Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).
Description

[0001] The present invention is related to a process for preparing a polyurethane material. More specifically the present invention is related to a process for preparing a polyurethane material using a polyoxyethylene polyoxypropylene polyol having a high oxyethylene content and a polyisocyanate having a high 4,4'-diphenylmethane diisocyanate (4,4'-MDI) content.

[0002] The preparation of polyurethane materials having a high hardblock content from polyols having a high oxyethylene content, polyisocyanates comprising at least 85% by weight of 4,4'-MDI or a variant thereof and water has been disclosed in WO 98/00450. The materials made are elastomers and hence show a glass transition temperature of less than 25°C. Further it has been disclosed in EP 608626 to produce shape memory polyurethane foams by reacting a polyisocyanate comprising a high amount of 4,4'-MDI and a polyol with a high oxyethylene content with water. The foams have a glass transition temperature above 25°C; the amounts of chain extender and cross-linker used are relatively low, leading to products with a limited hard-block content giving products which are not as stiff as sometimes desirable.

[0003] Surprisingly it has now been found that if a polyol is used which has a high oxyethylene content and a high level of primary hydroxyl groups together with an amount of a chain extender or cross-linker sufficient to provide a high hard block ratio, a polyurethane material is obtained which has a glass transition temperature of at least 25°C and shows a high stiffness at a given density. The material obtained shows less surface defects (improved mixing, less bubbles) and a relatively high “ductility” (i.e. not brittle). The combination of ingredients used for making these materials show a good wetting of fibrous materials and in particular of glass fibres which makes the process particularly suitable for reaction injection moulding (RIM), especially for reinforced RIM (RRIM) and structural RIM(SRIM).

[0004] Therefore the present invention is concerned with a process for preparing a polyurethane material having no glass transition temperature below 25°C, which process comprises reacting a polyisocyanate and an isocyanate-reactive composition, optionally in the presence of water in an amount of less than 5% by weight on the below isocyanate-reactive ingredients. Any isocyanate groups consumed in a preliminary step to produce modified polyisocyanates or any active hydrogens consumed with respect to the amount of isocyanate theoretically required for reacting with the amount of isocyanate-reactive hydrogen used in a formulation.

[0005] The materials prepared according to the present invention have no glass transition temperature, Tg, below 25°C and preferably not below 60°C.

[0006] The Tg is defined as the temperature at which the tan δ curve reaches its maximum value as measured by Dynamic Mechanical Thermal Analysis (DMTA) at 1 Hz and a heating rate of 3°C/min.

[0007] In the context of the present invention the following terms have the following meaning:

1) isocyanate index or NCO index or index:

   the ratio of NCO-groups over isocyanate-reactive hydrogen atoms present in a formulation, given as a percentage:

   \[ \frac{[\text{NCO}] \times 100}{[\text{active hydrogen}]} \] (%).

   In other words the NCO-index expresses the percentage of isocyanate actually used in a formulation with respect to the amount of isocyanate theoretically required for reacting with the amount of isocyanate-reactive hydrogen used in a formulation.

   It should be observed that the isocyanate index as used herein is considered from the point of view of the actual polymerisation process preparing the elastomer involving the isocyanate ingredient and the isocyanate-reactive ingredients. Any isocyanate groups consumed in a preliminary step to produce modified polyisocyanates (including such isocyanate-derivatives referred to in the art as prepolymers) or any active hydrogens consumed in a preliminary step (e.g. reacted with isocyanate to produce modified polyols or polyamines) are not taken into
account in the calculation of the isocyanate index. Only the free isocyanate groups and the free isocyanate-reactive hydrogens (including those of the water) present at the actual polymerisation stage are taken into account.

2) The expression "isocyanate-reactive hydrogen atoms" as used herein for the purpose of calculating the isocyanate index refers to the total of active hydrogen atoms in hydroxyl and amine groups present in the reactive compositions; this means that for the purpose of calculating the isocyanate index at the actual polymerisation process one hydroxyl group is considered to comprise one reactive hydrogen, one primary amine group is considered to comprise one reactive hydrogen and one water molecule is considered to comprise two active hydrogens.

3) Reaction system: a combination of components wherein the polyisocyanates are kept in one or more containers separate from the isocyanate-reactive components.

4) The expression "polyurethane material" as used herein refers to cellular or non-cellular products as obtained by reacting polyisocyanates with isocyanate-reactive hydrogen containing compounds, optionally using foaming agents, and in particular includes cellular products obtained with water as reactive foaming agent (involving the reaction of water with isocyanate groups yielding urea linkages and carbon dioxide and producing polyurea-urethane foams) and with polyls, aminoalcohols and/or polyamines as isocyanate-reactive compounds.

