

NOVEL (METH)ACRYLIC RESIN AND RESIN COMPOSITION UTILIZING SAME

TECHNICAL FIELD

The present invention relates to a novel (meth)acrylic resin. More specifically, it relates to a (meth)acrylic resin having a hydroquinone, catechol, or resorcin skeleton as well as a carboxy group in its molecule; and further a resin composition using the same applied suitably for adhesive agents is proposed.

BACKGROUND ART

Heretofore, (meth)acrylic resin having a carboxy group in its molecule has been widely used for photoresist ink compositions used for forming resist patterns in printed-wiring boards (see Patent Documents 1 and 2, etc.). The photoresist ink composition is used in order to form a desired wiring pattern through development. More specifically, an energy beam such as ultraviolet rays is irradiated to the (meth)acrylic resin composition under a mask having a pattern (wiring) to thereby crosslink the (meth)acryloyl group of the (meth)acrylic resin at exposed portions. Then, making use of alkali-solubility of the carboxy group of uncured (meth)acrylic resin, alkali-development is performed to thereby form a certain pattern.

The (meth)acrylic resin has also been used for adhesive agents. For example, it is used for a photo-curable dental adhesive agent in Patent Document 3.

However, it is designed for the application of dental adhesive agents in particular considering photo-curability around room temperature, water-resistant adhesion properties of cured material, etc. As described above, application of the (meth)acrylic resin for adhesive agents has not been sufficiently established.

Patent Document 1: Japanese Unexamined Patent Application, Publication No. S61-243869

Patent Document 2: Japanese Unexamined Patent Application, Publication No. H3-143911

Patent Document 3: Japanese Unexamined Patent Application, Publication No. H5-286822

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

The present invention has been made in view of the problems described above and relates to a novel (meth)acrylic resin having a carboxy group in its molecule. That is, the present invention proposes a novel (meth)acrylic resin that is suitably used for the application of adhesive agents and allows to attain freedom in handling, freedom in designing an adhesive agent, and high adhesion strength of adhesive agents.

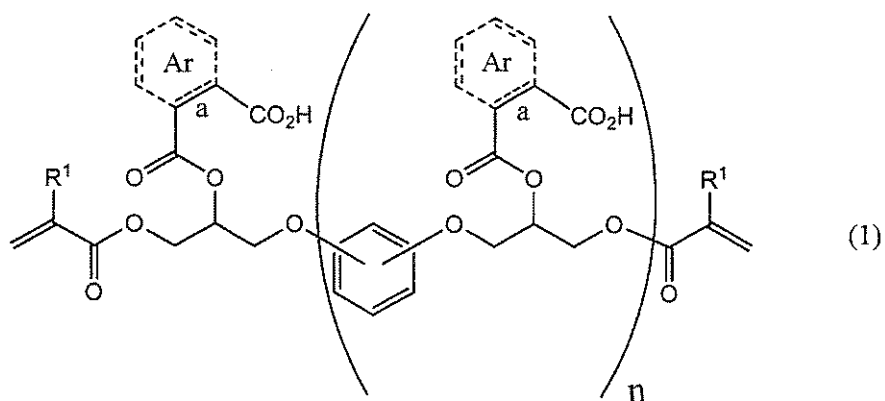
Means for Solving the Problems

The present inventors have performed diligent studies in view of the problems described above; as a result, have found that the compound resulting from reacting a (meth)acrylic acid

ester of an epoxy resin having a skeleton such as hydroquinone, resorcin, and catechol with an acid anhydride etc. exhibits a lower viscosity due to a lower molecular mass and may also have a higher polarity due to a lower carboxy group equivalent (molecular mass per one carboxy group) and therefore enhances adhesion strength and/or attains a promoting effect on thermosetting reaction when used as a component of adhesive agents, thereby completing the present invention.

Specifically, the present invention relates to the following 1) to 12). Here, in this specification, "(meth)acrylic" means one or both of "acrylic" and "methacrylic". Further, in this specification, "(meth)acryloyl" means one or both of "acryloyl" and "methacryloyl".

1) A (meth)acrylic resin represented by formula (1) below:



in the formula, the benzene ring Ar may be present or absent; when no benzene ring Ar exists, the bond "a" represents a single bond or a double bond;

n represents an integer of from 1 to 5; and R¹ represents

a hydrogen atom or a methyl group.

2) The (meth)acrylic resin according to 1), in which no benzene ring Ar exists in the formula (1).

3) The acrylic resin according to 1) or 2), in which R^1 is a hydrogen atom in the formula (1).

