H$$

(IVa)

wherein

R_1 to R_9, m, y, x and z are as defined in claim 30.

32. A polyurethane or polyurethane urea according to claim 30 or 31 in which the molecular weight range of the polycarbonate macrodiol is about 400 to about 5000.

33. A polyurethane or polyurethane urea according to claim 32 in which the molecular weight range of the polycarbonate macrodiol is about 400 to about 2000.

34. A polyurethane or polyurethane urea according to any

preceding claims in which the soft segment is a combination of PDMS or amino-terminated PDMS with a polyether of the formula (I) and/or a silicon-based polycarbonate.

35. A polyurethane or polyurethane urea according to any preceding claims in which the polyisocyanate (c) is a di or higher isocyanate selected from polymeric 4,4'-diphenylmethane diisocyanate (MDI),. MDI, methylene biscyclohexyl diisocyanate (H_{12}MDI), p-phenylene diisocyanate (p-PDI), trans-cyclohexane-1,4-diisocyanate (CHDI), 1,6-diisocyanatohexane (DICH), 1,5-diisocyanatonaphthalene (NDI), para-tetramethylxylenediisocyanate (p-TMXDI), meta-tetramethylxylene diisocyanate (m-TMXDI), 2,4-toluene diisocyanate (2,4-TDI) isomers or mixtures thereof or isophorone diisocyanate (IPDI).

36. A polyurethane or polyurethane urea according to claim 35 in which the polyisocyanate is MDI.

37. A polyurethane or polyurethane urea according to any preceding claims in which the di-functional chain extender (d) is a compound having two functional groups per molecule which are capable of reacting with an isocyanate group.

38. A polyurethane or polyurethane urea according to claim 37 in which the di-functional chain extender (d) has a molecular weight range of about 500 or less.

39. A polyurethane or polyurethane urea according to claim 38 in which the di-functional chain extender (d) has a molecular weight range of about 15 to about 500.

40. A polyurethane or polyurethane urea according to claim 39 in which the di-functional chain extender (d) has

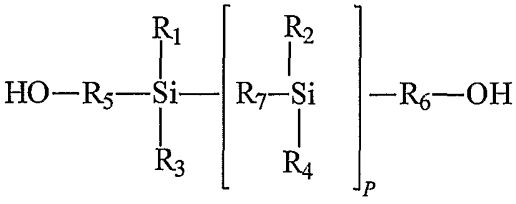
a molecular weight range of about 60 to about 450.

41. A polyurethane or polyurethane urea according to any one of the preceding claims in which the di-functional chain extender is selected from diol, diamine and silicone-containing chain extenders.

42. A polyurethane or polyurethane urea according to claim 41 in which the diol chain extender is selected from 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,12-dodecanediol,1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, p-xyleneglycol, 1,3-bis(4-hydroxybutyl) tetramethyldisiloxane, 1,3-bis(6-hydroxyethoxypropyl)tetramethyldisiloxane and 1,4-bis(2-hydroxyethoxy)benzene.

43. A polyurethane or polyurethane urea according to claim 41 in which the diamine chain extender is selected from 1,2-ethylenediamine, 1,3-propanediamine,1,4-butanediamine, 1,3-bis(3-aminopropyl)tetramethyldisiloxane, 1,3-bis(4-aminobutyl)tetramethyldisiloxane and 1,6-hexanediamine.

44. A polyurethane or polyurethane urea according to claim 41 in which the silicon-containing chain extender is a silicon-containing diol of the formula (V):



$$HO-R_5-\underset{R_3}{\overset{R_1}{Si}}-\left[R_7-\underset{R_4}{\overset{R_2}{Si}}\right]_p-R_6-OH$$

(V)

wherein

R_1, R_2, R_3, R_4, R_5 and R_6 are as defined in formula (III) in claim 22;

R_7 is as defined in formula (IV) in claim 30; and

q is 0 or greater.