5) The term "average nominal hydroxyl functionality" is used herein to indicate the number average functionality (number of hydroxyl groups per molecule) of the polyl or polyl composition on the assumption that this is the number average functionality (number of active hydrogen atoms per molecule) of the initiator(s) used in their preparation although in practice it will often be somewhat less because of some terminal unsaturation.

6) The word "average" refers to number average unless indicated otherwise.

7) The term "hard block ratio" refers to the amount (in pbw) of polyisocyanate + isocyanate-reactive materials having a molecular weight of 500 or less (wherein polyls having a molecular weight of more than 500 incorporated in the polyisocyanates are not taken into account) divided by the amount (in pbw) of all polyisocyanate + all isocyanate-reactive materials used.

8) The glass transition temperature is measured according to Dynamic Mechanical Thermal Analysis (DMTA) according to ISO/DIS 6721-5 at 3°C/min.

[0008] Preferably the polyisocyanate a) is selected from 1) a diphenylmethane diisocyanate comprising at least 40%, preferably at least 60% and most preferably at least 85% by weight of 4,4'-diphenylmethane diisocyanate and the following preferred variants of such diphenylmethane diisocyanate: 2) a carbodiimide and/or uretonimine modified variant of polyisocyanate 1), the variant having an NCO value of 20% by weight or more; 3) a urethane modified variant of polyisocyanate 1), the variant having an NCO value of 20% by weight or more and being the reaction product of an excess of polyisocyanate 1) and of a polyl having an average nominal hydroxyl functionality of 2-4 and an average molecular weight of at most 1000; 4) a prepolymer having an NCO value of 20% by weight or more and which is the reaction product of an excess of any of the aforementioned polyisocyanates 1-3) and of a polyl having an average nominal functionality of 2-6, an average molecular weight of 2000-12000 and preferably an hydroxyl value of 15 to 60 mg KOH/g, and 5) mixtures of any of the aforementioned polyisocyanates. Polyisocyanates 1), 2), 3) and mixtures thereof are preferred.

[0009] Polyisocyanate 1) comprises at least 40% by weight of 4,4'-MDI. Such polyisocyanates are known in the art and include pure 4,4'-MDI and isomeric mixtures of 4,4'-MDI and up to 60% by weight of 2,4'-MDI and 2,2'-MDI.

[0010] It is to be noted that the amount of 2,2'-MDI in the isomeric mixtures is rather at an impurity level and in general will not exceed 2% by weight, the remainder being 4,4'-MDI and 2,4'-MDI. Polyisocyanates as these are known in the art and commercially available; for example Suprasec™ MPR ex Huntsman Polyurethanes, which is a business of Huntsman International LLC (who owns the Suprasec trademark). The carbodiimide and/or uretonimine modified variants of the above polyisocyanate 1) are also known in the art and commercially available; e.g. Suprasec 2020, ex Huntsman Polyurethanes. Urethane modified variants of the above polyisocyanate 1) are also known in the art, see e.g. The ICI Polyurethanes Book by G. Woods 1990, 2nd edition, pages 32-35. Aforementioned prepolymer of polyisocyanate 1) having an NCO value of 20% by weight or more are also known in the art. Preferably the polyl used for making these prepolymer is selected from polyester polyls and polyether polyls and especially from polyoxyethylene polyoxypropylene polyls having an average nominal functionality of 2-4, an average molecular weight of 2500-8000, and preferably an hydroxyl
value of 15-60 mg KOH/g and preferably either an oxyethylene content of 5-25% by weight, which oxyethylene preferably is at the end of the polymer chains, or an oxyethylene content of 50-90% by weight, which oxyethylene preferably is randomly distributed over the polymer chains.

Mixtures of the aforementioned polyisocyanates may be used as well, see e.g. The ICI Polyurethanes Book by G. Woods 1990, 2nd edition pages 32-35. An example of such a commercially available polyisocyanate is Suprasec 2021 ex Huntsman Polyurethanes.

The other polyisocyanate b) may be chosen from aliphatic, cycloaliphatic, araliphatic and, preferably, aromatic polyisocyanates, such as toluene diisocyanate in the form of its 2,4 and 2,6-isomers and mixtures thereof and mixtures of diphenylmethane diisocyanates (MDI) and oligomers thereof having an isocyanate functionality greater than 2 known in the art as "crude" or polymeric MDI (polymethylene polyphenylene polyisocyanates). Mixtures of toluene diisocyanate and polymethylene polyphenylene polyisocyanates may be used as well.

