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(54) **Title:** METHOD FOR PREPARING URETHANE METHACRYLATE RESIN

(57) **Abstract:** The present invention relates to a method for the preparation of an urethane methacrylate resin composition comprising urethane methacrylate resin and reactive diluent, wherein the method comprises (1) preparing an urethane methacrylate resin by reacting at least a hydroxyl functional methacrylate and an isocyanate and optionally other alcohols in the presence of a reaction catalyst, whereby a secondary hydroxyalkyl methacrylate is used as methacrylate, and the isocyanate is an aromatic and/or aliphatic di- and/or tri- isocyanate, and (2) adding reactive diluent to the urethane methacrylate resin during and/or after its preparation, wherein a zirconium alkoxide and/or zirconium carboxylate is used as reaction catalyst and the process further comprises (3) adding a tertiary aromatic amine to the urethane methacrylate resin.



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METHOD FOR PREPARING URETHANE METHACRYLATE RESIN

The present invention relates to a method for the preparation of an urethane methacrylate resin composition comprising urethane methacrylate resin and
5 reactive diluent, wherein the method comprises (1) preparing an urethane methacrylate resin by reacting at least a hydroxyl functional methacrylate and an isocyanate and optionally other alcohols in the presence of a reaction catalyst, whereby a secondary hydroxyalkyl methacrylate is used as methacrylate, and the isocyanate is an aromatic and/or aliphatic di- and/or tri- isocyanate, and (2) adding reactive diluent to the
10 urethane methacrylate resin during and/or after its preparation.

Such methods are known in the art, see for example GB-A-2217722. A standard catalyst for the preparation of such urethane methacrylate resins are organo stannous compounds, in particular dibutyl tin dilaurate, since this catalyst is very effective in view of its rate, conversion and selectivity. However, this catalyst has a
15 negative toxicological profile, in other words it is poisonous and measures need to be taken to reduce or prevent environmental exposure. Consequently there is a need to replace such catalyst. Furthermore, the reaction of an isocyanate with a secondary hydroxyl functional methacrylate is much more difficult than with a primary hydroxyl functional methacrylate. Consequently a good catalyst for the reaction of primary
20 hydroxyl groups with an isocyanate is not per se a good catalyst for the reaction of secondary hydroxyl groups with an isocyanate. Moreover, as the catalysts are transition metal compounds, they can have a substantial negative influence on the cure reaction.

The object of the present invention is to perform the urethane
25 methacrylate resin preparation using a secondary hydroxyl functional methacrylate with a catalyst that is more environmentally benign, which catalyst has also a good selectivity, and at the same time has no or almost no negative influence on the curing efficiency of a resin composition comprising such urethane methacrylate resin and reactive diluent.

30 The inventors have surprisingly found that by using a zirconium alkoxide and/or a zirconium carboxylate as reaction catalyst, the reaction of a secondary hydroxyalkyl methacrylate with an aromatic and/or aliphatic di- and/or tri-isocyanate can be executed efficiently; and that the peranhydride initiated curing of a resin composition comprising such urethane methacrylate resin, reactive diluent and a
35 tertiary aromatic amine can in addition be effected efficiently.

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Accordingly, the present invention relates to a method for the preparation of an urethane methacrylate resin composition comprising urethane methacrylate resin and reactive diluent, wherein the method comprises

- 5 (1) preparing an urethane methacrylate resin by reacting at least a hydroxyl functional methacrylate and an isocyanate and optionally other alcohols in the presence of a reaction catalyst, whereby at least a secondary hydroxyalkyl methacrylate is used as methacrylate, and the isocyanate is an aromatic and/or aliphatic di- and/or tri- isocyanate, and a zirconium alkoxide and/or a zirconium carboxylate is used as reaction catalyst; and
- 10 (2) adding reactive diluent to the urethane methacrylate resin during and/or after its preparation to obtain a resin composition comprising urethane methacrylate resin, reactive diluent, and zirconium alkoxide and/or zirconium carboxylate; and
- 15 (3) adding a tertiary aromatic amine to the urethane methacrylate resin to obtain a resin composition comprising urethane methacrylate resin, reactive diluent, zirconium alkoxide and/or zirconium carboxylate, and a tertiary aromatic amine.