45. A polyurethane or polyurethane urea according to claim 44 in which the silicon-containing diol of the formula (V) is selected from 1,3-bis(4-hydroxybutyl)tetramethyl disiloxane (BHTD) (compound of formula (V) wherein R_1, R_2, R_3 and R_4 are methyl, R_5 and R_6 are butyl and R_7 is O), 1,4-bis(3-hydroxypropyl)tetramethyl disilylethylene (compound of formula (V) wherein R_1, R_2, R_3 and R_4 are methyl, R_5 and R_6 are propyl and R_7 is ethylene) and 1-4-bis(3-hydroxypropyl)tetramethyl disiloxane.

46. A polyurethane or polyurethane urea according to claims 44 or 45 in which the di-functional chain extender is a combination of a silicon-containing chain extender of formula (V) and a diol or diamine chain extender.

47. A polyurethane or polyurethane urea according to claim 46 in which the di-functional chain extender of formula (V) is BHTD and the diol chain extender is BDO.

48. A polyurethane or polyurethane urea according to claim 46 or 47 in which the molar percentage of silicon chain extender relative to the diol or diamine chain extender is about 1 to about 70%.

49. A polyurethane or polyurethane urea according to any one of the preceding claims in which the amount of hard segment is about 15 to about 100 wt%.

50. A polyurethane or polyurethane urea according to claim 49 in which the amount of hard segment is about 20 to about 70 wt%.

51. A polyurethane or polyurethane urea according to claim 50 in which the amount of hard segment is about 30 to about 60 wt%.

52. A polyurethane or polyurethane urea according to any one of the preceding claims in which the molecular weight range of the soft segment is about 300 to about 3000.

53. A polyurethane or polyurethane urea according to claim 52 in which the molecular weight range of the soft segment is about 300 to about 2500.

54. A polyurethane or polyurethane urea according to claim 53 in which the molecular weight range of the soft segment is about 500 to about 2000.

55. A polyurethane or polyurethane urea according to any one of the preceding claims in which the soft segment comprises macrodiols derived from 40 to 98 wt% of polysiloxane and 2 to 60 wt% of a polyether and/or polycarbonate macrodiol.

56. A polyurethane or polyurethane urea according to any one of the preceding claims in which the weight ratio of polysiloxane and/or silicon-based polycarbonate to polyether and/or polycarbonate in the soft segment is in the range of from 1:99 to 99:1.

57. A compound of formula (V) as defined in claim 9,

58. A process for preparing the polyurethane or polyurethane urea defined in any of claims 1 to 56 which comprises the steps of:
   (i) reacting components (a), (b) and (c) as defined in any one of claims 1 to 56 to form a prepolymer having terminally reactive

polyisocyanate groups; and

(ii) reacting the prepolymer with components (d) and (e) defined in any one of claims 1 to 56.

59. A process for preparing the polyurethane or polyurethane urea defined in any one of claims 1 to 56 which comprises the steps of:

(i) mixing components (a), (b), (d) and (e) defined in any one of claims 1 to 56; and

(ii) reacting the mixture with component (c) defined in any one of claims 1 to 56.

60. A process according to claim 59 in which step (i) is carried out at temperatures in the range of about 45 to about 100°C.

61. A process according to claim 59 or claim 60 in which a catalyst is added in step (i).

62. A polyurethane or polyurethane urea according to claim 61 in which the catalyst is stanneous octoate or dibutyl tin dilaurate.

63. A polyurethane or polyurethane urea according to any one of claims 58 to 62 in which polyurethane processing additives are added in step (i) selected from radical inhibitors, stabilisers, lubricants, dyes, pigments, inorganic fillers organic fillers and reinforcing materials.

64. A material, device, article or implant which is wholly or partly composed of the polyurethanes or polyurethane ureas defined in any one of claims 1 to 56.

