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(54) PMMA-BASED CAST POLYMERS HAVING IMPROVED MECHANICAL PROPERTIES

PMMA-BASIERTE GIESSPOLYMERE MIT VERBESSERTEN MECHANISCHEN EIGENSCHAFTEN

POLYMÈRES COULÉS À BASE DE PMMA PRÉSENTANT DES PROPRIÉTÉS MÉCANIQUES AMÉLIORÉES

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Description

Field of the invention

[0001] The invention relates to a composition for producing a PMMA-based cast polymer with a low styrene content using urea (derivatives) as a formulation constituent, and a hydrophilic inorganic compound as a filler. It is possible to produce PMMA-based cast polymers and mouldings having surprisingly high mechanical stability from the composition according to the invention.

Prior art

[0002] Poly(methylmethacrylate) (PMMA) foams are extensively described in the literature but have hitherto achieved little if any industrial significance. One reason therefor is the frequently described, but very complicated production via autoclave processes in which PMMA is loaded with gaseous blowing agents, e.g. CO_2 or N_2, under high pressures in an autoclave and then expanded by release of pressure.

[0003] PMMA plastics may be produced by various processes. One of these processes is chamber polymerization, also known as cast polymerization. This comprises thermal or photochemical polymerization of a pourable monomer solution between two glass plates separated from one another by a sealing rope. This monomer solution contains at least the monomer (MMA) and a polymerization initiator. Once polymerization is complete, the glass plates are removed from the resulting polymer and a polymer sheet is obtained.

[0004] These cast polymers made of PMMA have an elastic modulus of about 3000 to 3300 MPa.

[0005] Cast polymerization also allows for the use of comonomers and additives. Employable here are in principle all comonomers soluble in the respective monomer solution and copolymerizable with MMA.

[0006] The mechanical properties of the thus obtained PMMA-based polymers may be adjusted within certain narrow limits through the choice of the comonomers. However, it is not known that for example the elastic modulus can be increased beyond a value of for example 4000 MPa in this way.

[0007] Polymethyl methacrylimide (PMMI) is a polymer which is based on PMMA and has an elastic modulus of about 4000 MPa (e.g. Pleximid® TT70 manufactured by Röhm GmbH). However, this polymer cannot be produced by a cast polymerization.

[0008] US 4,816,492 describes the production of (meth)acrylate-based foams, wherein the monomer mixture is polymerized in the presence of blowing agents. The used blowing agents are halogenated hydrocarbons. Halogenated hydrocarbons, however, are problematic in that they have a severely adverse effect on the ozone layer and therefore are subject to significant environmental restrictions. Furthermore, the described foams produced exclusively from (meth)acrylates, vinyl acetate and chlorine-containing monomers do not have sufficient compressive strength.

[0009] EP 0 068 439 discloses the production of PMMA-based foams by polymerization of MMA in the presence of a blowing agent and subsequent foaming. 5 wt% to 40 wt % of the plasticizing agents, such as alkyl methacrylates having at least three least carbon atoms in the alkyl group, are employed to obtain foams. The use of hydrocarbons and/or hydrofluorocarbons as blowing agents is reported.

[0010] JP 2006045256 discloses using of a monomer mixture comprising 50% to 70% by weight of MMA, 14% to 30% by weight of (meth)acrylic acid, 10% to 20% by weight of styrene, and urea as a foaming agent to produce thermoplastic acrylic foams.

[0011] Likewise, describes JP 2002003635 using of a monomer mixture comprising 50% to 75% by weight of MMA, 14% to 27% by weight of (meth)acrylic acid, 10% to 20% by weight of styrene, and urea or urea derivatives as a foaming agent to produce thermoplastic acrylic foams.

[0012] JP 2013203954 discloses a method for producing an acrylic resin foam comprising the steps of (a) preparing a polymerizable solution containing a polymerizable monomer including maleic anhydride and methacrylamide, a foaming agent including urea, and a polymerization initiator; (b) polymerizing the polymerizable monomer mixture; and then (c) foaming the foamable polymer obtained in step (b). The foaming agent further includes an alcohol having a boiling point of 70°C to 180°C. Specifically, it is suggested to use the polymerizable monomer mixture comprising 35% to 60% by weight of MMA, 14% to 35% by weight of (meth)acrylic acid, 10% to 20% by weight of styrene and 1% to 10% by weight of maleic anhydride and methacrylamide.

[0013] Patent applications JP 2006045256, JP 2002003635 and JP 2013203954 all describe at least 10% by weight content of styrene in the polymerizable compositions. Styrene is regarded as a "reasonably anticipated to be a human carcinogen". Therefore, if possible, the amount of styrene monomer used in polymer compositions is reduced to minimum.

[0014] It was found that if styrene is used as one of the essential components of the monomer mixture, the solubility of urea or a urea derivative, which is used as a foaming agent, is greatly reduced. Moreover, the polymerization rate is also reduced. Furthermore, styrene causes the deterioration in weather resistance of the obtained foam.

[0015] JP 55139433 describes a method for producing an acrylic foam containing 50% to 96% by weight of MMA, 4%

to 35% by weight of acrylic and/or methacrylic acid as comonomers, urea foaming agent and 0.05% to 4% by weight of water. The preferable amount of styrene monomer in the monomer mixture is less than 5% by weight. This patent application does not mention or suggest any means for additional increasing the mechanical strength of the acrylic foam or the cast polymer for producing thereof.

[0016] US 2019/211124 relates to novel PMMA foams and also the production thereof. The production of the foams is carried out by means of a polymerization, for example a plate polymerization of monomer mixtures containing firstly a relevant proportion of MMA, or a syrup of a polymer consisting to a relevant proportion of MMA and a monomer mixture composed to a relevant proportion of MMA, preferably in the presence of a blowing agent which is not gaseous under polymerization conditions and/or a copolymerizable blowing agent. In a second step, the resulting, fully polymerized PMMA plate which has optionally also been subsequently loaded with blowing agent is then foamed by heating.

[0017] It was found that the use of small amounts of methacrylamide, N-alkylmethacrylamide and/or N,N-dialkylmethacrylamide as comonomers brings about a significant improvement in the mechanical properties of the foams obtained in this way.

[0018] US 2018/079882 relates to novel types of fine-cell PMMA foams and also to the production thereof. The recipes used in the production process include nucleating agents in addition to suitable blowing agents. The US 2018/079882 provides a simple-to-produce stable PMMA foam having very fine cells and very good properties.

[0019] The novel type of process for producing PMMA foams, comprises producing said foams by a polymerization, as by a slab polymerization for example, of monomer mixtures containing predominantly MMA and/or of a syrup consisting of a polymer consisting wholly or predominantly of MMA and a monomer mixture composed wholly or predominantly of MMA, in the presence of a nucleating agent and of a blowing agent that is non-gaseous under polymerization conditions. The fully polymerized PMMA slab thus obtained, which is laden with blowing agent, is then foamed up in a second step by heating while small and uniform cells are formed by the admixed nucleating agent.

[0020] This process is particularly characterized in that the nucleating agent comprises silicon oxide particles having a diameter between 4 and 1000 nm. The composition contains from 0.01 to 2.0 wt% of one or more initiators, from 2 to 20 wt% of one or more blowing agents, from 0.2 to 10 wt% of the silicon oxide particles with the diameter between 4 and 1000 nm, and from 70 to 97.79 wt% of a polymer-forming mixture, wherein said polymer-forming mixture consists of MMA and/or MMA repeat units to an extent of not less than 75 mol% and may be present as polymer and/or oligomer to an extent of from 0 to 80 wt%. This composition is initially polymerized at a temperature between 20°C and 100°C and subsequently foamed at a temperature between 130°C and 250°C.

[0021] JP S55 139433 discloses a composition for producing a PMMA-based cast polymer, characterized in that the composition contains 1-10 wt% of urea, 0.001-2.0 wt% of an initiator (AIBN), 0-5 wt% of a chain-transfer agent (Lauryl mercaptan), and 53-98.498 wt% of a monomer mixture consisting of 60-95 wt% of MMA, 5-40 wt% of (meth)acrylic acid and/or itaconic acid and less than 4 wt% of styrene, α-methylstyrene and/or chlorostyrene.For all PMMA-based foams disclosed in the prior art, it is common that they have a compressive strength which is too low for use in composite materials, such as particularly, sandwich constructions. For uses as core material in sandwich composites, the mechanical properties, especially the compressive strength, are of great importance since they have an influence on the manufacturing processes of the sandwich elements and on the mechanical properties of the sandwich elements.

Problem

[0022] The problem addressed by the present invention was that of providing a novel process for producing PMMA-based foams which does not exhibit the discussed disadvantages of the prior art. Particularly, the produced PMMA-based foamed material should be very resistant to mechanical stress. The foam should especially have a very high compressive strength. Additionally, such PMMA-based foams should have a low density, preferably between 30 kg/m^3 and 350 kg/m^3.

[0023] A further problem addressed by the present invention was that of providing a PMMA-based cast polymer which is readily foamable, while allowing high degrees of freedom with regard to the establishment of cell size, cell distribution and foam density. Such unfoamed cast polymers should show exceptional mechanical properties. Particularly, the PMMA-based cast polymer should have an elastic modulus of at least 4500 MPa measured at room temperature.

[0024] Further problems addressed by the present invention were those of providing a suitable PMMA-based polymer which, as a foam, may be readily and simply joined to a second material, e.g. in the form of an outer layer, by means of adhesive bonding, melting or by resin curing on the surface. It is also important to this end that the obtained PMMA foams are compatible with the resin systems or adhesives used for producing the sandwich elements.

Solution

[0025] The above-mentioned technical problems are solved by a novel composition which is usable for producing PMMA-based cast polymers and optionally PMMA-based foams thereof.

[0026] In the course of a thorough experimentation, among other things, it was surprisingly found that the presence of hydrophilic inorganic compounds not soluble in the monomer mixture allows to substantially increase the mechanical strength of the PMMA-based cast polymer. To achieve a good compatibility of such hydrophilic inorganic compounds with the polymer matrix, and sufficient distribution of such compounds, it was necessary to reduce the amount of styrene or its derivatives to less than 4 % by weight.

[0027] The object of the present invention is a composition for producing a PMMA-based cast polymer, characterized in that the composition contains 1% to 10% by weight of urea and/or urea derivatives, 0.001% to 2.0% by weight of an initiator, 0% to 20% by weight of a further non-polymerizable blowing agent, 0% to 5% by weight of a chain-transfer agent, 0.5% to 10% by weight of a hydrophilic inorganic compound essentially not soluble in the composition, and 53% to 98.498% by weight of a monomer mixture consisting of 60% to 95% by weight of MMA, 5% to 40% by weight of acrylic, methacrylic and/or itaconic acid, less than 4% by weight of styrene, α-methylstyrene and/or chlorostyrene, and 0% to 35% by weight of further MMA-copolymerizable monomers other than urea derivatives, wherein the inorganic hydrophilic compound has a methanol wettability of less than 30% by volume of methanol in a methanol/water mixture.

[0028] The term "methanol wettability" means in the context of the present invention that for the determination of the methanol wettability, described in EP 2515829 B1, in each case 0.2 g (± 0.005 g) of hydrophobic or hydrophobized particles are weighed into transparent centrifuge tubes. 8.0 ml portions of a methanol/water mixture with 10, 20, 30, 40, 50, 60, 70 or 80 vol.% methanol are added to each sample. The tubes are shaken for 30 seconds and then centrifuged at 2500 min^{-1} for 5 minutes. The methanol wettability is the defined as the volume per cent of methanol for which the sediment volume is 100%. The higher the number the higher the hydrophobicity.

[0029] An essential constituent of the inventive composition is a hydrophilic inorganic compound essentially not soluble in the composition. The hydrophilic inorganic compound is chosen from the group consisting of silica, metal oxides, metal hydroxides, metal silicates, talcum, and the mixtures thereof. The hydrophilic inorganic compound has an average diameter d_{50} of between 5 and 1000 nm.

[0030] The particle size d_{50} is determined according to ASTM 690-1992.

[0031] The term "inorganic compound" means in the context of the present invention that maximally one carbon atom is present in each molecule of the compound. Thus, SiC is an inorganic compound in the context of the present invention, whereas $Na_2C_2O_4$ is not.

[0032] The term "essentially not soluble" means in the context of the present invention that at least 90%, preferably at least 95%, more preferably at least 99% of the full amount of such a hydrophilic inorganic compound employed in the composition remains in the particulate state, not dissolved in the composition after at least 1 h of presence therein. The inorganic compounds, which react with one or more of the components of the inventive composition are not "essentially not soluble". Thus, lithium oxide would react with (meth)acrylic or itaconic acid present and is therefore not "essentially not soluble". The use of urea and/or urea derivatives as a constituent of the composition is an essential part of the invention, which, in combination with other features, brings about a marked improvement in the mechanical properties of the thus obtained cast polymers and the foams produced therefrom.

[0033] The urea derivatives present in the composition as an alternative to urea in accordance with the invention are preferably an N-alkylurea, for example N-methylurea, or N,N'-dialkylurea, such as N,N'-dimethylurea, unsubstituted or substituted 2-imidazolidones, such as 2-imidazolidone or N,N-dimethyl 2-imidazolidone, optionally further substituted 1-methyl-2-imidazolidinones and further cyclic urea derivatives.

[0034] In a further embodiment, the urea derivatives are at least partly copolymerizable with MMA urea derivatives, in particular N-(2-methacryloyloxyethyl)ethyleneurea. Hereinafter, in order to avoid ambiguity in terms of the overall composition, such copolymerizable with MMA urea derivatives are not considered as being a part of the monomer mixture.

[0035] The composition for producing a PMMA-based cast polymer consists of 1% to 10% by weight, preferably 2% to 8% by weight, particularly preferably 3% to 7% by weight of urea and/or urea derivatives, 0.001 to 2.0% by weight, preferably 0.002 to 1.0% by weight, particularly preferably 0.003% to 0.5% by weight of one or more initiators, 0% to 20% by weight of a further non-polymerizable blowing agent, 0% to 5% by weight of a chain-transfer agent, 0.5% to 10% by weight, preferably 1% to 8% by weight, particularly preferably 2% to 6% by weight of a hydrophilic inorganic compound and 53% to 98.498% by weight, preferably 57% to 96.999% by weight, more preferably 64.5% to 95.997% by weight of a monomer mixture.

[0036] The above-mentioned monomer mixture in turn consists of 60% to 95% by weight, preferably 70% to 90% by weight, particularly preferably 75% to 85% by weight, of MMA, 5% to 40% by weight, preferably 10% to 30% by weight, particularly preferably 15% to 25% by weight, of acrylic, methacrylic and/or itaconic acid, less than 4% by weight, preferably less than 2% by weight, particularly preferably less than 1% by weight of styrene, α-methylstyrene and/or chlorostyrene and 0% to 35% by weight, preferably 0% to 20% by weight, particularly preferably 0% to 10% by weight, very particularly preferably at least 0.1% by weight, of further MMA-copolymerizable monomers other than urea derivatives.

[0037] Particularly preferably, the composition according to the invention contains 2% to 8% by weight of urea and/or urea derivatives, 0.002% to 2.0% by weight of an initiator, 0% to 20% by weight of a further non-polymerizable blowing agent, 0% to 5% by weight of a chain-transfer agent, 1% to 8% by weight of a hydrophilic inorganic compound, and 57% to 96.998% by weight of a monomer mixture consisting of 70% to 90% by weight of MMA, 10% to 30% by weight of acrylic, methacrylic and/or itaconic acid, less than 4% by weight of styrene, α-methylstyrene and/or chlorostyrene, and 0% to 35% by weight of further MMA-copolymerizable monomers other than urea derivatives.

[0038] Particularly preferably, the monomer mixture contains essentially no styrene, α-methylstyrene and/or chlorostyrene, i.e. the amount of styrene, α-methylstyrene and/or chlorostyrene is less than 0.1% by weight, even more preferably less than 0.01% by weight of the monomer mixture.

[0039] While PMMA-based foams containing styrene and optionally maleic acid derivatives have proven mechanically very stable, the styrene proportion has been found to lead to incompatibility of the foams with certain resins. The foam produced from the composition according to the invention is therefore preferably free from styrene and maleic acid derivatives.

[0040] The optional further MMA-copolymerizable monomers in the monomer mixture may be crosslinkers. Such crosslinkers may be in particular ethylene glycol dimethacrylate, triallyl cyanurate, triallyl isocyanurate and/or allyl methacrylate. Further alternatives are di-, tri- or tetra(meth)acrylates. Any crosslinkers present may also be a mixture containing at least two of these crosslinkers. However, a high degree of covalent crosslinking is preferably not desired.

[0041] The monomer mixture present in the composition of the present invention preferably contains at least 0.1% by weight of the further MMA-copolymerizable monomers and, which are crosslinkers, in particular ethylene glycol dimethacrylate, triallyl cyanurate, triallyl isocyanurate, allyl methacrylate, or a mixture thereof.

[0042] Further optional MMA-copolymerizable monomers may be alkyl acrylates. These alkyl acrylates are preferably alkyl acrylates having 1 to 8 carbon atoms in the alkyl radical, particularly preferably ethyl acrylate, n-propyl acrylate or n-butyl acrylate. The acrylates as repeating units in the polymer especially increase the thermal stability of said polymer.

[0043] Monomers optionally present in addition to MMA, may also or in addition include alkyl methacrylates other than MMA. Such alkyl methacrylates are in particular those having 2 to 8 carbon atoms in the alkyl radical. Particular preference is given to ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate or 2-ethylhexyl methacrylate.

[0044] Further advantageously employable monomers of this category are in particular hydroxyl-functional alkyl (meth)acrylates. These are preferably 2-hydroxyethyl (meth)acrylate or 3-hydroxypropyl (meth)acrylate.

[0045] The monomer mixture preferably contains between 5% and 10% by weight of tert-butyl methacrylate, isopropyl methacrylate, tert-butyl acrylate and/or isopropyl acrylate.

[0046] The monomer mixture may optionally contain N-alkyl(meth)acrylamides having 1 to 12 carbon atoms in the alkyl group and no methacrylamide or N,N-dialkylmethacrylamides as MMA-copolymerizable monomers. The N-alkyl(meth)acrylamide is particularly preferably N-methylolmethacrylamide, 2-hydroxypropylmethacrylamide or N-isopropylmethacrylamide, especially preferably N-isopropylmethacrylamide.

[0047] Such N-alkyl(meth)acrylamides entail great advantages in terms of later joining with for example outer layers to afford sandwich components or other composite materials and an altogether better further processability in terms of adhesive bonding, welding or superficial resin curing. This is particularly the case when the present foams contain neither styrene nor maleic acid derivatives.

[0048] The chain-transfer agent which is optionally present in the inventive composition, is preferably a compound having from one to five mercaptan groups, a γ-terpinene or a mixture of at least two of these chain-transfer agents. The chain-transfer agent is particularly preferably pentaerythritol tetrathioglycolate, 2-mercaptoethanol, an alkyl mercaptan having from 2 to 12 carbon atoms, thioglycolic acid, a thioglycolate, γ-terpinene or a mixture of at least two of these chain-transfer agents.

[0049] Especially suitable non-copolymerizable blowing agents other than urea or urea derivatives are preferably n-heptane, MTBE, methyl ethyl ketone, an alcohol having one to four carbon atoms, such as tert-butanol, water, methylal, and/or tert-butyl methyl ether.

[0050] The composition can also contain further components. Examples of these further components include release agents, waxes, pigments, stabilizers, in particular UV stabilizers, and/or adhesion promoters.

[0051] Further object of the invention is a PMMA-based cast polymer, obtainable by polymerization of the composition according to the invention.

[0052] Another object of the invention is a process for producing a PMMA-based cast polymer, wherein the composition according to the invention, as described hereinabove, is polymerized at a temperature between 20°C and 100°C.

[0053] Optionally, the entirety of the composition or a part of the composition may be in the form of polymer and/or oligomer to an extent of up to 80% by weight at the beginning of the polymerization. This is what is known as a "syrup process" and is described further hereinbelow.

[0054] When oligomers or polymers are used, the polymerization is a so-called syrup polymerization which has proven useful in particular in a casting process between two plates. At the end of such a syrup polymerization, two PMMA types having different compositions may be present simultaneously as a mixture in the cast polymer or in the moulding or foam produced therefrom without any relevant influence on foaming.

[0055] The polymerization process, preferably in the form of a bulk polymerization, is carried out at a temperature between 20°C and 100°C, preferably between 30°C and 70°C.

[0056] Further object of the invention is a PMMA-based foam, obtainable by foaming of the cast polymer of the invention or by foaming of the at least partly polymerized composition according to the invention.

[0057] The PMMA-based foam preferably has a density between 30 kg/m^3 and 350 kg/m^3, particularly preferably between 50 and 300 kg/m^3_determined according to DIN EN ISO 1183 (Publication: 2013-04).

[0058] Another object of the invention is a process for producing a PMMA-based foam according to the invention, wherein the composition of the invention is polymerized at a temperature between 20°C and 100°C and is subsequently foamed at a temperature between 130°C and 250°C.

[0059] Foaming is preferably carried out - depending on the blowing agents used - at a temperature between 130°C and 250°C, more preferably between 150°C and 230°C.

[0060] The polymerization and/or foaming are preferably carried out in stages at different temperatures. It is possible, alternatively or in addition, to carry out the polymerization and the foaming at least partly simultaneously.

[0061] In such a simultaneous mode of operation, the process may optionally be performed in particular such that the polymerization is performed only incompletely, in this case preferably to a conversion of at least 80%, and the final end-polymerization is carried out during foaming. Such a process has the advantage that at the beginning of the foaming procedure, the remaining monomers have a plasticizing effect without any plasticizing compound remaining in the finished foam. In such an embodiment, the polymerization and the foaming would thus be carried out partly simultaneously at one foaming temperature.

[0062] The polymerization is preferably carried out in a shape-conferring vessel, in particular in the form of a chamber polymerization between two plates, for example glass plates. In the simplest case a rectangular tub may be concerned for example. Polymerization in such a tub later affords a sheet whose thickness has been determined by the fill level in the tank/the plate spacing. However, more complex shapes are also conceivable for the vessel. The polymerization is preferably carried out at a temperature between 30°C and 70°C. Employable initiators include not only well-known free-radical initiators, for example peroxides or azo initiators, but also redox systems or UV initiators.

[0063] Polymerization temperatures below 40°C apply particularly to these redox systems and UV initiators. UV initiators are initiated by irradiation with appropriate UV light, while redox initiators comprise two-component systems initiated by mixing the two components and the monomers.

[0064] Foaming may subsequently take place in the same vessel, in which case the volume increase is restricted to one direction, the open side of the vessel. However, the polymerized material can also be foamed without enclosure or in a suspended manner. Foaming is preferably carried out in an oven. As an alternative, it is also possible to bring about foaming by irradiation with IR radiation, in particular radiation having a wavelength in the range from 0.78 to 2.20 μm, preferably from 1.20 to 1.40 μm. Microwave foaming represents a further alternative. The combination of different methods, such as IR radiation, microwaves and/or heating in an oven, is also conceivable.

[0065] Foaming as well as the polymerization may each be carried out in a plurality of temperature stages as previously mentioned. The temperature may be raised later in the polymerization to additionally enhance the conversion and thereby reduce the residual monomer content. During foaming, the foaming temperature can be increased in stages in order to influence the cell distribution, the cell size and the number of cells.

[0066] It has surprisingly been found that using the composition according to the invention, it is possible to obtain a PMMA-based polymer having an elastic modulus measured at room temperature of more than 4500 MPa. By comparison a pure PMMA cast polymer has an elastic modulus in the range between 2800 and 3300 MPa.

[0067] The PMMA-based foams produced according to the invention have a surprisingly high strength coupled with a surprisingly low brittleness and may therefore find application in lightweight construction for example. Furthermore, owing to the good material properties, there is no need for the use of plasticizers, e.g. relatively long-chain alkyl (meth)acrylates or phthalates, which according to knowledge to date have a positive effect on the flowability or the foamability but at the same time have an adverse effect on the mechanical properties of the PMMA foam, in particular the strength.

[0068] It has been found that for the same cell structure as described in the prior art, a foam produced from a polymer having an elastic modulus X exhibits better mechanical properties than a foam produced from a polymer having an elastic modulus Y when X>Y. Therefore, the high elastic modulus of the polymer is a prerequisite for obtaining good mechanical properties of the foam.

[0069] The PMMA-based cast polymers produced according to the invention may be used in a variety of different applications. Examples of such uses include filled or transparent mouldings, glazing, in advertising materials, for production of films, in architectural building elements, as diffusers in lighting applications, in furniture construction, in boatbuilding, in vehicle construction, in the aerospace industry or in model building. It is especially preferable when said polymers are used for producing likewise inventive PMMA foams.

[0070] The PMMA-based foams produced according to the invention may also find a very wide variety of uses. Examples of such uses are weathering-resistant insulation materials, core material for sandwich composites, in blades of wind power plants, in boat- and shipbuilding and also in subsea applications, in lightweight construction, as packaging material, as energy absorbers in crash elements, in architectural building elements, as diffusers in lighting applications, in furniture construction, in vehicle construction, in the aerospace industry or in model building.

Examples

[0071] The PMMA polymers were produced in the casting process. To this end, glass chambers consisting of 2 glass plates (400x300 mm) held apart and sealed by a sealing tape (13 mm thickness) were filled with the monomer solution.

[0072] To produce the monomer solution, the ingredients were added together according to the formulations recited below (Tables 1-4) and stirred until all constituents were dissolved.

[0073] The thus produced and filled glass chambers were stored in a water bath at 40°C for the polymerization. After about 27h the glass chambers were end-polymerized at 115°C. The glass plates and the sealing rope were then removed. A hard and translucent polymer was obtained in all cases.

[0074] AEROSIL® OX50 (manufacturer: Evonik Resource Efficiency GmbH) was used as a hydrophilic inorganic compound.

[0075] Tensile tests for determining the elastic modulus of the polymers were performed using a Zwick/Roell Z030 instrument. Measurements were carried out at standard conditions of 23°C and 50% humidity. The samples were stored for at least 16 hours at identical conditions (23°C-50% humidity) prior to measurement. The results are shown in Table 5.

Table 1: Example 1

Example 1	wt%
Methyl methacrylate	69.45
Methacrylic acid	20.00
Butyl acrylate	1.00
Urea	5.00
Silica (AEROSIL® OX50)	4.00
2,2'-Azobis(2,4-dimethylvaleronitrile)	0.05
2-Ethylhexyl thioglycolate	0.50

Table 2: Comparative Example 1

Comparative Example 1	wt%
Methyl methacrylate	63.45
Methacrylic acid	20.00
Butyl acrylate	1.00
Styrene	6.00
Urea	5.00
Silica (AEROSIL® OX50)	4.00
2,2'-Azobis(2,4-dimethylvaleronitrile)	0.05
2-Ethylhexyl thioglycolate	0.50

Table 3: Comparative Example 2

Comparative Example 2	wt%
Methyl methacrylate	74.45
Methacrylic acid	20.00
Butyl acrylate	1.00
Silica (AEROSIL® OX50)	4.00

(continued)

Comparative Example 2	wt%
2,2'-Azobis(2,4-dimethylvaleronitrile)	0.05
2-Ethylhexyl thioglycolate	0.50

Table 4: Comparative Example 3

Comparative Example 3	wt%
Methyl methacrylate	74.45
Methacrylic acid	20.00
Butyl acrylate	1.00
Urea	4.00
2,2'-Azobis(2,4-dimethylvaleronitrile)	0.05
2-Ethylhexyl thioglycolate	0.50

Table 5: Elastic moduli

Elastic modulus comparison	Elastic modulus (MPa)
Example 1 (with urea and SiO_2)	*4900*
Comparative example 1 (with urea, SiO_2 and styrene)	*4400*
Comparative example 2 (no urea, with SiO_2)	*3600*
Comparative example 3 (with urea, no SiO_2)	*4500*

[0076] Table 5 shows the results of the measurement of the elastic moduli of the polymers prepared in Example 1 and comparative examples 1-3. The polymer prepared without the use of urea as a blowing agent and silica as a filler (comparative example 2), shows the lowest elastic modulus. The use of both urea and silica, but no styrene (example 1) shows the best results. The use of urea, silica and styrene leads to inferior results (comparative example 1) than in example 1, as well as the use of urea without silica (comparative example 3).

Claims

1. Composition for producing a PMMA-based cast polymer, **characterized in that** the composition contains 1% to 10% by weight of urea and/or urea derivatives, 0.001 to 2.0% by weight of an initiator, 0% to 20% by weight of a further non-polymerizable blowing agent, 0% to 5% by weight of a chain-transfer agent, 0.5% to 10% by weight of a hydrophilic inorganic compound essentially not soluble in the composition, and 53% to 98.498% by weight of a monomer mixture consisting of 60% to 95% by weight of MMA, 5% to 40% by weight of acrylic, methacrylic and/or itaconic acid, less than 4% by weight of styrene, α-methylstyrene and/or chlorostyrene, and 0% to 35% by weight of further MMA-copolymerizable monomers other than urea derivatives, wherein the inorganic hydrophilic compound has a methanol wettability of less than 30% by volume of methanol in a methanol/water mixture and wherein the methanol wettability is determined by the method mentioned in the specification.

2. Composition according to Claim 1, **characterized in that** the composition contains 2% to 8% by weight of urea and/or urea derivatives, 0.002 to 1.0% by weight of an initiator, 0% to 20% by weight of a further non-polymerizable blowing agent, 0% to 5% by weight of a chain-transfer agent, 1% to 8% by weight of a hydrophilic inorganic compound, and 57% to 96.999% by weight of a monomer mixture consisting of 70% to 90% by weight of MMA, 10% to 30% by weight of acrylic, methacrylic and/or itaconic acid, less than 2% by weight of styrene, α-methylstyrene and/or chlorostyrene, and 0% to 35% by weight of further MMA-copolymerizable monomers other than urea derivatives.

3. Composition according to at least one of Claims 1 or 2, **characterized in that** the monomer mixture contains essentially no styrene, α-methylstyrene and/or chlorostyrene.

4. Composition according to at least one of Claims 1 to 3, **characterized in that** the hydrophilic inorganic compound is chosen from the group consisting of silica, metal oxides, metal hydroxides, metal silicates, talcum, and the mixtures thereof.

5. Composition according to at least one of Claims 1 to 4, **characterized in that** the hydrophilic inorganic compound has an average diameter d_{50} of between 5 and 1000 nm, determined according to ASTM 690-1992.

6. Composition according to at least one of Claims 1 to 5, **characterized in that** the monomer mixture contains at least 0.01% by weight of the further MMA-copolymerizable monomers and **in that** these monomers are crosslinkers, in particular, ethylene glycol dimethacrylate, triallyl cyanurate, triallyl isocyanurate, allyl methacrylate, or a mixture thereof.

7. Composition according to at least one of Claims 1 to 6, **characterized in that** the urea derivatives are chosen from the group consisting of an N-alkylurea, an N,N'-dialkylurea, 2-imidazolidones, 1-methyl-2-imidazolidinones, and the mixtures thereof.

8. Composition according to at least one of Claims 1 to 7, **characterized in that** the urea derivatives are at least partly copolymerizable with MMA urea derivatives, in particular N-(2-methacryloyloxyethyl)ethyleneurea.

9. Composition according to at least one of Claims 1 to 8, **characterized in that** the monomer mixture contains between 5% and 10% by weight of tert-butyl methacrylate, isopropyl methacrylate, tert-butyl acrylate and/or isopropyl acrylate.

10. PMMA-based cast polymer, obtainable by polymerization of the composition according to at least one of Claims 1 to 9.

11. Process for producing a PMMA-based cast polymer, **characterized in that** the composition according to at least one of Claims 1 to 9, is polymerized at a temperature between 20°C and 100°C.

12. PMMA-based foam, obtainable by foaming of the cast polymer according to Claim 10 or by foaming of the at least partly polymerized composition according to at least one of Claims 1 to 9.

13. PMMA-based foam according to Claim 12, wherein the foam has a density of between 30 kg/m^3 and 350 kg/m^3, determined according to DIN EN ISO 1183.

14. Process for producing a PMMA-based foam according to at least one of Claims 12 to 13, **characterized in that** the composition according to at least one of Claims 1 to 9 is polymerized at a temperature between 20°C and 100°C and is subsequently foamed at a temperature between 130°C and 250°C.

15. Process according to Claim 14, **characterized in that** the polymerization and foaming are carried out at least partly simultaneously.

Patentansprüche

1. Zusammensetzung zur Herstellung eines PMMA-basierten Gusspolymerisats, **dadurch gekennzeichnet, dass** die Zusammensetzung 1 bis 10 Gew.-% Harnstoff und/oder Harnstoffderivate, 0,001 bis 2,0 Gew.-% eines Initiators, 0 bis 20 Gew.-% eines weiteren nicht polymerisierbaren Treibmittels, 0 bis 5 Gew.-% eines Reglers, 0,5 bis 10 Gew.-% einer hydrophilen anorganischen Verbindung, die in der Zusammensetzung im Wesentlichen nicht löslich ist, und 53 bis 98,498 Gew.-% einer Monomermischung, bestehend aus 60 bis 95 Gew.-% MMA, 5 bis 40 Gew.-% Acryl-, Methacryl- und/oder Itaconsäure, weniger als 4 Gew.-% Styrol, α-Methylstyrol und/oder Chlorstyrol und 0 bis 35 Gew.-% weiterer mit MMA copolymerisierbarer Monomere, bei denen es sich nicht um Harnstoffderivate handelt, enthält, wobei die anorganische hydrophile Verbindung eine Methanolbenetzbarkeit von weniger als 30 Vol.-% Methanol in einer Methanol/Wasser-Mischung aufweist und wobei die Methanolbenetzbarkeit nach der in der Beschreibung genannten Methode bestimmt wird.

2. Zusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** die Zusammensetzung 2 bis 8 Gew.-%

Harnstoff und/oder Harnstoffderivate, 0,002 bis 1,0 Gew.-% eines Initiators, 0 bis 20 Gew.-% eines weiteren nicht polymerisierbaren Treibmittels, 0 bis 5 Gew.-% eines Reglers, 1 bis 8 Gew.-% einer hydrophilen anorganischen Verbindung, und 57 bis 96,999 Gew.-% einer Monomermischung, bestehend aus 70 bis 90 Gew.-% MMA, 10 bis 30 Gew.-% Acryl-, Methacryl- und/oder Itaconsäure, weniger als 2 Gew.-% Styrol, α-Methylstyrol und/oder Chlorstyrol und 0 bis 35 Gew.-% weiterer mit MMA copolymerisierbarer Monomere, bei denen es sich nicht um Harnstoffderivate handelt, enthält.

3. Zusammensetzung nach mindestens einem der Ansprüche 1 oder 2, **dadurch gekennzeichnet, dass** die Monomermischung im Wesentlichen kein Styrol, α-Methylstyrol und/oder Chlorstyrol enthält.

4. Zusammensetzung nach mindestens einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** die hydrophile anorganische Verbindung aus der Gruppe bestehend aus Siliciumdioxid, Metalloxiden, Metallhydroxiden, Metallsilikaten, Talk und den Mischungen davon ausgewählt ist.

5. Zusammensetzung nach mindestens einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** die hydrophile anorganische Verbindung einen mittleren Durchmesser d_{50} zwischen 5 und 1000 nm, bestimmt gemäß ASTM 690-1992, aufweist.

6. Zusammensetzung nach mindestens einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** die Monomermischung mindestens 0,01 Gew.-% der weiteren mit MMA copolymerisierbaren Monomere enthält und dass es sich bei diesen Monomeren um Vernetzer, insbesondere Ethylenglykoldimethacrylat, Triallylcyanurat, Triallylisocyanurat, Allylmethacrylat oder eine Mischung davon, handelt.

7. Zusammensetzung nach mindestens einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** die Harnstoffderivate aus der Gruppe bestehend aus einem N-Alkylharnstoff, einem N,N'-Dialkylharnstoff, 2-Imidazolinonen, 1-Methyl-2-imidazolinonen und den Mischungen davon ausgewählt ist.

8. Zusammensetzung nach mindestens einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet, dass** es sich bei den Harnstoffderivaten um zumindest teilweise mit MMA copolymerisierbare Harnstoffderivate, insbesondere N-(2-Methacryloyloxyethyl)ethylenharnstoff, handelt.

9. Zusammensetzung nach mindestens einem der Ansprüche 1 bis 8, **dadurch gekennzeichnet, dass** die Monomermischung zwischen 5 und 10 Gew.-% tert-Butylmethacrylat, Isopropylmethacrylat, tert-Butylacrylat und/oder Isopropylacrylat enthält.

10. PMMA-basiertes Gusspolymerisat, das durch Polymerisation der Zusammensetzung nach mindestens einem der Ansprüche 1 bis 9 erhältlich ist.

11. Verfahren zur Herstellung eines PMMA-basierten Gusspolymerisats, **dadurch gekennzeichnet, dass** die Zusammensetzung nach mindestens einem der Ansprüche 1 bis 9 bei einer Temperatur zwischen 20 °C und 100 °C polymerisiert wird.

12. PMMA-basierter Schaumstoff, der durch Schäumen des Gusspolymerisats nach Anspruch 10 oder durch Schäumen der zumindest teilweise polymerisierten Zusammensetzung nach mindestens einem der Ansprüche 1 bis 9 erhältlich ist.

13. PMMA-basierter Schaumstoff nach Anspruch 12, wobei der Schaumstoff eine Dichte zwischen 30 kg/m^3 und 350 kg/m^3, bestimmt gemäß DIN EN ISO 1183, aufweist.

14. Verfahren zur Herstellung eines PMMA-basierten Schaumstoffs nach mindestens einem der Ansprüche 12 bis 13, **dadurch gekennzeichnet, dass** die Zusammensetzung nach mindestens einem der Ansprüche 1 bis 9 bei einer Temperatur zwischen 20 °C und 100 °C polymerisiert und anschließend bei einer Temperatur zwischen 130 °C und 250°C geschäumt wird.

15. Verfahren nach Anspruch 14, **dadurch gekennzeichnet, dass** die Polymerisation und die Schäumung zumindest teilweise simultan erfolgen.

Revendications

1. Composition pour la production d'un polymère coulé à base de PMMA, **caractérisée en ce que** la composition contient 1 % à 10 % en poids d'urée et/ou de dérivés d'urée, 0,001 à 2,0 % en poids d'un initiateur, 0 % à 20 % en poids d'un agent gonflant non polymérisable supplémentaire, 0 % à 5 % en poids d'un agent de transfert de chaîne, 0,5 % à 10 % en poids d'un composé inorganique hydrophile essentiellement non soluble dans la composition et 53 % à 98,498 % en poids d'un mélange de monomères constitué de 60 % à 95 % en poids de MMA, 5 % à 40 % en poids d'acide acrylique, méthacrylique et/ou itaconique, moins de 4 % en poids de styrène, d'α-méthylstyrène et/ou de chlorostyrène et 0 % à 35 % en poids de monomères copolymérisables avec le MMA supplémentaires autres que des dérivés d'urée, dans laquelle le composé hydrophile inorganique a une mouillabilité par du méthanol inférieure à 30 % en volume de méthanol dans un mélange méthanol/eau et dans laquelle la mouillabilité par du méthanol est déterminée par la méthode mentionnée dans la description.

2. Composition selon la revendication 1, **caractérisée en ce que** la composition contient 2 % à 8 % en poids d'urée et/ou de dérivés d'urée, 0,002 à 1,0 % en poids d'un initiateur, 0 % à 20 % en poids d'un agent gonflant non polymérisable supplémentaire, 0 % à 5 % en poids d'un agent de transfert de chaîne, 1 % à 8 % en poids d'un composé inorganique hydrophile et 57 % à 96,999 % en poids d'un mélange de monomères constitué de 70 % à 90 % en poids de MMA, 10 % à 30 % en poids d'acide acrylique, méthacrylique et/ou itaconique, moins de 2 % en poids de styrène, d'α-méthylstyrène et/ou de chlorostyrène et 0 % à 35 % en poids de monomères copolymérisables avec le MMA supplémentaires autres que des dérivés d'urée.

3. Composition selon au moins l'une des revendications 1 ou 2, **caractérisée en ce que** le mélange de monomères ne contient essentiellement pas de styrène, d'α-méthylstyrène et/ou de chlorostyrène.

4. Composition selon au moins l'une des revendications 1 à 3, **caractérisée en ce que** le composé inorganique hydrophile est choisi dans le groupe constitué par la silice, des oxydes métalliques, des hydroxydes métalliques, des silicates métalliques, le talc et les mélanges de ceux-ci.

5. Composition selon au moins l'une des revendications 1 à 4, **caractérisée en ce que** le composé inorganique hydrophile a un diamètre moyen d_{50}, déterminé selon la norme ASTM 690-1992, compris entre 5 et 1000 nm.

6. Composition selon au moins l'une des revendications 1 à 5, **caractérisée en ce que** le mélange de monomères contient au moins 0,01 % en poids des monomères copolymérisables avec le MMA supplémentaires et **en ce que** ces monomères sont des agents de réticulation, en particulier le diméthacrylate d'éthylèneglycol, le cyanurate de triallyle, l'isocyanurate de triallyle, le méthacrylate d'allyle ou un mélange de ceux-ci.

7. Composition selon au moins l'une des revendications 1 à 6, **caractérisée en ce que** les dérivés d'urée sont choisis dans le groupe constitué par une N-alkylurée, une N,N'-dialkylurée, des 2-imidazolidones, des 1-méthyl-2-imidazolidinones et les mélanges de celles-ci.

8. Composition selon au moins l'une des revendications 1 à 7, **caractérisée en ce que** les dérivés d'urée sont des dérivés d'urée au moins en partie copolymérisables avec le MMA, en particulier la *N*-(2-méthacryloyloxyéthyl)éthylèneurée.

9. Composition selon au moins l'une des revendications 1 à 8, **caractérisée en ce que** le mélange de monomères contient entre 5 % et 10 % en poids de méthacrylate de tert-butyle, de méthacrylate d'isopropyle, d'acrylate de tert-butyle et/ou d'acrylate d'isopropyle.

10. Polymère coulé à base de PMMA, pouvant être obtenu par polymérisation de la composition selon au moins l'une des revendications 1 à 9.

11. Procédé pour la production d'un polymère coulé à base de PMMA, **caractérisé en ce que** la composition selon au moins l'une des revendications 1 à 9 est polymérisée à une température comprise entre 20 °C et 100 °C.

12. Mousse à base de PMMA, pouvant être obtenue par moussage du polymère coulé selon la revendication 10 ou par moussage de la composition selon au moins l'une des revendications 1 à 9 au moins en partie polymérisée.

13. Mousse à base de PMMA selon la revendication 12, la mousse ayant une masse volumique, déterminée selon la

norme DIN EN ISO 1183, comprise entre 30 kg/m^3 et 350 kg/m^3.

14. Procédé pour la production d'une mousse à base de PMMA selon au moins l'une des revendications 12 à 13, **caractérisé en ce que** la composition selon au moins l'une des revendications 1 à 9 est polymérisée à une température comprise entre 20 °C et 100 °C et est par la suite moussée à une température comprise entre 130 °C et 250 °C.

15. Procédé selon la revendication 14, **caractérisé en ce que** la polymérisation et le moussage sont effectués au moins en partie simultanément.

REFERENCES CITED IN THE DESCRIPTION

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