

Two-stage process for producing semi-rigid solid polyurethane moulded items

5 The invention relates to a process for preparing solid, transparent to translucent polyurethane moulded items which, due to their elastic and optical properties, can be used, for instance, as an alternative material to rubber.

10 PUR catalysed resins based on polyesterpolyols are generally used to produce semi-rigid PU moulded items. They are particularly suitable for producing moulded items by the casting or injection moulding process because good results with respect to the hardness of the material and the solidification time can be obtained with these over a wide range of system variations. Complex engineering for machines, filling procedures, mould production and mould closures is not normally required, but may be applied in individual cases.

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The use of PUR catalysed resins based on polyetherpolyols is also known but is often not chosen because satisfactory and continuously producible high degrees of transparency can only be achieved by using more complicated engineering procedures. Production by the RIM process using catalysed resins which contain both reactive hydroxy and amine terminal groups and requires the use of special moulding and closure equipment, as has been described in accordance with EP 0 299 117 A1, may be mentioned here. Ultimately, however, when using PUR moulding compositions based on polyetherpolyols, the processing window is always very restricted so that, in contrast, PUR systems based on polyesterpolyols have always been used in preference.

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25 Astonishingly, this is the case even for applications in exposed areas where hydrolytic/microbial decomposition of the ester components is prevented only by the incorporation of often very costly protective additives.

30 It has now been found, surprisingly, that PUR moulding compositions based on etherpolyols can be advantageously processed in the same way as those based on esters to

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give transparent/translucent moulded items if they have been provided with a much higher average molecular weight, and thus an associated increase in viscosity, in a first process stage. A suitable process stage of this type is in particular the reaction described below with difunctional and/or higher functional components with terminal isocyanate groups to give so-called OH-prepolymers. Reaction with difunctional or higher functional carboxylic acids to give comparably extended ether/ester-polyols has also proven to be suitable.

The invention therefore provides a two-stage process for preparing compact, transparent PUR moulded items by the polyisocyanate/polyaddition process with a Shore A hardness of 40 to 90 by reacting

- a) organic and/or modified organic polyisocyanates with
 - b) at least one high molecular weight compound containing at least two reactive hydrogen atoms and optionally
 - c) low molecular weight chain-extending and/or cross-linking agents in the presence of
 - d) catalysts and
 - e) auxiliary agents and additives,
- characterised in that, as an at least one high molecular weight compound containing at least two reactive hydrogen atoms (b), the reaction product of
- (I) a linear EO/PO-polyetherpolyol with terminal EO groups and an EO/PO ratio of 15:85 to 40:60, an OH value of 56-28 and a functionality of 2.0,
- or

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(II) a mixture of a polyetherpolyol as specified under (I) with another, but higher functional, EO/PO-polyetherpolyol started with glycerine, trimethylolpropane, pentaerythritol or sugar (EO/PO ratio 15:85 to 40:60) with an OH value of 60-25,

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or

(III) mixtures of several linear and branched polyetherpolyols, each of which are composed in the way described under (I) and (II),

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or

(IV) a poly-THF-ether (C₄-ether) with an average molecular weight of 500 to 2000

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and also

(V) combinations of (I), (II), (III) and (IV),

when reacted with

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(A) TDI (2,4-TDI to 2,6-TDI in any ratio) and the prepolymers obtainable therefrom,

or

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(B) TDI-polynuclear isocyanates and the prepolymers obtainable therefrom,

or

(C) MDI (4,4'-MDI, 2,4'-MDI, 2,2'-MDI in any ratio) and the prepolymers obtainable therefrom,

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or

(D) MDI-polynuclear isocyanates and the prepolymers obtainable therefrom,

or

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(E) any other aromatic isocyanates obtainable on an industrial scale with a functionality of at least 2 (NDI, p-PDI), and the prepolymers obtainable therefrom,

10 or

(F) any other aliphatic isocyanates obtainable on an industrial scale with a functionality of at least 2 (IPDI, HDI, H-MDI) and the prepolymers obtainable therefrom,

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or

(G) isocyanate mixtures of (A) to (F).

20 Each of the prepolymers specified in (A) to (G) are obtained, for example, by reacting the isocyanates with an etherpolyol as described under (I) to (V) and are characterised by the presence of terminal, reactive NCO groups.

25 Reaction of the polyols described under (I) to (V) is also possible with (AA) difunctional and/or higher functional carboxylic acids such as, for example, adipic acid, glutaric acid, succinic acid and other representative of this class of substances and also their mixtures, instead of with isocyanates.

30 Furthermore, also "short-chain" reaction components such as H₂O, difunctional and trifunctional OH compounds, OH-amines, diamines and triamines, etc, which have been used in the preliminary reaction and have participated in the reaction and

specifically alter the properties of the material subsequently reacted to give a polyurethane.

5 The first reaction stage to give a polyol, as described above, does not necessarily require catalytic acceleration, in the case of the reaction of a diol etc. with diisocyanate, but does proceed substantially more rapidly after the addition of amines, metal salts, etc.