65. A material device, article or implant according to claim 64 selected from catheters; stylets; bone suture anchors; vascular, oesophageal and bilial stents; cochlear

implants; reconstructive facial surgery; controlled drug release devices; components in key hole surgery; biosensors; membranes for cell encapsulations; medical guidewires; medical guidepins; cannularizations; pacemakers, defibrillators and neurostimulators and their respective electrode leads; ventricular assist devices; orthopaedic joints or parts thereof; spinal discs; small joints; cranioplasty plates; intraoccular lenses; urological stents and other urological devices; stent/graft devices; device joining/extending/repair sleeves; heart valves; vein grafts; vascular access ports; vascular shunts; blood purification devices; casts for broken limbs; vein valve, angioplasty, electrophysiology and cardiac output catheters; tools and accessories for insertion of medical devices, infusion and flow control devices; toys and toy components; shape memory films; pipe couplings; electrical connectors; zero-insertion force connectors; Robotics; Aerospace actuators; dynamic displays; flow control devices; sporting goods and components thereof; body-conforming devices; temperature control devices; safety release devices; and heat shrink insulation.

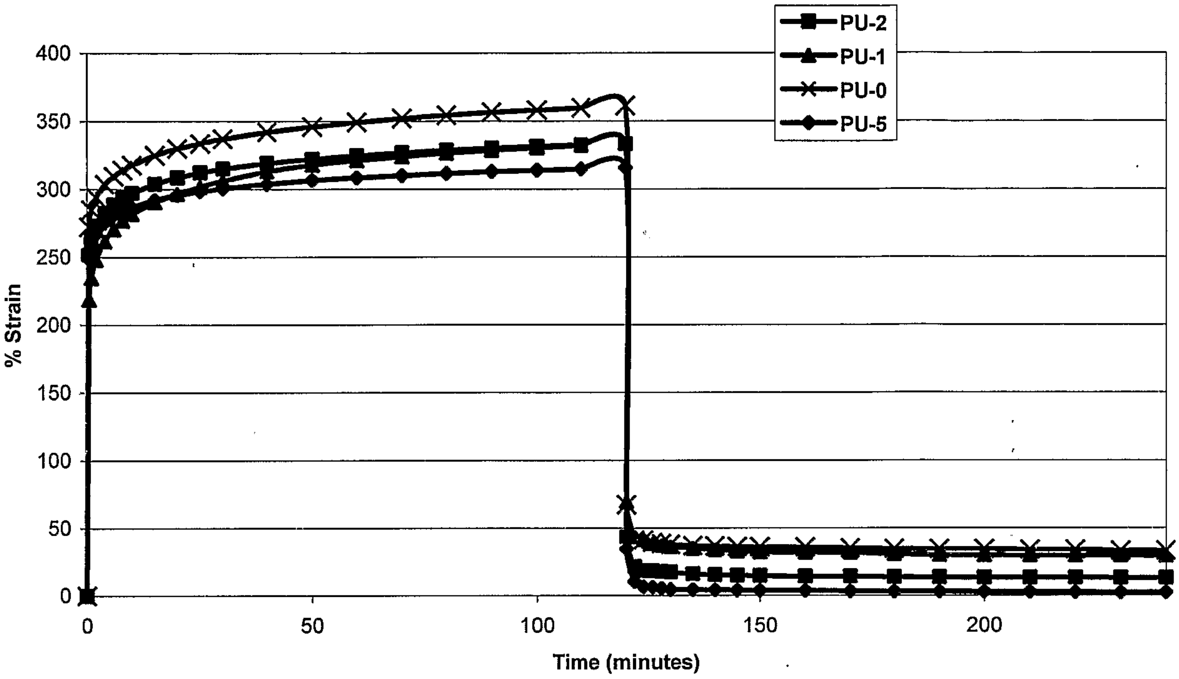

PU-2
PU-1
PU-0
PU-5
400
350
300
250
200
150
100
50
0
% Strain
0
50
100
150
200
Time (minutes)

