

PRESSURE SENSITIVE ADHESIVE SHEET, METHOD FOR MANUFACTURING THEREOF, AND METHOD FOR MANUFACTURING IMAGE DISPLAY DEVICE

TECHNICAL FIELD

5 **[0001]** The present invention relates to a photocurable pressure sensitive adhesive sheet and method for manufacturing thereof. The present invention also relates to a method for manufacturing an image display device using the pressure sensitive adhesive sheet.

BACKGROUND ART

10 **[0002]** Liquid crystal displays and organic EL displays are widely used as various kinds of image display devices of mobile phones, car navigation devices, personal computer monitors, televisions and so on. On a viewing-side outermost surface of an image display panel, a front transparent plate (also referred to as a “cover window” etc.) such as a transparent resin plate or a glass plate may be provided, for the purpose of, for example,
15 preventing damage to the image display panel due to impact from the outer surface. In addition, display devices provided with a touch panel on front surface of an image display panel become common recently.

[0003] In an image display device including a front transparent member such as a front transparent plate or a touch panel arranged on a front surface of an image display panel,
20 the front transparent member and the image display panel are bonded with a pressure sensitive adhesive sheet interposed therebetween. The pressure sensitive adhesive sheet may also be disposed between a touch panel and a front transparent plate. Since members are bonded together with a pressure sensitive adhesive sheet, peeling of a front transparent member by impacts of falling, etc. hardly occurs compared with a case where
25 a front transparent member is fixed to only a housing.

[0004] A colored layer (decorative printed layer) may be formed on the peripheral edge of a front transparent member for the purpose of decoration and light shielding. When a pressure sensitive adhesive is bonded to a transparent member having a decorative printed layer, bubbles are easily generated on the periphery of a printing level difference
30 portion. Accordingly, a pressure sensitive adhesive sheet having a large thickness is used to impart a level difference absorbency, so that a failure such as ingress of bubbles can be suppressed. When a pressure sensitive adhesive sheet having a large thickness is used, impact resistance tends to be improved.

[0005] A method has been proposed in which a pressure sensitive adhesive sheet

including a photocurable pressure sensitive adhesive composition is used to bond a front transparent member (see, for example, Patent Documents 1 and 2). The photocurable pressure sensitive adhesive composition contains a photopolymerizable polyfunctional monomer or oligomer in an unreacted state. A pressure sensitive adhesive sheet before
5 photocuring has high fluidity, and is therefore excellent in level difference absorbency, so that bubble can be prevented from being generated in the bonding interface or the vicinity of the printing level difference. After being bonded to an adherend, the pressure sensitive adhesive sheet is irradiated with an active ray and thus is photocured, the fluidity of the pressure sensitive adhesive is reduced, so that the adhesion retaining force is enhanced.

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PRIOR ART DOCUMENTS

[0006] Patent Document 1: WO2013/161666

Patent Document 2: JP 2014-227453 A

15 SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] In an image display device equipped with a front transparent member such as a cover window with larger in size than a display panel, the front transparent member is bonded to a housing with an adhesive tape or the like at a region outside the outer
20 peripheral edge of the display panel. That is, the front transparent member is fixed not only to a display panel surface with an interlayer filling pressure sensitive adhesive sheet but also to a housing with a pressure sensitive adhesive tape or the like.

[0008] In recent years, narrowing of the frames of display devices or popularization of bezel-less display devices has progressed mainly in mobile devices such as smartphones.

25 Due to popularization of narrow frame display devices and bezel-less display devices, the size of a display panel 10 becomes comparable to or greater than the size of a front transparent member 7. In this configuration, a housing 9 and the front transparent member 7 cannot be fixed to each other with an adhesive tape or the like, and it is necessary to fix the front transparent member 7 with a pressure sensitive adhesive sheet
30 alone (see FIG. 2). Accordingly, the pressure sensitive adhesive sheet is required to have higher adhesive strength, and also required to prevent occurrence of peeling by impacts of falling and the like.

