

[DESCRIPTION]

[Title of Invention]

DENTAL ADHESIVE COMPOSITION

5 [Technical Field]

[0001]

The present invention relates to a dental adhesive composition.

10 [Background Art]

[0002]

Two-agent type dental adhesive compositions are known to exhibit better adhesion to both tooth and to composite resin than one-agent type dental
15 adhesive compositions. Such adhesion can be obtained by applying a first agent containing both an acidic compound and water to a target, acid-etching the target, removing water not involved in adhesion by air blowing, and then applying a second agent
20 containing a polymerizable monomer and a photopolymerization initiator, followed by light irradiation.

[0003]

As a two-agent type dental adhesive
25 composition, for example, a dental adhesive system is disclosed that consists of a primer composition consisting of a polymerizable monomer having an acidic group, a polymerizable monomer having a hydroxyl group, and water, and a bonding composition
30 consisting of an acylphosphine oxide-based photopolymerization initiator and a polymerizable monomer (see PTL 1).

[Citation List]

[Patent Literature]

[0004]

[PTL 1]

5 Japanese Laid-Open Patent Publication No.
2000-016911

[Summary of Invention]

[Technical Problem]

10 [0005]

Conventional two-agent type dental adhesive compositions have a problem of decreasing strength over time in a wet environment.

[0006]

15 It is an object of the present invention to provide a dental adhesive composition that does not decrease in strength over time in the wet environment.

[Solution to Problem]

20 [0007]

According to one aspect of the present invention, a two-agent type dental adhesive composition includes: a first agent; and a second agent, wherein the first agent includes a
25 (meth)acrylate compound having an acid group, a (meth)acrylate compound having no acid group, water, and a water-soluble organic solvent, wherein the second agent includes a multifunctional (meth)acrylate compound, a photopolymerization
30 initiator, and a filler of 0 to 50 mass%, and wherein both the first agent and the second agent substantially do not contain 2-hydroxyethyl methacrylate.

[Advantageous Effects of Invention]

[0008]

5 According to one aspect of the present
invention, a dental adhesive composition that does
not decrease in strength over time in a wet
environment, can be provided.

[Description of Embodiments]

10 [0009]

 Hereinafter, embodiments of the present
invention will be described in detail.

[0010]

<Dental Adhesive Composition>

15 A dental adhesive composition according to
the present embodiment is a two-agent type dental
adhesive composition including a first agent and a
second agent.

[0011]

20 <First Agent>

 In the two-agent type dental adhesive
composition, the first agent, also referred to as a
pretreatment agent or a primer, includes a
(meth)acrylate compound having an acid group, a
25 (meth)acrylate compound having no acid group, water,
and a water-soluble organic solvent, and
substantially does not contain 2-hydroxyethyl
methacrylate.

[0012]

30 In the present specification, the term
(meth)acrylate refers to at least one selected from
acrylates or methacrylates.

[0013]

<(Meth)acrylate Compound having Acid Group>

Examples of the (meth)acrylate compound having an acid group include, but are not limited to, (meth)acrylates having a phosphate group, (meth)acrylates having a pyrophosphate group, (meth)acrylates having a carboxyl group, (meth)acrylates having a thiophosphate group, (meth)acrylates having a sulfonate group, (meth)acrylates having a phosphonate group, and the like.

[0014]

Examples of the (meth)acrylates having a phosphate group include 2-(meth)acryloyloxyethyl dihydrogen phosphate, bis[2-(meth)acryloyloxyethyl] hydrogen phosphate, 2-(meth)acryloyloxyethyl phenyl hydrogen phosphate, 6-(meth)acryloyloxyhexyl dihydrogen phosphate, 6-(meth)acryloyloxyhexyl phenyl hydrogen phosphate, 10-(meth)acryloyloxydecyl dihydrogen phosphate (hereinafter sometimes abbreviated as MDP), 1,3-di(meth)acryloyl propane-2-dihydrogen phosphate, 1,3-di(meth)acryloyl propane-2-phenyl hydrogen phosphate, bis[5-{2-(meth)acryloyloxyethoxycarbonyl} heptyl] hydrogen phosphate, and the like, and their acid chlorides, alkali metal salts, ammonium salts, and the like. Among these, 10-methacryloyloxydecyl dihydrogen phosphate (MDP) is preferred in terms of initial adhesion.

[0015]

Examples of the (meth)acrylates having a pyrophosphate group include bis(2-(meth)acryloyloxyethyl) pyrophosphate, bis(4-(meth)acryloyloxybutyl) pyrophosphate, bis(6-

(meth)acryloyloxyhexyl) pyrophosphate, bis(8-(meth)acryloyloxyoctyl) pyrophosphate, bis(10-(meth)acryloyloxydecyl) pyrophosphate, and the like, and their acid chlorides, alkali metal salts, ammonium salts, and the like.
[0016]

Examples of the (meth)acrylates having a carboxyl group include 4-(meth)acryloyloxyethyl trimellitic acid (hereinafter sometimes abbreviated as 4-MET), 4-(meth)acryloyloxyethyl trimellitic anhydride (hereinafter sometimes abbreviated as 4-META), 4-(meth)acryloyloxydecyl trimellitic acid, 4-(meth)acryloyloxydecyl trimellitic anhydride, 11-(meth)acryloyloxy-1, 1-undecanedicarboxylic acid, 1,4-di(meth)acryloyloxypyromellitic acid, 2-(meth)acryloyloxyethyl maleic acid, 2-(meth)acryloyloxyethyl phthalic acid, 2-(meth)acryloyloxyethyl hexahydrophthalic acid, and the like. Among these, 4-(meth)acryloyloxyethyl trimellitic anhydride (4-META) is preferred in terms of initial adhesion.
[0017]

