A curable liquid resin composition comprising: (A) a urethane (meth)acrylate having a structure derived from polypropylene glycol with a number average molecular weight of about 4,000 or less; (B) a urethane (meth)acrylate having a structure derived from a polypropylene glycol with a number average molecular weight of more than about 4,000; (C) a (meth)acrylate monomer; and (D) a polymerization initiator, wherein from about 50 to about 80 mass% of the component (C) is 2-ethylhexyl (meth)acrylate, and from about 50 to about 90 mass% of the component (D) is 1-hydroxycyclohexyl phenyl ketone is described and claimed. This composition, when cured, provides a cured product having low self-adhesiveness and a high stress relaxation rate. The composition is suitable for use as a Secondary Coating or as a Matrix Coating for Optical Fibers.
Title: Curable liquid resin composition

FIELD OF THE INVENTION

The present invention relates to a curable liquid resin composition which produces a cured product having low self-adhesiveness and a high stress relaxation rate.

BACKGROUND OF THE INVENTION

In the manufacture of optical fibers, a resin coating is provided over a glass fiber for protection and reinforcement immediately after the glass fiber is produced by spinning molten glass. As the resin coating, a structure is known in which a flexible primary coating layer is formed on a surface of the glass fiber and a more rigid secondary coating layer is applied over the primary coating layer. A structure is also known in which, for example, four or eight resin-coated optical fibers are placed side by side in a plane and bundled with a bundling material to produce a ribbon-shaped coating layer having a rectangular section. A resin composition for forming the primary coating layer is called a primary material, a resin composition for forming the secondary coating layer is called a secondary material, and a material for bundling optical fibers is called a ribbon matrix material.

The secondary material or the ribbon matrix material is generally positioned in the outermost layer during the production process. For example, an optical fiber coated with the cured secondary material is stored in a state in which the optical fiber is wound around a bobbin, and is then unwound from the bobbin when applying an ink layer or forming a ribbon. The optical fiber ribbon is also stored in a wound state so that portions of the ribbon are rubbed against each other when forming a cable. Since portions of the cured secondary material or the ribbon matrix materials come in contact in this manner, if the cured material has high adhesion, the optical fiber is not regularly wound around the bobbin and is not smoothly unwound, thereby hindering the production process.

As an attempt to decrease the self-adhesiveness of the cured product, a processing method of curing the material in a nitrogen atmosphere is known. However, adhesiveness increases if the material is cured in an atmosphere containing oxygen. Therefore, an effective solution in terms of the material is desired.

SUMMARY OF THE INVENTION

The first aspect of the instant claimed invention is a radiation curable liquid resin composition comprising:

(A) a urethane (meth)acrylate having a structure derived from polypropylene glycol with a number average molecular weight of about 4,000 or less;
(B) a urethane (meth)acrylate having a structure derived from a polypropylene glycol with a number average molecular weight of more then about 4000;
(C) a (meth)acrylate monomer; and
(D) a polymerization initiator;
wherein from about 50 to about 80 mass% of the component (C) is 2-ethylhexyl (meth)acrylate, and from about 50 to about 90 mass% of the component (D) is 1-hydroxycyclohexyl phenyl ketone.

The second aspect of the instant claimed invention is an optical fiber comprising the coating layer according to the first aspect of the instant claimed invention.
The third aspect of the instant claimed invention is an optical fiber ribbon comprising the coating layer according to the first aspect of the instant claimed invention.

The fourth aspect of the instant claimed invention is a process to coat an optical fiber with at least two radiation curable liquid resin compositions comprising

a) providing an optical fiber;

b) coating said optical fiber with a radiation curable coating, which is a primary coating, and optionally applying radiation to cure said primary coating;

c) coating said optical fiber with a second radiation curable coating, which is a secondary coating, applied over the primary coating;

d) applying radiation to cure said secondary coating; and optionally
e) coating said optical fiber with a matrix radiation curable coating and applying radiation to cure said matrix radiation curable coating;

wherein either the secondary coating or the optional matrix radiation curable coating is the composition of the first aspect of the instant claimed invention.

An object of the present invention is to provide a curable liquid resin composition which produces a cured product, used as a Secondary Coating or a Matrix Coating, where the product has low self-adhesiveness and a high stress relaxation rate.