It has surprisingly been found that, compared with the state of the art tin catalyst, a zirconium alkoxide or a zirconium carboxylate has no or almost no influence on the curing characteristics of the urethane methacrylate resin in the resin composition, both immediately after preparation (as demonstrated by gel time, peak time and/or peak temperature) as well after prolonged storage (as demonstrated by gel time drift tendency). It has surprisingly been found that the resin compositions according to the invention have low or even reduced gel time drift tendency.

WO-A-03074579 describes liquid resin compositions comprising (a)
25 an urethane (meth)acrylate, a Group IV metal compound, preferably a titanium or zirconium compound, and a phosphorus containing photoinitiator for UV- initiating the curing of the liquid resin composition. There is however no teaching in WO-A-03074579 that using a zirconium alkoxide or zirconium carboxylate as reaction catalyst in the preparation of an urethane methacrylate resin, obtained by reacting at least a
30 secondary hydroxyl functional methacrylate with an isocyanate, would result in selective urethane methacrylate resin preparation and at the same time in efficient peranhydride initiated curing of a resin composition comprising urethane methacrylate resin, reactive diluent and tertiary aromatic amine and also low or even reduced gel time drift tendency of such pre-accelerated resin compositions.

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Non-limiting examples of secondary hydroxyalkyl methacrylates are 2-hydroxypropyl methacrylate, 2-hydroxybutyl methacrylate, 3-hydroxybutyl methacrylate, 2-hydroxycyclohexyl methacrylate and glycerol-1,3-dimethacrylate. A preferred secondary hydroxyalkyl methacrylate is 2-hydroxypropyl methacrylate.

5 In a preferred embodiment of the invention, the methacrylate used for preparing the urethane methacrylate resin is a secondary hydroxyalkyl methacrylate. In an even more preferred embodiment of the invention, 2-hydroxypropyl methacrylate is used as secondary hydroxyalkyl methacrylate. In an even more preferred embodiment of the invention, the methacrylate used is 2-hydroxypropyl methacrylate.

10 Non-limiting examples of aromatic and/or aliphatic di- and/or tri-isocyanates used for preparing the urethane methacrylate resin are toluene diisocyanate (TDI), 4,4'-methylene diphenyl diisocyanate (MDI), hexanediisocyanate (HDI), isophorone diisocyanate (IPDI) TDI trimers, HDI trimers, and polymeric MDI (pMDI). Preferred aromatic and/or aliphatic di- and/or tri- isocyanates are toluene
15 diisocyanate (TDI), 4,4'-methylene diphenyl diisocyanate (MDI), hexanediisocyanate (HDI), isophorone diisocyanate (IPDI), TDI trimers, HDI trimers, and polymeric MDI (pMDI). Especially MDI and polymeric MDI are preferred diisocyanates. In a preferred embodiment of the invention, aromatic and/or aliphatic diisocyanate is used as isocyanate compound.

20 The catalyst used for preparing the urethane methacrylate resin is a zirconium alkoxide and/or a zirconium carboxylate. More preferably, the catalyst used is a zirconium (IV) alkoxide and/or a zirconium (IV) carboxylate. Even more preferably, the catalyst used is a zirconium alkoxide and even more preferably a zirconium (IV) alkoxide.

25 The amount of zirconium catalyst used for preparing the urethane methacrylate resin is preferably from 1 to 5000 ppm (relative to the total amount of reaction components used for preparing the urethane methacrylate resin).

The method for preparing the urethane methacrylate resin may be performed in the presence of the reaction product of the isocyanate with a polyol,
30 preferably a diol. Non-limiting examples of polyols are glycerol, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, polyethylene oxide, polypropylene oxide, ethoxylated bisphenol A , ethoxylated bisphenol F, propoxylated bisphenol A, propoxylated bisphenol F. Preferred diols are dipropylene glycol, tripropylene glycol, ethoxylated bisphenol A , ethoxylated bisphenol F, propoxylated
35 bisphenol A, propoxylated bisphenol F.

