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Radically curable urethane prepolymers and their use in dental materials

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(54) Title: RADICALLY CURABLE URETHANE PREPOLYMERS AND THEIR USE IN DENTAL MATERIALS

(54) Bezeichnung: RADIKALISCH HÄRTBARE URETHANPRÄPOLYMERE UND DEREN VERWENDUNG IN DENTALMASSEN

(57) Abstract: The invention relates to urethane prepolymers that are obtained by reacting: (A) 15 to 85 % by weight of one or more α,ω-terminated poly(meth)acrylate diols; (B) 0 to 30 % by weight of one or more radically curable, polyhydroxyfunctional compounds; (C) 14 to 60 % by weight of one or more polyisocyanates; (D) 1 to 40 % by weight of a monofunctional compound that reacts with isocyanate groups and that additionally comprises one or more radically curable groups. The invention further relates to the use of the inventive prepolymers.

(57) Zusammenfassung: Die Erfindung betrifft Urethanpräpolymere, erhältlich durch Umsetzung von: A) 15 bis 85 Gew.-% eines oder mehrerer α, ω-terminierter Poly(meth)acrylatdiole; B) 0 bis 30 Gew.-% einer oder mehrerer radikalisch härtbarer, polyhydroxyfunktioneller Verbindungen; C) 14 bis 60 Gew.-% eines oder mehrerer Polyisocyanat; D) 1 bis 40 Gew.-% einer gegenüber Isocyanatgruppen reaktiven monofunktionellen Verbindung, die zusätzlich über eine oder mehrere radikalisch härtbare Gruppierungen verfügt, sowie deren Verwendung.

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Abstract

Urethane prepolymers and their use

The invention relates to urethane prepolymers, obtainable by reaction of:

(A) 15 to 85 wt.-% of one or more α,ω-terminated poly(meth)acrylate diols,
(B) 0 to 30 wt.-% of one or more radically curable, polyhydroxy-functional compounds,
(C) 14 to 60 wt.-% of one or more polyisocyanates,
(D) 1 to 40 wt.-% of a monofunctional compound, reactive vis-à-vis isocyanate groups, which also contains one or more radically curable groupings.

as well as their use.

Radically curable urethane prepolymers and their use

The present invention describes di- or higher-functional radically curable urethane prepolymers and their use in polymerizable compounds. The invention furthermore describes the use of the polymerizable compounds in the dental field, for example as filling materials, stump build-up materials, fixing cements, temporary crown and bridge materials, dental materials, modelling materials or for the preparation of inlays, onlays, facing shells, crowns and bridges.

Materials suitable for such purposes advantageously display a high impact strength, high elasticity with high hardness as well as a small tendency to swell. These properties are largely determined by the monomers used.

In the state of the art, above all, ethylenically unsaturated compounds such as acrylic acid and/or methacrylic acid esters are described as suitable monomers.

In the dental industry, essentially 7,7,9-trimethyl-4,13-dioxo-3,14-dioxa-5,12-diazahexadecane-1,16-dioxy-dimethacrylate (e.g. Plex 666-1, Röhm) for example is used in particular from the group of the urethane(meth)acrylates, which with its low molecular weight has little elastifying effect and improves the impact strength only slightly.

To improve the elastifying properties and the impact strength, in the lacquer industry for example, a variety of polyurethane oligomers end-functionalized with (meth)acrylate groups which have polyester, polyether, polybutadiene and/or polycarbonate units are used with radically curable systems. However, these systems have a range of disadvantages:

Thus the ester bonds of the polyester urethane(meth)acrylates and of the polycarbonate urethane(meth)acrylates tend towards hydrolysis upon contact with moisture, whereby in particular the mechanical values of formulations prepared therefrom are reduced.

Polyether-based urethane(meth)acrylates show a clearly lower susceptibility to hydrolysis. However, these systems, due to their hydrophilicity, display an increased water absorption and thus an increased tendency to swell and lower strength, which involves a readiness to discolour. Such systems are therefore not suitable for aesthetically demanding applications.

A further disadvantage of the polyether urethane(meth)acrylates lies in their lack of resistance to oxidation as a result of the degradation of the oxidative polyether chain.

Although the polybutadiene urethane(meth)acrylates show excellent elastic properties, they are readily discoloured by the double bonds present through short-wave radiation as contained in sunlight.