Fig. 1

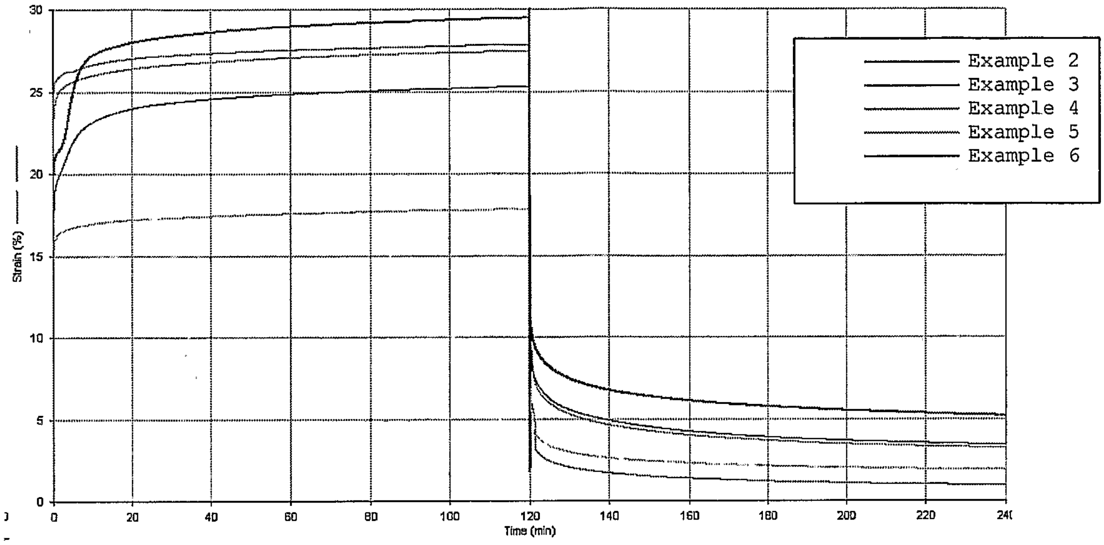

Strain (%)
Time (min)
30
25
20
15
10
5
0
0
20
40
60
80
100
120
140
160
180
200
220
240
Example 2
Example 3
Example 4
Example 5
Example 6

Fig. 2

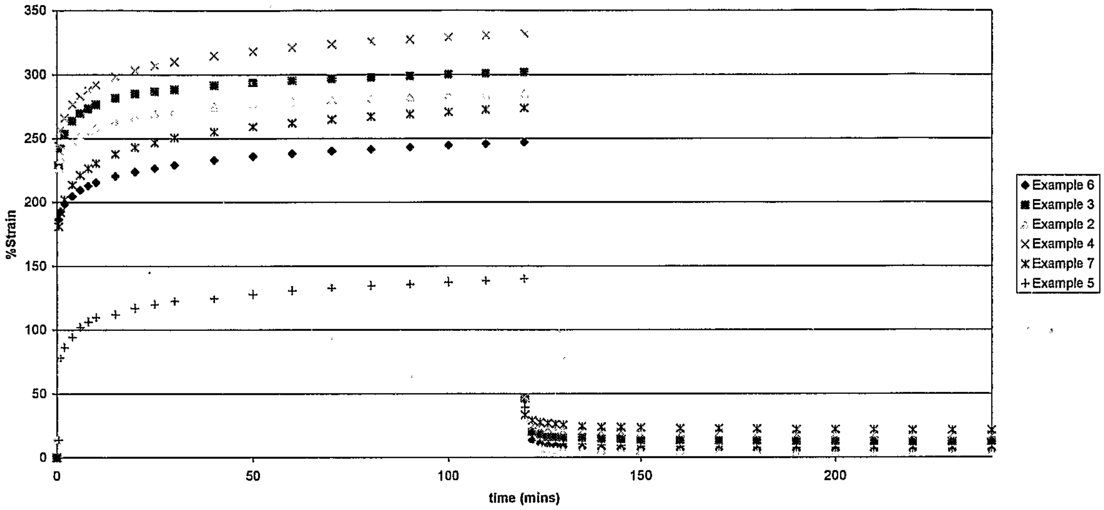

350
300
250
200
150
100
50
0
%Strain
0
50
100
150
200
time (mins)
◆ Example 6
■ Example 3
△ Example 2
× Example 4
✱ Example 7
+ Example 5