The inventors of the present invention have found that the above object can be achieved by combining two types of specific urethane (meth)acrylate s, a specific urethane (meth)acrylate monomer, and a specific polymerization initiator. This finding has led to the completion of the present invention.

The cured product obtained by curing the curable liquid resin composition of the present invention exhibits low self adhesion, excellent surface sliding properties, a high stress-relaxation rate, and high strength to an external stress.
DETAILED DESCRIPTION OF THE INVENTION

The urethane (meth)acrylate used as the component (A) of the present invention has a structure derived from polypropylene glycol having a number average molecular weight of about 4,000 or less, and is produced by, for example, reacting a polypropylene glycol having a number average molecular weight of about 4,000 or less, a diisocyanate, and a hydroxyl-group-containing (meth)acrylate. Specifically, the urethane (meth)acrylate is produced by reacting isocyanate groups of the diisocyanate with hydroxyl groups of the polyol and the hydroxyl group-containing (meth)acrylate.

As the method for reacting these compounds, a method of reacting the polyol, the diisocyanate, and the hydroxyl group-containing (meth)acrylate all together; a method of reacting the polyol with the diisocyanate, and reacting the resulting product with the hydroxyl group-containing (meth)acrylate; a method of reacting the diisocyanate with the hydroxyl group-containing (meth)acrylate, and reacting the resulting product with the polyol; a method of reacting the diisocyanate with the hydroxyl group-containing (meth)acrylate, reacting the resulting product with the polyol, and further reacting the resulting product with the hydroxyl group-containing (meth)acrylate; and the like can be given.

The polyol used is a polypropylene glycol having a number average molecular weight of about 4,000 or less, and preferably from about 500 to about 4,000. The number average molecular weight is determined by gel permeation chromatography (GPC method) as a polystyrene-reduced molecular weight.

The polypropylene glycol is commercially available as "PPG-400", "PPG1000", "PPG2000", "PPG3000", "EXCENOL 720", "EXCENOL 1020", and "EXCENOL 2020" (manufactured by Asahi Glass Urethane Co., Ltd.), and the like.
As examples of the diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3′-dimethyl-4,4′-diphenylmethane diisocyanate, 4,4′-diphenylmethane diisocyanate, 3,3′-dimethylphenylene diisocyanate, 4,4′-biphenylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, methylenebis(4-cyclohexylisocyanate), 2,2,4-trimethylhexamethylene diisocyanate, bis(2-isocyanateethyl)fumarate, 6-isopropyl-l,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, lysine diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated xylylene diisocyanate, tetramethylxylylene diisocyanate, 2,5(or 2,6)-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, and the like can be given. Of these, 2,4-tolylene diisocyanate, isophorone diisocyanate, xylylene diisocyanate, and methylenebis(4-cyclohexylisocyanate) are preferable.

These diisocyanates may be used either individually or in combination of two or more.

Examples of (meth)acrylates containing a hydroxyl group include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butaneopolyol mono(meth)acrylate, 2-hydroxyalkyl(meth)acryloyl phosphate, 4-hydroxycyclohexyl (meth)acrylate, 1,6-hexaneopolyol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethylene di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, and (meth)acrylates shown by the following formulas (1) and (2):

\[
\begin{align*}
\text{CH}_2=\text{C}(\text{R}^1)\text{- COOCH}_2\text{CH}_2\text{- (OCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{G}_2\text{H}_2\text{)}_n\text{HO} & \quad (1) \\
\text{CH}_2=\text{C}(\text{R}^1)\text{- COOCH}_2\text{CH(OH)CH}_2\text{- O-} & \quad (2)
\end{align*}
\]
wherein $R_1$ represents a hydrogen atom or a methyl group and $n$ is an integer from 1 to 15.

A compound obtained by the addition reaction of (meth)acrylic acid and a glycidyl group-containing compound such as an alkyl glycidyl ether, allyl glycidyl ether, or glycidyl (meth)acrylate may also be used. Of these hydroxyl group-containing (meth)acrylates, 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate are preferable.

These hydroxyl group-containing (meth)acrylate compounds may be used either individually or in combination of two or more.

The polyol, the diisocyanate, and the hydroxyl group-containing (meth)acrylate are preferably used so that the isocyanate groups included in the diisocyanate and the hydroxyl groups included in the hydroxyl group-containing (meth)acrylate are respectively 1.1 to 3 equivalents and 0.2 to 1.5 equivalents for one equivalent of the hydroxyl groups included in the polyol.