If prepolymers, having an NCO value of 20% by weight made from polyols having a molecular weight of 2000-12000, are used, the amount of these polyols in the prepolymer compared to the total amount of polyols having such molecular weight used in making the polyurethane material is preferably less than 50% and more preferably less than 30% by weight.

Polyol 1) having a high EO content and a high primary hydroxyl content is selected from those having an EO content of 50-100% and preferably 75-100% by weight calculated on the weight of the polyether polyol and a primary hydroxyl content of 70-100% and preferably of 80-100 % calculated on the number of primary and secondary hydroxyl groups in the polyol. These polyether polyols may contain other oxyalkylene groups like oxypropylene and/or oxybutylene groups. These polyols have an average nominal functionality of 3-8 and more preferably of 3-6, an average equivalent weight of 200-2000 and preferably of 200-1800 and a molecular weight of 600-8000, preferably of 600-5000. As long as there are sufficient oxyethylene groups at the end of the polymer chains so as to meet the requirement of the primary hydroxyl content the distribution of the oxyethylene and other oxyalkylene groups (if present) over the polymer chains may be of the type of a random distribution, a block copolymer distribution or a combination thereof. Mixtures of polyols may be used. Methods to prepare such polyols are known and such polyols are commercially available; examples are Caradol™ 3602 from Shell, Lupranol™ 9205 from BASF, Daltocel F526 ex Huntsman Polyurethanes (Daltocel is a trademark of Huntsman International LLC) and G2005 ex Uniqema.

The isocyanate-reactive chain extenders, which have a functionality of 2, may be selected from amines, amino- and alcohols and polyols; preferably polyols are used. Further the chain extenders may be aromatic, cycloaliphatic, araliphatic and aliphatic; preferably aliphatic ones are used. The chain extenders have a molecular weight of 500 or less. Most preferred are aliphatic diols having a molecular weight of 62-500, such as ethylene glycol, 1,3-propanediol, 2-methyl-1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-propanediol, 1,3-butanediol, 1,3-pentanediol, 1,2-hexanediol, 3-methylpentane-1,5-diol, 2,2-dimethyl-1,3-propanediol, diethylene glycol, dipropylene glycol and tripropylene glycol, and propoxylated and/or ethoxylated products thereof. The cross-linkers are isocyanate-reactive compounds having an average molecular weight 500 or less and a functionality of 3-8. Examples of such cross-linkers are glycerol, trimethylolpropane, pentaerythritol, sucrose, sorbitol, mono-, di- and triethanolamine, ethylenediamine, toluenediamine, diethylenetoluene diamine, polyoxyethylene polyols having an average nominal functionality of 3-8 and an average molecular weight of 500 or less like ethoxylated glycerol, trimethylol propane, pentaerythritol, sucrose and sorbitol having said molecular weight, and polyether diamines and triamines having an average molecular weight below 500; most preferred cross-linkers are the polyol cross-linkers. The amount of chain extenders and/or cross-linkers used is such that the hard block ratio is 0.60 or more and preferably at least 0.65.

The other isocyanate-reactive compounds, which may be used in an amount of 0-20% by weight and preferably of 0-10% by weight, may be selected from polyether polyamines, polyester polyols and polyether polyols (different from the above described ones) having a molecular weight of more than 500 and in particular from such other polyether polyols, which may be selected from polyoxyethylene polyols, polyoxypolypropylene polyols, polyoxyethylene polyoxypropylene polyols having an oxyethylene content of less than 50% by weight and polyoxyethylene polyoxypropylene polyols having a primary hydroxyl content of less than 70%. Preferred polyoxyethylene polyoxypropylene polyols are those having an oxyethylene content of 5-30% and preferably 10-25% by weight, wherein all the oxyethylene groups are at the end of the polymer chains (so-called EO capped polyols) and those having an oxyethylene content of 60-90% by weight and having all oxyethylene groups and oxypropylene groups randomly distributed and a primary hydroxyl content of 20-60%, calculated on the number of primary and secondary hydroxyl groups in the polyol. Preferably these other polyether polyols have an average nominal functionality of 2-6, more preferably 2-4 and an average molecular weight of 2000-10000, more preferably of 2500-8000.