10 In the case of an ether/ester reaction (AA), typical ester catalysts (Sn and Ti derivatives) are preferred. The reaction temperatures are preferably 20 to 100°C (types A-G), but higher temperatures are also possible and in situation (AA) are also advantageous.

15 The resulting OH value of the reaction products mentioned above is between 7 and 50 mg KOH/g, preferably between 10 and 28 mg KOH/g. The viscosity of the starting product is greatly increased by the process when performed in the conventional temperature range of 20 to 50°C.

20 Since, as specified above, low molecular weight components with hydroxy and amine terminal groups, or even H₂O, may be incorporated in the preliminary reaction described, the reaction may also be started with a higher OH or OH/NHX group content. The viscosity achieved is modified in accordance.

Examples**1. OH-prepolymer examples**5 **Table of examples**

	1.1	1.2	1.3	
Basic ether (a) EO/PO = (25:75) (OH value: 28 mg KOH/g)	98.95	97.95	98.65	wt.%
TDI	1.00			wt.%
MDI prepolymer (20 % NCO)		2.0		wt.%
IPDI			1.3	wt.%
Dabco (cryst.)	0.05	0.05	0.05	wt.%
Viscosity: start of reaction	270	275	265	mPa.s
(50°C): end of reaction	740	710	650	mPa.s
OH value of reaction product	22	22	22	mg KOH/g

1.1. **Method:**

10 After initial introduction of the OH component and raising the temperature to a constant 50°C, the Dabco constituent is dissolved and then the isocyanate component is added. The viscosity is determined after about 2 hours and this is found to be unaltered, with the same value even after 1 day and 7 days.

15 1.2 It is also possible to initially introduce only some of reactive OH component so that a more concentrated reaction mixture is present, Dabco and the isocyanate component also being added to this at 50°C. After reaction, the remaining amount of the OH reactive component is added and a product which is the same as that prepared by process 1.1. is obtained.

20 **2. Reaction examples**

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- 2.1 The unreacted basic polyol (a) in example table 1 is reacted with the following reaction partners:

5	A component	polyol (a)	93.87
		butanediol-1,4	6.00
		DBTL	0.03
		Dabco (cryst.)	0.10
10	B component	MDI prepolymer made from 4,4'-MDI, Desmodur CD and etherpolyol (a) with a NCO content of 20 %	
	Temperature of materials	35°C each	

15 The mixture A:B in the ratio 100:38 is processed with a conventional low pressure machine and poured into a mould and sealed. The moulded item with a thickness of 5 mm and a density of 1100 kg/m³ can be removed from the mould after 4 min. However, it is not transparent but has a white, milky appearance.

- 20 2.2 The reaction product from example 1.1 is used in the previous formulation. Using the same procedure and taking into account the low OH number of the OH prepolymer now used (A:B = 100:36), a transparent moulded item can be removed from the mould after 4 min.

- 25 2.3 As a variant of the formulation for the direct production of soles of shoes, the following variant is selected:

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5	A component	polyol (a)	92.97
		butanediol-1,4	6.00
		ethanediol	0.50
		DBTL	0.03
		Dabco (cryst.)	1.00
	B component	(see example 2.1)	
	Temperature of materials:	35°C each	

10 The reaction mixture prepared by screw-mixing in accordance with the Desma process (A:B = 100:41) is introduced into a mould held at 50°C and the mould is sealed in accordance with the Desma process.

15 After about 2.5 min the mould is opened and a milky-white moulded item is obtained onto which another PUR material can be sprayed in a subsequent step.

2.4 20 As described under 2.3, but replacing polyol (a) with polyol (1.1) and with appropriate adjustment of the mixing ratio (A:B = 100:39), however, a transparent moulded item can be removed from the mould after 2.5 min, onto which another PUR material can also be sprayed in a subsequent step.

Claims

1. Two-stage process for producing semi-rigid, solid polyurethane moulded items which have a high transparency, even with different thicknesses of moulded item, by reacting
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- a) organic and/or modified organic (poly)isocyanates with
- b) an etherpolyol, as described under (I)-(V), which is reacted in a first stage with OH reactive reaction partners such as aromatic and aliphatic isocyanate derivatives to give an OH-prepolymer with terminal OH groups, with
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- c) low molecular weight chain-extending and/or cross-linking agents in the presence of
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- d) amine and/or metal salt catalysts and
- e) auxiliary agents and additives,
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- characterised in that the OH-prepolymer (b) has an OH value of 7 to 56 mg KOH/g and no longer contains any reactive NCO groups.
2. Process according to Claim 1, characterised in that component b) contains a proportion of short-chain reaction constituents such as H₂O, difunctional and trifunctional OH compounds, OH-amines, diamines and triamines, which are also reacted to give OH-prepolymers.
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3. Process according to Claim 1, characterised in that component b) is prepared with the assistance of amine and/or metal salt catalysts.
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4. Process according to Claim 1, characterised in that component b) is the reaction product of an etherpolyol and a difunctional and/or higher functional





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carboxylic acid, which no longer contains any free reactive carboxylic acid groups.

5. Process according to Claim 1 for producing soles of shoes, parts of soles of shoes, industrial seals and rollers which are subject to mechanical stress.

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