Examples of the (meth)acrylates having a thiophosphate group include 2-(meth)acryloyloxyethyl dihydrogen thiophosphate, 3-(meth)acryloyloxypropyl dihydrogen thiophosphate, 4-(meth)acryloyloxybutyl dihydrogen thiophosphate, 5-(meth)acryloyloxypentyl dihydrogen thiophosphate, 6-(meth)acryloyloxyhexyl dihydrogen thiophosphate, 7-(meth)acryloyloxyheptyl dihydrogen thiophosphate, 8-(meth)acryloyloxyoctyl dihydrogen thiophosphate, 9-(meth)acryloyloxynonyl dihydrogen thiophosphate, 10-(meth)acryloyloxydecyl dihydrogen thiophosphate (hereinafter sometimes

abbreviated as MDTP), 11-(meth)acryloyloxyundecyl
dihydrogen thiophosphate, 12-
(meth)acryloyloxydodecyl dihydrogen thiophosphate,
13-(meth)acryloyloxytridecyl dihydrogen
5 thiophosphate, 14-(meth)acryloyloxytetradecyl
dihydrogen thiophosphate, 15-
(meth)acryloyloxypentadecyl dihydrogen thiophosphate,
16-(meth)acryloyloxyhexadecyl dihydrogen
thiophosphate, 17-(meth)acryloyloxyheptadecyl
10 dihydrogen thiophosphate, 18-
(meth)acryloyloxyoctadecyl dihydrogen thiophosphate,
19-(meth)acryloyloxynonadecyl dihydrogen
thiophosphate, 20-(meth)acryloyloxyicosyl dihydrogen
thiophosphate, and the like, and their acid chlorides,
15 alkali metal salts, ammonium salts, and the like.
Among these, 10-(meth)acryloyloxydecyl dihydrogen
thiophosphate (MDTP) is preferred in terms of initial
adhesion.

[0018]

20 Examples of the (meth)acrylates having a
sulfonate group include 2-(meth)acrylamide-2
methylpropane sulfonic acid, styrene sulfonic acid,
2-sulfoethyl (meth)acrylate, and the like.

[0019]

25 Examples of the (meth)acrylates having a
phosphonate group include 2-(meth)acryloyloxyethyl
phenyl phosphonate, 5-(meth)acryloyloxypropyl-3
phosphonopropionate, 6-(meth)acryloyloxyhexyl-3
phosphonopropionate, 10-(meth)acryloyloxydecyl-3
30 phosphonopropionate, 6-(meth)acryloyloxyhexyl-3
phosphonoacetate, 10-(meth)acryloyloxydecyl-3
phosphonoacetate, and the like, and their acid
chlorides, alkali metal salts, ammonium salts, and

the like.

[0020]

The (meth)acrylate compound having the acid group may be used alone or in combination of two or
5 more.

[0021]

The content of the (meth)acrylate compound having the acid group in the first agent is not particularly limited, but is, for example, 5 to 30
10 mass%, and preferably 10 to 20 mass%, for 100 mass% of the first agent. When the content of the (meth)acrylate compound having the acid group in the first agent is 5 to 30 mass%, the initial adhesion of the dental adhesive composition is improved.

15 [0022]

<(Meth)acrylate Compound having No Acid Group>

The (meth)acrylate compound having no acid group is not particularly limited, but is, for example, di(meth)acrylate compound. The di(meth)acrylate
20 compound is preferably di(meth)acrylate compounds having a molecular weight of less than 400, such as 2-hydroxy-1,3-dimethacryloyloxy propane, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol #200
25 dimethacrylate, 1,6-hexanediol dimethacrylate, 1,9-nonanediol dimethacrylate, 1,10-decanediol dimethacrylate, neopentyl glycol dimethacrylate, and the like, for example. The (meth)acrylate compound having no acid group may be used alone or in
30 combination of two or more.

[0023]

The content of the (meth)acrylate compound having no acid group in the first agent is not

particularly limited, but is, for example, 1 to 40 mass%, and preferably 5 to 25 mass%, for 100 mass% of the first agent. When the content of the (meth)acrylate compound having no acid group in the first agent is 1 to 40 mass%, the adhesion of the dental adhesive composition is improved, and the mechanical strength of the hardened body of the dental adhesive composition is improved.

[0024]

10 <Water>

As water, ion-exchanged water or distilled water is preferably used, although not particularly limited. When the first agent contains water, because the acid group of the (meth)acrylate having the acid group is dissociated, the solubility of the smear layer on the tooth surface is increased, and the tooth demineralization and the permeability into tooth of the dental adhesive composition as a primer, are improved. Therefore, when the tooth surface is pretreated with the first agent, the permeability into tooth of the dental adhesive composition as a primer is improved, and the adhesion of the dental adhesive composition is improved.

[0025]

25 The content of water in the dental composition is not particularly limited, but is, for example, preferably 1 to 50 mass%, and more preferably 5 to 40 mass%, for 100 mass% of the first agent. When the content of water in the dental composition is 1 to 50 mass%, the solubility of the smear layer on the tooth surface is increased, and the tooth demineralization and the permeability into tooth of the dental adhesive composition as a primer, are

improved.

[0026]

<Water-Soluble Organic Solvent>

Examples of the water-soluble organic
5 solvent include, but are not limited to, methanol,
ethanol, propanol, isopropanol, butanol, pentanol,
acetone, methyl ethyl ketone, methyl isobutyl ketone,
toluene, xylene, ethyl acetate, butyl acetate,
cellosolve, tetrahydrofuran, dioxane,
10 dichloromethane, chloroform, carbon tetrachloride,
trichloroethylene, dimethylformamide, dimethyl
sulfoxide, and the like. The water-soluble organic
solvent may be used alone or in combination of two or
more. Among these, ethanol, acetone, isopropanol, and
15 butanol are preferred.