Still further the other isocyanate-reactive compounds may be selected from polyesters, polyesteramides, polythioethers, polycarbonates, polycetalis, polyolefins or polysiloxanes. Polyester polyols which may be used include hydroxyl-terminated reaction products of dihydric alcohols such as ethylene glycol, propylene glycol, diethyleneglycol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol or cyclohexane dimethanol or mixtures of such dihydric alcohols, and...
dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric and adipic acids or their dimethyl esters, sebacic acid, phthalic anhydride, tetrachlorophthalic anhydride or dimethyl terephthalate or mixtures thereof. Polyesteramides may be obtained by the inclusion of aminoalcohols such as ethanolamines in polyesterification mixtures.

Polythioether polyols, which may be used, include products obtained by condensing thioglycol either alone or with other glycols, alkylene oxides, dicarboxylic acids, formaldehyde, amino-alcohols or aminocarboxylic acids. Polycarbonate polyols which may be used include products obtained by reacting diols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol or teraethylene glycol with diaryl carbonates, for example diphenyl carbonate, or with phosgene. Polyacetel polyols which may be used include those prepared by reacting glycols such as diethylene glycol, triethylene glycol or hexanediol with formaldehyde. Suitable polyacetics may also be prepared by polymerising cyclic acetals. Suitable polyolefin polyols include hydroxy-terminated butadiene homo- and copolymers and suitable polysiloxane polyols include polydimethylsiloxane diols.

Mixtures of the aforementioned other isocyanate-reactive compounds may be used as well. Preferably the other isocyanate-reactive compounds are polyols selected from the above preferred ones.

The polyols may comprise dispersions or solutions of addition or condensation polymers in polyols of the types described above. Such modified polyols, often referred to as "polymer polyols" have been fully described in the prior art and include products obtained by the in situ polymerisation of one or more vinyl monomers, for example styrene and/or acrylonitrile, in the above polyether polyols, or by the in situ reaction between a polyisocyanate and an amino- and/or hydroxy-functional compound, such as triethanolamine, in the above polyol. Polyoxyalkylene polyols containing from 1 to 50% of dispersed polymer are particularly useful. Particle sizes of the dispersed polymer of less than 50 microns are preferred.

During the last years several methods have been described to prepare polyether polyols having a low level of unsaturation. These developments have made it possible to use polyether polyols at the higher end of the molecular weight range since such polyols can now be prepared with an acceptably low level of unsaturation. According to the present invention polyols having a low level of unsaturation may be used as well.

Still further the following optional ingredients may be used: catalysts enhancing the formation of urethane bonds like tin catalysts like tin octoate and dibutyltindilaurate, tertiary amine catalysts like triethylenediamine and imidazoles like dimethylimidazol and other catalysts like maleate esters and acetate esters; surfactants; foam stabilisers like siloxane-oxyalkylene copolymers; fire retardants; smoke suppressants; UV-stabilizers; colorants; microbial inhibitors; organic and inorganic fillers and internal mould release agents. Further external mould release agents may be used. A particularly preferred class of catalyst is an alkali metal or alkaline earth metal carboxylate salt. The catalyst may be a salt of any metal of Groups IA and IIA of the Periodic Table but in general the alkali metal salts are preferred like potassium and sodium salts, especially the potassium salts. If desired mixtures of such salts may be used like a mixture of a potassium and a sodium salt.

A catalytically effective amount of the salt will usually be in the range of 0.1 to 10, preferably 0.2-5 parts by weight per 100 parts by weight of reactants.

Although other polyurethane catalysts may be used together with the carboxylate salt catalysts, like the generally known tertiary amine catalysts and tin catalysts, it is preferred that the materials are made in the absence of other catalysts in particular in the absence of tertiary amine and tin catalysts.

The carboxylate may be selected from aliphatic carboxylates having 2-10 carbon atoms like acetate, hexanoate, 2-ethylhexanoate and octanoate.

Especially the carboxylate may be selected from those having the formula R-E-A-COO- wherein

- A is a hydrocarbon diradical having 1-6 preferably 1-3 carbon atoms;
- E is -O- or

and

R is X-R1-(OR2)n wherein X is CH2- or OH-, R1 is a hydrocarbon diradical having 1-8 and preferably 1-4 carbon atoms, R2 is a hydrocarbon diradical having 2-4 and preferably 2 or 3 carbon atoms and n is 0 to 10, preferably 0-5.