When reacting these compounds, it is preferable to use a urethanization catalyst such as copper naphthenate, cobalt naphthenate, zinc naphthenate, dibutyltin dilaurate, triethylamine, 1,4-diazabicyclo[2.2.2]octane, or 2,6,7-trimethyl-1,4-diazabicyclo[2.2.2]octane in an amount of 0.01 to 1 part by mass for 100 parts by mass of the reactants. The reaction temperature is preferably 10 to 90°C, and particularly preferably 30 to 80°C.

The hydroxyl group-containing (meth)acrylate may be partially replaced with a compound having a functional group which can be added to an isocyanate group. As examples of such compound, γ-mercaptoptrimethoxysilane, γ-aminotrimethoxysilane, or the like can be given. Use of these compounds improves adhesion to a substrate such as glass.

The urethane (meth)acrylate of component (A) is added to the curable liquid resin composition of the present invention in an amount of preferably from about 20 to about 50 mass%, and particularly preferably from about 25 to about 40 mass%.
The urethane (meth)acrylate used as the component (B) of the present invention has a structure derived from polypropylene glycol having a number average molecular weight of more than about 4,000, and may be prepared by using polypropylene glycol having a number average molecular weight of more than about 4,000 instead of the polypropylene glycol having a number average molecular weight of about 4,000 or less used for preparing the urethane (meth)acrylate of the component (A).

A polypropylene glycol having a number average molecular weight of more than about 4,000, preferably from about 6,000 to about 20,000, more preferably from about 7,000 to about 18,000, and particularly preferably from about 7,000 to about 16,000 is used.

The commercially available products such as "PREMINOL PML S-X4008", "PREMINOL PML S-4011", "PREMINOL PML S-X3008", "PREMINOL PML S-3011", "PREMINOL PML S-X3015", "PREMINOL PML 4016", "PREMINOL PML 7001", "PREMINOL PML 7003", and "PREMINOL PML 7012" (manufactured by Asahi Glass Urethane Co., Ltd.), and the like can also be used.

In order to reduce self adhesion, the urethane (meth)acrylate of the component (B) is added to the curable liquid resin composition of the present invention in an amount of preferably from about 0.5 to about 7 mass%, and particularly preferably from about 1 to about 5 mass%.

To the extent not inhibiting the effect of the curable liquid resin composition of the present invention, other urethane (meth)acrylates (urethane (meth)acrylate (B')) may optionally be added in addition to the urethane (meth)acrylate (A) and the urethane (meth)acrylate (B). As examples of such a urethane (meth)acrylate, urethane (meth)acrylate which does not contain a polyol component and is obtained by reacting a diisocyanate compound and a hydroxyl group-containing (meth)acrylate compound can be given. The diisocyanate compound and the hydroxyl group-containing (meth)acrylate mentioned above as raw materials for synthesizing the
component (A) may be preferably used as a diisocyanate compound and a hydroxyl group-containing (meth)acrylate used for synthesizing the urethane (meth)acrylate (B').

As preferable examples of the urethane (meth)acrylate (B') other than the component (A) and the component (B), a reaction product of 2-hydroxyethyl (meth)acrylate and 2,4-tolylene diisocyanate at a molar ratio of 2:1, an equimolar reaction product of 2-hydroxypropyl (meth)acrylate, 2,4-tolylene diisocyanate, and 2-hydroxyethyl (meth)acrylate, and the like can be given.

The amount of the urethane (meth)acrylate (B') other than the component (A) and the component (B) to be added to the curable liquid resin composition of the present invention is preferably from about 20 to about 70 mass%, and particularly from about 30 to about 45 mass%.