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The amount of secondary hydroxyl functional methacrylate used for preparing the urethane methacrylate resin is preferably chosen such that for each mole of isocyanate group at least one mole of secondary hydroxyl functional methacrylate is present. In one embodiment, a slight stoichiometric excess of the secondary hydroxyl functional methacrylate is added to ensure that only a minimum level of isocyanate groups remain after an acceptable reaction period in order to prevent that unreacted isocyanate will copolymerize with the reactive diluent (being an ethylenically unsaturated monomer that is added to the resin during and/or after its preparation) on subsequent curing. In this embodiment, the process of the invention preferably further comprises adding another reactive diluent than a secondary hydroxyl functional methacrylate during the preparation of the urethane methacrylate resin and optionally adding additional reactive diluent (not necessarily the same as that used during the preparation) after the preparation of the urethane methacrylate resin. In another embodiment, an excess of the secondary hydroxyl functional methacrylate is added, resulting in that unreacted secondary hydroxyl functional methacrylate remains after the reaction period which secondary hydroxyl functional methacrylate is a reactive diluent for the prepared resin. In this embodiment, the method according to the invention optionally further comprises adding, to the urethane methacrylate resin during and/or after its preparation, another reactive diluent than the secondary hydroxyalkyl methacrylate used for the preparation of the urethane methacrylate resin.

The amount of optional polyol described above used for preparing the urethane methacrylate resin can vary within wide ranges as long as an excess of isocyanate is present. The molar ratio between OH groups of the polyol and NCO groups of the isocyanate is generally higher than 0.01, more preferably higher than 0.05 and even more preferably higher than 0.1. The molar ratio between OH groups of the polyol and NCO groups of the isocyanate is preferably lower than 0.95, more preferably lower than 0.9 and even more preferably lower than 0.7.

In a preferred embodiment of the invention, the method for preparing the urethane methacrylate resin comprises mixing the isocyanate component(s) with the zirconium catalyst, optionally adding the polyol to such mixture to allow reaction of the isocyanate with the polyol, preferably at a temperature of between 20 and 90°C, to obtain a first reaction product, and adding the secondary hydroxyl functional methacrylate, preferably at a temperature of between 20 and 90°C, to allow reaction with the first reaction product. To prevent premature polymerization of the monomers in the reaction mixture, conventional vinyl inhibitors may be used during the preparation

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of the resin, for example inhibitors like for instance benzoquinone, hydroquinone, tert.butyl catechol.

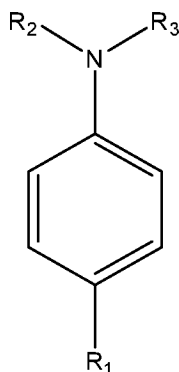
The method according to the invention further comprises adding a tertiary aromatic amine to the urethane methacrylate resin after its preparation, to
5 obtain a resin composition comprising an urethane methacrylate resin diluted in reactive diluent, zirconium alkoxide and/or zirconium carboxylate, which resin composition is pre-accelerated with a tertiary aromatic amine. It has surprisingly been found that such resin compositions have low or even reduced gel time drift tendency and that such resin compositions can be efficiently radical copolymerized (cured) with a
10 peranhydride. In a preferred embodiment, the tertiary aromatic amine is added to the urethane methacrylate resin diluted in reactive diluent. In case the urethane methacrylate resin is not yet diluted in reactive diluent, the tertiary aromatic amine is preferably pre-mixed with reactive diluent and the so-obtained mixture is added to the urethane methacrylate resin.

15 The present invention thus also relates to a thermosetting resin composition comprising (a) an urethane methacrylate resin prepared by reacting at least a hydroxyl functional methacrylate and an isocyanate and optionally other alcohols in the presence of a reaction catalyst, wherein at least a secondary hydroxyalkyl methacrylate is used as methacrylate and the isocyanate is an aromatic
20 and/or aliphatic di- and/or tri- isocyanate, and (b) a reactive diluent, wherein the resin composition further comprises (c) a tertiary aromatic amine and (d) a zirconium alkoxide and/or a zirconium carboxylate. The amounts and types of the reaction components for obtaining the urethane methacrylate resin are preferably as described above. The amount of zirconium alkoxide and zirconium carboxylate in the resin
25 composition is preferably from 1 to 5000 ppm (relative to the urethane methacrylate resin).

The zirconium alkoxide is preferably a zirconium (IV) alkoxide. The zirconium carboxylate is preferably a zirconium (IV) carboxylate. Even more preferably, the resin composition comprises a zirconium alkoxide and even more preferably a
30 zirconium (IV) alkoxide.