[0009] Further, in narrow frame display devices and bezel-less display devices, high

dimensional stability is required in assembly of an image display device and conveyance of a product-in-process. Before photocuring, the photocurable pressure sensitive adhesive sheet used for bonding a front transparent member is soft, and thus is excellent in level difference absorbency. After being bonded to an adherend and before being photocuring, a pressure sensitive adhesive sheet made flexible for imparting a level difference absorbency to the sheet has a pressure sensitive adhesive having high fluidity, and is thus easily deformed when an external force is applied in conveyance or processing, so that positional displacement may occur between bonded members. Further, when the pressure sensitive adhesive has high fluidity, a problem with processability such as glue missing of the pressure sensitive adhesive sheet may occur at the time of peeling a release sheet temporarily attached to a surface of the pressure sensitive adhesive sheet.

[0010] In view of the situations described above, an object of the present invention is to provide a pressure sensitive adhesive sheet which has both of a level difference absorbency and processability before being photocured and which is excellent in impact resistance and adhesive durability after being photocured.

MEANS FOR SOLVING THE PROBLEMS

[0011] The present invention relates to a photocurable pressure sensitive adhesive sheet in which a pressure sensitive adhesive composition is formed in a sheet shape. The pressure sensitive adhesive composition that forms a photocurable pressure sensitive adhesive sheet contains an acryl-based base polymer having a crosslinked structure, a photopolymerizable polyfunctional compound, and a photopolymerization initiator. The photopolymerizable polyfunctional compound is a compound having two or more photopolymerizable functional groups per molecule, and it is preferable to use a compound having three or more photopolymerizable functional groups per molecule.

[0012] The pressure sensitive adhesive sheet may have a storage elastic modulus of 100 to 250 kPa at 25°C and 1 Hz, and a gel fraction of 25 to 70%. The pressure sensitive adhesive sheet may have a storage elastic modulus of 4.5 kPa or more at 25°C and 10^{-7} Hz. The pressure sensitive adhesive sheet may have an adhesive strength of 4 N/10 mm or more to glass.

[0013] The acryl-based base polymer contained in the pressure sensitive adhesive sheet preferably has crosslinked structure in which an isocyanate crosslinker or the like is introduced into an acryl-based base polymer having a weight average molecular weight of

300,000 or more. The acryl-based base polymer is preferably an acryl-based base polymer containing 5 to 30 parts by weight of a hydroxy group-containing monomer based on 100 parts by weight of the total of monomer components. Preferably, the pressure sensitive adhesive sheet contains 1 to 6 parts by weight of a photopolymerizable polyfunctional compound based on 100 parts by weight of the acryl-based base polymer.

[0014] The pressure sensitive adhesive sheet can be formed by applying a composition, which contains an acryl-based base polymer, a crosslinker and a photopolymerizable polyfunctional compound, on a substrate in a sheet shape, and introducing a crosslinker-associated crosslinked structure into the acryl-based base polymer.

10 [0015] For example, the pressure sensitive adhesive sheet of the present invention is used for bonding a transparent member in an image display device in which the transparent member is arranged on a viewing-side surface. An image display device can be formed by bonding the pressure sensitive adhesive sheet to the transparent member, and then irradiating the pressure sensitive adhesive sheet with an active ray to photocure the pressure sensitive adhesive composition.

15 [0016] The photocured pressure sensitive adhesive sheet may have a storage elastic modulus of 180 to 400 kPa at 25°C and 1 Hz. The glass transition temperature of the photocured pressure sensitive adhesive sheet may be -3°C or lower. The gel fraction of the photocured pressure sensitive adhesive sheet may be 65 to 95%. The loss tangent peak-top value of the photocured pressure sensitive adhesive sheet may be 1.5 or more. The adhesive strength of the photocured pressure sensitive adhesive sheet to glass may be 4 N/10 mm or more.

EFFECTS OF THE INVENTION

25 [0017] The pressure sensitive adhesive sheet of the present invention has both of a level difference absorbency and processability before being photocured, and is excellent in impact resistance and adhesive durability after being photocured. An image display device in which a cover window or the like is bonded to a viewing-side surface using the pressure sensitive adhesive sheet of the present invention is excellent in bonding reliability, and can be adapted to narrow frames display devices and bezel-less display devices.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. 1 is a sectional view showing an example of a configuration of a pressure sensitive adhesive sheet with a release film.