In principle, urethane(meth)acrylates can also be prepared from low-molecular aliphatic and/or aromatic diols. However, these do not show elastic and impact strength-modifying properties as good as those of the above-named urethane(meth)acrylates which contain soft segments on polyester, polyether, polybutadiene and/or polycarbonate units.

There is therefore a substantial demand for monomers which in curable compounds lead to an improvement in impact strength, good elasticity with high hardness and swell only slightly.

Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is solely for the purpose of providing a context for the present invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this application.

The present invention provides urethane prepolymers which can be obtained by reaction of:

(A) 15 to 85 wt.-%, preferably 20 to 80 wt.-% of one or more α,ω-terminated poly(meth)acrylate diols,

(B) 0 to 30 wt.-%, preferably 0 to 20 wt.-% of one or more radically curable, polyhydroxy-functional compounds,

(C) 14 to 60 wt.-%, preferably 18 to 50 wt.-% of one or more polyisocyanates,

(D) 1 to 40 wt.-%, preferably 2 to 35 wt.-% of a monofunctional compound reactive vis-à-vis isocyanate groups, which also contains one or more radically curable groupings.

Surprisingly, compounds which were formulated with the monomers according to the invention show an extremely small degree of swelling.

Furthermore, the monomers are toxicologically acceptable and are therefore suitable in particular for use in the dental field.

The α,ω-terminated poly(meth)acrylate diols of the component (A) are compounds which contain two terminal hydroxyl groups. Suitable starting compounds for building up these α,ω-terminated poly(meth)acrylate diols and the preparation process for these compounds are described in detail in EP-B1-0 622 378 and EP-B1-0 205 846. They are commercially available from Tego under the name "Tego-Diol".

The component (B) is radically curable compounds, for example (meth)acrylate-based, which in accordance with DIN 53 240 display OH numbers preferably from 40 to 700 mg KOH/g and particularly preferably from 80 to 500 mg KOH/g.

Suitable representatives are for example polyhydroxy-group-containing polyester(meth)acrylate prepolymers as described in US-A-4 206 205, DE-

OS-40 40 290, DE-OS-33 16 592, DE-OS-37 04 098 and in "UV & EB Curing Formulations for Printing Inks Coatings and Paints", ed. R. Holman and P. Oldring, published by SITA Technology, London (England) 1988, p 36 ff.

Alternatively, polyhydroxy-group-containing polyepoxy(meth)acrylate prepolymers which are accessible by reaction of polyepoxides with (meth)acrylic acid, and/or polyhydroxy-group-containing polyurethane(meth)acrylate prepolymers can also be used.

Particularly preferred representatives are polyhydroxy-group-containing polyepoxy(meth)acrylate prepolymers, such as 2,2-bis[p-(2'-hydroxy-3'-methacryloyloxypropoxy)-phenyl]-propane (bis-GMA) or 2,2-bis-[p-(2'hydroxy-3'-acryloyloxypropoxy)-phenyl]-propane (bis-GA) and polyhydroxy-group-containing (meth)acrylate esters such as glycerol mono(meth)acrylate, trimethylolpropane mono(meth)acrylate or pentaerythritol di(meth)acrylate.

Suitable polyisocyanates of the component (C) are of an aliphatic, cycloaliphatic and/or aromatic nature and contain at least two free isocyanate groups. Preferably, diisocyanates $X(NCO)_2$ are used, X representing an aliphatic hydrocarbon radical with 2 to 12 C atoms, a cycloaliphatic hydrocarbon radical with 5 to 18 C atoms, an aromatic hydrocarbon radical with 6 to 16 C atoms and/or an araliphatic hydrocarbon radical with 7 to 15 C atoms.

Examples of such diisocyanates are: 1,4-tetramethylene diisocycanate, 1,6-hexamethylene diisocycanate (HDI), 2,4,4-trimethyl-hexamethylene diisocycanate, isophorone diisocycanate, 4,4'-dicyclohexylmethane diisocycanate, meta- and para-tetramethylxylene diisocycanate, 1,4-phenylene diisocycanate, 2,6- and 2,4-toluene diisocycanate, 1,5-naphthylene diisocycanate, 2,4' and 4,4'-diphenylmethane diisocycanate.

It is naturally also possible to use, or also use a proportion of, the higher-functional polyisocyanates known from polyurethane chemistry or else modified polyisocyanates, for example containing carbodiimide groups, allophanate groups, isocyanurate groups and/or biuret groups. Particularly preferred isocyanates are isophorone diisocyanate and 2,4,4-trimethylhexamethylene diisocyanate.