As examples of the (meth)acrylate monomer of the component (C), monofunctional (meth)acrylates such as, for example, (meth)acrylates having an alkyl group such as butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, amyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, iso-octyl (meth)acrylate, nonyl (meth)acrylate, iso-nonyl (meth)acrylate, decyl (meth)acrylate, iso-decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, and lauryl (meth)acrylate; (meth)acrylates having an alicyclic structure such as isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentany1 (meth)acrylate, dicyclopentenyl (meth)acrylate, 4-butylcyclohexyl (meth)acrylate, and cyclohexyl (meth)acrylate;

(meth)acrylates having an aromatic ring such as benzyl (meth)acrylate; and other (meth)acrylates such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl acrylate, stearyl (meth)acrylate, iso-stearyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate,
methoxypolyethylene glycol (meth)acrylate, methoxy polypropylene glycol (meth) acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, and 7-amino-3,7-dimethyloctyl (meth)acrylate; as well as polyfunctional (meth)acrylates such as trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth) acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropanetrioxyethyl (meth) acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, di(meth) acrylate of diol of ethylene oxide or propylene oxide adduct of bisphenol A, di(meth)acrylate of diol of ethylene oxide or propylene oxide adduct of hydrogenated bisphenol A, epoxy(meth)acrylate obtained by the addition of (meth)acrylate to diglycidyl ether of bisphenol A, triethylene glycol divinyl ether, and the like can be given.

As examples of the commercially available products of the above monofunctional (meth)acrylates, "Aronix M-IH", "Aronix M-113", "Aronix M-114", and "Aronix M-117" (manufactured by Toagosei Co., Ltd.), "KAYARAD TCHOS", "KAYARADR629", and "KAYARADR644" (manufactured by Nippon Kayaku Co., Ltd.), "IBXA" and "Viscoat 3700" (manufactured by Osaka Organic Chemical Industry, Ltd.); and as the commercially available polyfunctional (meth)acrylates, "Yupimer UV SA1002" and "Yupimer UV SA2007" (manufactured by Mitsubishi Chemical Corp.), "Viscoat 700" (manufactured by Osaka Organic Chemical Industry, Ltd.), "KAYARADR-604", "KAYARADDPCA-20", "KAYARADDPCA-30", "KAYARADDPCA-60", "KAYARADDPCA-120", "KAYARADHX-620", "KAYARADD-310", and "KAYARADD-330" (manufactured by Nippon Kayaku Co., Ltd.), "ARONIX M-210", "ARONIX M-215", "ARONIX M-315", and "ARONIX M-325" (manufactured by Toagosei Co., Ltd.), and the like can be given.
In the present invention, from about 50 to about 80 mass%, and preferably from about 55 to about 70 mass% of the (meth)acrylate monomer of the component (C) is 2-ethylhexyl(meth)acrylate.

The amount of the (meth)acrylate monomer of the component (C) in the curable liquid resin composition of the present invention is preferably 20 to 50 mass%, and more preferably from about 25 to about 35 mass%.

As the polymerization initiator used as the component (D), a photopolymerization initiator or a heat polymerization initiator can be used.

When curing the curable liquid resin composition of the present invention using heat, a heat polymerization initiator such as a peroxide or an azo compound can be used. As specific examples of the heat polymerization initiator, benzoyl peroxide, t-butyl-oxybenzoate, azobisisobutyronitrile, and the like can be given.

When curing the curable liquid resin composition of the present invention using light, a photopolymerization initiator is used. In addition, a photosensitizer may optionally be added. Given as examples of the photopolymerization initiator are 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropane-1-one, 2-hydroxy-2-methyl-1-phenylpropane-1-one, thioxanethone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propane-1-one, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyloxyphosphine oxide; "IRGACURE 184", "IRGACURE 369", "IRGACURE 651", "IRGACURE 500", "IRGACURE 907", "CG1 1700", "CG1 1750", "CG1 1850", "CG24-61", "Darocur 1116", and "Darocur 1173" (manufactured by Ciba Specialty Chemicals Co.); "Lucirin LR8728"
(manufactured by BASF); and "Ubecryl P36" (manufactured by UCB). As examples of the photosensitizer, triethylamine, diethylamine, N-methylidethanol amine, ethanolamine, 4-dimethylaminobenzoic acid, 4-methyl dimethylaminobenzoate, 4-ethyl dimethylaminobenzoate, 4-isoamyl dimethylaminobenzoate; "Ubecryl P102", "Ubecryl P103", "Ubecryl P104", and "Ubecryl P105" (manufactured by UCB); and the like can be given.

In the present invention, from about 50 to about 90 mass%, and preferably from about 65 to about 90 mass% of the polymerization initiators of the component (D) is 1-hydroxycyclohexyl phenyl ketone. If the amount of 1-hydroxycyclohexyl phenyl ketone is less than about 50 mass%, surface curability (a sticking power) decreases, and if more than about 80 mass%, there is a tendency for the cure speed to decrease.