Preferably the tertiary aromatic amine has the following structure:

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in which R₁=H, C₁-C₅ alkyl, O(C₁-C₅)alkyl; R₂ and R₃ are independently selected from C₁-C₄ alkyl optionally substituted with hydroxyl or (poly) ether groups. Preferably, R₁= CH₃. Preferably R₂ and/or R₃ are CH₃, C₂H₅, C₂H₄OH, C₃H₇ and

5 CH₂CH(OH)CH₃.

Very suitable examples of tertiary aromatic amines are, for instance, 4-methoxy-N,N-dimethylaniline (R₁=OCH₃, R₂ and R₃=CH₃), N,N-diethanolaniline (R₁=H R₂,R₃=CH₂CH₂OH), N-methyl N-ethanol aniline (R₁=H R₂=CH₃, R₃=CH₂CH₂OH), N,N-diethanoltoluidine (R₁=CH₃ R₂,R₃=CH₂CH₂OH), N,N-diethanolaniline mono-methylether (R₁=H R₂=CH₂CH₂OH, R₃=CH₂CH₂OCH₃), N,N-diethanolaniline dimethylether (R₁=H R₂,R₃=CH₂CH₂OCH₃), N,N-diisopropanol aniline (R₁=H R₂,R₃=CH₂CH(OH)CH₃), N,N-diisopropanoltoluidine (R₁=CH₃ R₂,R₃=CH₂CH(OH)CH₃), N,N-diisopropanoltoluidine monomethyl ether (R₁=CH₃ R₂=CH₂CH(OCH₃)CH₃, R₃=CH₂CH(OH)CH₃), N,N-diisopropanoltoluidine dimethyl ether (R₁=CH₃ R₂,R₃=CH₂CH(OCH₃)CH₃), N,N-diglycidyl-4-glycidyloxyaniline (R₁=OCH₂CHOCH₂ R₂,R₃= OCH₂CHOCH₂ and N,N-diglycidylaniline (R₁=H R₂,R₃= OCH₂CHOCH₂),. Also N,N-ethoxylated or N,N-propoxylated anilines, respectively ethoxylated or propoxylated toluidines may suitably be used and are considered to be encompassed in the group of suitable tertiary aromatic amines.

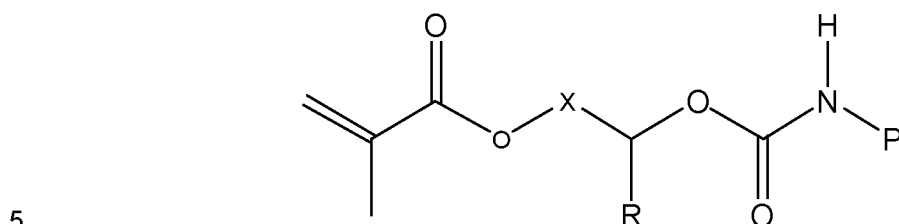
The resin composition preferably comprises from 30 up to and including 85 wt.% of urethane methacrylate resin. The amount of reactive diluent in the resin composition is in the range from 15 up to and including 70 wt.%. As used herein, all amounts in wt.% are given relative to the total weight of the urethane methacrylate resin (a) and reactive diluent (b), unless otherwise specified.

The amount of tertiary aromatic amine relative to the total amount of compounds (a) and (b) is preferably from 0.01 up to and including 10 wt.%, more

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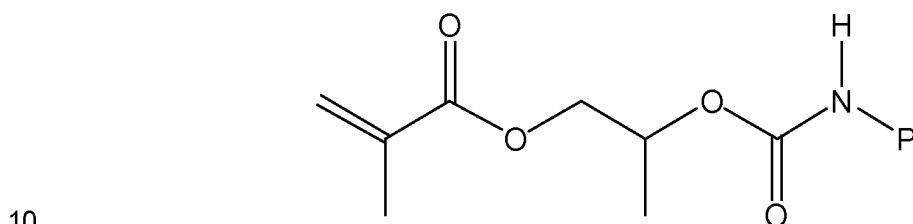
preferably from 0.05 up to and including 8 wt.% and even more preferably from 0.1 up to and including 5 wt.%.

The urethane methacrylate resin preferably has the following structural formula (1):



in which X= C1-C10 (cyclo)alkyl or C1-C30 alkoxy; R = C1-C4 alkyl and P = a residue of the isocyanate optionally attached to a polymer. Preferably X= C1-C6 (cyclo)alkyl.