4) A resin composition containing the (meth)acrylic resin according to any one of 1) to 3).

5) The resin composition according to 4), further containing a photo-polymerization initiator.

6) The resin composition according to 4) or 5), further containing a thermal radical polymerization initiator.

7) The resin composition according to any one of 4) to 6), further containing an inorganic filler.

8) The resin composition according to any one of 4) to 7), further containing a hydrazide compound.

9) The resin composition according to any one of 4) to 8), further containing a silane coupling agent.

10) An adhesive agent for electronic parts, using the resin composition according to any one of 4) to 9).

11) An adhesive agent for liquid crystal display cells, using the resin composition according to any one of 4) to 9).

12) A liquid crystal display cell, adhered using the adhesive agent for liquid crystal display cells according to 11).

Effects of the Invention

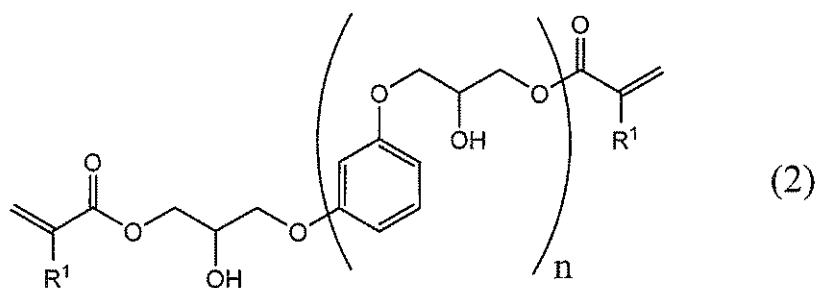
The (meth)acrylic resin of the present invention is very

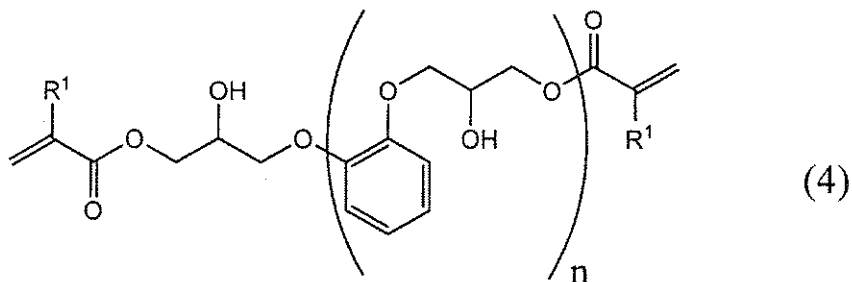
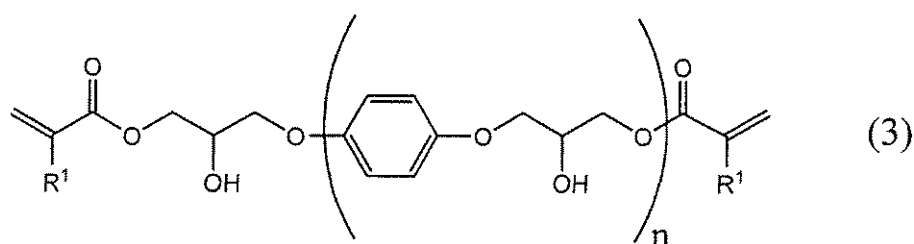
suitably used for the application of adhesive agents. That is, since it has a carboxy group in its molecule and also the carboxy equivalent is lower, improvement in adhesion strength of adhesive agents and a promoting effect on thermosetting reaction can be achieved. Furthermore, its lower molecular mass allows its easy handling and also provides a feature of easy of design when used as an adhesive agent even without using dilution agents such as organic solvents since it is unlikely to be restricted with respect to viscosity of other ingredients.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

Hereinafter, the present invention is explained in detail.

The (meth)acrylic resin of the present invention represented by the above-noted formula (1) can be obtained by reacting an epoxy acrylate resin, represented by formulas (2) to (4) shown below, with an acid anhydride of 0.1 to 30 mole equivalents preferably 1 to 10 mole equivalents in the presence of a reaction catalyst. The reaction temperature is preferably from 0°C to 100°C and more preferably from 10°C to 40°C. Here, n and R^1 in the formulas (2) to (4) mean those identical to n and R^1 in the above-noted formula (1).





The reaction catalyst is not particularly limited thereto; for example, bases may be used, and organic bases are preferable. Tertiary amines are particularly preferable. A mixture of two or more may also be used; in a particularly preferable embodiment, a mixture of 4-(methyldamino)pyridine and triethylamine is used.