[0027]

The content of the water-soluble organic
solvent in the first agent is not particularly limited,
but is, for example, 10 to 50 mass%, and preferably
20 20 to 40 mass%, for 100 mass% of the first agent.
When the content of the water-soluble organic solvent
in the dental adhesive composition is 10 mass% or
more, the uniformity of the dental composition is
improved, and when 50 mass% or less, the adhesion of
25 the dental adhesive composition as a primer is
improved.

[0028]

<Other Component>

The first agent may further contain a
30 photopolymerization initiator, a tertiary amine, a
polymerization inhibitor, and a filler.

[0029]

Examples of the photopolymerization

initiator include, but are not particularly limited to, α -diketone compounds such as camphorquinone; acylphosphine oxide compounds such as 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2,4,6-trimethoxybenzoyldiphenylphosphine oxide, 2,6-dimethylbenzoyldiphenylphosphine oxide, 2,6-dimethoxybenzoyldiphenylphosphine oxide; benzyl ketal, diacetyl ketal, benzyl dimethyl ketal, benzyl diethyl ketal, benzyl bis(2-methoxyethyl) ketal, 4,4'-dimethyl(benzyl dimethyl ketal), anthraquinone, 1-chloroanthraquinone, 2-chloroanthraquinone, 1,2-benzanthraquinone, 1-hydroxyanthraquinone, 1-methylantraquinone, 2-ethylanthraquinone, 1-bromoanthraquinone, thioxanthone, 2-isopropylthioxanthone, 2-nitrothioxanthone, 2-methylthioxanthone, 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2,4-diisopropylthioxanthone, 2-chloro-7-trifluoromethylthioxanthone, thioxanthone-10,10-dioxide, thioxanthone-10-oxide, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzophenone, bis(4-dimethylaminophenyl) ketone, 4,4'-bis(diethylamino) benzophenone, and compounds containing an azide group. The photopolymerization initiator may be used alone or in combination of two or more.

[0030]

The content of the photopolymerization initiator in the first agent is not particularly limited, but is, for example, 0.01 to 5 mass%, and preferably 2 to 4 mass%, for 100 mass% of the first agent. When the content of the photopolymerization initiator in the first agent is 0.01 to 5 mass%, the adhesion of the dental adhesive composition is

improved, and the storage stability of the dental adhesive composition as a primer is improved.

[0031]

5 The tertiary amine may function as a polymerization accelerator. The tertiary amine is not particularly limited, but is preferably an aromatic tertiary amine such as ethyl 4-dimethylaminobenzoate, and the like, for example. When the tertiary amine is contained, the content of the tertiary amine in the first agent is not particularly limited, but is, for example, 0.01 to 3 mass%, and preferably 0.1 to 1 mass%, for 100 mass% of the first agent.

[0032]

15 The polymerization inhibitor is not particularly limited, but is dibutylhydroxytoluene, 2,6-t-butyl-2,4-xyleneol, and the like, for example. When the polymerization inhibitor is included, the content of the polymerization inhibitor in the first agent is not particularly limited, but is, for example, 0.01 to 3 mass%, and preferably 0.1 to 1 mass%, for 100 mass% of the first agent.

[0033]

25 The filler is not particularly limited, but is preferably an inorganic filler, such as colloidal silica, fine particle silica whose surface is hydrophobized, aluminum oxide, and the like. When the filler is contained, the content of the filler in the first agent is not particularly limited, but is, for example, 0.01 to 30 mass%, and is preferably 0.1 to 10 mass%, for 100 mass% of the first agent.

[0034]

<Excluded Component in First Agent>

The first agent substantially does not

contain 2-hydroxyethyl methacrylate (hereinafter sometimes abbreviated as HEMA). As used herein, "substantially does not contain" means that the target ingredient, such as HEMA, is not intentionally
5 included. The target ingredient that is "substantially does not contained" may be included as an unavoidable impurity. The content of the target ingredient as the unavoidable impurity is preferably less than 1%.

10 [0035]

When the first agent substantially contains 2-hydroxyethyl methacrylate (HEMA), the strength of the hardened layer of the dental adhesive composition decreases over time due to water absorption. In
15 contrast, in the present embodiment, when the first agent substantially does not contain 2-hydroxyethyl methacrylate (HEMA), a decrease in strength over time of the hardened layer of the dental adhesive composition due to water absorption can be minimized.

20 [0036]

For the same reason as 2-hydroxyethyl methacrylate (HEMA), it is preferable that the first agent substantially does not contain a monofunctional (meth)acrylate compound having a hydroxyl group, such
25 as 2,3-dihydroxypropyl methacrylate, and a monofunctional (meth)acrylamide, such as N,N-diethylacrylamide.

[0037]

The first agent preferably has a pH of 1.2
30 to 2.0, more preferably 1.5 to 2.0. When the pH of the first agent is set to 1.2 to 2.0, the solubility of the smear layer on the tooth surface and the tooth demineralization are improved, and the adhesion of

the dental adhesive composition is improved.

[0038]

<Second Agent>

In the two-agent type dental adhesive
5 composition, the second agent, also referred to as a
bonding agent (or bond), includes a multifunctional
(meth)acrylate compound, a photopolymerization
initiator, and a filler of 0 to 50 mass%, and
substantially does not contain 2-hydroxyethyl
10 methacrylate (HEMA).