The polymerization initiator (D) is used in the curable liquid resin composition of the present invention in an amount of preferably from about 0.1 to about 10 mass%, and particularly preferably from about 0.3 to about 7 mass%.

The curable liquid resin composition of the present invention may further comprise a silicone compound having an average molecular weight of from about 1,500 to about 35,000 as a component (E). The component (E) plays an important role in obtaining effects of improving peelability for removing the outermost layer optical fibers formed from the resin composition of the present invention from the adjacent layer thereof. If the average molecular weight of the component (E) is less than about 1,500, sufficient effects of improving peelability may not be obtained. If the average molecular weight of the component (D) exceeds about 35,000, the effects of improving peelability may be insufficient. The average molecular weight is more preferably from about 1,500 to about 20,000, still more preferably from about 1,500 to about 20,000, and particularly preferably from about 3,000 to about 15,000.
It is preferable that the component (E) not include a polymerizable group such as an ethylenically unsaturated group. If the component (E) does not contain a polymerizable group, excellent peelability can be maintained even after subjecting the optical fibers to a heat history.

As examples of the silicone compound, polyether-modified silicone, alkyl-modified silicone, urethane acrylate-modified silicone, urethane-modified silicone, methylstyril-modified silicone, epoxy polyether-modified silicone, alkylaralkyl polyether-modified silicone, and the like can be given. Of these, polyether-modified silicone is particularly preferable. As the polyether-modified silicone, a polydimethylsiloxane compound in which at least one silicon atom is bonded to a group \( \text{R}^{14}(\text{R}^{15}\text{O})_{s}\text{R}^{16}\) - (wherein \( \text{R}^{14} \) represents a hydroxyl group or an alkoxy group having 1 to 10 carbon atoms, \( \text{R}^{15} \) represents an alkylene group having 2 to 4 carbon atoms (\( \text{R}^{15} \) may have two or more different alkylene groups), \( \text{R}^{16} \) represents an alkylene group having 2 to 12 carbon atoms, and \( s \) is an integer of 1 to 20) is preferably used. As \( \text{R}^{15} \) in the above, an ethylene group and a propylene group are preferable, with an ethylene group being particularly preferable. As the commercially available products of the silicone compound which does not include a polymerizable group such as an ethylenically unsaturated group, "SH28PA" (manufactured by Dow Corning Toray Silicone Co., Ltd., dimethylpolysiloxane-polyoxyalkylene copolymer), "Paintad 19" and "Paintad 54" (manufactured by Dow Corning Toray Co., Ltd., dimethylpolysiloxane-polyoxyalkylene copolymer), "Silaplane FM0411" (manufactured by Chisso Corp.), "SF8428" (manufactured by Dow Corning Toray Co., Ltd., dimethylpolysiloxane-polyoxyalkylene copolymer (including side chain OH)), "BYK UV3510" (manufactured by BYK-Chemie Japan., dimethylpolysiloxane-polyoxyalkylene copolymer), and "DC57" (manufactured by Dow Corning Toray Co., Ltd., dimethylpolysiloxane-polyoxyalkylene copolymer), and the like can be given. As the commercially available products of the silicone compound which has a polymerizable group such as an ethylenically unsaturated group, "Tego Rad
2300" and "Tego Rad 2200N" (manufactured by Tego Chemie Service) can be given.

The component (E) is added to the composition in an amount of preferably from about 0.1 to about 50 mass%, more preferably from about 0.5 to about 40 mass%, and particularly preferably from about 1 to about 20 mass% from the viewpoint of ensuring peelability, strength, and weather resistance of the outermost layer.

Additives such as antioxidants, coloring agents, UV absorbers, light stabilizers, heat polymerization inhibitors, leveling agents, surfactants, preservatives, plasticizers, lubricants, solvents, fillers, aging preventives, wettability improvers, and coating surface improvers may be added to the curable liquid resin composition of the present invention in addition to the above-described components.


Other oligomers, polymers, or additives may optionally be included in the composition of the present invention insofar as the characteristics of the composition are not impaired.
As examples of such other oligomers or polymers, polyester (meth)acrylate, epoxy (meth)acrylate, polyamide (meth)acrylate, siloxane polymers having a (meth)acryloyloxy group, glycidyl methacrylate, and the like can be given.

From the viewpoint of handling properties and applicability, the viscosity of the curable liquid resin composition of the present invention at 25°C is preferably from about 0.1 to about 10 Pa·s, more preferably from about 1 to about 8 Pa·s, and particularly preferably from about 2 to about 6 Pa·s.

An aspect of the instant claimed invention is a process to coat an optical fiber with at least two curable liquid resin compositions comprising

a) providing an optical fiber;

b) coating said optical fiber with a radiation curable coating, which is a primary coating, and optionally applying radiation to cure said primary coating;

c) coating said optical fiber with a second radiation curable coating, which is a secondary coating, applied over the primary coating; and

d) applying radiation to cure said secondary coating; and optionally

e) coating said optical fiber with a matrix radiation curable coating and applying radiation to cure said matrix radiation curable coating,

wherein either the secondary coating or the optional matrix radiation curable coating is the composition of Claim 1.

It is known in the art how to manufacture optical fibers and coat them with one or more radiation curable liquid resin compositions. The one or more radiation curable liquid resin compositions may include a Primary Coating, a Secondary Coating and an Ink Coating. Primary Coatings, Secondary Coatings (not of this invention) and Ink Coatings for optical fiber are commercially available from JSR Corporation in Japan, http://www.jsr.co.jp/jsr_e/

and other countries.

The arrangement of optical fibers into a ribbon configuration is standardized based on either industry standard or government standard or both depending upon where the optical fiber is manufactured and used. People of ordinary skill in the art of optical fibers know what type of ribbon configurations are acceptable in what jurisdiction.

The composition of the present invention when used either as a Secondary Coating or as a Matrix coating may be cured by applying heat or radiation. It is preferable under most circumstances to cure by applying radiation. Radiation used herein refers to infrared rays, visible light, ultraviolet rays, X-rays, electron beams, α-rays, β-rays, γ-rays, and the like.

The product of the process is either a coated optical fiber (if the composition of the instant claimed invention is used as a Secondary Coating) or an "optical fiber ribbon" (if the composition of the instant claimed invention is used as a Matrix Coating) which is one or more optical fibers arranged in a ribbon configuration.

When the curable liquid resin composition of the present invention is used as a secondary material or ribbon matrix material for optical fibers, the Young's modulus of the product obtained after curing is preferably from about 100 to about 2,500 MPa. {When used as a primary material for optical fibers, the Young's modulus of the cured product is preferably from about 0.5 to about 3 MPa.}

When a 5% extension distortion is given to the cured product at 50% humidity, the stress relaxation time, which is defined as the time required for the stress to decrease to 37% of the initial stress, is usually about 10 minutes or less, preferably five minutes or less, and particularly preferably three minutes or less.
EXAMPLES

The present invention is described below in more detail by examples. However, the present invention is not limited to these examples.

Synthesis Example 1: synthesis of urethane (meth)acrylate (A)

A reaction vessel equipped with a stirrer was charged with 10.68 g of 2,4-tolylene diisocyanate, 0.012 g of 2,6-di-t-butyl-p-cresol, and 0.039 g of dibutyltin dilaurate. The mixture was cooled with ice to 10°C or below while stirring. After the addition of 30.65 g of a ring-opening polymer of propylene oxide having a number average molecular weight of 1,000, the mixture was allowed to react for two hours with stirring while controlling the liquid temperature at 35°C or less. Then, 7.12 g of hydroxyethyl acrylate was added dropwise and the mixture was stirred for a further three hours at 70 to 75°C. The reaction was terminated when the residual isocyanate content was reduced to 0.1 wt% or less to obtain a urethane acrylate with a structure having hydroxyethyl acrylate bonded to both ends of propylene oxide via 2,4-tolylene diisocyanate. The resulting urethane acrylate is referred to as "UA-1".