Compounds of the component (D) contain a functional group which is reactive vis-à-vis isocyanates, for example a hydroxy group or amino group, and also have one or more radically curable groupings. The radically curable groupings are preferably (meth)acrylate-based. The representatives of this component (D) can also be used as a mixture.

Suitable representatives are for example 2-hydroxy(meth)acrylate, 2-hydroxypropyl (meth)acrylate, glycerol di(meth)acrylate and/or trimethylolpropane di(meth)acrylate. Particularly preferred are 2-hydroxyethyl methacrylate (HEMA) and/or 2-hydroxyethyl acrylate (HEA).

For the preparation of the urethane prepolymers according to the invention, for example the components (A) to (C) are introduced first into a reactor or fed individually in metered quantities and converted to an NCO-containing prepolymer under anhydrous conditions, for example in a temperature range from –20°C to 160°C, preferably in a temperature range from 0°C to 130°C and particularly preferably a temperature range from 20°C to 100°C.

The equivalence ratio of isocyanate groups to compounds reactive vis-à-vis isocyanate groups is 1.1:1 to 8:1, preferably 1.5:1 to 4:1.

The isocyanate polyaddition reaction can take place in the presence of catalysts known from polyurethane chemistry, for example organotin compounds such as dibutyltin dilaurate or amine catalysts such as diazabicyclo[2.2.2]octane. Furthermore, the synthesis can take place both in the melt and in a suitable solvent which can be added before or during the prepolymer preparation. Suitable solvents are for example acetone, 2-butanone, tetrahydrofurane, dioxane, dimethylformamide, N-methyl-2-pyrrolidone (NMP), ethyl acetate, alkyl ethers of ethylene and propylene glycol and aromatic hydrocarbons. The use of ethyl acetate as solvent is particularly preferred.

Measured doses of the component (D) are added complete or portionwise to the NCO-containing prepolymers accompanied by stirring and reacted for example in a temperature range from –20°C to 160°C, preferably in a temperature range from 0°C to 130°C and particularly preferably a temperature range from 20°C to 100°C. The quantity of component (D) to be used depends on the still present unreacted isocyanate groups of the prepolymer. The measurement of the isocyanate content of the prepolymer takes place for example according to DIN 53 185.

For example, the average by weight of the molecular weight (M_w) obtained from GPC measurements against polystyrene standards can lie between 400 and 200,000 g/mol, preferably between 500 and 100,000 g/mol and particularly preferably between 600 and 50,000 g/mol. Naturally, the molecular weights can also lie outside these ranges provided it allows the use of the polyurethane prepolymers according to the invention.

The urethane prepolymers according to the invention are suitable for example for the preparation of curable compounds such as dental compounds or for coating, pouring and gluing of substrates.

Curable formulations, for example for use in the dental field, preferably contain the following components:

(C1) 1 to 70 wt.-%, in particular 2 to 50 wt.-% of urethane prepolymer according to the invention,

(C2) 8.9 to 70 wt.-%, in particular 10 to 60 wt.-% of one or more radically polymerizable monomers,

(C3) 10 to 90 wt.-%, in particular 10 to 87.9 wt.-% fillers, (C4) 0.1 to 5 wt.-%, in particular 0.1 to 3 wt.-% initiators and optionally activators,

(C5) 0 to 30 wt.-%, in particular 0 to 20 wt.-% additives, optionally pigments, thixotropic auxiliaries, plasticizers.

The compounds formulated with the urethane prepolymers according to the invention are characterized by particularly good impact strength, good elasticity with high hardness and a surprisingly small tendency to swell.

As component (C2) are used mono-, di- or higher-functional ethylenically unsaturated compounds, preferably acrylate- and/or methacrylate-based. These can contain both monomeric and higher-molecular oligomeric or polymeric acrylates. Furthermore, they can be used alone or in mixture in the formulations.

Suitable monomers are for example the acrylic acid and methacrylic acid esters of mono-, di- or higher-functional alcohols. As examples there can be named: methyl (meth)acrylate, iso-butyl (meth)acrylate, ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate (TEGDMA), hexanediol di(meth)acrylate, dodecanediol di(meth)acrylate and trimethylolpropane tri(meth)acrylate.