[0039]

<Multifunctional (Meth)acrylate Compound>

The multifunctional (meth)acrylate
compound in the second agent is not particularly
15 limited, but is preferably a di(meth)acrylate
compound, more preferably containing both a
di(meth)acrylate compound having a molecular weight
of 400 or more and a di(meth)acrylate compound having
a molecular weight of less than 400.

20 [0040]

Examples of the di(meth)acrylate compound
having a molecular weight of 400 or more include
aliphatic di(meth)acrylate compounds having a
molecular weight of 400 or more and aromatic
25 di(meth)acrylate compounds having a molecular weight
of 400 or more.

[0041]

Specific examples of the aliphatic
di(meth)acrylate compounds having a molecular weight
30 of 400 or more include 1,6-bis-[2-
methacryloyloxyethoxycarbonylamino]-2,4,4-
trimethylhexane (UDMA), polyethylene glycol #400
dimethacrylate, polyethylene glycol #600

dimethacrylate, polyethylene glycol #1000
dimethacrylate, and the like, for example.

[0042]

Specific examples of the aromatic
5 di(meth)acrylate compounds having a molecular weight
of 400 or more include bisphenol A diglycidyl
methacrylate (Bis-GMA), 2-(4-
(meth)acryloyloxydiethoxyphenyl)-2-(4-
(meth)acryloyloxytriethoxyphenyl) propane, 2-(4-
10 (meth)acryloyloxydipropoxyphenyl)-2-(4-
(meth)acryloyloxytriethoxyphenyl) propane, 2,2-
bis(4-(meth)acryloyloxypropoxyphenyl) propane, 2,2-
bis(4-(meth)acryloyloxyisopropoxyphenyl) propane,
and the like.

15 [0043]

The di(meth)acrylate compound having a
molecular weight of less than 400 is not particularly
limited, but is preferably a di(meth)acrylate
compound having a molecular weight of less than 300.

20 [0044]

Examples of the di(meth)acrylate compound
having a molecular weight of less than 300 include 2-
hydroxy-1,3-dimethacryloyloxypropane, diethylene
glycol dimethacrylate, triethylene glycol
25 dimethacrylate, polyethylene glycol #200
dimethacrylate, 1,6-hexanediol dimethacrylate, 1,9-
nonanediol dimethacrylate, 1,10-decanediol
dimethacrylate, neopentyl glycol dimethacrylate, and
the like. Among these, di(meth)acrylate compounds
30 containing a hydroxyl group are preferred, and 2-
hydroxy-1,3-dimethacryloyloxypropane is more
preferred.

[0045]

The content of the multifunctional (meth)acrylate compound in the second agent is not particularly limited, but is, for example, 50 to 99 mass%, and preferably 60 to 95 mass%, for 100 mass% of the second agent. When the content of the multifunctional (meth)acrylate compound in the second agent is 50 to 99 mass%, the adhesion of the dental adhesive composition is improved, and the mechanical strength of the hardened body of the dental adhesive composition is improved.

[0046]

The proportion of the content of the di(meth)acrylate compound having a molecular weight of less than 400 to the content of the di(meth)acrylate compound having a molecular weight of 400 or more in the second agent is freely-determined, but is preferably 0.5 to 2, and even more preferably 0.8 to 1.4. When the proportion of the content of the di(meth)acrylate compound having a molecular weight of less than 400 to the content of the di(meth)acrylate compound having a molecular weight of 400 or more in the second agent is 0.5 to 2, adhesion of the dental adhesive composition is improved.

[0047]

<Photopolymerization Initiator>

Examples of the photopolymerization initiator in the second agent include, but are not particularly limited to, α -diketone compounds such as camphorquinone; acylphosphine oxide compounds such as 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2,4,6-trimethoxybenzoyldiphenylphosphine oxide, 2,6-dimethylbenzoyldiphenylphosphine oxide, 2,6-

dimethoxybenzoyldiphenylphosphine oxide; benzyl
ketal, diacetyl ketal, benzyl dimethyl ketal, benzyl
diethyl ketal, benzyl bis(2-methoxyethyl) ketal,
4,4'-dimethyl(benzyl dimethyl ketal), anthraquinone,
5 1-chloroanthraquinone, 2-chloroanthraquinone, 1,2-
benzanthraquinone, 1-hydroxyanthraquinone, 1-
methylantraquinone, 2-ethylanthraquinone, 1-
bromoanthraquinone, thioxanthone, 2-
isopropylthioxanthone, 2-nitrothioxanthone, 2-
10 methylthioxanthone, 2,4-dimethylthioxanthone, 2,4-
diethylthioxanthone, 2,4-diisopropylthioxanthone, 2-
chloro-7-trifluoromethylthioxanthone, thioxanthone-
10,10-dioxide, thioxanthone-10-oxide, benzoin methyl
ether, benzoin ethyl ether, benzoin isopropyl ether,
15 benzoin isobutyl ether, benzophenone, bis(4-
dimethylaminophenyl) ketone, 4,4'-bis(diethylamino)
benzophenone, and compounds containing an azide group.
The photopolymerization initiator may be used alone
or in combination of two or more.

20 [0048]

The content of the photopolymerization
initiator in the second agent is not particularly
limited, but is, for example, 0.01 to 8 mass%, and
preferably 3 to 6 mass%, for 100 mass% of the second
25 agent. When the content of the photopolymerization
initiator in the second agent is 0.01 to 8 mass%, the
adhesion of the dental adhesive composition is
improved, and the storage stability of the dental
adhesive composition as a bonding agent is improved.