FIG. 2 is a sectional view showing an example of a configuration of an image display device.

5 FIGS. 3 and 4 are sectional views showing an example of a stacking configuration of an optical film with a pressure sensitive adhesive sheet.

FIG. 5A is a photograph showing a state of an interlayer adhesiveness test, and FIG. 5B is a photograph for observing a sample in which streaky bubbles are generated in the interlayer adhesiveness test.

10 FIG. 6 is a schematic view showing an arrangement of a sample in an impact resistance test.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0019] FIG. 1 shows a pressure sensitive adhesive sheet with a release film in which
15 release films 1 and 2 are temporarily attached, respectively, to both surfaces of a pressure sensitive adhesive sheet 5. FIG. 2 is a sectional view showing an example of a configuration of an image display device in which a front transparent plate 7 is fixed using the pressure sensitive adhesive sheet.

[0020] [Physical Properties of Pressure Sensitive Adhesive Sheet]

20 The pressure sensitive adhesive sheet is obtained by depositing a pressure sensitive adhesive composition in a sheet shape. The pressure sensitive adhesive composition contains an acryl-based base polymer having a crosslinked structure, a photopolymerizable polyfunctional compound and a photopolymerization initiator. The pressure sensitive adhesive sheet is photocurable. Preferably, the pressure sensitive
25 adhesive sheet has high transparency. The total light transmittance of the pressure sensitive adhesive sheet is preferably 85% or more, more preferably 90% or more. The haze of the pressure sensitive adhesive sheet is preferably 1.5% or less, more preferably 1% or less.

[0021] From the viewpoint of imparting a level difference absorbency to the pressure
30 sensitive adhesive sheet to prevent ingress of bubbles to the vicinity of a printing level difference, the storage elastic modulus at a temperature of 25°C and a frequency of 1 Hz ($G'_{25^\circ\text{C}}$) of the pressure sensitive adhesive sheet before photocuring is preferably 250 kPa or less, more preferably 200 kPa or less, further preferably 180 kPa or less. On the other

hand, the storage elastic modulus $G'_{25^{\circ}\text{C}}$ of the pressure sensitive adhesive sheet before photocuring is preferably 100 kPa or more, more preferably 110 kPa or more from the viewpoint of suppressing positional displacement after the pressure sensitive adhesive sheet is bonded to an adherend and securing processing dimensional stability.

5 **[0022]** The storage elastic modulus at a temperature of 25°C and a frequency of 10^{-7} Hz of the pressure sensitive adhesive sheet before photocuring is preferably 4.5 kPa or more, more preferably 5 kPa or more, further preferably 5.5 kPa or more. If the storage elastic modulus at a frequency of 10^{-7} Hz is within the above-described range, the pressure sensitive adhesive sheet is hardly plastically deformed even by distortion at low speeds, and plastic deformation distortion of the pressure sensitive adhesive sheet is small in conveyance and processing of a product-in-process after the pressure sensitive adhesive sheet is bonded to an adherend, so that processing dimensional stability tends to be improved.

15 **[0023]** The storage elastic modulus of the pressure sensitive adhesive sheet at a temperature of 25°C and a frequency of 10^{-7} Hz before photocuring is preferably 20 kPa or less, more preferably 15 kPa or less, further preferably 10 kPa or less. When the storage elastic modulus at a frequency of 10^{-7} Hz is in the above-described range, the pressure sensitive adhesive has moderate softness in a high-temperature environment, and therefore, the level difference absorbency can be secured.

20 **[0024]** When photocuring is performed after the pressure sensitive adhesive sheet is bonded to an adherend, the storage elastic modulus of the pressure sensitive adhesive sheet is increased by photopolymerization reaction (photocuring) of a photopolymerizable polyfunctional compound. The storage elastic modulus of the photocured pressure sensitive adhesive sheet at a temperature of 25°C and a frequency of 1 Hz ($G'_{25^{\circ}\text{C}}$) is preferably 180 kPa or more, more preferably 200 kPa or more, further preferably 210 kPa or more. Bonding reliability tends to be improved as the storage elastic modulus $G'_{25^{\circ}\text{C}}$ of the photocured pressure sensitive adhesive sheet increases.

30 **[0025]** On the other hand, from the viewpoint of imparting moderate viscosity to the pressure sensitive adhesive sheet to secure wettability, and adhesive durability against impact in falling or the like, the storage elastic modulus $G'_{25^{\circ}\text{C}}$ of the photocured pressure sensitive adhesive sheet is preferably 400 kPa or less, more preferably 350 kPa or less, further preferably 300 kPa or less, especially preferably 280 kPa or less.

[0026] The glass transition temperature of the photocured pressure sensitive adhesive

sheet is preferably -3°C or lower, more preferably -5°C or lower, further preferably -6°C or lower. The glass transition temperature of the photocured pressure sensitive adhesive sheet is preferably -20°C or higher, more preferably -15°C or higher, further preferably -13°C or higher. When the glass transition temperature is within the above-mentioned
5 range, the pressure sensitive adhesive sheet tends to be excellent in impact resistance because it has appropriate viscosity even over a low-temperature range.

[0027] The loss tangent ($\tan \delta$) peak-top value (*i.e.*, $\tan \delta$ at glass transition temperature) of the photocured pressure sensitive adhesive sheet is preferably 1.5 or more, more preferably 1.6 or more, further preferably 1.7 or more, especially preferably 1.75 or more.

10 A pressure sensitive adhesive sheet having a large $\tan \delta$ peak-top value tends to exhibit a high viscous behavior, leading to excellent impact resistance.

[0028] The upper limit of the $\tan \delta$ peak-top value of the photocured pressure sensitive adhesive sheet is not particularly limited, but is generally 3.0 or less. From the viewpoint of the adhesion retaining force, the $\tan \delta$ peak-top value is preferably 2.5 or less, more
15 preferably 2.3 or less, further preferably 2.1 or less.

[0029] In measurement of the physical properties of the photocured pressure sensitive adhesive sheet, a pressure sensitive adhesive sheet photocured so as to have residual C=C bonds in an amount of 15% or less as determined by infrared spectroscopy is used. The storage elastic modulus G' , glass transition temperature and $\tan \delta$ peak-top value of the
20 pressure sensitive adhesive sheet are determined by measurement of viscoelasticity. Unless otherwise specified, measurement frequency is 1 Hz. The glass transition temperature is a temperature at which $\tan \delta$ is maximum (peak-top temperature). The loss tangent ($\tan \delta$) is a ratio (G''/G') between the storage elastic modulus G' and the loss elastic modulus G'' . The storage elastic modulus G' corresponds to a part stored as elastic
25 energy in deformation of a material, and is an index indicating a degree of hardness. As the storage elastic modulus of the pressure sensitive adhesive sheet increases, the adhesion retaining force tends to become higher, leading to suppression of peeling caused by strain. The loss elastic modulus G'' corresponds to a loss energy part scattered and lost by internal friction etc. in deformation of a material, and indicates the degree of viscosity.
30 As the loss tangent ($\tan \delta$) increases, the pressure sensitive adhesive sheet tends to become more viscous, and exhibit a deformation behavior closer to that of liquid, leading to a decrease in rebound elastic energy.

[0030] From the viewpoint of imparting moderate flexibility for imparting a level

difference absorbency while securing processing dimensional stability by setting the storage elastic modulus $G'_{25^{\circ}\text{C}}$ to 100 kPa or more, the gel fraction of the pressure sensitive adhesive sheet before photocuring is preferably 25 to 70%. The gel fraction of the pressure sensitive adhesive sheet before photocuring is more preferably 30 to 65%, further preferably 33 to 60%, especially preferably 35 to 55%. From the viewpoint of securing both bonding reliability and impact resistance, the gel fraction of the photocured pressure sensitive adhesive sheet is preferably 65 to 95%, more preferably 70 to 93%, further preferably 75 to 90%.