Fig. 3

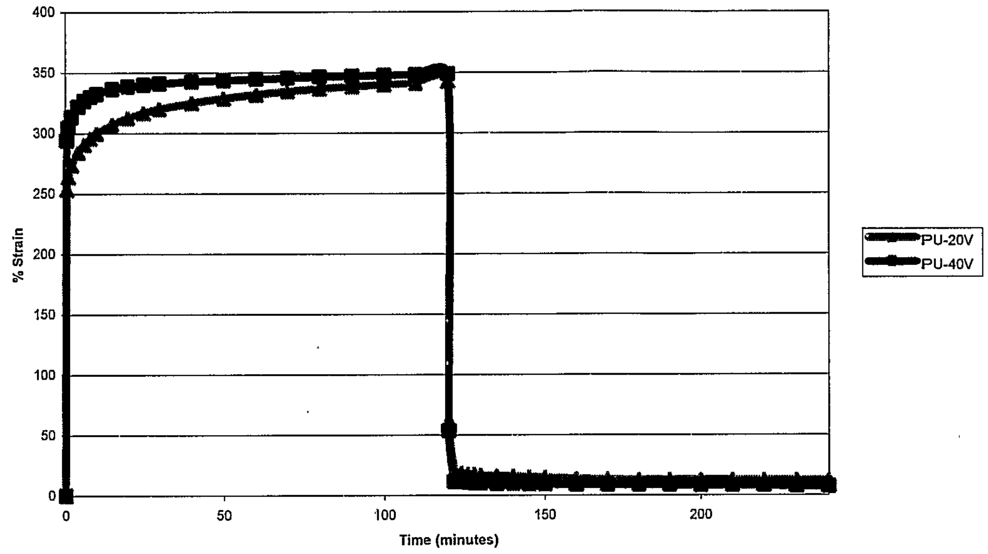

400
350
300
250
200
150
100
50
0
% Strain
0
50
100
150
200
Time (minutes)
PU-20V
PU-40V

Fig. 4

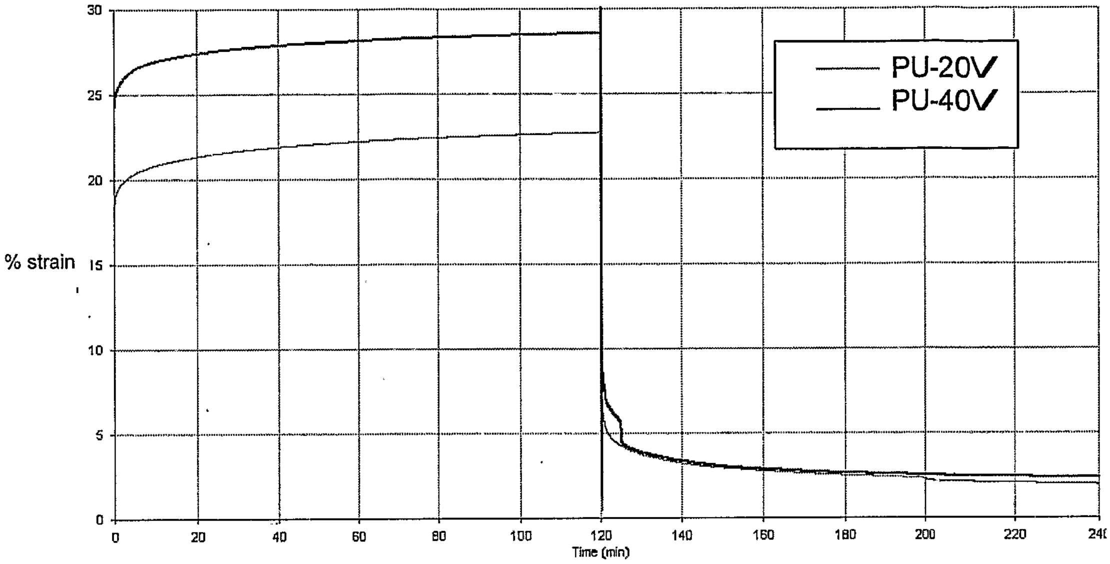

% strain
30
25
20
15
10
5
0
0
20
40
60
80
100
120
140
160
180
200
220
24
Time (min)
PU-20V
PU-40V

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/001662

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. 7: C08G 18/48, 18/61, 18/12, 18/10, 18/65, 18/66