30 [0049]

<Filler>

The second agent may include the filler.
The content of the filler in the second agent is 0 to

50 mass%, and preferably 0.1 to 20 mass%. That is, when the second agent includes the filler, the filler of more than 50 mass% is not contained.

[0050]

5 When the content of the filler in the second agent exceeds 50 mass%, the operability may be impaired and the adhesion may be reduced because the polymerized component is reduced. In contrast, when the content of the filler in the second agent is 50
10 mass% or less, the dispersibility of the second agent is improved and the storage stability of the dental adhesive composition as a bonding agent is improved.

[0051]

<Other Ingredient>

15 The second agent may further include a tertiary amine, and a polymerization inhibitor.

[0052]

 The tertiary amine in the second agent may function as a polymerization accelerator, as in the
20 first agent. The tertiary amine in the second agent is not particularly limited, but is preferably an aromatic tertiary amine such as ethyl 4-dimethylaminobenzoate, and the like, for example. When the tertiary amine is contained, the content of
25 the tertiary amine in the second agent is not particularly limited, but is, for example, 0.01 to 5 mass%, and preferably 1 to 4 mass%, for 100 mass% of the second agent.

[0053]

30 The polymerization inhibitor in the second agent is not particularly limited but is dibutylhydroxytoluene, 2,6-t-butyl-2,4-xyleneol, and the like, for example. When the polymerization

inhibitor is included, the content of the polymerization inhibitor in the second agent is not particularly limited, but is, for example, 0.01 to 3 mass%, and preferably 0.1 to 1 mass%, for 100 mass% of the second agent.

[0054]

<Excluded Component in Second Agent>

The second agent substantially does not contain 2-hydroxyethyl methacrylate (HEMA). When the second agent substantially contains HEMA, the strength of the hardened layer of the dental adhesive composition decreases over time due to water absorption. In contrast, in the present embodiment, when the second agent substantially does not contain HEMA, a decrease in strength over time of the hardened layer of the dental adhesive composition due to water absorption can be minimized.

[0055]

For the same reason as 2-hydroxyethyl methacrylate (HEMA), it is preferable that the second agent substantially does not contain a monofunctional (meth)acrylate compound having a hydroxyl group, such as 2,3-dihydroxypropyl methacrylate, and a monofunctional (meth)acrylamide, such as N,N-diethylacrylamide.

[0056]

It is preferable that the second agent substantially does not contain the (meth)acrylate compound having an acid group. When the second agent substantially contains the (meth)acrylate compound having an acid group, some types of photopolymerization initiators may cause degradation, resulting in a decrease in polymerizability. In

contrast, when the second agent substantially does not contain the (meth)acrylate compound having an acid group, the storage stability of the photopolymerization initiator in the second agent can
5 be improved and the decrease in polymerizability in the dental adhesive composition can be minimized.

[0057]

It is even more preferable that the second agent substantially does not contain a chemical
10 polymerization initiator. When the second agent contains the chemical polymerization initiator, the storage stability of the second agent as a bonding agent may decrease. Examples of such chemical polymerization initiators include vanadium compounds
15 such as vanadium acetylacetonate.

[0058]

Because both the first agent and the second agent of the dental adhesive composition according to the present embodiment substantially do not contain
20 2-hydroxyethyl methacrylate (HEMA) as described above, the composition is resistant to strength degradation over time in a wet environment. Therefore, according to the present embodiment, the dental adhesive composition that improves adhesion and improves the
25 mechanical strength of the hardened body can be obtained.

[0059]

<Mode of Use of Dental Composition>

The dental adhesive composition according
30 to the present embodiment is used by applying the first agent described above to a target, followed by air blowing, and then applying the second agent described above to the target. Here, the target may

be either tooth or restorations (composite resin
prostheses and the like). The air blowing may be
performed by a publicly-known method and may be
performed immediately after application of the first
5 agent.
[0060]

The manner in which the first agent is
applied to the target is freely-determined, but for
example, the first agent may be applied to the target
10 by a publicly-known method. The manner in which the
second agent is applied to the target is freely-
determined, but for example, the second agent may be
applied to the target to which the first agent is
applied by a publicly-known method.
15 [0061]

The dental adhesive composition according
to the present embodiment can be used in the same
manner as the conventional two-agent type dental
adhesive composition by being used in such a manner,
20 and is therefore easy to handle as a two-agent type
dental adhesive composition.
[0062]

<Application of Dental Adhesive Composition>

The application of the dental adhesive
25 composition according to the present embodiment is
not particularly limited but may include various
dental materials. Examples of the application of the
dental adhesive composition according to the present
embodiment include dental cement, dental adhesive,
30 dental temporary sealing material, dental coating
material, dental hard resin, dental cutting resin
material, dental temporary restorative material,
dental filler, dentifrice, and the like. Among these,

the dental adhesive composition of the present embodiment is suitably used for dental adhesive.

[Example]

5 [0063]

Hereinafter, the present invention will be further described using Examples and Comparative Examples. In the following, "part" and "%" are based on mass unless otherwise specified. In addition,
10 various tests and evaluations are performed according to the following methods.

[0064]

<Test Sample (First Agent)>

A first agent, which constitutes a two-
15 agent type dental adhesive composition, was prepared with the formulation presented in Table 1. The first agent, which was formulated in Table 1, had a pH of 1.5.