Also advantageously usable is bisphenol-A di(meth)acrylate as well as the ethoxy- or propoxylated di(meth)acrylates derived therefrom. The monomers described in US-A-3 066 112 based on bisphenol-A and glycidyl(meth)acrylate or their derivatives resulting from the addition of isocyanates are also suitable.

Particularly suitable are also the diacrylic and dimethacrylic acid esters of bis(hydroxymethyl)-tricyclo[5.2.1.$0^{2.6}$]-decane named in DE-C-28 16 823 and the diacrylic and dimethacrylic acid esters of the compounds of bis(hydroxymethyl)-tricyclo[5.2.1.$0^{2.6}$]-decane extended by 1 to 3 ethylene oxide and/or propylene oxide units.

Urethane(meth)acrylates, such as 7,7,9-trimethyl-4,13-dioxo-5,12-diazahexadecane-1,16-dioxy-dimethacrylate (UDMA), can also be a constituent of the component (C2).

Fillers according to component (C3) can be inorganic fillers, for example quartz, ground glasses, non-water-soluble fluorides such as CaF_2, silica gels such as silicic acid, in particular pyrogenic silicic acid and granulates thereof. Cristobalite, calcium silicate, zirconium silicate, zeolites, including the molecular sieves, metal oxide powders, such as aluminium or zinc oxides or their mixed oxides, barium sulphate, yttrium fluoride, calcium carbonate can also be used as fillers.

Fluoride-releasing fillers, for example complex inorganic fluorides of the general formula A_nMF_m as described in DE-A-44 45 266, can be used or added. A represents a mono- or polyvalent cation, M a metal of the IIIrd, IVth, Vth main or sub-group, n an integer from 1 to 3 and m an integer from 4 to 6.

Organic fillers can also be a constituent of the component (C3). As examples there can be named customary methyl methacrylate-based bead polymers and copolymers, which can be obtained for example from Röhm under the name "Plexidon" or "Plex".

For better incorporation into the polymer matrix, it can be advantageous to hydrophobize the named fillers and, if present, X-ray-opaque additives. The quantity of silane used is usually 0.5 to 10 wt.-% relative to inorganic fillers, preferably 1 to 6 wt.-%, quite particularly preferably 2 to 5 wt.-% relative to inorganic fillers. Customary hydrophobing agents are silanes, for example trimethoxymethacryloxypropyl silane. The maximum average particle size of the inorganic fillers is preferably 15 μm, in particular 8 μm. Fillers with an average particle size of < 3 μm are quite particularly preferably used.

By initiators according to component (C4) are meant initiator systems which effect the radical polymerization of the monomers, for example photoinitiators and/or so-called redox-initiator systems and/or thermal initiators.

Suitable as photoinitiators are for example α-diketones such as camphorquinone, in combination with secondary and tertiary amines, or mono- and bisacylphosphinic oxides such as 2,4,6-trimethylbenzoyldiphenyl-phosphinic oxide and bis-(2,6-dichlorobenzoyl)-4-n-propylphenyl-phosphinic oxide. However, other compounds of this type as described in European patent publications EP-A-0 073 413, EP-A-0 007 508, EP-A-0 047 902, EP-A-0 057 474 and EP-A-0 184 095 are also suitable.

Organic peroxide compounds together with so-called activators are suitable as redox initiator systems. In particular, compounds such as lauroyl peroxide, benzoyl peroxide and p-chlorobenzoyl peroxide and p-methylbenzoyl peroxide can be considered as organic peroxide compounds.

Suitable as activators are, for example, tertiary aromatic amines, such as the N,N-bis-(hydroxyalkyl)-3,5-xylidines known from US-A-3 541 068 as well as N,N-bis-(hydroxyalkyl)-3,5-di-t-butylanilines known from DE-A-26 58 530, in particular N,N-bis-(β-oxybutyl)-3,5-di-t-butylaniline as well as N,N-bis-(hydroxyalkyl)-3,4,5-trimethylaniline.

Well-suited activators are also the barbituric acids and barbituric acid derivatives described in DE-B-14 95 520 as well as the malonyl sulfamides described in EP-A-0 059 451. Preferred malonyl sulfamides are 2,6-dimethyl-4-isobutylmalonyl sulfamide, 2,6-diisobutyl-4-propylmalonyl sulfamide, 2,6-dibutyl-4-propylmalonyl sulfamide, 2,6-dimethyl-4-ethylmalonyl sulfamide and 2,6-dioctyl-4-isobutylmalonyl sulfamide.