A may be selected from diradicals like -CH2-, -CH2CH2-, -CH2CH2CH2-.
The most preferred diradical is \(-\text{CH}=\text{CH}_2\) or

\[-\text{CH}_2=\text{C}=\text{CH}_2\]
The polyols used were not dried before use and likely have contained a minor amount of residual water, reason why a density of 929 and 957 kg/m$^3$ was obtained.

Caradol™ SA 3602, ex Shell is a polyol having a nominal hydroxyl functionality of 3, an OH-value of 36 mg KOH/g, an oxyethylene content of about 77% by weight and a primary hydroxy content of about 90%. DABCO EG is an amine catalyst from AirProducts. The polyisocyanate is a polyisocyanate having an NCO value of 26.2% by weight and which is a mixture of 1) a polyisocyanate made by reacting 42.55 pbw of MDI comprising more than 95% by weight of 4,4'-MDI and 5.05 pbw of a mixture of tripropylene glycol, propylene glycol and 1,3-butanediol (59/18.79/22.21, /w/w/w) and of 2) Suprasec 2020 (52.4 pbw) (a uretonimine-modified MDI from a polyisocyanate comprising more than 95% w 4,4'-MDI having an NCO value of 29.5% by weight ex Huntsman Polyurethanes). Polyol 1 is a sorbitol initiated polyoxyethylene polyol having an OH value of 187 mg KOH/g and a molecular weight of 1800.

Claims

1. A process for preparing a polyurethane material having no glass transition temperature below 25°C, which process comprises reacting a polyisocyanate and an isocyanate-reactive composition, optionally in the presence of water in an amount of less than 5% by weight on the below isocyanate-reactive composition, wherein the reaction is conducted at an isocyanate index of 80 to 140, the polyisocyanate consists of a) 80-100% by weight of diphenylmethane diisocyanate comprising at least 40% by weight of 4,4'-diphenylmethane disiocyanate and/or a variant of said diphenylmethane disiocyanate which variant is liquid at 25°C and has an NCO value of at least 20% by weight (polyisocyanate a), and b) 20-0% by weight of another polyisocyanate (polyisocyanate b), and wherein the isocyanate-reactive composition consists of a) 80-100% by weight of a polyether polyol having an average nominal functionality of 3-8, an average equivalent weight of 200-2000, an average molecular weight of 600-8000, an oxyethylene (EO) content of 50-100% by weight and a primary hydroxyl content of 70-100% calculated on the number of primary and secondary hydroxyl groups in the polyol, b) an isocyanate-reactive chain extender and/or cross linker in an amount such that the hard block ratio is 0.60 or more and c) 20-0% by weight of one or more other isocyanate-reactive compounds excluding water, the amount of polyol a) and isocyanate-reactive compound c) being calculated on the total amount of this polyol a) and compound c).

2. Process according to claim 1 wherein the material has no glass transition temperature below 60°C, the diphenylmethane disiocyanate comprises at least 85% by weight of 4,4'-diphenylmethane disiocyanate and/or a variant of said disiocyanate which variant is liquid at 25°C and has an NCO value of at least 20% by weight, the oxyethylene content in the polyether polyol is 75-100% by weight and the hard block ratio is at least 0.65.

3. Process according to claims 1-2 wherein the material has a density of more than 500 kg/m$^3$.

4. Process according to claims 1-3 wherein the isocyanate index is 90-110.

5. Material made according to the process of claims 1-4.
Patentansprüche

1. Verfahren zur Herstellung eines Polyurethanmaterials, das keine Glasübergangstemperatur von unterhalb von 25°C hat, wobei das Verfahren das Umsetzen eines Polysiloxanats und einer Isocyanatreaktiven Zusammensetzung, ggf. in Gegenwart von Wasser in einer Menge von wenigstens 5 Gew.% bezogen auf die Isocyanatreaktive Zusammensetzung unten, umfasst, wobei die Reaktion bei einem Isocyanat-Index von 80 bis 140 durchgeführt wird, das Isocyanat aus a) 80-100 Gew.% Diphenylmethandiisocyanat aus wenigstens 40 Gew.% 4,4'-Diphenylmethandiisocyanat und/oder einer Variante des Diphenylmethandiisocyanats, wobei die Variante bei 25°C flüssig ist und einen NCO-Wert von wenigstens 20 Gew.% hat (Polyisocyanat a), und b) 20-0 Gew.% eines weiteren Polysiloxanats (Polyisocyanat b) besteht, und wobei die Isocyanatreaktive Zusammensetzung aus a) 80-100 Gew.% eines Polyetherpolyols mit einer zahlenmittleren Funktionalität von 3-8, einem Durchschnittsmolekulargewicht von 200-2000, einem Durchschnittsmolekulargewicht von 60-8000, einem Oxyethylengehalt (EO) von 50-100 Gew.% und einem primären Hydroxylgehalt von 70-100%, bezogen auf die Anzahl der primären und sekundären Hydroxylgruppen im Polyol, b) einem Isocyanatreaktiven Kettenverlängerer und/oder Vernetzer in einer solchen Menge, dass das Hartblockverhältnis 0,60 oder mehr ist und c) 20-0 Gew.% eines oder mehrerer Isocyanatreaktiver Verbindungen einschließlich Wasser besteht, wobei die Menge an Polyol a) und Isocyanatreaktiver Verbindung c) auf die Gesamtmenge dieses Polyols a) und Verbindung c) bezogen berechnet ist.