[0065]

[Table 1]

PRIMER FORMULATION	[wt%]
ACETONE	25
GDMA	15
TEGDMA	5
AEROSIL R972	5
4-META	10
MDP	10
DISTILLED WATER	25
CQ	1
EPA	1
TPO	2
BHT	1
TOTAL	100

[0066]

5 The specifications of ingredients indicated
by abbreviations or product names in Table 1 are as
follows.

[0067]

GDMA: 2-hydroxy-1,3-dimethacryloyloxypropane
10 TEGDMA: triethylene glycol dimethacrylate
AEROSIL (registered trademark) R972: fine
particle silica surface-treated with
dimethyldichlorosilane (DDS) (manufactured by Nippon
Aerosil Co., Ltd.)
15 4-META: 4-methacryloyloxyethyl trimellitic
anhydride

MDP: 10-methacryloyloxydecyl dihydrogen
phosphate

CQ: camphorquinone

EPA: ethyl 4-dimethylaminobenzoate

5 TPO: 2,4,6-trimethoxybenzoyldiphenylphosphine
oxide

BHT: dibutylhydroxytoluene

[0068]

<Test Sample (Second Agent)>

10 A second agent, which constitutes the two-
agent type dental adhesive composition, was prepared
with the formulation presented in Table 2.

[0069]

[Table 2]

BONDING AGENT FORMULATION [wt%]	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3	EXAMPLE 4	EXAMPLE 5	EXAMPLE 6	EXAMPLE 7	COMPARA- TIVE EXAMPLE 1	COMPARA- TIVE EXAMPLE 2	COMPARA- TIVE EXAMPLE 3
Bis-GMA	13		13	13	13	13	18	13	13	13
BPE-200		13								
UDMA	30	30	30	30	30	30	30	30	30	30
GDMA	45	45			45	45		30	15	15
TEGDMA			45				45			
NPG				45						
HEMA								15	30	15
MDP										15
CQ	2	2	2	2	2	2	2	2	2	2
EPA	2	2	2	2	2	2	2	2	2	2
TPO	2	2	2	2	2	2	2	2	2	2
BHT	1	1	1	1	1	1	1	1	1	1
AEROSIL RX50	5	5	5	5				5	5	5
AEROSIL R812					5					
AEROSIL RX200						5				
TOTAL	100	100	100	100	100	100	100	100	100	100

[0070]

5 The specifications of ingredients indicated by abbreviations or product names in Table 2 are as follows.

[0071]

Bis-GMA: bisphenol A diglycidyl methacrylate
BPE-200: ethoxylated bisphenol A dimethacrylate
UDMA: 1,6-bis-[2-methacryloyloxyethoxycarbonylamino]-2,4,4-trimethylhexane
5 GDMA: 2-hydroxy-1,3-dimethacryloyloxypropane
TEGDMA: triethylene glycol dimethacrylate
NPG: neopentyl glycol dimethacrylate
HEMA: 2-hydroxyethyl methacrylate
10 MDP: 10-methacryloyloxydecyl dihydrogen phosphate
CQ: camphorquinone
EPA: ethyl 4-dimethylaminobenzoate
TPO: 2,4,6-trimethoxybenzoyldiphenylphosphine
15 oxide
BHT: dibutylhydroxytoluene
AEROSIL (registered trademark) RX50: fine particle silica surface-treated with hexamethyldisilazane (manufactured by Nippon Aerosil Co., Ltd.)
20 AEROSIL (registered trademark) R812: fine particle silica surface-treated with hexamethyldisilazane (manufactured by Nippon Aerosil Co., Ltd.)
25 AEROSIL (registered trademark) RX200: fine particle silica surface-treated with hexamethyldisilazane (manufactured by Nippon Aerosil Co., Ltd.)
[0072]
30 <Shear Adhesion Strength>

The shear adhesion strength was measured with reference to the adhesion test according to ISO 29022 (2013). Bovine mandibular anterior teeth were

embedded with room temperature polymerized resin. Then, enamel and dentin were exposed using #120 SiC water-resistant abrasive paper, and the test surface was polished using #400 SiC water-resistant abrasive paper. A self-etching primer (the first agent or a first fluid) was applied to the test surface using an applicator and allowed to stand for 10 seconds. A bond (the second agent or a second fluid) was then applied using an applicator. After the bond was equalized with low-pressure air, a plastic mold with a hole of 2.38 mm in diameter was placed on the test surface, and the mold was irradiated with light using a light irradiator (G-Light Prima II Plus, manufactured by GC Corporation) for 10 seconds to harden the bond. The hole was filled with a composite resin (Clearfil AP-X, manufactured by Kuraray Noritake Dental Inc.) and irradiated with light using the light irradiator for 20 seconds. The mold was removed so that no load was applied to the specimen, and the specimen was stored in water at 37°C for 24 hours. After measuring the dimensions of the obtained specimen, a shear adhesion test was performed using a universal testing machine (EZ-S, manufactured by Shimadzu Corporation) (crosshead speed: 1 mm/min), and the shear adhesion strength was calculated from the dimensions and the stress values obtained in the shear adhesion test. The measurement was performed by setting N=5. The shear adhesion strength was evaluated for enamel on the following criteria: excellent: 35 MPa or more; good: 25 MPa or more and less than 35 MPa; and poor: less than 25 MPa, and for dentin on the following criteria: excellent: 45 MPa or more; good: 35 MPa or more and less than 45 MPa; and poor: less than 35 MPa.

The results are presented in Table 3.