The acid anhydride may be exemplified by maleic acid anhydride, dihydro maleic acid anhydride (succinic acid anhydride), phthalic acid anhydride, etc. In addition, the (meth)acrylic resin represented by the above-noted formula (1) can be obtained even using maleic acid, dihydro maleic acid (succinic acid), phthalic acid, etc. in place of the acid anhydrides by appropriately adjusting the additive amount.

An organic solvent may also be used in the synthesis. The organic solvent used may be exemplified by 2-butanon, methylene chloride, etc.; a mixture of two or more may also be used.

The (meth)acrylic resin of the present invention is preferably the resins having a resorcin skeleton rather than the resins having a hydroquinone or catechol skeleton. The reason is that the resorcin skeleton shows lower symmetry than that of the hydroquinone skeleton and is easily available compared to the catechol skeleton, and curing reaction of resins is faster. Furthermore, acrylic resins are more preferable than methacrylic resins in view of reaction speed. It is also preferred that maleic acid anhydride is used as the acid anhydride in order to reduce the carboxy equivalent.

The resin composition using the (meth)acrylic resin of the present invention is favorably applied for adhesive agents. In this case, the content of the (meth)acrylic resin is preferably from 0.01 to 95 parts by mass based on 100 parts by mass of the total amount of the resin composition. Furthermore, it is more preferably from 0.1 to 90 parts by mass and particularly preferably from 1 to 80 parts by mass. The remaining parts are of photo-polymerization initiator, thermal radical polymerization initiator, inorganic filler, thermosetting agent, silane coupling agent, etc.

The photo-polymerization initiator, which the resin composition of the present invention may include, is not particularly limited as long as a radical is generated upon being irradiated with an energy beam such as ultraviolet rays and visible light to thereby initiate a chain polymerization reaction and may be exemplified by benzyl dimethyl ketal, 1-hydroxycyclohexyl phenyl ketone, diethylthioxantone,

benzophenone, 2-ethyl anthraquinone, 2-hydroxy-2-methylpropiophenone, 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propane, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, etc. When used as an adhesive agent for liquid crystal display cells described below and in use at portions directly contacting a liquid crystal, those having a (meth)acryloyl group in their molecules are preferably used in view of staining properties to the liquid crystal; for example, a reaction product between 2-methacryloyloxyethyl isocyanate and 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one is favorably used. The compound can be obtained by producing in accordance with the method described in WO 2006/027982. The content of the photo-polymerization initiator is typically from 0.1 to 10 parts by mass and preferably from 0.2 to 5 parts by mass based on 100 parts by mass of the total amount of the resin composition of the present invention.

The thermal radical polymerization initiator, which the resin composition of the present invention may include, is not particularly limited as long as a radical is generated upon being heated to thereby initiate a chain polymerization reaction and may be exemplified by organic peroxides, azo compounds, benzoin compounds, benzoin ether compounds, acetophenone compounds, benzopinacol, etc.; and benzopinacol is favorably used. For example, Kayamek A, Kayamek M, Kayamek R, Kayamek L, Kayamek LH, Kayamek SP-30C, Perdox CH-50L, Perdox BC-FF, Kadox B-40ES, Perdox 14, Trigonox 22-70E, Trigonox 23-C70, Trigonox 121, Trigonox 121-50E, Trigonox 121-

LS50E, Trigonox 21-LS50E, Trigonox 42, Trigonox 42LS, Kayaester P-70, Kayaester TMPO-70, Kayaester CND-C70, Kayaester O, Kayaester O-50E, Kayaester AN, Kayabutyl B, Perdox 16, Kayacarbon BIC-75, Kayacarbon AIC-75 (by Kayaku Akzo Co.), Permek N, Permek H, Permek S, Permek F, Permek D, Permek G, Perhexa H, Perhexa HC, Perhexa TMH, Perhexa C, Perhexa V, Perhexa 22, Perhexa MC, Percure AH, Percure AL, Percure HB, Perbutyl H, Perbutyl C, Perbutyl ND, Perbutyl L, Percumyl H, Percumyl D, Perloyl IB, Perloyl IPP, Perocta ND (by NOF Co.), etc. are commercially available as the organic peroxides. VA-044, V-070, VPE-0201, VSP-1001 (by Wako Pure Chemical Industries, Ltd.), etc. are also commercially available as the azo compounds. The content of the thermal radical polymerization initiator is preferably from 0.0001 to 10 parts by mass, more preferably from 0.0005 to 7 parts by mass, and particularly preferably from 0.001 to 3 parts by mass based on 100 parts by mass of the total amount of the resin composition of the present invention.

The inorganic filler, which the resin composition of the present invention may include, may be exemplified by molten silica, crystalline silica, silicon carbide, silicon nitride, boron nitride, calcium carbonate, magnesium carbonate, barium sulfate, calcium sulfate, mica, talc, clay, alumina, magnesium oxide, zirconium oxide, aluminum hydroxide, magnesium hydroxide, calcium silicate, aluminum silicate, lithium aluminum silicate, zirconium silicate, barium titanate, glass fiber, carbon fiber, molybdenum disulfide, asbestos, etc.; in

which, molten silica, crystalline silica, silicon nitride, boron nitride, calcium carbonate, barium sulfate, calcium sulfate, mica, talc, clay, alumina, aluminum hydroxide, calcium silicate, and aluminum silicate are preferable; and molten silica, crystalline silica, alumina, and talc are more preferable. These inorganic fillers may also be used in a combination of two or more. When used as an adhesive agent for liquid crystal display cells described below, the average particle diameter is appropriately no greater than 3 μm and preferably no greater than 2 μm , since excessively large average particle diameters thereof may cause problems such that a gap cannot be properly formed at the time of laminating upper and lower glass substrates when producing liquid crystal display cells with a narrower gap. The particle diameter can be measured by a laser diffraction-scattering type particle size distribution measuring apparatus (dry type) (by Seishin Enterprise Co., LMS-30).

The content of the inorganic filler in the resin composition is typically from 1 to 60 parts by mass, preferably from 5 to 60 parts by mass, and more preferably from 10 to 50 parts by mass based on 100 parts by mass of the total amount of the resin composition of the present invention. In cases where the content of the inorganic filler is excessively low, adhesion strength may be decreased, and the degradation of adhesive strength after moisture absorption may be larger since moisture-resistant reliability may also be poor. On the other hand, in cases where the content of the

inorganic filler is excessively large, gaps of liquid crystal display cells may not be formed.

The thermosetting agent, which the resin composition of the present invention may include, is not particularly limited (except for the above-noted thermal radical polymerization initiators) and may be exemplified by polyvalent amines, polyhydric phenols, hydrazide compounds, etc.; and in particular, hydrazide compounds are favorably used. For example, aromatic hydrazides such as salicylic acid hydrazide, terephthalic acid dihydrazide, isophthalic acid dihydrazide, 2,6-naphthoic acid dihydrazide, 2,6-pyridine dihydrazide, 1,2,4-benzene trihydrazide, 1,4,5,8-naphthoic acid tetrahydrazide, and pyromellitic acid tetrahydrazide may be exemplified. In cases of aliphatic hydrazide compounds, for example, formhydrazide, acetohydrazide, propionic acid hydrazide, oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, pimelic acid dihydrazide, 1,4-cyclohexane dihydrazide, tartaric acid dihydrazide, malic acid dihydrazide, iminodiacetic acid dihydrazide, N,N'-hexamethylene bis-semicarbazide, citric acid trihydrazide, nitriloacetic acid trihydrazide, cyclohexane tricarboxylic acid trihydrazide; dihydrazide compounds having a hydantoin skeleton, preferably a valine hydantoin skeleton (skeleton where a carbon atom of a hydantoin ring is substituted with an isopropyl group), such as 1,3-bis(hydrazinocarbonyl)-5-isopropyl hydantoin; tris(1-hydrazinocarbonyl-methyl)isocyanurate, tris(2-

hydrazinocarbonyl-ethyl)isocyanurate, tris(2-hydrazinocarbonyl-ethyl)isocyanurate, tris(3-hydrazinocarbonyl-propyl)isocyanurate, and bis(2-hydrazinocarbonyl-ethyl)isocyanurate may be exemplified. In view of the balance between curing reactivity and latency, isophthalic acid dihydrazide, malonic acid dihydrazide, adipic acid dihydrazide, tris(1-hydrazinocarbonyl-methyl)isocyanurate, tris(2-hydrazinocarbonyl-ethyl)isocyanurate, tris(2-hydrazinocarbonyl-ethyl)isocyanurate, and tris(3-hydrazinocarbonyl-propyl)isocyanurate are preferable; and tris(2-hydrazinocarbonyl-ethyl)isocyanurate is particularly preferable. In cases of using the thermosetting agent, the amount used is preferably from 0.1 to 20 parts by mass and more preferably from 1 to 10 parts by mass based on 100 parts by mass of the total amount of the resin composition of the present invention; a mixture of two or more may also be used.

The silane coupling agent, which the resin composition of the present invention may include, may be exemplified by 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropyl methyldimethoxysilane, 3-glycidoxypropyl methyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyl trimethoxysilane, N-phenyl-γ-aminopropyl trimethoxysilane, N-(2-aminoethyl)-3-aminopropyl methyldimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyl trimethoxysilane, 3-aminopropyl triethoxy silane, 3-mercaptopropyl trimethoxysilane, vinyltrimethoxysilane, N-(2-(vinylbenzylamino)ethyl)-3-aminopropyl trimethoxysilane hydrochloride, 3-methacryloxypropyl trimethoxysilane, 3-

chloropropyl methyldimethoxysilane, 3-chloropropyl trimethoxysilane, etc. The content of the silane coupling agent in the resin composition is preferably from 0.05 to 3 parts by mass based on 100 parts by mass of the total amount of the resin composition of the present invention.

The resin composition of the present invention may contain a curable resin, as another resin component, consisting of one or more selected from epoxy resins, (meth)acrylated epoxy resins, and partially (meth)acrylated epoxy resins. For example, an epoxy resin, a mixture of an epoxy resin and a (meth)acrylated epoxy resin, a (meth)acrylated epoxy resin, and a partially (meth)acrylated epoxy resin may be exemplified. When used as an adhesive agent for liquid crystal display cells and in use at portions directly contacting a liquid crystal in particular, those exhibiting lower staining properties and solubility to the liquid crystal are preferable. Examples of preferable epoxy resins are bisphenol A type epoxy resins, bisphenol F type epoxy resins, bisphenol S type epoxy resins, phenol novolak type epoxy resins, cresol novolak type epoxy resins, bisphenol A novolak type epoxy resins, bisphenol F novolak type epoxy resins, alicyclic epoxy resins, aliphatic chain epoxy resins, glycidyl ester type epoxy resins, glycidyl amine type epoxy resins, hydantoin type epoxy resins, isocyanurate type epoxy resins, and phenol novolak type epoxy resins having a triphenolmethane skeleton; in addition, diglycidyl-etherified compounds of bifunctional phenols, diglycidyl-etherified

compounds of bifunctional alcohols, and halogenated compounds or hydrogen additives thereof; but which are not exclusive. A (meth)acryloylated epoxy resin or a partially (meth)acryloylated epoxy resin can be obtained by a well-known reaction between an epoxy resin and a (meth)acrylic acid. For example, it can be obtained by adding a (meth)acrylic acid, a catalyst (e.g., benzyl dimethyl amine, triethyl amine, benzyl trimethyl ammonium chloride, triphenylphosphine, triphenylstibine, etc.), and a polymerization inhibitor (e.g., methoquinone, hydroquinone, methylhydroquinone, phenothiazine, dibutylhydroxytoluene, etc.) to an epoxy resin in predetermined equivalent ratios to conduct an esterification reaction at from 80°C to 110°C. The epoxy resin of raw material, which is not particularly limited, is preferably bifunctional or higher functional epoxy resins; examples thereof are bisphenol A type epoxy resins, bisphenol F type epoxy resins, bisphenol S type epoxy resins, phenol novolak type epoxy resins, cresol novolak type epoxy resins, bisphenol A novolak type epoxy resins, bisphenol F novolak type epoxy resins, alicyclic epoxy resins, aliphatic chain epoxy resins, glycidyl ester type epoxy resins, glycidyl amine type epoxy resins, hydantoin type epoxy resins, isocyanurate type epoxy resins, and phenol novolak type epoxy resins having a triphenolmethane skeleton; in addition, diglycidyl-etherified compounds of bifunctional phenols, diglycidyl-etherified compounds of bifunctional alcohols, and halogenated compounds or hydrogen additives thereof. Among these, from the viewpoint

of staining properties to liquid crystals, bisphenol type epoxy resins and novolak type epoxy resins are more preferable. Additionally, the ratio between epoxy group and (meth)acryloyl group, which is not particularly limited thereto, may be appropriately selected from the viewpoints of adaptability to processes and staining properties to liquid crystals.

The resin composition of the present invention may be further compounded with a monomer or an oligomer of (meth)acrylic acid ester as required. For example, the monomer or oligomer may be exemplified by a reaction product between dipentaerythritol and (meth)acrylic acid, a reaction product between dipentaerythritol-caprolactone and (meth)acrylic acid, etc.; but which are not particularly restrictive.

The resin composition of the present invention may be further compounded with organic fillers and additives such as pigments, leveling agents, antifoam agents, and solvents as required.

An exemplary method to obtain the resin composition of the present invention is the method shown below. Initially, a photo-polymerization initiator, another (meth)acrylic resin, an epoxy resin, etc. are heated and dissolved in the (meth)acrylic resin of the present invention and which are then cooled to room temperature, followed by being mixed with an inorganic filler, a silane coupling agent, a thermal radical polymerization initiator, a thermosetting agent, etc., which are then mixed more uniformly by conventional mixing devices such as triple rolls, sand mills, and ball mills and

filtered through a metal mesh, thereby the resin composition of the present invention can be produced.

The resin composition of the present invention is very useful for an adhesive agent for electronic parts. The adhesive agent for electronic parts may be exemplified by an adhesive agent for flexible printed-wiring boards, an adhesive agent for TABs, an adhesive agent for semiconductors, an adhesive agent for various displays, etc., but which are not exclusive.

The resin composition of the present invention is also very useful as an adhesive agent for liquid crystal display cells, in particular as a liquid crystal sealing agent. Liquid crystal display cells are exemplified below for the cases where the resin composition of the present invention is used as a liquid crystal sealing agent.

In the liquid crystal display cell produced using the adhesive agent for liquid crystal display cells of the present invention, a pair of substrates where predetermined electrodes have been formed are oppositely disposed with a predetermined gap, a periphery thereof is sealed with the liquid crystal sealing agent of the present invention, and a liquid crystal is encapsulated in the gap. The type of the liquid crystal encapsulated is not particularly limited. Here, the substrates are formed of a combination of substrates such as glass, quartz, plastic, and silicon, in which at least one of the substrates is light-transmissive. In the production method, a spacer (space control material) such as of glass fiber is

added to the liquid crystal sealing agent of the present invention, then the liquid crystal sealing agent is coated on one of the pair of substrates using a dispenser, a screen printing device, etc., followed by provisional curing at from 80°C to 120°C as required. Then, a liquid crystal is added drop-wise inside a weir of the liquid crystal sealing agent, and another glass substrate is superimposed under vacuum to create a gap. After creating the gap, UV rays are irradiated at a site of the liquid crystal sealing agent by a UV-ray irradiation device to cause photocuring. Irradiation amount of the UV rays is preferably from 500 to 6000 mJ/cm² and more preferably from 1000 to 4000 mJ/cm². By curing afterward for 1 to 2 hours at from 90°C to 130°C as required, the liquid crystal display cell of the present invention can be obtained. The liquid crystal display cell of the present invention obtained in this way is free from display failure due to contamination of liquid crystal and is excellent in adhesion properties and moisture-resistant reliability. The spacer may be exemplified by glass fiber, silica beads, polymer beads, etc. The diameter thereof, which depends on the purpose, is typically from 2 μm to 8 μm and preferably from 4 μm to 7 μm. The amount used is typically from 0.1 to 4 parts by mass, preferably from 0.5 to 2 parts by mass, and more preferably about from 0.9 to 1.5 parts by mass based on 100 parts by mass of the liquid crystal sealing agent of the present invention.

The novel (meth)acrylic resin of the present invention is very suitably used for the application of adhesive agents.

That is, since it has a carboxy group in its molecule and also the carboxy equivalent is lower, improvement in adhesion strength of adhesive agents and a promoting effect on thermosetting reaction can be achieved. Furthermore, its lower molecular mass allows easy handling thereof and also provides a feature of easy design when used as an adhesive agent, since it is unlikely to be restricted with respect to viscosity of other ingredients. The resin composition using the (meth)acrylic resin of the present invention is very useful as an adhesive agent for electronic parts or an adhesive agent for liquid crystal display cells.

EXAMPLES

Hereinafter, the present invention is explained more specifically with reference to synthesis examples and examples, but to which the present invention is not limited. In addition, expressions with the term "part" or "%" in the specification are on a mass basis unless indicated otherwise.

Synthesis Example 1: Synthesis of Acrylated Resorcin Diglycidyl Ether

181.2 g of resorcin diglycidyl ether (by Nagase Chemtex Co.) was dissolved in 266.8 g of toluene, and to which 0.8 g of dibutyl hydroxy toluene was added as a polymerization inhibitor, followed by raising the temperature to 60°C. Then, 117.5 g of acrylic acid of 100% equivalent to the epoxy group was added and the temperature was further raised to 80°C, and

0.6 g of trimethyl ammonium chloride as a reaction catalyst was added thereto, followed by stirring at 98°C for about 30 hours to obtain a reaction liquid. The reaction liquid was rinsed with water followed by distilling away the toluene, thereby obtaining 253 g of an intended epoxy acrylate of resorcin diglycidyl ether (acrylated resorcin diglycidyl ether).

Synthesis Example 2: Synthesis of Maleic Acid Anhydride Adduct of Acrylated Resorcin Diglycidyl Ether

To 3.66 g of epoxy acrylate of resorcin diglycidyl ether resulting from Synthesis Example 1, 0.049 g of 4-dimethylamino pyridine, 6.07 g of triethylamine, and 1000 mL of methylene chloride were added, and which were dissolved by stirring at room temperature, to which then 11.8 g of maleic acid anhydride was added, followed by stirring at room temperature overnight. The resulting reaction liquid was rinsed three times with dilute hydrochloric acid and then three times with water followed by distilling away methylene chloride, thereby obtaining 5 g of acrylated resorcinol diglycidyl ether having a carboxy group in its molecule. LC MS (m/z) = 561 (M-H), IR 1705 cm^{-1} (COOH).

(Preparation of Sealing Agent for Liquid Crystal Dropping Process)

Example 1

In accordance with the ratios shown in Table 1 below, the

acrylic resin of the present invention synthesized in Synthesis Example 2 was heated and dissolved at 90°C, the photo-polymerization initiator was heated and dissolved therein followed by cooling to room temperature, to which then the silane coupling agent, the silica, and the thermosetting agent were added and stirred, followed by dispersing by a three roll mill and filtering through a metal mesh (635 mesh), thereby preparing the sealing agent for liquid crystal dropping process of Example 1.

Comparative Examples 1 to 2

Furthermore, similarly in accordance with the ratios shown in Table 1 below, the acrylic resin of the present invention synthesized in Synthesis Example 1 was heated to 90°C, the photo-polymerization initiator was heated and dissolved therein followed by cooling to room temperature, to which then the silane coupling agent, the silica, the thermosetting agent, and the curing accelerator were added and stirred, followed by dispersing by a three roll mill and filtering through a metal mesh (635 mesh), thereby preparing the sealing agents for liquid crystal dropping process of Comparative Examples 1 and 2.

Evaluation tests were performed by the methods below.

(Test of Moisture-Resistant Adhesion Strength)

1 g of 5 μ m glass fiber as a spacer was added to 100 g of the resulting liquid crystal sealing agents, which were then

mixed and stirred. The liquid crystal sealing agents were coated on a glass substrate of 50 mm by 50 mm, and a glass piece of 1.5 mm by 1.5 mm was stuck on the liquid crystal sealing agents to irradiate UV rays of 3000 mJ/cm^2 by a UV irradiation device, which were then placed in an oven to thermally cure at 120°C for 1 hour. The test pieces were placed in a pressure cooker tester (TPC-411, by Tabai Espec Co.) for 12 hours under a condition of 121°C , 2 atoms, and 100% humidity, then shear adhesion strengths of the glass pieces were measured by a bond tester (SS-30WD, by Seishin Trading Co.). The results are shown in Table 1.

(Test of Curing Speed)

The resulting liquid crystal sealing agents were measured for complex viscosity coefficients by a dynamic viscoelastic modulus measuring apparatus (Rheosol-G5000, by UBM Co.). The dynamic viscoelastic modulus measuring apparatus was set as follows: cone was a parallel cone of 20 mm diameter, frequency was 1 Hz, strain degree was 3 degrees, and the measurement temperature was raised from 30°C to 120°C at a rate of 18°C/min and maintained at 120°C afterward. The times when the viscosity reached $10000 \text{ Pa}\cdot\text{s}$ are shown in Table 1.

[Table 1]

			Example 1	Compara tive Example 1	Compara tive Example 2
#1	Novel acrylic resin	Acid anhydride adduct of epoxy acrylate of resorcin diglycidyl ether	16 parts		
#2	Acrylic resin	Epoxy acrylate of resorcin diglycidyl ether		16 parts	16 parts
#3	Thermosetting agent	Tris(2-hydrazinocarbonyl-ethyl) isocyanurate	1 part	1 part	1 part
#4	Silane coupling agent	3-Glycidioxypropyl trimethoxysilane	0.1 part	0.1 part	0.1 part
#5	Inorganic filler	Silica	3 parts	3 parts	3 parts
#6	Photo-polymerization initiator	Reaction product between 2-methacryloyloxyethyl isocyanate and 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one	1 part	1 part	1 part
#7	Curing accelerator	1,3,5-Tris(2-carboxyethyl) isocyanurate		1 part	
Test of moisture-resistant adhesion strength			50 MPa	30 MPa	50 MPa
Test of curing speed			4 sec	4 sec	8 sec

#1 : Synthesized in Synthesis Example 2.

#2 : Synthesized in Synthesis Example 1.

#3 : HCIC (by Japan Finechem Co.)

HCIC was used after finely milling to average particle diameter 1.5 μm and maximum particle diameter 5 μm by a jet mill.

#4 : Sila-Ace S510 (by Chisso Co.)

#5 : Admafine SE2 (by Admatechs Co.)

#6 : Synthesized by the method described in WO 2006/027982.

#7 : CIC acid (by Shikoku Chemicals Co.)

CIC acid was used after finely milling to average particle diameter 1.5 μm and maximum particle diameter 5 μm by a jet mill.

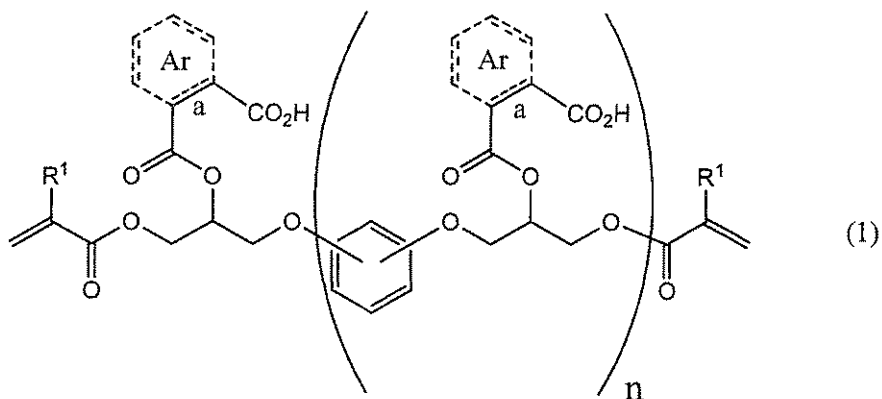
It is understood from the results of Table 1 that, in Comparative Example 1, the time to reach 10000 Pa·s is fast because of containing CIC acid but the moisture-resistant adhesion strength is poor. It is understood that, in Comparative Example 2, the moisture-resistant adhesion strength is high because of not containing CIC acid but the curing speed is slow. On the other hand, in Example 1, the time to reach 10000 Pa·s is fast even without using CIC acid and also the moisture-resistant adhesion strength is high. Consequently, the (meth)acrylic resin of the present invention allows to enhance both of moisture-resistant adhesion strength and curing ability at the same time.

INDUSTRIAL APPLICABILITY

The novel (meth)acrylic resin of the present invention and resin compositions using the same are very useful as an adhesive agent for electronic parts particularly as a liquid crystal sealing agent.

CLAIMS

1. A (meth)acrylic resin represented by formula (1) below:



wherein, benzene ring Ar may be present or absent; when no benzene ring Ar exists, bond "a" represents a single bond or a double bond;

n represents an integer of from 1 to 5; and R¹ represents a hydrogen atom or a methyl group.

2. The (meth)acrylic resin according to claim 1, wherein no benzene ring Ar exists in the formula (1).

3. The (meth)acrylic resin according to claim 1 or 2, wherein R¹ is a hydrogen atom in the formula (1).

4. A resin composition, comprising the (meth)acrylic resin according to any one of claims 1 to 3.

5. The resin composition according to claim 4, further comprising a photo-polymerization initiator.

6. The resin composition according to claim 4 or 5, further comprising a thermal radical polymerization initiator.
7. The resin composition according to any one of claims 4 to 6, further comprising an inorganic filler.
8. The resin composition according to any one of claims 4 to 7, further comprising a hydrazide compound.
9. The resin composition according to any one of claims 4 to 8, further comprising a silane coupling agent.
10. An adhesive agent for electronic parts, using the resin composition according to any one of claims 4 to 9.
11. An adhesive agent for liquid crystal display cells, using the resin composition according to any one of claims 4 to 9.
12. A liquid crystal display cell, adhered using the adhesive agent for liquid crystal display cells according to claim 11.