For further acceleration, the polymerization is in this case preferably carried out in the presence of heavy-metal compounds and ionogenic halogen or pseudohalogen. Copper is particularly suitable as heavy metal, chloride ion as halide. The heavy metal is suitably used in the form of soluble organic compounds. Likewise, the halide and pseudohalide ions are suitably used in the form of soluble salts, as examples there can be named the soluble amine hydrochlorides as well as quaternary ammonium chloride compounds.

If the dental compounds according to the invention contain a redox initiator system comprising organic peroxide and activator, peroxide and activator are preferably present in parts of the dental compound according to the invention physically separated from one another and are homogeneously mixed together only immediately before use. If organic peroxide, copper compound, halide and malonyl sulfamide and/or barbituric acid are present next to each other, it is particularly useful for the organic peroxide, malonyl sulfamide and/or barbituric acid and the combination of copper compound/halide to be present in three constituents physically separated from one another. For example, the combination of copper compound/halide, polymerizable monomers and fillers can be kneaded to a paste and the other components kneaded to two separate pastes in the above-described manner each with a small quantity of fillers or in particular thixotropic auxiliaries, such as silanized silicic acid, and a plasticizer, for example phthalate. On the other hand, the polymerizable monomers can also be present together with organic peroxide and fillers. Alternatively, a distribution of organic peroxide, copper compound, halide and malonyl sulfamide and/or barbituric acid can be realized according to DE-A-199 28 238.

As representatives of the component (C5), soluble organic polymers can for example be used to increase the flexibility of the compounds. Suitable are for example polyvinyl acetate as well as copolymers based on vinyl chloride/vinyl acetate, vinyl chloride/vinyl isobutyl ether and vinyl acetate/maleic acid dibutyl ether. Well-suited as additional plasticizers are for example dibutyl, dioctyl and dinonyl phthalates or adipates as well as higher-molecular polyphthalic acid and adipic acid esters. There can also be used as thixotropic auxiliaries, in addition to pyrogenic silicic acids, modified layered silicates (bentonites) or organic modifiers, for example on the basis of hydrogenated castor oils.

Furthermore, retardants as described in EP-A-0 374 824 as component (d) can also be contained as additives in the formulations.

The components according to the invention can be distributed for example over two pastes as follows:

- Paste 1: Parts of C3, parts of C4, C5
- Paste 2: C1, C2, parts of C3, parts of C4.

Dental materials which contain the urethane prepolymers according to the invention can be used for example as filling materials, cements, temporary crown and bridge materials, facing plastics, prosthesis materials, orthodontic materials, plastics for fissure sealing, modelling plastics or model plastics.

The urethane prepolymers according to the invention and formulations prepared therefrom are also suitable for the gluing and coating of substrates. As examples can be named the coating of wood, metal, glass or plastic. Furthermore, the urethane prepolymers according to the invention and formulations prepared therefrom are also suitable for the preparation of moulded bodies.

Preferably, compounds containing the urethane prepolymers according to the invention are formulated as two-component mixtures, these preferably being packed into a cartouche system and the compounds applied via a static or dynamic mixing set, homogeneously mixed and cured.

In the following, the invention is explained in more detail by means of examples, the latter not to be seen as limiting the invention in any way.

Examples

Preparation example 1: Urethane acrylate

212 g (approx. 0.2 mol) Tego-Diol BD-1000, 70 g ethyl acetate and 0.1 g dibutyltin dilaurate are introduced into a 2l 3-neck flask equipped with thermometer, reflux cooler, mechanical stirrer and drying tube, and 126 g (0.6 mol) trimethyl-hexamethylene diisocyanate added in measured doses, accompanied by cooling, over a period of 30 minutes. The reaction mixture is stirred for 20 hours at room temperature until the isocyanate content has fallen to 7.7%. 91 g hydroxyethylacrylate is added accompanied by cooling. After 72 hours at room temperature, an isocyanate value of 0 is recorded, at which the reaction is ended. The ethyl acetate can be distilled off in fine vacuum.