[0073]

<Polymerization Rate>

A ring of 10 mm in diameter and 1.0 mm thick,
 5 made of a OHP sheet, was placed on a glass slide, and
 the ring was overfilled with the second agent while
 ensuring that no air bubbles were formed. An OHP sheet
 was then placed thereon, and pressure welded using
 glass slides. Using the light irradiator (G-Light
 10 Prima II Plus, manufactured by GC Corporation), light
 irradiation at one point in the center was applied on
 the back and front surfaces for 10 seconds each to
 harden the bond. Five minutes after preparation, for
 the hardened body obtained, the peak after
 15 polymerization was measured using the ATR method of
 FT-IR (NICOLET (registered trademark) iS50,
 manufactured by Thermo Fisher Scientific Inc.).
 Similarly, the bond before hardening was measured by
 FT-IR and the peak before polymerization was measured.
 20 The peaks before and after polymerization were
 compared, and the polymerization rate was calculated
 from the following equation. All measurements were
 performed by setting N=5. The polymerization rate was
 evaluated based on the following criteria: excellent:
 25 75% or more; good: 60% or more and less than 75%; and
 poor: less than 60%. The results are presented in
 Table 3.

[0074]

[Equation 1]

$$POLYMERIZATION\ RATE = 1 - \frac{\frac{AFTER\ POLYMERIZATION\ C = C(1640\ cm^{-1})}{AFTER\ POLYMERIZATION\ (1610\ cm^{-1})}}{\frac{BEFORE\ POLYMERIZATION\ C = C(1640\ cm^{-1})}{BEFORE\ POLYMERIZATION\ (1610\ cm^{-1})}}$$

[0075]

<Bending Strength>

The bending strength was measured by the bending test according to ISO 4049 (2019). A glass plate and a mold made of an OHP sheet for measuring dimensions were placed on a metal plate, and the mold was filled with the bond (the second fluid). Pressure bonding was performed using OHP sheets and glass plates. From the outside of the glass plates, light irradiation at nine points was applied to the back and front surfaces of the glass plate for 10 seconds each using the light irradiator (G-Light Prima II Plus, manufactured by GC Corporation) to harden the bonds. After standing in a thermostatic chamber at 37°C for 15 minutes, the specimen was removed from the mold, deburred using #320 water-resistant abrasive paper, and stored in water at 37°C for 24 hours or for 1 week. After measuring the dimensions of the obtained specimen, a three-point bending test was performed using a universal testing machine (AG-IS, manufactured by Shimadzu Corporation) (crosshead speed: 1 mm/min). From the dimensions and the stress values obtained in the three-point bending test, the three-point bending strength was calculated and the bending strength after 1 day (24 hours) and after 1 week was measured. All measurements were performed by setting N=5. The bending strength was evaluated on the following criteria: excellent: 120 MPa or more; good: 100 MPa or more and less than 120 MPa; and poor: less than 100 MPa. The results are presented in Table 3.

[0076]

<Decrease Rate of Bending Strength>

The decrease rate of bending strength was calculated from the following equation from the bending strength after one day and after one week obtained by the above bending test. When the decrease rate of bending strength is negative, it indicates an increase in bending strength. This is because the water absorption of the hardened dental adhesive composition was suppressed, and furthermore, the decrease in polymerizability was reduced, and the polymerization progressed over time. The results are presented in Table 3.

[0077]

[Equation 2]

$$\text{DECREASE RATE OF BENDING STRENGTH (\%)} = \frac{\text{BENDING STRENGTH AFTER ONE DAY} - \text{BENDING STRENGTH AFTER ONE WEEK}}{\text{BENDING STRENGTH AFTER ONE DAY}} \times 100$$

15

[0078]

<Vickers Hardness>

The Vickers hardness was measured by a Vickers hardness test. A ring of 15 mm in diameter and 1.5 mm thick, made of a OHP sheet, was placed on a glass slide, and the ring was overfilled with the bond (the second fluid) while ensuring that no air bubbles were formed. An OHP sheet was then placed thereon, and pressure welded using glass slides. Using the light irradiator (G-Light Prima II Plus, manufactured by GC Corporation), light irradiation at one point in the center and eight points on the circumference was applied on the back and front surfaces for 10 seconds each to harden the bond. The obtained hardened body was polished sequentially using #1200, #2400, and #4000 SiC water-resistant abrasive paper, and stored in water at 37°C for 24

hours or for 1 week. The Vickers hardness of the obtained specimen after 1 day (24 hours) and after 1 week was measured using a micro-Vickers tester (HNV-G21D1, manufactured by Shimadzu Corporation) (HV 0.2, retention time 10 seconds, 3 specimens, N=5 per specimen). The Vickers hardness was evaluated on the following criteria: excellent: 25HV or more; good: 20HV or more and less than 25HV; and poor: less than 20HV. The results are presented in Table 3.

10 [0079]

<Decrease Rate in Vickers Hardness>

The decrease rate in Vickers hardness was calculated from the Vickers hardness after one day and after one week obtained by the above Vickers hardness test, using the following equation. The results are presented in Table 3.

[0080]

[Equation 3]

$$\text{DECREASE RATE OF VICKERS HARDNESS (\%)} = \frac{\text{VICKERS HARDNESS AFTER ONE DAY} - \text{VICKERS HARDNESS AFTER ONE WEEK}}{\text{VICKERS HARDNESS AFTER ONE DAY}} \times 100$$

20

[0081]

<Water Absorption amount>

The water absorption amount was measured by a water absorption test according to ISO 4049 (2019). A ring of 15 mm in diameter and 1.0 mm thick, made of a OHP sheet, was placed on a glass slide, and the ring was overfilled with the bond (the second fluid) while ensuring that no air bubbles were formed. An OHP sheet was then placed thereon, and pressure welded using glass slides. Using the light irradiator (G-Light Prima II Plus, manufactured by GC Corporation), light irradiation at one point in the center and eight

points on the circumference was applied on the back and front surfaces for 20 seconds each to harden the bond. The obtained hardened body was stored as a test specimen in a desiccator in a thermostat set at 37°C.