The urethane methacrylate resin more preferably has the following structural formula (2):



in which P a residue of the isocyanate optionally attached to a polymer.

For clarity purpose, a reactive diluent is a diluent for the urethane methacrylate resin which diluent is able to copolymerize with the urethane methacrylate resin. Ethylenically unsaturated compounds can be advantageously used as reactive diluent such as styrene, α -methylstyrene, 4-methylstyrene, (meth)acrylates, vinyl ethers, a vinyl esters, vinyl amines or vinyl amides or a mixture of at least two of these compounds. Preferably, styrene and/or methacrylates are used as reactive diluent. More preferably, methacrylates are used as reactive diluent. Suitable examples of (meth)acrylate reactive diluents are hydroxyl ethyl (meth)acrylate, hydroxyl propyl (meth)acrylate, butyl (meth)acrylate, hexyl (meth)acrylate and cyclohexyl (meth)acrylate, phenoxyethyl (meth)acrylate, tetrahydro furfuryl (meth)acrylate, allyl (meth)acrylate, PEG200 di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, 2,3-butanedioldi(meth)acrylate, 1,6-hexanediol di(meth)acrylate and its isomers, diethyleneglycol di(meth)acrylate, triethyleneglycol di(meth)acrylate, glycerol di(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolpropane tri(meth)acrylate neopentyl glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, PPG250

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di(meth)acrylate, tricyclodecane dimethylol di(meth)acrylate, 1,10-decanediol di(meth)acrylate and/or tetraethylene glycol dimethacrylate. Preferred methacrylate reactive diluents are hydroxyl ethyl (meth)acrylate, hydroxyl propyl (meth)acrylate, 1,4-butanediol di(meth)acrylate, neopentylglycol di(meth)acrylate, PEG200

5 di(meth)acrylate, triethyleneglycol di(meth)acrylate and/or tripropylene glycol di(meth)acrylate.

In a preferred embodiment, 2-hydroxypropyl methacrylate is present as reactive diluent as in such a case an excess of 2-hydroxypropyl methacrylate can be employed in the urethane synthesis. Other preferred reactive diluents, in view of their

10 labeling, are butane diol di methacrylate, PEG200 dimethacrylate and trimethylolpropane trimethacrylate

In the resin composition according to the invention also fillers can be present. A wide variety of fillers can be applied like for instance, without being limited thereto, silica, sand, cement, mica and talc. The resin composition may also be

15 coloured by means of pigments. In the resin composition according to the invention also reinforcing fibers can be present, such as for example glass fibres, natural fibres and carbon fibres. Besides fibres and/or fillers, other additives may be present in the resin compositions according to the invention such as for instance low profile additives.

The resin composition according to the invention in addition optionally

20 contains a filler in a weight ratio of 0.05:1 to 20:1, preferably in a weight ratio of 0.2:1 to 3:1, relative to the total weight of urethane methacrylate resin and the reactive diluent..

Thermosetting resin compositions harden by chemical reaction, often generating heat when they are formed, and cannot be melted or readily re-formed once hardened. The resin compositions are liquids at normal temperatures and pressures,

25 so can be used to impregnate reinforcements, for instance fibrous reinforcements, especially glass fibres, and/or fillers may be present in the resin composition, but, when treated with suitable radical forming initiators, the various unsaturated components of the resin composition crosslink with each other via a free radical copolymerization mechanism to produce a hard, thermoset plastic mass (also referred to as cured,

30 structural part).

The resin composition according to the invention preferably further comprises one or more inhibitors. The inhibitor of the resin composition of the invention can be any radical inhibitor known to the skilled man, preferably chosen from the group of phenolic compounds, stable radicals like galvinoxyl and N-oxyl based compounds