Preparation example 2: Urethane methacrylate

212 g (approx. 0.2 mol) Tego-Diol BD-1000, 140 g acetone and 0.1 g dibutyltin dilaurate are introduced first into a 2l 3-neck flask equipped with thermometer, reflux cooler, mechanical stirrer and drying tube, and 84 g (0.4 mol) trimethyl-hexamethylene diisocyanate added in measured does, accompanied by cooling, over a period of 30 minutes. The reaction mixture is stirred for 20 hours at room temperature until the isocyanate content has fallen to 3.7%. 53 g hydroxyethyl methacrylate is added, accompanied by cooling. After 72 hours at room temperature, an isocyanate value of 0.1 is recorded, at which the reaction is ended. The ethyl acetate can be distilled off in fine vacuum.

Application examples

10 g catalyst and 100 g base paste each are kneaded from the constituents listed in Table 1 and Table 2. These are packed into 10:1 cartouches from Mixpack, Rotkreuz. To apply them, they are pressed through a static mixing device by means of a dispenser and mixed, so that curing occurs within several minutes.

Table 1:

Catalyst			
Component	**Constituent**	**Quantity [g]**	**Wt.-%**
C3	Fluoroaluminosilicate glass powder (Ø<12µm)	3.4	34
C3	Silanized microfine silicic acid (HDKH 2000, Wacker, Burghausen)	0.7	7
C4	1-benzyl-5-phenyl barbituric acid	0.1	1
C4	3,5,5-trimethylhexanoic acid tertiary butyl ester	0.06	0.6
C5	2,2-bis-4-(2-hydroxyethoxyphenyl)-propane-bis-acetate	5.74	57.4

Table 2:

Application example 1			
Component	**Base 1**	**Quantity [g]**	**Wt.-%**
C3	Fluoroaluminosilicate glass powder (Ø<12µm) silanized with methacryloxypropyl trimethoxy silane	25	25
C3	Silanized microfine silicic acid (HDKH 2000, Wacker)	7	7
C4	Bis-(1-phenylpentane-1,3-dionato)-copper(II)	0.00775	0.00775
C4	(β-phenylethyl)-dibutyl-ammonium-chloride	0.352	0.352
C1	Urethane acrylate: Preparation example 1	13.6	13.6
C2	2,2-bis-4(acryloxy-bisethylene glycol)-phenylpropane	54.04025	54.04025

Application example 2			
Component	**Base 2**	**Quantity [g]**	**Wt.-%**
C3	Fluoroaluminosilicate glass powder (Ø<12µm) silanized with methacryloxypropyl trimethoxy silane	25	25
C3	Silanized microfine silicic acid (HDKH 2000, Wacker)	7	7
C4	Bis-(1-phenylpentane-1,3-dionato)-copper(II)	0.00775	0.00775
C4	(ß-phenylethyl)-dibutyl-ammonium-chloride	0.352	0.352
C1	Urethane methacrylate: Preparation example 2	13.6	13.6
C2	2,2-bis-4(acryloxy-bisethylene glycol)-phenylpropane	54.04025	54.04025

Comparison example 1		
Base 3	**Quantity [g]**	**Wt.-%**
Fluoroaluminosilicate glass powder (Ø<12µm) silanized with methacryloxypropyl trimethoxy silane	25	25
Silanized microfine silicic acid (HDKH 2000, Wacker)	7	7
Bis-(1-phenylpentane-1,3-dionato)-copper(II)	0.00775	0.00775
(ß-phenylethyl)-dibutyl-ammonium-chloride	0.352	0.352
Polyesterurethane-acrylate 98-446 (Rahn)	13.6	13.6
2,2-bis-4(acryloxy-bisethylene glycol)-phenylpropane	54.04025	54.04025

Comparison example 2		
Base 4	**Quantity [g]**	**Wt.-%**
Fluoroaluminosilicate glass powder (Ø<12μm) silanized with methacryloxypropyl trimethoxy silane	25	25
Silanized microfine silicic acid (HDKH 2000, Wacker)	7	7
Bis-(1-phenylpentane-1,3-dionato)-copper(II)	0.00775	0.00775
(β-phenylethyl)-dibutyl-ammonium-chloride	0.352	0.352
Polyesterurethane-acrylate BR-372 (Bomar)	13.6	13.6
2,2-bis-4(acryloxy-bisethylene glycol)-phenylpropane	54.04025	54.04025

The following measurement values were obtained with the cured testpieces:

Table 3:

Base	Polyurethane (meth)acrylate	Linear swelling, 7d in 36°C H_20 [%]	E-modulus [Mpa]	Bending on fracture [mm]	Impact strength [kJ/m^2]
1	Urethane acrylate: Preparation example 1	0.2	1450	1.7	9.41
2	Urethane methacrylate: Preparation example 2	0.25	1200	1.3	9.97
3	Polyesterurethane-acrylate 98-446 (Rahn)	0.35	900	1.4	4.89
4	Polyetherurethane-acrylate BR-372 (Bomar)	0.4	1000	1.2	4.42

Measurement methods: E-modulus and bending: 3-point bending test; Impact strength = Notched impact strength; Linear swelling after storage of testpieces for 7 days in water at 36°C; figure as % of the starting length.