Synthesis Example 2: synthesis of urethane (meth) acrylate (B)

A reaction vessel equipped with a stirrer was charged with 1.59 g of 2,4-tolylene diisocyanate, 0.012 g of 2,6-di-t-butyl-p-cresol, and 0.039 g of dibutyltin dilaurate. The mixture was cooled with ice to 10°C or below while stirring. After the addition of 1.06 g of hydroxyethyl acrylate dropwise while controlling the temperature at 20°C or less, the mixture was allowed to react for one hour while stirring. Then, 45.78 g of a ring-opening polymer of propylene oxide with a number average molecular weight of 10,000 and the mixture was stirred for a further three hours at 70 to 75°C. The reaction was terminated when the residual isocyanate content was reduced to 0.1 wt% or less to obtain a urethane acrylate with a structure having hydroxyethyl acrylate bonded to both ends of propylene oxide via 2,4-tolylene diisocyanate. The resulting urethane acrylate is referred to as "UA-2".
Synthesis Example 3: synthesis 1 of urethane (meth)acrylate (B')

A reaction vessel equipped with a stirrer was charged with 41.4 g of 2,4-tolylene diisocyanate, 0.02 g of 2,6-di-t-butyl-p-cresol, 0.08 g of dibutyltin dilaurate, and 0.008 g of phenothiazine. The mixture was cooled to 20°C with stirring. After addition of 27.6 g of 2-hydroxyethyl acrylate dropwise, the mixture was allowed to react for one hour while stirring and controlling the temperature at 25°C or lower. After further addition of 30.9 g of 2-hydroxypropyl acrylate, the mixture was reacted at about 60°C with stirring. The reaction was terminated when the residual isocyanate concentration was 0.1 wt% or less to obtain a urethane acrylate which is an equimolar reaction product of 2,4-tolylene diisocyanate, 2-hydroxyethyl acrylate, and 2-hydroxypropyl acrylate. The resulting urethane acrylate is referred to as "UA-3".

Synthesis Example 4: synthesis 2 of urethane (meth)acrylate (B')

A reaction vessel equipped with a stirrer was charged with 42.9 g of 2,4-tolylene diisocyanate, 0.02 g of 2,6-di-t-butyl-p-cresol, 0.08 g of dibutyltin dilaurate, and 0.008 g of phenothiazine. The mixture was cooled to 20°C with stirring. After the addition of 57.1 g of 2-hydroxyethyl acrylate dropwise, the mixture was allowed to react for one hour at room temperature while stirring and controlling the temperature at 25°C or lower. The reaction was terminated when the residual isocyanate concentration was 0.1 wt% or less to obtain a urethane acrylate having a structure with 2-hydroxypropyl acrylate bonded to both ends of 2,4-tolylene diisocyanate. The resulting urethane acrylate is referred to as "UA-4".

Examples 1 to 2 and Comparative Examples 1 to 5

A reaction vessel equipped with a stirrer was charged with the components listed in Table 1. The mixture was then stirred for one hour while controlling the liquid temperature at 50°C to obtain a curable liquid resin composition.
Test Example 1

The curable liquid resin compositions obtained in the above examples and comparative examples were cured using the following method to prepare specimens. The specimens were evaluated as follows. The results are shown in Table 1.

1. Preparation of test specimen

The curable liquid resin composition was applied to a glass plate using a 250 µm thickness applicator bar and cured by applying ultraviolet rays at a dose of 1 J/cm² in air to obtain a test film.

2. Measurement of Young's modulus

The film was cut into a strip-shaped sample having an extension part width of 6 mm and a length of 25 mm. The sample was subjected to a tensile test at a temperature of 23°C and a humidity of 50%. The Young's modulus was calculated from the tensile strength at a strain of 2.5% and a tensile rate of 1 mm/min.

3. Breaking strength and breaking elongation

Breaking strength and breaking elongation of the test sample were measured using a tensile tester ("AGS-50G" manufactured by Shimadzu Corp.).

Tensile rate 50 mm/min
Benchmark distance (measurement distance) 25 mm
Measurement temperature 23°C
Relative humidity 50% RH

4. Measurement of stress-relaxation time

The film was cut into a strip-shaped sample with a width of 6 mm and a length of 25 mm. A strain of 5% was applied to the sample at a rate of 1,000 mm/minute at a temperature of 23°C and a humidity of 50%. Changes in the stress were monitored by suspending the cross head of a tensile tester ("Autograph AGS-50G" manufactured by Shimazu Corp.). A period of time in
which the stress was reduced to 37% of the initial stress was determined as the stress relaxation time.

(5) Sticking power

The adhesive of the cured products of the compositions obtained in Examples and Comparative Examples was evaluated. The liquid composition was applied to a sliding glass plate using a 381 µm thickness applicator. The applied liquid composition was irradiated with ultraviolet rays at a dose of 0.1 J/cm² in a nitrogen atmosphere to obtain a cured film with a thickness of about 200 µm. The cured film on the sliding glass plate was allowed to stand for 24 hours at a temperature of 23°C and a humidity of 50%. A sample in the shape of a strip having an extension part with a width of 10 mm was prepared from the cured film. An adhesion test of the sample was carried out according to JIS Z0237 using a tensile tester. The adhesion was determined from the tensile strength at a tensile rate of 50 mm/min.
Table 1

<table>
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<tr>
<th></th>
<th>Example</th>
<th>Comparative Examples (not examples of the instant claimed invention)</th>
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<td>2-Ethylhexyl acrylate</td>
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<td>Irgacure 184</td>
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<tr>
<td>Irganox 245</td>
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<td>Young's modulus (MPa)</td>
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<td>Breaking strength (MPa)</td>
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<td>Breaking elongation (%)</td>
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<td>Stress-relaxation time (relative value)</td>
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<tr>
<td>Sticking power (N/m)</td>
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In Table 1:

"Lucirin TPO": 2,4,6-trimethylbenzoyldiphenylphosphine oxide (manufactured by Ciba Speciality Chemicals Co., Ltd.)
"Irgacure 184": 1-hydroxycyclohexyl phenyl ketone (manufactured by Ciba Specialty Chemicals Co., Ltd.)
"Irganox 245": ethylenbis(oxyethylene)bis[3-(5-tert-butyl-4-hydroxy-m-tolyl)propionate] (manufactured by Ciba Specialty Chemicals Co., Ltd.)
"SH28PA": dimethylpolysiloxane polyoxyalkylene copolymer (manufactured by Dow Corning Toray Co., Ltd.)
All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (i.e., meaning "including, but not limited to," unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed.

No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-
described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.
Claims

1. A curable liquid resin composition comprising:
   (A) a urethane (meth)acrylate having a structure derived from polypropylene glycol with a number average molecular weight of about 4,000 or less;
   (B) a urethane (meth)acrylate having a structure derived from a polypropylene glycol with a number average molecular weight of more than about 4,000;
   (C) a (meth)acrylate monomer; and
   (D) a polymerization initiator;

   wherein from about 50 to about 80 mass% of the component (C) is 2-ethylhexyl (meth)acrylate, and from about 50 to about 90 mass% of the component (D) is 1-hydroxycyclohexyl phenyl ketone.

2. The curable liquid resin composition according to claim 1, which is used for forming an optical fiber Secondary coating layer.

3. The curable liquid resin composition according to claim 1, which is used for a Matrix coating for one or more optical fibers.

4. A coating layer obtained by curing the curable liquid resin composition according to claim 1.

5. An optical fiber comprising the coating layer according to Claim 1.

6. An optical fiber ribbon comprising the coating layer according to Claim 1.
7. A process to coat an optical fiber with at least two curable liquid resin compositions comprising
   a) providing an optical fiber;
   b) coating said optical fiber with a radiation curable coating, which is a primary coating, and optionally applying radiation to cure said primary coating;
   c) coating said optical fiber with a second radiation curable coating, which is a Secondary coating, applied over the Primary coating; and
   d) applying radiation to cure said Secondary coating; and optionally
   e) coating said optical fiber with a Matrix radiation curable coating and applying radiation to cure said Matrix radiation curable coating, wherein either the Secondary coating or the optional Matrix radiation curable coating is the composition of Claim 1.
**INTERNATIONAL SEARCH REPORT**

**International application No**
PCT/NL2008/050179

**A. CLASSIFICATION OF SUBJECT MATTER**

| INV. | C09D4/06 | C09D175/00 | C09D11/00 | C03C25/00 | G02B6/00 |

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

- C09D
- C03C
- G02B
- C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

- EPO-Internal
- WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<td>WO 2005/087874 A (DSM IP ASSETS BV [NL]; JSR CORP [JP]; YAMAGUCHI HIROSHI [JP]; KAMO SAT) 22 September 2005 (2005-09-22) examples 3,4; table 1</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

- Special categories of cited documents:
  - 'X': later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - 'Y': document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  - 'Z': document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  - 'A': document member of the same patent family

**Date of the actual completion of the international search**

12 June 2008

**Date of mailing the international search report**

27/06/2008

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**Authorized officer**

Droghetti, Anna
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