[0031] The gel fraction of the pressure sensitive adhesive sheet can be determined as a content of components insoluble in a solvent such as ethyl acetate, and specifically, the gel fraction is determined as a weight fraction (unit: % by weight) of insoluble components after immersion of the pressure sensitive adhesive layer in ethyl acetate at 23°C for 7 days to the sample before immersion. Generally, the gel fraction of the polymer is equal to a crosslinking degree, and the gel fraction becomes higher as the number of crosslinked moieties in the polymer increases. The gel fraction (introduction amount of crosslinked structure) can be adjusted within a desired range by a method for introducing a crosslinked structure, the type and the amount of a crosslinker, and the like.

[0032] The adhesive strength of the pressure sensitive adhesive sheet before photocuring is preferably 4 N/10 mm or more, more preferably 6 N/10 mm or more, further preferably 7 N/10 mm or more, especially preferably 8 N/10 mm or more. When the adhesive strength of the pressure sensitive adhesive sheet before photocuring is in the above-described range, it is possible to suppress peeling and positional displacement of the pressure sensitive adhesive sheet from an adherend at the time of conveyance and processing of a product-in-process after the pressure sensitive adhesive sheet is bonded to the adherend. When the adhesive strength of the pressure sensitive adhesive sheet before photocuring is within the above-mentioned range, peeling at an interface between an adherend and a pressure sensitive adhesive sheet can be suppressed at the time of peeling a release film 1 (heavily peelable film) temporarily attached to one surface of the pressure sensitive adhesive sheet after a release film 2 (lightly peelable film) temporarily attached to the other surface is peeled to bond the pressure sensitive adhesive sheet to the adherend.

[0033] The adhesive strength of the fully cured pressure sensitive adhesive sheet is preferably 4 N/10 mm or more, more preferably 4.5 N/10 mm or more, further preferably 5

N/10 mm or more. When the adhesive strength of the photocured pressure sensitive adhesive sheet is within the above-mentioned range, peeling of the pressure sensitive adhesive sheet from the adherend can be prevented even in case of occurrence of stress by strain or an impact of falling or the like.

5 **[0034]** The adhesive strength is determined by a peeling test conducted at a tension speed of 300 mm/minute and a peeling angle of 180° with a glass plate used as an adherend. Unless otherwise specified, the adhesive strength is a measured value at 25°C.

[0035] The thickness of the pressure sensitive adhesive sheet is not particularly limited, and may be set according to the type, shape and the like of an adherend. When a member
10 having a printing level difference, such as a front transparent plate, is used as the adherend, the thickness of the pressure sensitive adhesive sheet is preferably greater than the thickness of the printing level difference. The thickness of the pressure sensitive adhesive sheet to be used for bonding a front transparent plate (cover window) is preferably 30 μm or more, more preferably 40 μm or more, further preferably 50 μm or
15 more. When the thickness of the pressure sensitive adhesive sheet is increased, the level difference absorbency and impact resistance tend to be improved. The upper limit of the thickness of the pressure sensitive adhesive sheet is not particularly limited, but is preferably 500 μm or less, more preferably 300 μm or less, further preferably 250 μm or less from the viewpoint of, for example, productivity of the pressure sensitive adhesive
20 sheet.

[0036] [Compositions of Pressure Sensitive Adhesive]

Composition of the pressure sensitive adhesive is not particularly limited, and pressure sensitive adhesives containing a base polymer such as an acryl-based polymer, a
silicone-based polymer, a polyester, a polyurethane, a polyamide, a polyvinyl ether, a vinyl
25 acetate/vinyl chloride copolymer, a modified polyolefin, an epoxy-based polymer, a fluorine-based polymer, or a polymer based on a rubber such as a natural rubber or a synthetic rubber can be appropriately selected. Particularly, an acryl-based pressure sensitive adhesive is preferably used because it is excellent in optical transparency, exhibits moderate wettability, cohesive strength and pressure sensitive adhesive properties such as
30 adhesiveness, and is also excellent in weather resistance, heat resistance and the like.

[0037] <Base Polymer>

The acryl-based base polymer contains a (meth)acrylic acid alkyl ester as a main constituent monomer component. In this specification, the “(meth)acryl” means acryl

and/or methacryl.