The testpieces prepared with the base pastes 3 and 4 not according to the invention display an increased swelling, a reduced E-modulus and a much reduced impact strength compared with the testpieces made from pastes according to the invention (base 1 and 2).

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. Urethane prepolymers, obtainable by reaction of:

(A) 15 to 85 wt.-% of one or more α,ω-terminated poly(meth)acrylate diols;

(B) 0 to 30 wt.-% of one or more radically curable, polyhydroxy-functional compounds;

(C) 14 to 60 wt.-% of one or more polyisocyanates; and

(D) 1 to 40 wt.-% of a monofunctional compound, reactive vis-à-vis isocyanate groups, which also contains one or more radically curable groupings.

2. Urethane prepolymers according to claim 1, wherein the representatives of the component (B) display OH numbers from 40 to 700 mg KOH/g.

3. Urethane prepolymers according to claim 1 or 2:

wherein component (B) is selected from the group consisting of polyhydroxy-group-containing polyester(meth)acrylate prepolymers, polyhydroxy-group-containing polyepoxy(meth)acrylate prepolymers and polyhydroxy-group-containing polyurethane(meth)acrylate prepolymers.

4. Urethane prepolymers according to any one of claims 1 to 3, wherein the representatives of the component (C) are of an aliphatic, cycloaliphatic and/or aromatic nature and display at least two free isocyanate groups.

5. Urethane prepolymers according to any one of claims 1 to 4, wherein the representatives of the component (C) are diisocyanates $X(NCO)_2$, X representing an aliphatic hydrocarbon radical with 2 to 12 C atoms, a cycloaliphatic hydrocarbon radical with 5 to 18 C atoms, an aromatic hydrocarbon radical with 6 to 16 C atoms and/or an araliphatic hydrocarbon radical with 7 to 15 C atoms.

6. Urethane prepolymers according to any one of claims 1 to 5, wherein the representatives of the component (D) have a hydroxy group and, as radically curable groupings, (meth)acrylate groups.

7. Use of the urethane prepolymers according to any one of claims 1 to 6 for the preparation of dental compounds and the gluing, coating or pouring of substrates.

8. The use of the urethane prepolymers according to claim 7 for the preparation of filling materials, stump build-up materials, fixing cements, temporary crown and bridge materials, dental materials, model materials, inlays, onlays, facing shells, crowns and bridges.

9. Compositions, containing:

(C1) 1 to 70 wt.-% of at least one urethane prepolymer according to one of claims 1 to 6,

(C2) 8.9 to 70 wt.-% of one or more radically polymerizable monomers, (C3) 10 to 90 wt.-% fillers,

(C4) 0.1 to 5 wt.-% initiators and optionally activators,

(C5) 0 to 30 wt.-% additives optionally pigments, thixotropic auxiliaries, plasticizers.

10. Compositions according to claim 9, wherein component (C2) is selected from mono-, di- and/or higher-functional acrylic acid and/or methacrylic acid esters, which can contain both monomeric and higher-molecular oligomeric or polymeric acrylates and are used alone or in a mixture.

11. Use of the compositions according to any one of claims 9 to 10 in the dental field.

12. The use of the composition according to claim 11 as filling material, stump build-up material, fixing cement, temporary crown and bridge material, dental material, model material, inlay, onlay, facing shell, crowns and bridges.

13. Kit for the preparation of dental materials optionally containing an applicator for the dispensing of dental materials, optionally a static mixing set, at least one cartouche with at least two chambers which are filled with a composition according to any one of claims 9 to 10.

14. A cured composition according to any one of claims 9 to 10.

15. An applicator, containing at least one cartouche, containing a composition according to any one of claims 9 to 10.

16. Urethane prepolymers substantially as hereinbefore described with reference to Examples 1 and 2.

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