2. Verfahren nach Anspruch 1, wobei das Material keine Glasübergangstemperatur von unterhalb von 60°C hat, das Diphenylmethan-Diisocyanat wenigstens 85 Gew.% an 4,4'-Diphenylmethan-Diisocyanat und/oder einer Variante dieses Diisocyanats, wobei die Variante bei 25°C flüssig ist und einen NCO-Wert von wenigstens 20 Gew.% hat, umfasst, der Oxyethylengehalt im Polyetherpolyol 75-100 Gew.% ist und das Hartblockverhältnis wenigstens 0,65 ist.

3. Verfahren nach den Ansprüchen 1-2, wobei das Material eine Dichte von mehr als 500 kg/m³ besitzt.

4. Verfahren nach Anspruch 1-3, wobei der Isocyanatindex 90-110 ist.


Revendications

1. Procédé pour la préparation d’une matière polyuréthane ayant une température de transition vitreuse inférieure à 25°C, procédé qui comprend la réaction d’un polyisocyanate et d’une composition réactive avec les isocyanates, éventuellement en présence d’eau en une quantité inférieure à 100 % en poids sur la composition réactive avec les isocyanates ci-dessous, dans laquelle la réaction est conduite à un indice d’isocyanate de 80 à 140, le polyisocyanate consistant en a) 80 à 100 % en poids de diphenylméthane-diisocyanate comprenant au moins 40 % en poids de 4,4'-diphenylméthane-diisocyanate et/ou d’un variant dudit diphenylméthane-diisocyanate, variant qui est liquide à 25°C et qui a un indice de NCO d’au moins 20 % en poids (polyisocyanate a), et b) 20 à 0 % en poids d’un autre polyisocyanate (polyisocyanate b), et dans laquelle la composition réactive avec les isocyanates consiste en a) 80 à 100 % en poids d’un polyétherpolyol ayant une fonctionnalité nominale moyenne de 3 à 8, un poids équivalent moyen de 200 à 2000, un poids moléculaire moyen de 600 à 8000, une teneur en oxyéthylène (EO) de 50 à 100 % en poids et une teneur en groupes hydroxyle primaires de 70 à 100 %, calculée sur le nombre de groupes hydroxyle primaires et secondaires dans le polyol, b) un agent d’allongement de chaîne et/ou agent de réticulation, réactif avec les isocyanates, dans une quantité telle que la proportion de blocs durs soit égale ou supérieure à 0,60 et c) 20 à 0 % en poids d’un ou plusieurs autres composés réactifs avec les isocyanates, à l’exclusion de l’eau, la quantité de polyol a) et de composé c) réactif avec les isocyanates étant calculée sur la base de la quantité totale de ce polyol a) et de ce composé c).

2. Procédé suivant la revendication 1, dans lequel une matière a une température de transition vitreuse inférieure à 60°C, le diphenylméthane-diisocyanate comprend au moins 85 % en poids de 4,4'-diphenylméthane-diisocyanate et/ou d’un variant dudit diisocyanate, variant qui est liquide à 25°C et qui a un indice de NCO d’au moins 20 % en poids, la teneur en oxyéthylène dans le polyétherpolyol est comprise dans l’intervalle de 75 à 100 % en poids et la proportion de blocs durs est d’au moins 0,65.

3. Procédé suivant les revendications 1 et 2, dans lequel la matière a une masse volumique supérieure à 500 kg/m³.
4. Procédé suivant les revendications 1 à 3, dans lequel l'indice d'isocyanate est compris dans l'intervalle de 90 à 110.

5. Matière préparée suivant le procédé des revendications 1 à 4.