35 and/or phenothiazines. Suitable examples of inhibitors that can be used in the resin

compositions according to the invention are, for instance, 2-methoxyphenol, 4-methoxyphenol, 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butylphenol, 2,4,6-trimethylphenol, 2,4,6-tris-dimethylaminomethyl phenol, 4,4'-thio-bis(3-methyl-6-t-butylphenol), 4,4'-isopropylidene diphenol, 2,4-di-t-butylphenol, 6,6'-di-t-butyl-2,2'-methylene di-p-cresol, hydroquinone, 2-methylhydroquinone, 2-t-butylhydroquinone, 2,5-di-t-butylhydroquinone, 2,6-di-t-butylhydroquinone, 2,6-dimethylhydroquinone, 2,3,5-trimethylhydroquinone, catechol, 4-t-butylcatechol, 4,6-di-t-butylcatechol, benzoquinone, 2,3,5,6-tetrachloro-1,4-benzoquinone, methylbenzoquinone, 2,6-dimethylbenzoquinone, naphthoquinone, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine-4-ol (a compound also referred to as TEMPOL), 1-oxyl-2,2,6,6-tetramethylpiperidine-4-one (a compound also referred to as TEMPON), 1-oxyl-2,2,6,6-tetramethyl-4-carboxyl-piperidine (a compound also referred to as 4-carboxy-TEMPO), 1-oxyl-2,2,5,5-tetramethylpyrrolidine, 1-oxyl-2,2,5,5-tetramethyl-3-carboxylpyrrolidine (also called 3-carboxy-PROXYL), aluminium-N-nitrosophenyl hydroxylamine, diethylhydroxylamine, phenothiazine and/or derivatives or combinations of any of these compounds.

Advantageously, the amount of inhibitor in the resin composition according to the invention is in the range of from 0.00001 to 5 % by weight, preferably from 0.0001 to 2 % by weight, more preferably, from 0.001 to 1 % by weight. Preferred inhibitors are stable radicals like TEMPOL, TEMPON, 4-carboxy TEMPO, 3-carboxy proxyl and hydroquinones and catechols. In this case for some applications it is even more preferred to employ a combination of a stable radical inhibitor with an hydroquinone or catechol. A very suitable combination is TEMPOL with catechol or t-butyl catechol.

Curing of the resin composition according to the invention is preferably performed by mixing the resin composition with a peranhydride.

Accordingly, the present invention also relates to a process for preparing a radically cured structural part by curing the resin composition according to the invention or obtained with the process according to the invention with a peranhydride. The curing is performed by mixing the resin composition with a peranhydride. The amount of peranhydride relative to the total amount of compounds (a) and (b) is from 0.01 up to and including 30 wt.%, more preferably from 0.05 up to and including 20 wt.% and even more preferably from 0.1 up to and including 15 wt.%. The molar amount of peranhydride relative to the molar amount of tertiary aromatic amine is preferably from 0.1 up to and including 10. The curing is preferably effected at

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a temperature in the range of from -20 to +150 °C, more preferably in the range of from -20 to +100 °C and even more preferably in the range of from -20 to + 40 °C. The present invention further also relates to structural objects as are being obtained by mixing the resin composition according to the invention with a peranhydride as

5 described above and curing at appropriate conditions. These structural objects have excellent mechanical properties. The present invention therefore also relates to the use of the resin composition according to the invention together with peranhydride in adhesive applications, automotive parts, boats, roofing, construction, containers, relining, pipes, tanks, flooring, windmill blades or chemical anchoring.

10 The invention is now demonstrated by means of a series of examples and comparative examples. All examples are supportive of the scope of claims. The invention, however, is not restricted to the specific embodiments as shown in the examples.

15 Example 1 and Comparative Experiments A-D

A 300 ml reaction flask equipped with a mechanical stirrer was charged with 31.7 g MDI (4,4'-methylene diphenyl diisocyanate) and 0.015g catalyst (see Table1). Next 3.9 gram dipropylene glycol was slowly added maintaining the temperature below 55 °C. After the addition was finished, the reaction mixture was

20 stirred for an additional 15 min before slowly adding 94.9 g 2-hydroxypropyl methacrylate (HPMA) at such a rate that the temperature of the reaction was kept below 90 °C. After full addition of the HPMA, the reaction mixture was kept at 90 °C for an additional hour. Next 0.9g Tempol, 3.3g N,N-diisopropanoltoluidine (=N,N-bis(2-hydroxy propyl)-p-toluidine; being a tertiary aromatic amine), and 65g butane

25 dioldimethacrylate were added and the reaction mixture was cooled to room temperature after which a diluted urethane methacrylate resin was obtained.

Viscosity was determined analogous to ISO 3219 using a physica MC1 viscometer equipped with a Z2 spindle.