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)
IPC: C08G 18/-

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)
WPAT & JAPIO (Search terms: polyurethan+, cross-link+, polysilox+)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 393 858 A (MEIJS et al.) 28 February 1995 See column 2 line 50 to column 3 line 56 and claims 5 and 18.	1,11-15,35-43,58,64-65
Y		1-6,58-65
X	Derwent abstract accession no. 86-209555/32, Class A96 D21 (A25), JP 61143417 A (NIPPON MECTRON KK) 1 July 1986. See abstract	1-6,58-60
Y		1-6,58-65
Y	US 6 140 452 A (FELT et al.) 31 October 2000 See column 18 line 64 to column 19 line 18.	1-6,58-65
Y	Derwent abstract accession no. 12670E/07, Class A25 Q63, JP 57002340 A (ASAHI GLASS KK) 7 January 1982 See abstract	1-6, 58-65

☒ 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

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search
20 December 2004

Date of mailing of the international search report
20 JAN 2005

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
E-mail address: pct@ipaustralia.gov.au
Facsimile No. (02) 6285 3929

Authorized officer

ALBERT S. J. YONG
Telephone No : (02) 6283 2160

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 627 724 B (MEIJS et al.) 30 September 2003 See column 7 lines 43-64, column 8 lines 9-22, column 3 lines 49-57, the Examples and claim 12.	1-6, 58-65
Y	US 6 420 452 B (GUNATILLAKE et al.) 16 July 2002 See column 5 line 65 to column 7 line 18, column 8 lines 1-10 and the Examples.	1-6, 58-65
Y	US 6 313 254 B (MEIJS et al.) 6 November 2001 See column 7 line 45 to column 8 line 26, the Examples and claims 11 and 46.	1-6, 58-65
Y	EP 1 254 916 A (AORTECH BIOMATERIALS PTY LTD) See whole document.	1-6, 58-65
X Y	Derwent abstract accession no. 89-170393/23, Class P32, JP 011 13041 A (WADA SEIMITSU SHIKE) 1 May 1989. See abstract.	1,58 1, 58, 64-65

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet attached.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: *1-56 & 58-65*

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Supplemental Box
(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No: III

The international application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to from a single general inventive concept. In coming to this conclusion the International Searching Authority has found that there are different inventions as follows:

1. Claims 1 to 56 and 58 to 65 are directed to a cross-linked polyurethane or polyurethane urea which comprises a soft and/or hard segment. It is considered that the polyurethane comprises a first "special technical feature".

2. Claim 57 is directed to a cyclotetrasiloxane compound per se. It is considered that the said compound comprises a second "special technical feature".

Since the abovementioned groups of claims do not share either of the technical features identified, a "technical relationship" between the inventions, as defined in PCT rule 13.2 does not exist. Accordingly the international application does not relate to one invention or to a single inventive concept.

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	5393858	AU	80065/91	EP	0536223	EP	1293525
		WO	9200338				
JP	61143417	JP	1113041				
US	6140452	AU	18264/97	AU	24701/95	AU	28842/99
		AU	33969/99	AU	71786/98	AU	85486/01
		CA	2189643	CA	2243154	CA	2244197
		CN	1340330	EP	0830114	EP	0873145
		EP	0886506	EP	1230902	EP	1313411
		US	5556429	US	5795353	US	5888220
		US	6079868	US	6248131	US	6306177
		US	2001004710	US	2002156531	US	2003195628
		US	2003220649	WO	0217825	WO	9530388
		WO	9726847	WO	9820939	WO	9944509
JP	57002340						
US	6627724	AU	41924/97	BR	9711536	CA	2267276
		CN	1299382	EP	0938512	EP	1254916
		US	6313254	US	2003018156	WO	9813405
US	6420452	AU	82013/98	BR	9811689	CA	2296642
		EP	1000070	WO	9903863	AU	41924/97
		BR	9711536	CA	2267276	CN	1299382
		EP	0938512	EP	1254916	US	6313254
		US	2003018156	WO	9813405		
JP	1113041	JP	61143417				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX