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(54) **Adhesive compositions for easy application and improved durability**

Klebstoffzusammensetzungen für einfaches Auftragen und verbesserte Haltbarkeit

Compositions adhésives pour une application facile et une durabilité améliorée

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EP 2 281 860 B9

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Description

TECHNICAL FIELD

5 **[0001]** This invention relates to adhesive compositions having an improved set of physical properties especially at elevated temperatures yet having low modulus and thus capable of being easily applied.

BACKGROUND OF THE INVENTION

10 **[0002]** Pressure-sensitive adhesives (PSA) have been known and used for a long time in the art, as they provide many desirable characteristics such as ease of application and a wide range of performance characteristics. Some of the common pressure-sensitive adhesives are formulations based upon acrylates, natural rubbers, synthetic rubbers, vinyl acetates, and silicones. Acrylic PSAs are of particular utility in that they are relatively low in cost, adhere well to a variety of different surfaces, and can be formulated to build adhesion to a surface. Many examples of acrylic pressure sensitive adhesives are described in Pressure Sensitive Adhesives Technology, 1st Edition, 1996, Istvan Benedek and Luc J. Heymans, which is incorporated here by reference. An important factor affecting the performance of an acrylic pressure sensitive adhesive is the shear adhesion failure temperature, commonly referred to as SAFT. SAFT defines the upper working temperature of an adhesive and is the upper temperature limit at which the adhesive is able to support a certain amount of weight. However, acrylic PSAs typically have poor high temperature performance. In general, the ease of application of an acrylic pressure-sensitive adhesive relates to the ability of the adhesive to flow or conform to a given substrate with only minimal external force being applied. The greater an adhesive's ability to flow and/or reflow over a surface, the greater its ability to bond to the surface due to higher contact area.

15 **[0003]** Viscoelastic property characterization of adhesives is an important and most successful rheological tool to study the adhesive's performance. Generally, the viscoelasticity of adhesives is most often determined by dynamic mechanical analysis (DMA). In principle, the adhesion process can be followed easily by using viscoelastic and dynamic mechanical rheological measurements, as the formation of bonds between adhesive and substrate and the flow of an adhesive onto a substrate is reflected in the change of viscoelastic properties. For example, the degree to which the adhesive exhibits more solid-like or liquid-like properties is dependent upon both temperature and time. With dynamic mechanical analysis, a sinusoidal force or stress is applied to an adhesive sample and the resulting sinusoidal deformation or strain is monitored. The sample strain response lags behind the input stress wave with respect to time and this lag is known as the phase angle, δ . The ratio of the dynamic stress to the dynamic strain yields the complex modulus, G^* , which can be further broken down to yield the storage (or elastic) modulus, G' , and the loss (or viscosity) modulus, G'' . The storage modulus, G' , represents the ability of the adhesive to store energy and it is related to the stiffness of the material. The loss modulus, G'' represents the heat dissipated by the adhesive as a result of the material's given molecular motions and this reflects the flow characteristics of the composition. The ratio of the loss and storage moduli provides another useful quantity called $\tan \delta$ (tan delta), where $\tan \delta = G''/G'$. $\tan \delta$ is associated with the viscoelasticity of the adhesive where a low value (less than 1.0) indicates more solid-like viscoelasticity and a high value (greater than 1.0) reflects more liquid-like viscoelasticity. The values of G^* , G' and G'' are dependent upon temperature and frequency. Accordingly, the ability of the adhesive to flow at a given temperature will be reflected by its storage and loss moduli and $\tan \delta$ values.

20 **[0004]** EP 1 639 987 A1 refers to a dental adhesive composition comprising (a) at least one carboxylic acid functional polymer; (b) at least one acid derivative with stronger acidity than the carboxylic acid functional polymer (a), substituted with at least one polymerizable ethylenically unsaturated group; (c) 0.1 to 10 weight % of water; wherein the carboxylic acid functional polymer (a) and the acid derivative (b) are present at least in an amount effective that the dental composition exhibit shear thinning and/or a viscosity from 1.0 to 20 Pas, when measured with a plate/plate geometry and at a shear rate of 0.5 to 1 s⁻¹.

25 **[0005]** What is desired is an adhesive composition having improved resistance to deformation in a shear mode at an elevated temperature, i.e., a high SAFT value, as well as ease of application which is reflected in a $\tan \delta$ value of greater than 0.8 as measured at room temperature.

BRIEF SUMMARY OF THE INVENTION

30 **[0006]** The primary object of the invention is to provide an adhesive composition comprising at least two curing stages, whereby the composition possess excellent wet out characteristics after a first curing stage, and improved stiffness and temperature resistance after a second sequential curing stage.

35 **[0007]** More particularly, the object of the invention is to provide an adhesive composition having a specific minimum $\tan \delta$ value resulting from a first curing stage and a specific minimum elastic modulus value and shear adhesion failure temperature value resulting from a second sequential curing stage.

[0008] More particularly still, the object of the invention is to provide an adhesive composition having excellent wet out characteristics as reflected in a tan delta value of at least 0.5, preferably greater than 0.5, more preferably greater than 0.8 as measured at 20 °C resulting from a first curing stage, and improved stiffness and temperature resistance as reflected in a storage elastic modulus of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²), respectively, which result from a second sequential curing stage.

[0009] In general, the above objects and advantages of the present invention are attained most broadly by an adhesive composition as defined in Claim 1. Further, especially preferred embodiments are the subject-matter of the respective dependent claims or sub-claims, respectively.

[0010] Especially, the above objects and advantages of the present invention are attained most broadly by an adhesive composition which is free of a mono-functionalized oligomer and encompasses a combination of 1) a crosslinkable acrylic copolymer, 2) a multi-functionalized crosslinkable oligomer, and 3) a photoinitiator which initiates polymerization of the oligomer.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0011] The terms "comprises," "comprising," or any other variation thereof, are intended to cover a non-exclusive inclusion, such that a process, method, article, or apparatus that comprises a list of elements does not include only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. An element preceded by "comprises ... a" does not, without more constraints, preclude the existence of additional identical elements in the process, method, article, or apparatus that comprises the element.

[0012] As used herein, the term "adhesive" refers to a viscoelastic material which adheres instantaneously to most substrates with the application of slight pressure and remains permanently tacky. An adhesive within the meaning of the term as used herein if it has the properties of a pressure-sensitive adhesive per se or functions as a pressure-sensitive adhesive by admixture with tackifiers, plasticizers or other additives. For more information concerning pressure sensitive adhesives, in general, see for example, Pressure Sensitive Adhesives and Applications, 2nd Ed., by István Benedek (Marcel Dekker 2005) and Handbook of Adhesive Technology, 2nd Ed., edited by A. Pizzi and K. L. Mittal (Marcel Dekker 2003).

[0013] A "copolymer" as used herein, refers to polymers formed by the polymerization of reaction of at least two different monomers. For example, the term "copolymer" includes the co-polymerization reaction product of ethylene and an α -olefin, such as 1-hexene. The term "copolymer" is also inclusive of, for example, the co-polymerization of a mixture of ethylene, propylene, 1-propene, 1-butene, 1-hexene, and 1-octene. As used herein, a copolymer identified in terms of a plurality of monomers, e.g., "propylene ethylene copolymer", refers to a copolymer in which either monomer may copolymerize in a higher weight or molar percent than the other monomer or monomers. However, the first listed monomer preferably polymerizes in a higher weight percent than the second listed monomer.

Crosslinkable Acrylic Copolymers

[0014] A wide variety of crosslinkable acrylate copolymers can be used and are known in the polymer and adhesive arts, as are methods of preparing the monomers and polymers. Generally, acrylic copolymers are capable of undergoing a crosslinking polymerization reaction with itself or other polymerizable compounds to form a three-dimensional structure and may be further defined as either solvent-borne or solvent-free acrylic copolymers. In preferred embodiments of the invention, the crosslinkable acrylic copolymer is a solvent-borne acrylic copolymer. In other preferred embodiments, the crosslinkable acrylic copolymer is a solvent-free acrylic copolymer. Solvent-borne acrylic copolymers are adhesives in which volatile organic compounds are the major solvent or dispersant. In contrast, solvent-free acrylic copolymers have an absence of any organic solvent in adhesive. In some embodiments of the present invention, acrylate copolymers may include a comonomer selected from the group consisting of acrylamide, acrylonitrile, acrylic acid, alpha-methyl styrene, butyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, glycidylmethacrylate, 2-hydroxyethylmethacrylate, hexyl acrylate, hydroxyethyl acrylate, isobornyl acrylate, isobutyl acrylate, isooctyl acrylate, isodecyl acrylate, isononyl acrylate, methacrylic acid, methyl acrylate, methacrylonitrile, n-vinyl caprolactam, nonyl acrylate, caprolactam, propyl acrylate, tert-butyl acrylate, vinyl acetate, vinyl pyrrolidone, styrene, and combinations thereof.

[0015] Examples of useful monomers for the acrylate copolymers include, but not exclusively, the following groups:

Group A - acrylic acid esters of an alkyl alcohol (preferably a non-tertiary alcohol), the alcohol containing from 1 to 14 (preferably from 4 to 14) carbon atoms and include, for example, methyl acrylate, ethyl acrylate, n-butyl acrylate, t-butyl acrylate, hexyl acrylate, isooctyl acrylate, 2-ethylhexyl acrylate, isononyl acrylate, isobornyl acrylate, phenoxyethyl acrylate, decyl acrylate, and dodecyl acrylate;

Group B - methacrylic acid esters of an alkyl alcohol (preferably a non-tertiary alcohol), the alcohol containing from 1 to 14 (preferably from 4 to 14) carbon atoms and include, for example, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate and t-butyl methacrylate;

Group C - (meth)acrylic acid monoesters of polyhydroxy alkyl alcohols such as 1,2-ethanediol, 1,2-propanediol, 1,3-propane diol, the various butyl diols, the various hexanediols, glycerol, such that the resulting esters are referred to as hydroxyalkyl (meth)acrylates;

Group D - multifunctional (meth)acrylate esters such as 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, glycerol diacrylate, glycerol triacrylate, and neopentyl glycol diacrylate although these monomers are generally not preferred for reactive extrusion or melt blending;

Group E - macromeric (meth)acrylates such as (meth)acrylate-terminated styrene oligomers and (meth)acrylate-terminated polyethers, such as are described in PCT Patent Application WO 84/03837 and European Patent Application EP 140941; and

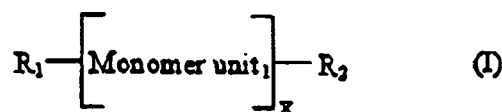
Group F - (meth)acrylic acids and their salts with alkali metals, including, for example, lithium, sodium, and potassium, and their salts with alkaline earth metals, including, for example, magnesium, calcium, strontium, and barium.

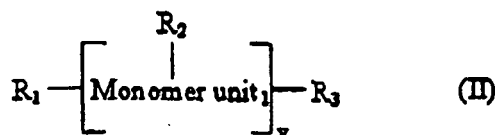
[0016] In preferred embodiments of the present invention, the crosslinkable acrylate copolymer includes a comonomer comprising ethyl acrylate, 2-ethylhexyl acrylate, methyl acrylate, vinyl acetate and combinations thereof. In other preferred embodiments, the crosslinkable acrylate copolymer is a solvent-borne crosslinkable acrylate copolymer comprising a comonomer which includes 2-ethylhexyl acrylate, methyl acrylate, vinyl acetate and combinations thereof. An example of a commercially available solvent-borne acrylate copolymer suitable for use in the present invention includes Cytec GMS 2480 from Cytec Industries, Inc., West Paterson, New Jersey, U.S.A. Cytec GMS 2480 acrylic copolymer is also an example of a thermally and chemically-curable solvent-borne adhesive which includes a crosslinking agent comprising aluminum (III) acetylacetonate (AlAcAc).

[0017] In still other preferred embodiments, the crosslinkable acrylate copolymer includes a benzophenone-functionalized acrylic copolymer, preferably a benzophenone-functionalized solvent-free acrylic copolymer comprising 2-ethylhexyl acrylate or butyl acrylate comonomer. In still yet other preferred embodiments, the crosslinkable acrylate copolymer is a solvent-free crosslinkable benzophenone-functionalized acrylate copolymer which includes a copolymer comprising 2-ethylhexyl acrylate or butyl acrylate comonomer. Examples of such acrylate copolymers are commercially available solvent-free acrylate copolymers sold under the trademark acResin®, particularly, acResin® A260 UV from BASF Corporation, Charlotte, North Carolina, U.S.A. The acResin® A260 UV acrylic copolymer is also an example of a UV radiation-curable solvent-free adhesive having a chemically built-in photoreactive chemical moiety.

Multi-functionalized Crosslinkable Oligomers

[0018] A multi-functionalized crosslinkable oligomer referred to herein is an oligomer having two or more chemically functional moieties capable of undergoing a crosslinking polymerization reaction with itself or other polymerizable compounds to form a three-dimensional structure. The "oligomer" portion of multi-functionalized oligomers refers to a polymer-like compound consisting of a finite number of monomer units, in contrast to a polymer which, at least in principle, consists of an unlimited number of monomers. The upper limit of monomer units is typically less than 50, preferably less than 25 and most preferably, less than 10. The term "telomere" is sometimes used synonymously with oligomer. The oligomer may comprise a single molecular structure as the monomer unit or different molecular structures as comonomer units. Examples of typical oligomeric monomer and comonomer units suitable for use in the present invention include, but are not limited to, acrylate, acrylic, epoxy, polyether, polyol, polyester, saturated and unsaturated rubber, polyurethane and combinations thereof. In a preferred embodiment of the present invention, the oligomeric monomer or comonomer unit is polyurethane. The functional moieties of multi-functionalized oligomers may include, for example, di-functional moieties with terminally positioned moieties, one at each end of the oligomer, or tri-functional moieties, typically comprising one grafted moiety within the oligomer chain and two terminally positioned moieties. Multi-functionalized oligomers useful in the adhesive composition may include, but are not limited to, the represented by structures (I), (II) and (III) shown below:





[0019] Where R_1 , R_2 and R_3 represent functional moieties and may be the same or different functional moiety. In the exemplary structures above, terminal functionalized oligomers are shown in structures (I) and (III), while a terminal and grafted functionalized oligomer is shown in structure (II). Examples of suitable functional moieties include, but not limited to, an acrylate moiety, epoxy moiety, hydroxy moiety and combinations thereof. In one preferred embodiment of the invention, the functional moiety is an acrylate moiety. In another preferred embodiment of the invention, the functional moiety is epoxy or epoxy and hydroxy. As described above, the monomer unit may include one or two or more chemically different repeating units. Examples of commercially available multi-functionalized crosslinkable oligomers include, but are not limited to, urethane multi-acrylate functionalized oligomer, such as, for example, CN 962, CN 964, CN 965, CN 934 and CN 972 from Sartomer Company, Inc, Exton, Pennsylvania, U.S.A.; and ACTI-LANE 130, 170, 270, and 290 supplied by Akzo Nobel Resins, Baxley, Georgia, U.S.A.; GE-NOMER 4269 from Rahn U.S.A. Corporation, Aurora, Illinois, U.S.A; and Ebecryl 230, 270, 8803, 4827, and 6700 from UCB Chemicals, Smyrna, Georgia, U.S.A.

Photoinitiator

[0020] A photoinitiator refers to any compound that, by exposure to electromagnetic radiation, undergoes a photoreaction, producing one or more reactive species. These reactive species are capable of initiating the polymerization of reaction of other polymerizable compounds within the composition, and may include, for example, free-radical species and cationic species. In general, most free-radical photoinitiators are reactive to UV radiation having a wavelength between 200 to 400 nm, but some free-radical species have been developed to react to radiation in the IR range. Cationic photoinitiators produce Brönsted or Lewis acid and can be activated by exposure to UV or electron beam radiation. In preferred embodiment of the present invention, a photoinitiator polymerizes the multi-functionalized oligomer. Exemplary photoinitiators useful for polymerizing the functionalized oligomers include acetophenones, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoin, benzophenones, thioxanthenes, onium salts, and combination thereof. Suitable free radical photoinitiators can include benzoin ethers, such as benzoin methyl ether or benzoin isopropyl ether, substituted benzoin ethers, such as anisoin methyl ether, substituted acetophenones, such as 2,2-diethoxyacetophenone and 2,2-dimethoxy-2-phenylacetophenone, substituted alpha-ketols, such as 2-methyl-2-hydroxypropionophenone, aromatic sulfonyl chlorides, such as 2-naphthalene-sulfonyl chloride, and photoactive oximes, such as 1-phenyl-1,2-propanedione-2(O-ethoxycarbonyl)oxime. Free radical photoinitiators for use in the compositions of the invention include, but are not limited to, commercially available compounds such as Irgacure 651 and 819 from CIBA Specialty Chemicals Corp.; Tarrytown, New Jersey, U.S.A. An exemplary cationic photoinitiator which is commercially available includes [4-[(2-Hydroxytetradecyl)oxy]phenyl]phenyliodonium hexafluoroantimonate from Aldrich Chemical Company, Milwaukee, Wisconsin, U.S.A.

Crosslinking Agent

[0021] A crosslinking agent referred to herein is any substance that promotes or regulates intermolecular covalent bonding between acrylic copolymer chains, linking them together to create a more rigid structure. Exemplary crosslinking agents useful for polymerizing acrylic copolymers, particularly, solvent-borne acrylic copolymers include amino resins, aziridines, melamines, isocyanates, metal acid esters, metal chelates, multifunctional propylene imines, and polycarbo-diimides. In preferred embodiments of the present invention, the crosslinking agent include metal acid esters comprising aluminum(III) acetylacetonate (AlAcAc), chromium(III) acetylacetonate (CrAcAc), iron(III) acetylacetonate (FeAcAc), cobalt(II) acetylacetonate (CoAcAc), nickel(II) acetylacetonate (NiAcAc), manganese(III) acetylacetonate (MnAcAc), titanium(IV) acetylacetonate (TiAcAc), zinc(II) acetylacetonate (ZnAcAc), zirconium(IV) acetylacetonate (ZrAcAc), and combinations thereof. In a more preferred embodiment, the crosslinking agent is aluminum (III) acetylacetonate (AlAcAc).

The crosslinking agent may be added as a separate component during fabrication of the adhesive compositions or may have been previously incorporated into the solvent-borne acrylic copolymer by a supplier of the same.

[0022] The term "curing" is typically used as a synonym for crosslinking but can also refer to a combination of additional polymerization reaction plus crosslinking. Curing of crosslinkable adhesive compositions, particularly, acrylic based adhesives may be accomplished generally by thermal, chemical and/or radiation crosslinking techniques. In general, thermal crosslinking includes evaporation or drying of a solvent or dispersant from the adhesive composition. Thermal crosslinking may further include a chemical crosslinking reaction involving the use of one or more crosslinking agents which are activated by the evaporation of solvent from the adhesive composition. For those preferred embodiments employing solvent-borne crosslinkable acrylic copolymers, the acrylic copolymer undergoes thermal and chemical induced crosslinking reactions during a first curing stage by evaporation of a solvent of the adhesive composition. Radiation crosslinking techniques include exposure to electromagnetic radiation of any frequency and preferably include infrared (IR) radiation, visible light, ultraviolet (UV) radiation, X-rays and gamma rays. Radiation crosslinking also includes electron beam radiation methods and exposure to sunlight. For those preferred embodiment employing crosslinkable benzophenone-functionalized acrylic copolymers, particularly, crosslinkable solvent-free benzophenone-functionalized acrylic copolymers, the acrylic copolymer undergoes radiation induced crosslinking reaction during the first curing stage by exposure to UV or electron beam radiation, preferably UV radiation and more preferably UV radiation having a wavelength of less than 300 nm. In all embodiments of the present invention, the crosslinkable multi-functionalized oligomer or oligomers undergo a radiation induced crosslinking reaction during a second curing stage by exposure to UV radiation from a UV bulb or sunlight, preferably, UV radiation having a wavelength of least 200 nm, more preferably by UV radiation having a wavelength of between 300 to 500 nm, and most preferably, by UV radiation having a wavelength of between 320 to 380 nm.

[0023] The present invention will be explained in the following in detail and on a more general level:

According to a first aspect of the present invention, there is provided an adhesive composition comprising:

(a) a crosslinkable acrylic copolymer;

(b) a multi-functionalized crosslinkable oligomer;

(c) a photoinitiator which initiates polymerization of the oligomer and is present in an amount of between 0.1 to 5% by weight relative to the dry weight of the acrylic copolymer; and

wherein the composition is free of a mono-functionalized oligomer and has:

(i) a first curing stage whereupon the composition exhibits a $\tan \delta$ value greater than 0.8 as measured at 20 °C, and

(ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

[0024] The acrylic copolymer may be a solvent-borne or solvent-free acrylic copolymer.

[0025] The acrylic copolymer may be crosslinked during the first curing stage by evaporation of a solvent or exposure to light having a wavelength less than 300 nm.

[0026] The oligomer may be present in an amount of between 5 to 40% by weight relative to the dry weight of the acrylic copolymer.

[0027] The oligomer may be crosslinked during the second curing stage by exposure to light having a wavelength of at least 200 nm.

[0028] Especially, the oligomer may be crosslinked during the second curing stage by exposure to light having a wavelength of between 300 to 500 nm.

[0029] Particularly, the oligomer may be crosslinked during the second curing stage by exposure to light having a wavelength of between 320 to 440 nm.

[0030] Usually, the composition may exhibit a $\tan \delta$ value of less than 0.8 as measured at 20 °C after the second curing stage.

[0031] Furthermore, the composition may exhibit a room temperature shear adhesion value of least 500 hours at 5 lb/in² (0.352 Kg/cm²) after the second curing stage.

[0032] The acrylic copolymer may comprise a comonomer selected from the group consisting of acrylamide, acrylonitrile, acrylic acid, alpha-methyl styrene, butyl acrylate, ethyl acrylate, n-butyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, glycidylmethacrylate, 2-hydroxyethylmethacrylate, hexyl acrylate, hydroxyethyl acrylate, isobornyl acrylate,

isobutyl acrylate, iso-octyl acrylate, isodecyl acrylate, isononyl acrylate, methacrylic acid, methyl acrylate, methacrylonitrile, n-vinyl caprolactam, nonyl acrylate, caprolactam, propyl acrylate, tert-butyl acrylate, vinyl acetate, vinyl pyrrolidone, styrene, and combinations thereof.

[0033] Also, the acrylic copolymer may be a solvent-borne acrylic copolymer comprising 2-ethylhexyl acrylate and vinyl acetate comonomers.

[0034] Especially, the acrylic copolymer may be a solvent-free benzophenone-functionalized acrylic copolymer.

[0035] Especially, the acrylic copolymer may be a solvent-free benzophenone-functionalized acrylic copolymer comprising 2-ethylhexyl acrylic or butyl acrylic comonomers.

[0036] In addition, the composition as described before may further comprise a crosslinking agent which reacts with the solvent-borne or solvent-free acrylic copolymer.

[0037] The crosslinking agent may be selected from the group consisting of amino resins, aziridines, melamines, isocyanates, metal acid esters, metal chelates, multifunctional propylene imines, and polycarbodiimides.

[0038] Also, the crosslinking agent may be selected from the group consisting of aluminum(III) acetylacetonate (AlAcAc), chromium(III) acetylacetonate (CrAcAc), iron(III) acetylacetonate (FeAcAc), cobalt(II) acetylacetonate (CoAcAc), nickel(II) acetylacetonate (NiAcAc), manganese(III) acetylacetonate (MnAcAc), titanium(IV) acetylacetonate (TiAcAc), zinc(II) acetylacetonate (ZnAcAc), zirconium(IV) acetylacetonate (ZrAcAc), and combinations thereof.

[0039] Especially, the crosslinking agent may be aluminum (III) acetylacetonate (AlAcAc).

[0040] The oligomer may comprise a functional moiety selected from the group consisting of acrylate, epoxy, hydroxy, and combinations thereof.

[0041] Especially, the functional moiety of the oligomer may be acrylate.

[0042] Also, the functional moiety of the oligomer may be epoxy.

[0043] The oligomer may comprise a monomer or comonomer selected from the group consisting of acrylate, acrylic, epoxy, polyether, polyol, polyester, saturated and unsaturated rubber, polyurethane and combinations thereof.

[0044] The photoinitiator may be selected from the group consisting of acetophenones, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoin, benzophenones, thioxanthenes, onium salts, and combination thereof.

[0045] Especially, the composition may exhibit a visible light transmission of between 80 to 100%.

[0046] Furthermore, according to another aspect of the present invention, there is provided an adhesive composition comprising:

(a) a crosslinkable acrylic copolymer comprising comonomers selected from the group consisting of ethyl acetate, 2-ethylhexyl acrylate, methyl acrylate, vinyl acetate and combinations thereof;

(b) a multi-functionalized crosslinkable oligomer comprising a functional moiety selected from the group consisting of acrylate, epoxy, hydroxy, and combinations thereof;

(c) a photoinitiator which initiates polymerization of the oligomer;

(d) a crosslinking agent which reacts with the acrylic copolymer; and

wherein the composition is free of a mono-functionalized oligomer and has:

(i) a first curing stage whereupon the composition exhibits a $\tan \delta$ value greater than 0.8 as measured at 20 °C, and

(ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

[0047] The acrylic copolymer may be a solvent-borne acrylic copolymer.

[0048] The oligomer may present in an amount of between 5 to 40% by weight relative to the dry weight of the acrylic copolymer.

[0049] The photoinitiator may be present in an amount of between 0.5 to 5% by weight relative to the dry weight of the acrylic copolymer.

[0050] The acrylic copolymer may be crosslinked during the first curing stage by evaporation of a solvent.

[0051] The crosslinking agent may be selected from the group consisting of aluminum(III) acetylacetonate (AlAcAc), chromium(III) acetylacetonate (CrAcAc), iron(III) acetylacetonate (FeAcAc), cobalt(II) acetylacetonate (CoAcAc), nickel(II) acetylacetonate (NiAcAc), manganese(III) acetylacetonate (MnAcAc), titanium(IV) acetylacetonate (TiAcAc), zinc(II) acetylacetonate (ZnAcAc), zirconium(IV) acetylacetonate (ZrAcAc), and combinations thereof.

[0052] The oligomer may comprise a monomer or comonomer selected from the group consisting of acrylate, acrylic,

epoxy, ether polyol, ester, saturated and unsaturated rubber, urethane and combinations thereof.

[0053] The photoinitiator may be selected from the group consisting of acetophenone, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoin, benzophenone, thioxanthone, and combination thereof.

[0054] The oligomer may be crosslinked during the second curing stage by exposure to light having a wavelength of at least 200 nm.

[0055] The oligomer may be crosslinked during the second curing stage by exposure to light having a wavelength of between 320 to 440 nm.

[0056] The composition may exhibit a tan delta value of less than 0.8 as measured at 20 °C after the second curing stage.

[0057] The composition may exhibit a room temperature shear adhesion value of least 500 hours at 5 lb/in² (0.352 Kg/cm²) after the second curing stage.

[0058] Further, the composition may exhibit a visible light transmission of between 80 to 100%.

[0059] Furthermore, according to yet another aspect of the present invention, there is provided an adhesive composition comprising:

(a) a solvent-borne crosslinkable acrylic copolymer comprising comonomers selected from the group consisting of ethyl acetate, 2-ethylhexyl acrylate, methyl acrylate and vinyl acetate and combinations thereof;

(b) a multi-functionalized crosslinkable oligomer comprising an acrylate functional moiety and a urethane monomer or comonomer; wherein the oligomer is present in an amount of between 5 to 40% by weight relative to the dry weight of the acrylic copolymer;

(c) a photoinitiator which initiates polymerization of the oligomer and is present in an amount of between 0.5 to 5% by weight relative to the dry weight of the acrylic copolymer;

(d) a crosslinking agent which reacts with the acrylic copolymer; and

wherein the composition is free of a mono-functionalized oligomer and has:

(i) a first curing stage whereupon the composition exhibits a tan δ value greater than 0.8 as measured at 20 °C, and

(ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

[0060] The acrylic copolymer may be crosslinked during the first curing stage by evaporation of a solvent.

[0061] The oligomer may be crosslinked during the second curing stage by exposure to light having a wavelength of at least 200 nm.

[0062] Especially, the oligomer may be crosslinked during the second curing stage by exposure to light having a wavelength of between 320 to 440 nm.

[0063] The composition may exhibit a tan delta value of less than 0.8 as measured at 20 °C after the second curing stage.

[0064] Further, the composition may exhibit a room temperature shear adhesion value of least 500 hours at 5 lb/in² (0.352 Kg/cm²) after the second curing stage.

[0065] The photoinitiator may be selected from the group consisting of acetophenone, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoin, benzophenone, thioxanthone, and combinations thereof.

[0066] E.g. the photoinitiator may be an aryl phosphineoxide or aryl sulfonium or aryl iodonium salt of hexafluorophosphate.

[0067] The crosslinking agent may be selected from the group consisting of aluminum(III) acetylacetonate (AlAcAc), chromium(III) acetylacetonate (CrAcAc), iron(III) acetylacetonate (FeAcAc), cobalt(II) acetylacetonate (CoAcAc), nickel(II) acetylacetonate (NiAcAc), manganese(III) acetylacetonate (MnAcAc), titanium(IV) acetylacetonate (TiAcAc), zinc(II) acetylacetonate (ZnAcAc), zirconium(IV) acetylacetonate (ZrAcAc), and combinations thereof.

[0068] The composition may exhibit a visible light transmission of between 80 to 100%.

[0069] Further, according to even yet another aspect of the present invention, there is provided an adhesive composition comprising:

(a) a benzophenone-functionalized crosslinkable acrylic copolymer;

(b) a multi-functionalized crosslinkable oligomer;

(c) a photoinitiator which initiates polymerization of the oligomer; and

wherein the composition is free of a mono-functionalized oligomer and has:

(i) a first curing stage whereupon the composition exhibits a $\tan \delta$ value greater than 0.8 as measured at 20 °C, and

(ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

[0070] The acrylic copolymer may be a solvent-free benzophenone-functionalized acrylic copolymer.

[0071] Also, the acrylic copolymer may further comprise 2-ethylhexyl acrylate or butyl acrylate comonomers.

[0072] Especially, the acrylic copolymer may be crosslinked during the first curing stage by exposure to light having a wavelength less than 300 nm.

[0073] The oligomer may comprise an acrylate functional moiety and a urethane monomer or comonomer.

[0074] Especially, the oligomer may be present in an amount of between 5 to 40% by weight relative to the dry weight of the acrylic copolymer.

[0075] The photoinitiator may be present in an amount of between 0.5 to 5% by weight relative to the dry weight of the acrylic copolymer.

[0076] Further, the oligomer may be crosslinked during the second curing stage by exposure to light having a wavelength greater than 300 nm.

[0077] Especially, the oligomer may be crosslinked during the second curing stage by exposure to light having a wavelength of between 320 to 440 nm.

[0078] Especially, the composition may exhibit a $\tan \delta$ value of less than 0.8 as measured at 20 °C after the second curing stage.

[0079] Further, the composition may exhibit a room temperature shear adhesion value of least 500 hours at 5 lb/in² (0.352 Kg/cm²) after the second curing stage.

[0080] The photoinitiator may be selected from the group consisting of acetophenone, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoin, benzophenone, thioxanthone, and combination thereof.

[0081] Especially, the composition may exhibit a visible light transmission of between 80 to 100%.

[0082] Finally, according to even yet another aspect of the present invention, there is provided an adhesive composition comprising:

(a) a solvent-free benzophenone-functionalized crosslinkable acrylic copolymer comprising 2-ethylhexyl acrylate or butyl acrylate comonomers;

(b) a multi-functionalized crosslinkable oligomer comprising an acrylate functional moiety and a urethane monomer or comonomer; wherein the oligomer is present in an amount of between 5 to 40% by weight relative to the dry weight of the acrylic copolymer;

(c) a photoinitiator which initiates polymerization of the oligomer and is present in an amount of between 0.5 to 5% by weight relative to the dry weight of the acrylic copolymer; and

wherein the composition is free of a mono-functionalized oligomer and has:

(i) a first curing stage whereupon the composition exhibits a $\tan \delta$ value greater than 0.8 as measured at 20 °C, and

(ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

[0083] The acrylic copolymer may crosslinked during the first curing stage by exposure to light having a wavelength less than 300 nm.

[0084] The oligomer may be crosslinked during the second curing stage by exposure to light having a wavelength greater than 300 nm.

[0085] The oligomer may be crosslinked during the second curing stage by exposure to light having a wavelength of between 320 to 440 nm.

[0086] The composition may exhibit a $\tan \delta$ value of less than 0.8 as measured at 20 °C after the second curing stage.

[0087] Further, the composition may exhibit a room temperature shear adhesion value of least 500 hours at 5 lb/in²

(0.352 Kg/cm²) after the second curing stage.

[0088] Especially, the photoinitiator is selected from the group consisting of acetophenone, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoin, benzophenone, thioxanthone, and combination thereof.

[0089] Also, the composition may exhibit a visible light transmission of between 80 to 100%.

[0090] Although specific embodiments of the present invention will now be described with reference to the drawings, it should be understood that such embodiments are by way of example only and merely illustrative of but a small number of the many possible specific embodiments which can represent applications of the principles of the present invention.

EXAMPLES

EXAMPLES 1-11

[0091] Examples 1-11 are illustrative of adhesive solutions comprising a solvent-borne crosslinkable acrylic copolymer and multi-functionalized crosslinkable oligomer according to the present invention. In a brown reaction vessel was placed an acrylic copolymer in the amounts shown in Table 1 and solvent to provide a mixture having a 43% total solids content. Representative solvents can be organic, and include, for example, acetone, cyclopentanone, 1,2-dimethoxyethane (glyme), ethyl acetate, heptane, hexane, isopropyl alcohol, methylene chloride, methyl-ethyl-ketone, methyl formate, nitromethane, pentanedione, toluene and the like. The multi-functionalized oligomer was then added neat to the acrylic copolymer/solvent mixture in the amounts shown in Table 1 and stirred. Once the oligomer was thoroughly mixed, the photoinitiator was added in the amounts shown in Table 1 along with a sufficient amount of solvent to adjust the mixture to one having a total solids content of 43%.

TABLE 1

Example	Acrylic Copolymer	Multi-Functional Oligomers		Photoinitiator
	Cytec 2480 (gram)	CN965 (gram)	CN964 (gram)	Irganox 819 (gram)
1	100	4.3	0	0.43
2	100	8.6	0	0.43
3	100	12.9	0	0.43
4	100	17.2	0	0.43
5	100	0	4.3	0.43
6	100	0	8.6	0.43
7	100	0	12.9	0.43
8	100	0	17.2	0.43
9	100	6.45	2.15	0.43
10	100	4.3	4.3	0.43
11	100	2.15	6.45	0.43

COMPARATIVE EXAMPLES 1-4

[0092] Comparative Examples 1-4 are illustrative of adhesive solutions comprising a solvent-borne acrylic copolymer and a combination of mono-functionalized and multi-functionalized oligomers. In a brown reaction vessel were placed the components shown in Table 2 in the same manner as described above for Examples 1-11, except that a combination of a mono-functionalized oligomer and multi-functionalized oligomer was used.

TABLE 2

Comparative Example	Acrylic Copolymer	Multi-Functional Oligomers		Mono-Functional Oligomer	Photoinitiator
	Cytec 2480 (gram)	CN965 (gram)	CN964 (gram)	Ebecryl CL 1039 (gram)	Irganox 819 (gram)
1	100	4.3	0	4.3	0.43

(continued)

Comparative Example	Acrylic Copolymer	Multi-Functional Oligomers		Mono-Functional Oligomer	Photoinitiator
	Cytec 2480 (gram)	CN965 (gram)	CN964 (gram)	Ebecryl CL 1039 (gram)	Irganox 819 (gram)
2	100	6.45	0	6.45	0.43
3	100	0	4.3	4.3	0.43
4	100	0	6.45	6.45	0.43

[0093] The adhesive solutions described above were coated onto a 90 lb polycoated natural Kraft release liner at a 12 mil wet thickness to yield a 3.5 gram/100 in² dry coating weight. The samples were dried at 23 °C for 10 minutes.

First Curing Stage of Adhesive Compositions

[0094] The above prepared coated samples of Examples 1-11 and Comparative Examples 1-4 were dried at 90 °C in a forced air oven for an additional 10 minutes. The samples were removed from the oven and allowed to cool for 5 minutes.

Second Curing Stage of Adhesive Compositions

[0095] A 2.0 mil clear Mylar film is laminated to the adhesive surface to form a test specimen for peel, tack and shear testing under Conditions A through D (described below). A silicone coated Mylar film is laminated to the adhesive surface to form a free test specimen for Rheology testing under Conditions E and F (described below). Each specimen was subjected to UV radiation using a Fusion UV D bulb at 15 feet/minute, 300 watts/inch. The Fusion UV D bulb has a range of spectral output between 340 to 440 nm.

Test Conditions

[0096] The release liner was removed from the test specimen prior to testing. Test specimens were subjected to the following conditions described below in Table 3 prior to testing.

TABLE 3

Conditions

A	1 st curing stage was completed before specimen is applied to a test panel for testing with no 2 nd curing stage and a 30 minute dwell time before testing.
B	1 st curing stage was completed before specimen is applied to a test panel for testing with 2 nd curing stage completed after application to the panel and a 30 minute dwell time before testing.
C	1 st curing stage was completed before specimen is applied to a test panel with 2 nd curing stage was completed after application to the panel and a 24 hour dwell time before testing.
D	1 st and 2 nd curing stages were completed before specimen is applied to a test panel and 30 minute dwell time before testing.
E	1 st curing stage was completed. Specimen was not applied to test panel.
F	1 st and 2 nd curing stages were completed. Specimen was not applied to test panel.

Test Methods

180° Peel Force Testing

[0097] 180° Peel Force measurements were determined as follows: A strip of tape is applied to a standard test panel (stainless steel) with controlled pressure. The tape is peeled from the panel at 180° angle at a rate of 12 inch/minute, during which time the force required to effect peel is measured. The peel force was determined using an Instron tensile tester in accordance with Pressure Sensitive Tape Council (PSTC)-16 Procedure A test method. The results are shown in Table 4.

TABLE 4

Example	Under Condition A (lb/in)	Under Condition B (lb/in)	Under Condition C (lb/in)	Under Condition D (lb/in)
1	4.5	4.6	4.7	4.1
2	5.0	4.2	5.0	3.3
3	4.8	4.1	4.5	2.7
4	5.2	3.8	4.3	3.1
5	4.6	4.3	5.1	4.0
6	5.0	4.1	4.2	2.6
7	5.2	3.6	3.8	2.5
8	5.0	3.2	3.6	2.4
9	4.8	3.9	4.8	3.1
10	4.8	3.8	4.6	3.1
11	4.6	3.8	4.4	2.9

Loop Tack Testing

[0098] Loop Tack measurements were determined as follows: A Mylar test specimen described above was then cut into strips 1 inch wide by 7 inches long. The specimen was brought into contact with a 24 mm x 24 mm (one square inch) surface of stainless steel test panel, with the only force applied being the weight of the pressure sensitive article itself. The specimen was then removed from the panel, with the force to remove the adhesive from the adherent measured by a recording instrument. The loop tack was determined using an Instron tensile tester in accordance with Pressure Sensitive Tape Council (PSTC)-16 Procedure A test method. The results are shown in Table 5.

TABLE 5

Example	Under Condition A (lb/in)	Under Condition D (lb/in)
1	3.7	2.8
2	3.4	2.2
3	4.1	1.7
4	4.7	1.2
5	3.0	2.0
6	4.4	1.8
7	5.6	1.2
8	5.1	0.6
9	3.0	1.6
10	3.5	1.3
11	3.5	1.1

Shear Adhesion Failure Temperature Testing

[0099] Shear Adhesion Failure Temperatures were determined as follows: A Mylar test specimen described above was then cut into strips 1 inch wide by 7 inches long. One end of the specimen was mounted onto stainless steel test panel with a total contact area of one square inch. A 1 kilogram weight attached to the opposite end of the specimen. The specimen was heated to a temperature of 100 F (38 °C) and allowed to equilibrate for 20 minutes at this temperature. The temperature of the specimen was increased at a rate of 0.5°/min to a maximum temperature of 425 °F (218 °C). The temperature at which the specimen becomes detached from the test panel was recorded. The Shear Adhesion Failure temperature was determined in accordance with Pressure Sensitive Tape Council (PSTC)-101 test method. The results are shown in Table 6.

EP 2 281 860 B9

TABLE 6

Example	Under Condition C (degrees F)
1	>425
2	>425
3	>425
4	>425
5	>425
6	>425
7	>425
8	>425
9	>425
10	>425
11	>425
Comparative Example	
1	380
2	323
3	343
4	358

Heated Shear Testing

[0100] Heated Shear was determined identically as described above for Shear Adhesion Failure Temperature, except that the specimen was heated to a temperature of 320 °F (160 °C) and the amount of time to failure, i.e., where specimen becomes detached from the test panel, was recorded. If no failure was observed, testing was stopped after 10,000 minutes. Heated Shear was determined in accordance with Pressure Sensitive Tape Council (PSTC)-107 Procedure G test method. The results are shown in Table 7.

TABLE 7

Example	Under Condition C (min)
1	>10,000
2	>10,000
3	>10,000
4	>10,000
5	>10,000
6	>10,000
7	>10,000
8	>10,000
9	>10,000
10	>10,000
11	>10,000

Room Temperature Shear Testing

[0101] Room Temperature Shear was determined identically as described above for Shear Adhesion Failure Temperature, except that a 2.3 kilogram weight was attached to the un-mounted end of the specimen and the specimen was heated to a temperature of 72 °F (22 °C). The amount of time to failure, i.e., where specimen becomes detached from the test panel, was recorded. If no failure was observed, testing was stopped after 500 hours. Room temperature shear was determined in accordance with Pressure Sensitive Tape Council (PSTC)-107 Procedure G test method. Room Temperature Shear was determined in accordance with Pressure Sensitive Tape Council (PSTC)-107 Procedure A test

EP 2 281 860 B9

method. The results are shown in Table 8.

TABLE 8

Example	Under Condition C (hours)
1	>500
2	>500
3	>500
4	>500
5	>500
6	>500
7	>500
8	>500
9	>500
10	>500
11	>500

DMA (Rheology) Testing

[0102] Rheology measurements were determined as follows: The specimen is secured to a dynamic mechanical analyzer, Model RDA III supplied by TA Instruments, New Castle, Delaware, U.S.A. Specifically, the specimen is placed on the bottom plate parallel plate rheometer having a thickness of 1.5 mm and 8 mm diameter and equilibrated at 20 °C. The top plate is pressed onto the specimen forming about a 1 mm gap. The specimen is heated to a maximum temperature of 70 °C and at a rate of 3°/min. Various measurements such as the storage modulus (or elastic modulus), G' ; the loss modulus, G'' ; the complex modulus, G^* , [the square root of the sum of (G') .sup.2 + (G'') .sup.2]; and the δ (tan delta), (ratio of the loss modulus divided by the storage modulus), and complex viscosity were recorded or calculated as function of time as the material sets. A temperature sweep at 10 radians/seconds and a strain of 0.1% were employed for the purpose of measuring the flow properties of the material in its molten state. The results are shown in Tables 9-11.

TABLE9

Example	Under Condition E		Under Condition F	
	Elastic Modulus at 20 °C (kPa)	Elastic Modulus at 70 °C (kPa)	Elastic Modulus at 20 °C (kPa)	Elastic Modulus at 70 °C (kPa)
1	145	30	280	53
2	116	27	405	75
3	92	25	417	83
4	70	19	628	115
5	166	32	334	55
6	138	27	579	81
7	107	25	739	98
8	88	20	1161	132
9	119	28	368	70
10	120	28	417	71
11	125	28	489	81
Comparative Example				
1	83	24	344	57
2	65	20	491	74
3	95	23	438	59
4	71	20	663	82

TABLE 10

Example	Under Condition E		Under Condition F	
	Tan delta at 20 °C	Tan delta at 70 °C	Tan delta at 20 °C	Tan delta at 70 °C
1	0.88	0.50	0.77	0.47
2	0.87	0.45	0.71	0.42
3	0.86	0.42	0.70	0.41
4	0.99	0.40	0.68	0.40
5	0.80	0.48	0.75	0.44
6	0.95	0.49	0.76	0.45
7	1.03	0.44	0.69	0.41
8	1.20	0.43	0.64	0.39
9	0.80	0.45	0.69	0.41
10	0.93	0.45	0.70	0.43
11	0.92	0.45	0.67	0.40
Comparative Example				
1	0.69	0.48	0.87	0.44
2	0.66	0.46	0.83	0.39
3	0.70	0.50	0.84	0.42
4	0.70	0.49	0.89	0.36

TABLE 11

Example	Complex Viscosity Under Condition E (kPa)
1	20500
2	14000
3	12000
4	9600
5	20600
6	19000
7	15000
8	14000
9	14000
10	16000
11	17000
Comparative Example	
1	10000
2	7300
3	11500
4	8600

[0103] It will be apparent to those skilled in the art that modifications and additions can be made to the various embodiments described above, without departing from the true scope and spirit of the present invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments set forth herein and that such embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows.

[0104] The present invention is further elucidated by the following items (aspects):

Item 1: An adhesive composition comprising:

(d) a crosslinkable acrylic copolymer;

(e) a multi-functionalized crosslinkable oligomer;

(f) a photoinitiator which initiates polymerization of the oligomer and is present in an amount of between 0.1 to 5% by weight relative to the dry weight of the acrylic copolymer; and

wherein the composition is free of a mono-functionalized oligomer and has:

(i) a first curing stage whereupon the composition exhibits a $\tan \delta$ value greater than 0.8 as measured at 20 °C, and

(ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

Item 2: The composition as defined in item 1 wherein the acrylic copolymer is a solvent-borne or solvent-free acrylic copolymer.

Item 3: The composition as defined in item 1 wherein the acrylic copolymer is crosslinked during the first curing stage by evaporation of a solvent or exposure to light having a wavelength less than 300 nm.

Item 4: The composition as defined in item 1 wherein the oligomer is present in an amount of between 5 to 40% by weight relative to the dry weight of the acrylic copolymer

Item 5: The composition as defined in item 1 wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of at least 200 nm.

Item 6: The composition as defined in item 1 wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of between 300 to 500 nm.

Item 7: The composition as defined in item 1 wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of between 320 to 440 nm.

Item 8: The composition as defined in item 1 wherein the composition exhibits a $\tan \delta$ value of less than 0.8 as measured at 20 °C after the second curing stage

Item 9: The composition as defined in item 1 wherein the composition exhibits a room temperature shear adhesion value of at least 500 hours at 5 lb/in² (0.352 Kg/cm²) after the second curing stage.

Item 10: The composition as defined in item 1 wherein the acrylic copolymer comprises a comonomer selected from the group consisting of acrylamide, acrylonitrile, acrylic acid, alpha-methyl styrene, butyl acrylate, ethyl acrylate, n-butyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, glycidylmethacrylate, 2-hydroxyethylmethacrylate, hexyl acrylate, hydroxyethyl acrylate, isobornyl acrylate, isobutyl acrylate, iso-octyl acrylate, isodecyl acrylate, isononyl acrylate, methacrylic acid, methyl acrylate, methacrylonitrile, n-vinyl caprolactam, nonyl acrylate, caprolactam, propyl acrylate, tert-butyl acrylate, vinyl acetate, vinyl pyrrolidone, styrene, and combinations thereof.

Item 11: The composition as defined in item 1 wherein the acrylic copolymer is a solvent-borne acrylic copolymer comprising 2-ethylhexyl acrylate and vinyl acetate comonomers.

Item 12: The composition as defined in item 1 wherein the acrylic copolymer is a solvent-free benzophenone-functionalized acrylic copolymer.

Item 13: The composition as defined in item 1 wherein the acrylic copolymer is a solvent-free benzophenone-functionalized acrylic copolymer comprising 2-ethylhexyl acrylate or butyl acrylic comonomers.

Item 14: The composition as defined in item 1 further comprising a crosslinking agent which reacts with the solvent-

borne or solvent-free acrylic copolymer.

Item 15: The composition as defined in item 14 wherein the crosslinking agent is selected from the group consisting of amino resins, aziridines, melamines, isocyanates, metal acid esters, metal chelates, multifunctional propylene imines, and polycarbodiimides.

Item 16: The composition as defined in item 14 wherein the crosslinking agent is selected from the group consisting of aluminum(III) acetylacetonate (AlAcAc), chromium(III) acetylacetonate (CrAcAc), iron(III) acetylacetonate (FeAcAc), cobalt(II) acetylacetonate (CoAcAc), nickel(II) acetylacetonate (NiAcAc), manganese(III) acetylacetonate (MnAcAc), titanium(IV) acetylacetonate (TiAcAc), zinc(II) acetylacetonate (ZnAcAc), zirconium(IV) acetylacetonate (ZrAcAc), and combinations thereof.

Item 17: The composition as defined in item 14 wherein the crosslinking agent is aluminum (III) acetylacetonate (AlAcAc).

Item 18: The composition as defined in item 1 wherein the oligomer comprises a functional moiety selected from the group consisting of acrylate, epoxy, hydroxy, and combinations thereof.

Item 19: The composition as defined in item 18 wherein the functional moiety of the oligomer is acrylate.

Item 20: The composition as defined in item 18 wherein the functional moiety of the oligomer is epoxy.

Item 21: The composition as defined in item 1 wherein the oligomer comprises a monomer or comonomer selected from the group consisting of acrylate, acrylic, epoxy, polyether, polyol, polyester, saturated and unsaturated rubber, polyurethane and combinations thereof.

Item 22: The composition as defined in item 1 wherein the photoinitiator is selected from the group consisting of acetophenones, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoines, benzophenones, thioxanthenes, onium salts, and combination thereof.

Item 23: The composition as defined in item 1 wherein the composition exhibits a visible light transmission of between 80 to 100%.

Item 24: An adhesive composition comprising:

- (a) a crosslinkable acrylic copolymer comprising comonomers selected from the group consisting of ethyl acetate, 2-ethylhexyl acrylate, methyl acrylate, vinyl acetate and combinations thereof;
- (b) a multi-functionalized crosslinkable oligomer comprising a functional moiety selected from the group consisting of acrylate, epoxy, hydroxy, and combinations thereof;
- (c) a photoinitiator which initiates polymerization of the oligomer;
- (d) a crosslinking agent which the acrylic copolymer; and

wherein the composition is free of a mono-functionalized oligomer and has:

- (i) a first curing stage whereupon the composition exhibits a $\tan \delta$ value greater than 0.8 as measured at 20 °C, and
- (ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

Item 25: The composition as defined in item 24 wherein the acrylic copolymer is a solvent-borne acrylic copolymer.

Item 26: The composition as defined in item 24 wherein the oligomer is present in an amount of between 5 to 40% by weight relative to the dry weight of the acrylic copolymer.

Item 27: The composition as defined in item 24 wherein the photoinitiator is present in an amount of between 0.5 to 5% by weight relative to the dry weight of the acrylic copolymer.

Item 28: The composition as defined in item 24 wherein the acrylic copolymer is crosslinked during the first curing stage by evaporation of a solvent

Item 29: The composition as defined in item 24 wherein the crosslinking agent is selected from the group consisting of aluminum(III) acetylacetonate (AlAcAc), chromium(III) acetylacetonate (CrAcAc), iron(III) acetylacetonate (FeAcAc), cobalt(II) acetylacetonate (CoAcAc), nickel(II) acetylacetonate (NiAcAc), manganese(III) acetylacetonate (MnAcAc), titanium(IV) acetylacetonate (TiAcAc), zinc(II) acetylacetonate (ZnAcAc), zirconium(IV) acetylacetonate (ZrAcAc), and combinations thereof.

Item 30: The composition as defined in item 24 wherein the oligomer comprises a monomer or comonomer selected from the group consisting of acrylate, acrylic, epoxy, ether polyol, ester, saturated and unsaturated rubber, urethane and combinations thereof.

Item 31: The composition as defined in item 24 wherein the photoinitiator is selected from the group consisting of acetophenone, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoin, benzophenone, thioxanthone, and combination thereof.

Item 32: The composition as defined in item 24 wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of at least 200 nm.

Item 33: The composition as defined in item 24 wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of between 320 to 440 nm.

Item 34: The composition as defined in item 24 wherein the composition exhibits a tan delta value of less than 0.8 as measured at 20 °C after the second curing stage.

Item 35: The composition as defined in item 24 wherein the composition exhibits a room temperature shear adhesion value of least 500 hours at 5 lb/in² (0.352 Kg/cm²) after the second curing stage.

Item 36: The composition as defined in item 24 wherein the composition exhibits a visible light transmission of between 80 to 100%.

Item 37: An adhesive composition comprising:

(a) a solvent-borne crosslinkable acrylic copolymer comprising comonomers selected from the group consisting of ethyl acetate, 2-ethylhexyl acrylate, methyl acrylate and vinyl acetate and combinations thereof;

(b) a multi-functionalized crosslinkable oligomer comprising an acrylate functional moiety and a urethane monomer or comonomer; wherein the oligomer is present in an amount of between 5 to 40% by weight relative to the dry weight of the acrylic copolymer;

(c) a photoinitiator which initiates polymerization of the oligomer and is present in an amount of between 0.5 to 5% by weight relative to the dry weight of the acrylic copolymer;

(d) a crosslinking agent which reacts with the acrylic copolymer; and

wherein the composition is free of a mono-functionalized oligomer and has:

(i) a first curing stage whereupon the composition exhibits a tan δ value greater than 0.8 as measured at 20 °C, and

(ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

Item 38: The composition as defined in item 37 wherein the acrylic copolymer is crosslinked during the first curing

stage by evaporation of a solvent.

Item 39: The composition as defined in item 37 wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of at least 200 nm.

Item 40: The composition as defined in item 37 wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of between 320 to 440 nm.

Item 41: The composition as defined in item 37 wherein the composition exhibits a tan delta value of less than 0.8 as measured at 20 °C after the second curing stage.

Item 42: The composition as defined in item 37 wherein the composition exhibits a room temperature shear adhesion value of least 500 hours at 5 lb/in² (0.352 Kg/cm²) after the second curing stage.

Item 43: The composition as defined in item 37 wherein the photoinitiator is selected from the group consisting of acetophenone, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoin, benzophenone, thioxanthone, and combinations thereof.

Item 44: The composition as defined in item 37 wherein the photoinitiator is an aryl phosphineoxide or aryl sulfonium or aryl iodonium salt of hexafluorophosphate.

Item 45: The composition as defined in item 37 wherein the crosslinking agent is selected from the group consisting of aluminum(III) acetylacetonate (AlAcAc), chromium(III) acetylacetonate (CrAcAc), iron(III) acetylacetonate (FeAcAc), cobalt(II) acetylacetonate (CoAcAc), nickel(II) acetylacetonate (NiAcAc), manganese(III) acetylacetonate (MnAcAc), titanium(IV) acetylacetonate (TiAcAc), zinc(II) acetylacetonate (ZnAcAc), zirconium(IV) acetylacetonate (ZrAcAc), and combinations thereof.

Item 46: The composition as defined in item 37 wherein the composition exhibits a visible light transmission of between 80 to 100%.

Item 47: An adhesive composition comprising:

(a) a benzophenone-functionalized crosslinkable acrylic copolymer;

(b) a multi-functionalized crosslinkable oligomer;

(c) a photoinitiator which initiates polymerization of the oligomer; and

wherein the composition is free of a mono-functionalized oligomer and has:

(i) a first curing stage whereupon the composition exhibits a tan δ value greater than 0.8 as measured at 20 °C, and

(ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

Item 48: The composition as defined in item 47 wherein the acrylic copolymer is a solvent-free benzophenone-functionalized acrylic copolymer.

Item 49: The composition as defined in item 47 wherein the acrylic copolymer further comprising 2-ethylhexyl acrylate or butyl acrylate comonomers.

Item 50: The composition as defined in item 47 wherein the acrylic copolymer is crosslinked during the first curing stage by exposure to light having a wavelength less than 300 nm.

Item 51: The composition as defined in item 47 wherein the oligomer comprises an acrylate functional moiety and a urethane monomer or comonomer.

Item 52: The composition as defined in item 47 wherein the oligomer is present in an amount of between 5 to 40% by weight relative to the dry weight of the acrylic copolymer.

Item 53: The composition as defined in item 47 wherein the photoinitiator is present in an amount of between 0.5 to 5% by weight relative to the dry weight of the acrylic copolymer.

Item 54: The composition as defined in item 47 wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength greater than 300 nm.

Item 55: The composition as defined in item 47 wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of between 320 to 440 nm.

Item 56: The composition as defined in item 47 wherein the composition exhibits a tan delta value of less than 0.8 as measured at 20 °C after the second curing stage.

Item 57: The composition as defined in item 47 wherein the composition exhibits a room temperature shear adhesion value of least 500 hours at 5 lb/in² (0.352 Kg/cm²) after the second curing stage.

Item 58: The composition as defined in item 47 wherein the photoinitiator is selected from the group consisting of acetophenone, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoin, benzophenone, thioxanthone, and combination thereof.

Item 59: The composition as defined in item 47 wherein the composition exhibits a visible light transmission of between 80 to 100%.

Item 60: An adhesive composition comprising:

(a) a solvent-free benzophenone-functionalized crosslinkable acrylic copolymer comprising 2-ethylhexyl acrylate or butyl acrylate comonomers;

(b) a multi-functionalized crosslinkable oligomer comprising an acrylate functional moiety and a urethane monomer or comonomer; wherein the oligomer is present in an amount of between 5 to 40% by weight relative to the dry weight of the acrylic copolymer;

(c) a photoinitiator which initiates polymerization of the oligomer and is present in an amount of between 0.5 to 5% by weight relative to the dry weight of the acrylic copolymer; and

wherein the composition is free of a mono-functionalized oligomer and has:

(i) a first curing stage whereupon the composition exhibits a tan value greater than 0.8 as measured at 20 °C, and

(ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

Item 60: The composition as defined in item 60 wherein the acrylic copolymer is crosslinked during the first curing stage by exposure to light having a wavelength less than 300 nm.

Item 61: The composition as defined in item 60 wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength greater than 300 nm.

Item 62: The composition as defined in item 60 wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of between 320 to 440 nm.

Item 63: The composition as defined in item 60 wherein the composition exhibits a tan delta value of less than 0.8 as measured at 20 °C after the second curing stage.

Item 64: The composition as defined in item 60 wherein the composition exhibits room temperature shear adhesion

value of least 500 hours at 5 lb/in² (0.352 Kg/cm²) after the second curing stage.

Item 65: The composition as defined in item 60 wherein the photoinitiator is selected from the group consisting of acetophenone, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoin, benzophenone, thioxanthone, and combination thereof.

Item 66: The composition as defined in item 60 wherein the composition exhibits a visible light transmission of between 80 to 100%.

Claims

1. An adhesive composition comprising:

- (a) a crosslinkable acrylic copolymer;
- (b) a multi-functionalized crosslinkable oligomer;
- (c) a photoinitiator which initiates polymerization of the oligomer and is present in an amount of between 0.1 to 5% by weight relative to the dry weight of the acrylic copolymer; and

wherein the composition is free of a mono-functionalized oligomer and has:

- (i) a first curing stage whereupon the composition exhibits a tan δ value greater than 0.8 as measured at 20 °C, and
- (ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

2. The composition as defined in claim 1 wherein the acrylic copolymer is a solvent-borne or solvent-free acrylic copolymer and/or wherein the acrylic copolymer is crosslinked during the first curing stage by evaporation of a solvent or exposure to light having a wavelength less than 300 nm.

3. The composition as defined in claim 1 or 2 wherein the oligomer is present in an amount of between 5 to 40% by weight relative to the dry weight of the acrylic copolymer and/or wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of at least 200 nm.

4. The composition as defined in any of the preceding claims wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of between 300 to 500 nm and/or wherein the oligomer is crosslinked during the second curing stage by exposure to light having a wavelength of between 320 to 440 nm.

5. The composition as defined in any of the preceding claims wherein the composition exhibits a tan δ value of less than 0.8 as measured at 20 °C after the second curing stage and/or wherein the composition exhibits a room temperature shear adhesion value of least 500 hours at 5 lb/in² (0.352 Kg/cm²) after the second curing stage.

6. The composition as defined in any of the preceding claims wherein the acrylic copolymer comprises a comonomer selected from the group consisting of acrylamide, acrylonitrile, acrylic acid, alpha-methyl styrene, butyl acrylate, ethyl acrylate, n-butyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, glycidylmethacrylate, 2-hydroxyethylmethacrylate, hexyl acrylate, hydroxyethyl acrylate, isobornyl acrylate, isobutyl acrylate, iso-octyl acrylate, isodecyl acrylate, isononyl acrylate, methacrylic acid, methyl acrylate, methacrylonitrile, n-vinyl caprolactam, nonyl acrylate, caprolactam, propyl acrylate, tert-butyl acrylate, vinyl acetate, vinyl pyrrolidone, styrene, and combinations thereof.

7. The composition as defined in any of the preceding claims wherein the acrylic copolymer is a solvent-borne acrylic copolymer comprising 2-ethylhexyl acrylate and vinyl acetate comonomers and/or wherein the acrylic copolymer is a solvent-free benzophenone-functionalized acrylic copolymer and/or wherein the acrylic copolymer is a solvent-free benzophenone-functionalized acrylic copolymer comprising 2-ethylhexyl acrylic or butyl acrylic comonomers.

8. The composition as defined in any of the preceding claims further comprising a crosslinking agent which reacts with the solvent-borne or solvent-free acrylic copolymer.

9. The composition as defined in claim 8 wherein the crosslinking agent is selected from the group consisting of amino

resins, aziridines, melamines, isocyanates, metal acid esters, metal chelates, multifunctional propylene imines, and polycarbodiimides and/or wherein the crosslinking agent is selected from the group consisting of aluminum(III) acetylacetonate (AlAcAc), chromium(III) acetylacetonate (CrAcAc), iron(III) acetylacetonate (FeAcAc), cobalt(II) acetylacetonate (CoAcAc), nickel(II) acetylacetonate (NiAcAc), manganese(III) acetylacetonate (MnAcAc), titanium (IV) acetylacetonate (TiAcAc), zinc(II) acetylacetonate (ZnAcAc), zirconium(IV) acetylacetonate (ZrAcAc), and combinations thereof and/or wherein the crosslinking agent is aluminum (III) acetylacetonate (AlAcAc).

10. The composition as defined in any of the preceding claims wherein the oligomer comprises a functional moiety selected from the group consisting of acrylate, epoxy, hydroxy, and combinations thereof.

11. The composition as defined in claim 10 wherein the functional moiety of the oligomer is acrylate and/or wherein the functional moiety of the oligomer is epoxy.

12. The composition as defined in any of the preceding claims wherein the oligomer comprises a monomer or comonomer selected from the group consisting of acrylate, acrylic, epoxy, polyether, polyol, polyester, saturated and unsaturated rubber, polyurethane and combinations thereof.

13. The composition as defined in any of the preceding claims wherein the photoinitiator is selected from the group consisting of acetophenones, aryl phosphineoxides, aryl sulfonium and aryl iodonium salts of hexafluorophosphate, benzyl/benzoin, benzophenones, thioxanthenes, onium salts, and combination thereof.

14. The composition as defined in any of the preceding claims wherein the composition exhibits a visible light transmission of between 80 to 100%.

15. The composition as defined in any of the preceding claims, wherein the composition comprises:

- (a) a crosslinkable acrylic copolymer comprising comonomers selected from the group consisting of ethyl acetate, 2-ethylhexyl acrylate, methyl acrylate, vinyl acetate and combinations thereof;
- (b) a multi-functionalized crosslinkable oligomer comprising a functional moiety selected from the group consisting of acrylate, epoxy, hydroxy, and combinations thereof;
- (c) a photoinitiator which initiates polymerization of the oligomer;
- (d) a crosslinking agent which reacts with the acrylic copolymer; and

wherein the composition is free of a mono-functionalized oligomer and has:

- (i) a first curing stage whereupon the composition exhibits a tan value greater than 0.8 as measured at 20 °C, and
- (ii) a second sequential curing stage whereupon the composition exhibits a storage modulus value of at least 300,000 Pa at 20 °C and a shear adhesion failure temperature of at least 425 °F (218.3 °C) at 1 Kg/in² (0.155 Kg/cm²).

Patentansprüche

1. Klebstoffzusammensetzung, umfassend:

- (a) ein vernetzbares Acrylcopolymer;
- (b) ein multifunktionalisiertes vernetzbares Oligomer;
- (c) einen Photoinitiator, der die Polymerisation des Oligomers initiiert und in einer Menge von zwischen 0,1 bis 5 Gew.-% in Bezug auf das Trockengewicht des Acrylcopolymers vorhanden ist; und

wobei die Zusammensetzung frei von einem monofunktionalisierten Oligomer ist und Folgendes aufweist:

- (i) eine erste Härstungsstufe, wonach die Zusammensetzung bei einer Messung von 20 °C einen tan-δ-Wert von mehr als 0,8 aufweist, und
- (ii) eine zweite sequenzielle Härstungsstufe, wonach die Zusammensetzung bei 20 °C einen Speichermodulwert von mindestens 300.000 Pa und bei 1 kg/in² (0,155 kg/cm²) eine Scherhaftungs-Ausfalltemperatur von mindestens 425 °F (218,3 °C) aufweist.

2. Zusammensetzung nach Anspruch 1, wobei das Acrylcopolymer ein lösungsmittelbasiertes oder lösungsmittelfreies Acrylcopolymer ist und/oder wobei das Acrylcopolymer während der ersten Härtungsstufe durch Verdampfung eines Lösungsmittels oder Aussetzung einem Licht mit einer Wellenlänge von weniger als 300 nm vernetzt wird.
- 5 3. Zusammensetzung nach Anspruch 1 oder 2, wobei das Oligomer in einer Menge von zwischen 5 bis 40 Gew.-% in Bezug auf das Trockengewicht des Acrylcopolymers vorhanden ist und/oder wobei das Oligomer während der zweiten Stufe durch Aussetzung einem Licht mit einer Wellenlänge von mindestens 200 nm vernetzt wird.
- 10 4. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Oligomer während der zweiten Härtungsstufe durch Aussetzung einem Licht mit einer Wellenlänge von zwischen 300 bis 500 nm vernetzt wird und/oder wobei das Oligomer während der zweiten Härtungsstufe durch Aussetzung einem Licht mit einer Wellenlänge zwischen 320 bis 440 nm vernetzt wird.
- 15 5. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei die Zusammensetzung nach der zweiten Härtungsstufe bei einer Messung von 20 °C einen $\tan\delta$ -Wert von weniger als 0,8 aufweist und/oder wobei die Zusammensetzung nach der zweiten Härtungsstufe einen Raumtemperatur-Scherhaftungswert von mindestens 500 Stunden bei 5 lb/in² (0,352 kg/cm²) aufweist.
- 20 6. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Acrylcopolymer ein Comonomer umfasst, das ausgewählt ist aus der Gruppe, bestehend aus Acrylamid, Acrylonitril, Acrylsäure, alpha-Methylstyrol, Butylacrylat, Ethylacrylat, n-Butylacrylat, Ethylacrylat, 2-Ethylhexylacrylat, Glycidylmethacrylat, 2-Hydroxyethylmethacrylat, Hexylacrylat, Hydroxyethylacrylat, Isobornylacrylat, Isobutylacrylat, Isooctylacrylat, Isodecylacrylat, Isononylacrylat, Methacrylsäure, Methylacrylat, Methacrylonitril, n-Vinylcaprolactam, Nonylacrylat, Caprolactam, Propylacrylat, tert-Butylacrylat, Vinylacetat, Vinylpyrrolidon, Styrol und Kombinationen davon.
- 25 7. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Acrylcopolymer ein lösungsmittelbasiertes Acrylcopolymer ist, das 2-Ethylhexylacrylat- und Vinylacetat-Comonomere umfasst und/oder wobei das Acrylcopolymer ein lösungsmittelfreies Benzophenon-funktionalisiertes Acrylcopolymer ist und/oder wobei das Acrylcopolymer ein lösungsmittelfreies Benzophenon-funktionalisiertes Acrylcopolymer ist, das 2-Ethylhexylacryl- oder Butylacryl-Comonomere umfasst.
- 30 8. Zusammensetzung nach einem der vorstehenden Ansprüche, ferner umfassend ein Vernetzungsmittel, das mit dem lösungsmittelbasierten oder lösungsmittelfreien Acrylcopolymer reagiert.
- 35 9. Zusammensetzung nach Anspruch 8, wobei das Vernetzungsmittel ausgewählt ist aus der Gruppe, bestehend aus Aminoharzen, Aziridinen, Melaminen, Isocyanaten, Metallsäureestern, Metallchelaten, multifunktionellen Propylenimin und Polycarbodiimiden und/oder wobei das Vernetzungsmittel ausgewählt ist aus der Gruppe, bestehend aus Aluminium(III)-acetylacetonat (AlAcAc), Chrom(III)-acetylacetonat (CrAcAc), Eisen(III)-acetylacetonat (FeAcAc), Kobalt(II)-acetylacetonat (CoAcAc), Nickel(II)-acetylacetonat (NiAcAc), Mangan(III)-acetylacetonat (MnAcAc), Titan(IV)-acetylacetonat (TiAcAc), Zink(II)-acetylacetonat (ZnAcAc), Zirkonium(IV)-acetylacetonat (ZrAcAc) und Kombinationen davon und/oder wobei das Vernetzungsmittel ein Aluminium(III)-acetylacetonat (AlAcAc) ist.
- 40 10. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Oligomer eine funktionelle Einheit umfasst, die ausgewählt ist aus der Gruppe, bestehend aus Acrylat, Epoxy, Hydroxy und Kombinationen davon.
- 45 11. Zusammensetzung nach Anspruch 10, wobei die funktionelle Einheit des Oligomers Acrylat ist und/oder wobei die funktionelle Einheit des Oligomers Epoxy ist.
- 50 12. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Oligomer ein Monomer oder Comonomer umfasst, das ausgewählt ist aus der Gruppe, bestehend aus Acrylat, Acryl, Epoxy, Polyether, Polyol, Polyester, gesättigtem und ungesättigtem Kautschuk, Polyurethan und Kombinationen davon.
- 55 13. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei der Photoinitiator ausgewählt ist aus der Gruppe, bestehend aus Acetophenonen, Arylphosphinoxiden, Arylsulfonium- und Aryliodoniumsalzen von Hexafluorophosphat, Benzyl/Benzoinen, Benzophenonen, Thioxanthonen, Oniumsalzen und Kombinationen davon.
14. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei die Zusammensetzung eine Lichtdurchlässigkeit im sichtbaren Bereich von zwischen 80 bis 100% aufweist.

15. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei die Zusammensetzung Folgendes umfasst:

- (a) ein vernetzbares Acrylcopolymer, das Comonomere umfasst, die ausgewählt sind aus der Gruppe, bestehend aus Ethylacetat, 2-Ethylhexylacrylat, Methylacrylat, Vinylacetat und Kombinationen davon;
- (b) ein multifunktionalisiertes vernetzbares Oligomer, das eine funktionelle Einheit umfasst, die ausgewählt ist aus der Gruppe, bestehend aus Acrylat, Epoxy, Hydroxy und Kombinationen davon;
- (c) einen Photoinitiator, der die Polymerisation des Oligomers initiiert;
- (d) ein Vernetzungsmittel, das mit dem Acrylcopolymer reagiert; und

wobei die Zusammensetzung frei von einem monofunktionalisierten Oligomer ist und Folgendes aufweist:

- (i) eine erste Härstungsstufe, wonach die Zusammensetzung bei einer Messung von 20 °C einen $\tan\delta$ -Wert von mehr als 0,8 aufweist, und
- (ii) eine zweite sequenzielle Härstungsstufe, wonach die Zusammensetzung bei 20 °C einen Speichermodulwert von mindestens 300.000 Pa und bei 1 kg/in² (0,155 kg/cm²) eine Scherhaftungs-Ausfalltemperatur von mindestens 425 °F (218,3 °C) aufweist.

Revendications

1. Composition adhésive qui comprend:

- (a) un copolymère acrylique réticulable;
- (b) un oligomère réticulable multi-fonctionnalisé;
- (c) un photoinitiateur qui initie la polymérisation de l'oligomère et est présent en une quantité d'environ 0,1 à 5 % en poids par rapport au poids sec du copolymère acrylique; et

la composition étant dépourvue d'oligomère mono-fonctionnalisé et ayant:

- (i) une première étape de durcissement après laquelle la composition présente une valeur $\tan \delta$ supérieure à 0,8 telle que mesurée à 20 °C, et
- (ii) une seconde étape de durcissement séquentielle après laquelle la composition présente une valeur de module de stockage d'au moins 300.000 Pa à 20 °C et une température de défaut d'adhérence sous cisaillement d'au moins 425°F (218,3 °C) à 1 kg/po² (0,155 kg/cm²).

2. Composition selon la revendication 1, dans laquelle le copolymère acrylique est un copolymère acrylique à base de solvant ou sans solvant et/ou dans laquelle le copolymère acrylique est réticulé durant la première étape de durcissement par évaporation d'un solvant ou exposition à une lumière ayant une longueur d'onde inférieure à 300 nm.

3. Composition selon la revendication 1 ou 2, dans laquelle l'oligomère est présent en une quantité comprise entre 5 et 40 % en poids par rapport au poids sec du copolymère acrylique et/ou dans laquelle l'oligomère est réticulé durant la seconde étape de durcissement par exposition à une lumière ayant une longueur d'onde d'au moins 200 nm.

4. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'oligomère est réticulé durant la seconde étape de durcissement par exposition à une lumière ayant une longueur d'onde comprise entre 300 et 500 nm et/ou dans laquelle l'oligomère est réticulé durant la seconde étape de durcissement par exposition à une lumière ayant une longueur d'onde comprise entre 320 et 440 nm.

5. Composition selon l'une quelconque des revendications précédentes, dans laquelle la composition présente une valeur $\tan \delta$ inférieure à 0,8 telle que mesurée à 20 °C après la seconde étape de durcissement et/ou dans laquelle la composition présente une valeur d'adhérence sous cisaillement à température ambiante d'au moins 500 heures à 5 lb/po² (0,352 kg/cm²) après la seconde étape de durcissement.

6. Composition selon l'une quelconque des revendications précédentes, dans laquelle le copolymère acrylique comprend un comonomère choisi dans le groupe constitué par l'acrylamide, l'acrylonitrile, l'acide acrylique, l'alpha-méthyl-styrène, l'acrylate de butyle, l'acrylate d'éthyle, l'acrylate de n-butyle, l'acrylate d'éthyle, l'acrylate de 2-éthylhexyle, le méthacrylate de glycidyle, le méthacrylate de 2-hydroxyéthyle, l'acrylate d'hexyle, l'acrylate d'hydroxyé-

thyle, l'acrylate d'isobornyle, l'acrylate d'isobutyle, l'acrylate d'iso-octyle, l'acrylate d'isodécyle, l'acrylate d'isononyl, l'acide méthacrylique, l'acrylate de méthyle, le méthacrylonitrile, le n-vinyl caprolactame, l'acrylate de nonyle, le caprolactame, l'acrylate de propyle, l'acrylate de tert-butyle, l'acétate de vinyle, la vinyl pyrrolidone, le styrène, et leurs combinaisons.

7. Composition selon l'une quelconque des revendications précédentes, dans laquelle le copolymère acrylique est un copolymère acrylique à base de solvant comprenant des comonomères d'acrylate de 2-éthylhexyle et d'acétate de vinyle et/ou dans laquelle le copolymère acrylique est un copolymère acrylique à fonction benzophénone dépourvu de solvant et/ou dans laquelle le copolymère acrylique est un copolymère acrylique à fonction benzophénone dépourvu de solvant comprenant des comonomères 2-éthylhexyl acryliques ou butyl acryliques.

8. Composition selon l'une quelconque des revendications précédentes, comprenant en outre un agent de réticulation qui réagit avec le copolymère acrylique à base de solvant ou dépourvu de solvant.

9. Composition selon la revendication 8, dans laquelle l'agent de réticulation est choisi dans le groupe constitué par les résines amino, les aziridines, les mélamines, les isocyanates, les esters d'acides métalliques, les chélates de métaux, les propylène imines multifonctionnelles, et les polycarbodiimides et/ou dans laquelle l'agent de réticulation est choisi dans le groupe constitué par l'acétylacétonate d'aluminium (III) (AlAcAc), l'acétylacétonate de chrome (III) (CrAcAc), l'acétylacétonate de fer (III) (FeA-cAc), l'acétylacétonate de cobalt (II) (CoAcAc), l'acétylacétonate de nickel (II) (NiAcAc), l'acétylacétonate de manganèse (III) (MnAcAc), l'acétylacétonate de titane (IV) (TiAcAc), l'acétylacétonate de zinc (II) (ZnAcAc), l'acétylacétonate de zirconium (IV) (ZrAcAc), et leurs combinaisons et/ou dans laquelle l'agent de réticulation est l'acétylacétonate d'aluminium (III) (AlAcAc).

10. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'oligomère comprend une fraction fonctionnelle choisie dans le groupe constitué par un acrylate, un époxy, un hydroxy, et leurs combinaisons.

11. Composition selon la revendication 10, dans laquelle la fraction fonctionnelle de l'oligomère est un acrylate et/ou dans laquelle la fraction fonctionnelle de l'oligomère est un groupe époxy.

12. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'oligomère comprend un monomère ou un comonomère choisi dans le groupe constitué par un acrylate, l'acrylique, un époxy, un polyéther, un polyol, un polyester, un caoutchouc saturé ou insaturé, un polyuréthane et les combinaisons de ceux-ci.

13. Composition selon l'une quelconque des revendications précédentes, dans laquelle le photoinitiateur est choisi dans le groupe constitué par les acétophénones, les oxydes d'aryl phosphine, les sels d'aryl sulfonium et d'aryl iodonium d'hexafluorophosphate, les benzyle/benzoïnes, les benzophénones, les thioxanones, les sels d'onium, et leurs combinaisons.

14. Composition selon l'une quelconque des revendications précédentes, dans laquelle la composition présente une transmission de la lumière visible comprise entre 80 et 100%.

15. Composition selon l'une quelconque des revendications précédentes, ladite composition comprenant:

- (a) un copolymère acrylique réticulable comprenant des comonomères choisis dans le groupe constitué par l'acétate d'éthyle, l'acrylate de 2-éthylhexyle, l'acrylate de méthyle, l'acétate de vinyle et leurs combinaisons;
- (b) un oligomère réticulable multifonctionnalisé comprenant une fraction fonctionnelle choisie dans le groupe constitué par un acrylate, un époxy, un hydroxy, et leurs combinaisons;
- (c) un photoinitiateur qui initie la polymérisation de l'oligomère;
- (d) un agent de réticulation qui réagit avec le copolymère acrylique; et

la composition étant dépourvue d'oligomère mono-fonctionnalisé et ayant:

- (i) une première étape de durcissement après laquelle la composition présente une valeur $\tan \delta$ supérieure à 0,8 telle que mesurée à 20 °C, et
- (ii) une seconde étape de durcissement séquentielle après laquelle la composition présente une valeur de module de stockage d'au moins 300.000 Pa à 20 °C et une température de défaut d'adhérence sous cisaillement d'au moins 425°F (218,3 °C) à 1 kg/po² (0,155 kg/cm²).

REFERENCES CITED IN THE DESCRIPTION

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