Molecular weight Mw was determined with GPC calibrated with

30 polystyrene standards analogous to ISO 16014-1 and ISO 16016014-3, set n° 1, whereby the eluent used is prepared by adding 20 ml acetic acid to 2.5 l THF (BHT stable); and the chromatographic conditions were as follows : Flow: 1.0 ml/min.; Column temperature: 40 °C; Refractive index detector temperature: 40 °C.

Curing was performed using 50 g resin to which 15 g Perkadox 20S,

35 a peranhydride obtained from AkzoNobel, was added. The curing was monitored by

means of standard gel time equipment. This is intended to mean that both the gel time (T_{gel} or $T_{25 \rightarrow 35^\circ\text{C}}$) and peak time (T_{peak} or $T_{25 \rightarrow \text{peak}}$) were determined by exotherm measurements according to the method of DIN 16945 when curing the resin with the peroxides as indicated in the Examples and Comparative Examples. The equipment used therefore was a Soform gel timer, with a Peakpro software package and National Instruments hardware; the waterbath and thermostat used were respectively Haake W26, and Haake DL30.

Also the gel-time drift (Gtd) was calculated. This was done on the basis of the gel times determined at different dates of curing according to formula 1:

$$\text{Gtd} = (T_{25 \rightarrow 35^\circ\text{C}} \text{ at } y\text{-days} - T_{25 \rightarrow 35^\circ\text{C}} \text{ after mixing}) / T_{25 \rightarrow 35^\circ\text{C}} \text{ after mixing} \times 100\%$$

(formula 1)

with "y" indicating the number of days after mixing.

Table 1

	Catalyst	Visco (mPa*s)	Mw	Gel time (min)	Peak time (min)	Peak temp. (°C)	GTD (%) (y=90)
Example 1	Zr tetra butoxide	63	1083	4.0	5.3	144	0
Comp A	Zr tetra acetylacetonate	62	1051	3.5	4.8	143	-6
Comp B	Ti tetrabutoxide	73	1136	4.2	5.8	144	10
Comp C	Dibutyl tin dilaurate DBTDL	63	1085	4.0	5.3	144	2
Comp D	No catalyst	Almost no polymer formed					

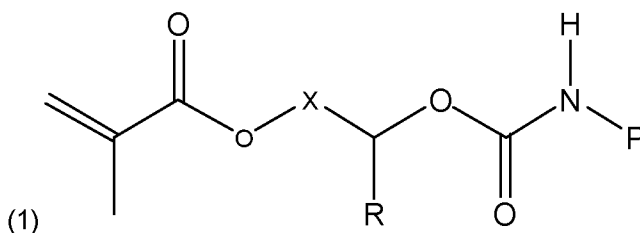
The results in this table clearly show that only by employing the zirconium catalysts according to the invention, it is possible to have a good alternative for the environmentally suspected tin compounds. It should be noted that, with respect to gel time drift, the catalysts according to the invention show even a small improvement (Example 1 vs Comp C). Using the acetylacetonate salt of zirconium the Mw is slightly lower, the reactivity differs and a negative drift, indicative of a tendency to gel, is present (Comp A). With the titanium complex however (Comp B) the viscosity became too high which is an indication of side reactions during the urethane synthesis,

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and in addition, the pre-accelerated resin composition suffers from gel time drift. When no catalyst is applied (Comp D), IR analysis showed that almost no polymer is formed since almost all isocyanate was still present.

CLAIMS

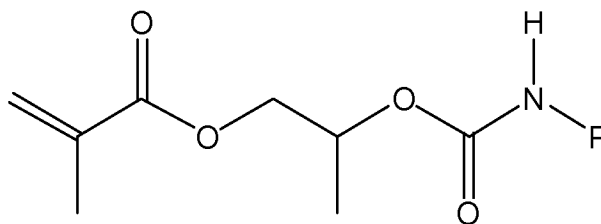
1. Method for the preparation of an urethane methacrylate resin composition comprising urethane methacrylate resin and reactive diluent, wherein the method comprises
 - (1) preparing an urethane methacrylate resin by reacting at least a hydroxyl functional methacrylate and an isocyanate in the presence of a reaction catalyst, whereby a secondary hydroxyalkyl methacrylate is used as methacrylate, and the isocyanate is an aromatic and/or aliphatic di- and/or tri- isocyanate, and
 - (2) adding reactive diluent to the urethane methacrylate resin during and/or after its preparation, characterized in that a zirconium alkoxide and/ or a zirconium carboxylate is used as reaction catalyst and the process further comprises
 - (3) adding a tertiary aromatic amine to the urethane methacrylate resin.
2. Method according to claim 1, wherein 2-hydroxypropyl methacrylate is used as secondary hydroxyalkyl methacrylate.
3. Method according to claim 1 or 2, wherein the catalyst is a zirconium (IV) alkoxide and/or a zirconium (IV) carboxylate.
4. Method according to claim 1 or 2, wherein the catalyst is a zirconium alkoxide.
5. Method according to anyone of the preceding claims, wherein the preparing of the urethane methacrylate resin is performed in the presence of the reaction product of a polyol and the isocyanate.
6. Method according to anyone of the preceding claims, wherein the urethane methacrylate resin is according to following formula