5 The volume (V) and weight (m1) of the constant-volume specimen were repeatedly determined until the mass loss was less than or equal to 0.1 g per 24 hours. The specimen was immersed in distilled water in a sample container and left in the thermostat set at
10 37°C for 1 week, after which the weight (m2) of the weighed specimen was determined. The water absorption amount was calculated from the following equation. The measurement was performed by setting N=5. The water absorption amount was evaluated the following
15 criteria: excellent: less than 50 µg/mm³; good: 50 µg/mm³ or more and less than 60 µg/mm³; and poor: 60 µg/mm³ or more. The results are presented in Table 3.
[0082]

[Equation 4]

$$WATER\ ABSORPTION\ AMOUNT = \frac{m2 - m1}{V}$$

20

[0083]

[Table 3]

EVALUATION		EXAMPLE 1	EXAMPLE 2	EXAMPLE 3	EXAMPLE 4	EXAMPLE 5	EXAMPLE 6	EXAMPLE 7	COMPARATIVE EXAMPLE 1	COMPARATIVE EXAMPLE 2	COMPARATIVE EXAMPLE 3
ADHESIVE STRENGTH TO SHEAR [MPa]	ENAMEL	39.9	40.1	37.7	39.1	37.4	40.3	36.5	34.5	30.2	32.4
	DENTIN	48.2	46.6	49.1	47.2	46.9	49.2	48	44.9	39.6	41.4
POLYMERIZATION RATE [%]		75.8	75.4	77.7	79.2	77.1	75	76.1	84	85.9	73.4
BENDING STRENGTH (AFTER ONE DAY) [MPa]		129	118.8	125.1	116.9	128	130	123.7	126.5	124.8	121.3
BENDING STRENGTH (AFTER ONE WEEK) [MPa]		126.1	123.6	124.9	118.8	124.4	129.3	121.6	120.4	108.3	109.3
DECREASE RATE OF BENDING STRENGTH [%]		2.2	-4.0	0.2	-1.6	2.8	0.5	1.7	4.8	13.2	9.9
VICKERS HARDNESS (AFTER ONE DAY) [HV]		26.3	24.9	27.2	28.2	27	26.7	28.5	23.2	17.7	18.4
VICKERS HARDNESS (AFTER ONE WEEK) [HV]		25.5	24.4	26.6	27.1	26.1	26.3	27.8	21.4	15.1	16.5
DECREASE RATE OF VICKERS HARDNESS [%]		3.0	2.0	3.7	3.9	3.3	1.5	3.1	7.8	14.7	10.3
WATER ABSORPTION AMOUNT [$\mu\text{g}/\text{mm}^3$]		41	41.3	32.2	23.8	39.8	37	33.5	62.8	78.7	68.3

[0084]

5 From Table 1 to 3, it can be seen that when the second agents of Examples 1 to 7 are used, all items are excellent or good, indicating that the

adhesive compositions exhibit good adhesion and are resistant to strength degradation over time in a wet environment.

[0085]

5 In contrast, when HEMA is blended (Comparative Examples 1, 2) and when HEMA and MDP are blended (Comparative Example 3) in the second agent, it can be seen that the bending strength and the Vickers hardness decrease after 1 week of immersion
10 in water.

[0086]

 Although the embodiments of the present invention have been described above, the present invention is not limited to specific embodiments, and
15 various modifications and changes are possible within the scope of the invention described in the claims.

[0087]

 The present application claims priority to Japanese Patent Application No. 2021-17790, filed
20 February 5, 2021, with the Japanese Patent Office, the contents of which are incorporated herein by reference in their entirety.

[CLAIMS]

[Claim 1]

A two-agent type dental adhesive composition comprising:
5 a first agent; and
a second agent,
wherein the first agent includes
a (meth)acrylate compound having an
acid group,
10 a (meth)acrylate compound having no
acid group,
water, and
a water-soluble organic solvent,
wherein the second agent includes
15 a multifunctional (meth)acrylate
compound,
a photopolymerization initiator, and
a filler of 0 to 50 mass%, and
wherein both the first agent and the second
20 agent substantially do not contain 2-hydroxyethyl
methacrylate.

[Claim 2]

The dental adhesive composition according
25 to claim 1, wherein the multifunctional
(meth)acrylate compound in the second agent contains
a di(meth)acrylate compound having a molecular weight
of 400 or more and a di(meth)acrylate compound having
a molecular weight of less than 400.

30

[Claim 3]

The dental adhesive composition according
to claim 2, wherein a proportion of a content of the

di(meth)acrylate compound having the molecular weight of less than 400 to a content of the di(meth)acrylate compound having the molecular weight of 400 or more in the second agent is 0.5 to 2.

5

[Claim 4]

The dental adhesive composition according to claim 2 or 3, wherein the di(meth)acrylate compound having the molecular weight of 400 or more in the
10 second agent includes an aromatic di(meth)acrylate compound and an aliphatic di(meth)acrylate compound.

[Claim 5]

The dental adhesive composition according
15 to any one of claims 2 to 4, wherein the di(meth)acrylate compound having the molecular weight of less than 400 in the second agent is a di(meth)acrylate compound containing a hydroxyl group.

20 [Claim 6]

The dental adhesive composition according to any one of claims 1 to 5, wherein the second agent substantially does not contain the (meth)acrylate compound having the acid group.

25

[Claim 7]

The dental adhesive composition according to any one of claims 1 to 6, wherein a pH of the first agent is 1.2 to 2.0.

30

[Claim 8]

The dental adhesive composition according to any one of claims 1 to 7, wherein the dental

adhesive composition is used by applying the first agent to a target, followed by air blowing, and then applying the second agent to the target.