in which X= C1-C10 (cyclo)alkyl or C1-C30 alkoxy; R = C1- C4 alkyl and P = a residue of the isocyanate.

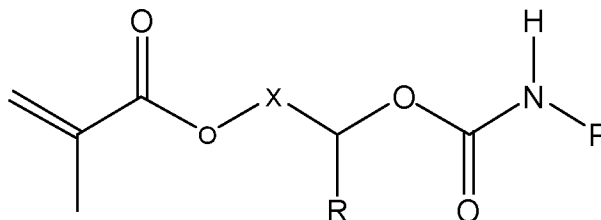
7. Method according to anyone of the preceding claims, wherein urethane methacrylate resin is according to the following formula (2)

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in which P a residue of the isocyanate.

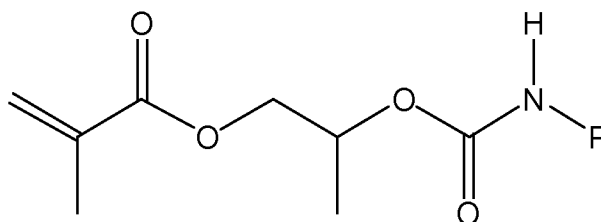
8. Resin composition comprising (a) an urethane methacrylate resin prepared by reacting at least a hydroxyl functional methacrylate and an isocyanate in the presence of a reaction catalyst, wherein a secondary hydroxyalkyl methacrylate is used as methacrylate and the isocyanate is an aromatic and/or aliphatic di- and/or tri- isocyanate, and (b) a reactive diluent, wherein the resin composition further comprises (c) a tertiary aromatic amine and (d) a zirconium alkoxide and/or a zirconium carboxylate.
9. Resin composition according to claim 8, wherein the amount of zirconium alkoxide and zirconium carboxylate in the resin composition is from 1 to 5000 ppm (relative to the urethane methacrylate resin).
10. Resin composition according to claim 8 or 9, wherein the zirconium alkoxide is a zirconium (IV) alkoxide and the zirconium carboxylate is a zirconium (IV) carboxylate.
11. Resin composition according to anyone of claims 8-10, wherein the resin composition comprises a zirconium alkoxide.
12. Resin composition according to anyone of claims 8-11, wherein the preparation of the urethane methacrylate resin is performed in the presence of the reaction product of a polyol and the isocyanate.
13. Resin composition according to anyone of claims 8-12, wherein 2-hydroxypropyl methacrylate is used as secondary hydroxyalkyl methacrylate.
14. Resin composition according to anyone of claims 8-13, wherein the resin composition comprises urethane methacrylate resin according to following formula (1)



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in which X= C1-C10 (cyclo) alkyl or C1-C30 alkoxy; R = C1- C4 alkyl and P = a residue the isocyanate.

15. Resin composition according to claim 14, wherein the urethane methacrylate resin is according to the following formula (2)



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in which P a residue of the isocyanate.

16. Process for preparing a radically cured structural part, characterized in that the curing is performed by mixing a resin composition obtained by a method according to anyone of claims 1-7 or by mixing a resin composition according to anyone of claims 8-15 with a peranhydride.
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17. Cured structural part obtained by mixing a resin composition obtained by a method according to anyone of claims 1-7 or a resin composition according to anyone of claims 8-15 with a peranhydride.
18. Use of the cured structural part of claim 17 in adhesive applications, automotive, boats, chemical anchoring, roofing, construction, containers, relining, pipes, tanks, flooring or windmill blades.
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