[0038] As the (meth)acrylic acid alkyl ester, a (meth)acrylic acid alkyl ester with the alkyl group having 1 to 20 carbon atoms is preferably used. The alkyl group of the (meth)acrylic acid alkyl ester may have a branch or may have a cyclic alkyl group.

5 **[0039]** Specific examples of the (meth)acrylic acid alkyl ester having a linear or branched alkyl group include methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, s-butyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, isopentyl (meth)acrylate, neopentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, isotridodecyl (meth)acrylate, tetradecyl (meth)acrylate, isotetradecyl (meth)acrylate, pentadecyl (meth)acrylate, cetyl (meth)acrylate, heptadecyl (meth)acrylate, octadecyl (meth)acrylate, isooctadecyl (meth)acrylate, nonadecyl (meth)acrylate and aralkyl (meth)acrylate.

15 **[0040]** Specific examples of the (meth)acrylic acid alkyl ester having a cycloaliphatic alkyl group include (meth)acrylic acid cycloalkyl esters such as cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate, cycloheptyl (meth)acrylate and cyclooctyl (meth)acrylate; (meth)acrylic acid esters having a dicyclic aliphatic hydrocarbon ring, such as isobornyl (meth)acrylate; and (meth)acrylic acid esters having a tri-or-more-cyclic aliphatic hydrocarbon ring, such as dicyclopentanyl (meth)acrylate, dicyclopentanyloxyethyl (meth)acrylate, tricyclopentanyl (meth)acrylate, 1-adamantyl (meth)acrylate, 2-methyl-2-adamantyl (meth)acrylate and 2-ethyl-2-adamantyl (meth)acrylate.

[0041] The amount of the (meth)acrylic acid alkyl ester based on the total amount of monomer components for forming an acryl-based base polymer is preferably 40% by weight or more, more preferably 50% by weight or more, further preferably 60% by weight or more. From the viewpoint of ensuring that the glass transition temperature (T_g) of the base polymer is within an appropriate range, the amount of the (meth)acrylic acid alkyl ester having a linear or branched alkyl group having 4 to 10 carbon atoms based on the total amount of constituent monomer components in the acryl-based base polymer is preferably 30% by weight or more, more preferably 40% by weight or more, further preferably 45% by weight or more.

[0042] The acryl-based base polymer preferably contains an acryl-based monomer unit having a crosslinkable functional group as a copolymer component. When the base

polymer contains a crosslinkable functional group, the base polymer can be reacted with the crosslinker to adjust the gel fraction of the pressure sensitive adhesive within a desired range.

[0043] Examples of the acryl-based monomer having a crosslinkable functional group include hydroxy group-containing monomers and carboxy group-containing monomers. For example, when an isocyanate-based crosslinker is used, a crosslinked structure is introduced by reaction of a hydroxy group with an isocyanate group. When an epoxy-based crosslinker is used, a crosslinked structure is introduced by reaction of a carboxy group with an epoxy group. It is preferable that in particular, a hydroxy group-containing monomer is used as a copolymerization component for the base polymer, and a crosslinked structure is introduced by an isocyanate-based crosslinker. When the base polymer includes a hydroxy group-containing monomer as a monomer unit, the crosslinkability of the base polymer is improved, and cloudiness of the pressure sensitive adhesive under a high-temperature and high-humidity environment tends to be suppressed, so that a pressure sensitive adhesive having high transparency is obtained.

[0044] Examples of the hydroxyl group-containing monomer include (meth)acrylic acid esters such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 6-hydroxyhexyl (meth)acrylate, 8-hydroxyoctyl (meth)acrylate, 10-hydroxydecyl (meth)acrylate, 12-hydroxylauryl (meth)acrylate and (4-hydroxymethylcyclohexyl)-methyl (meth)acrylate. Among them, 2-hydroxyethyl acrylate (Tg of homopolymer: -15°C) and 4-hydroxybutyl acrylate (Tg of homopolymer: -32°C) are preferable because they considerably contribute to enhancement of adhesive strength, and can suppress cloudiness of the pressure sensitive adhesive sheet in a high-humidity environment. 4-hydroxybutyl acrylate is especially preferable because it has a low glass transition temperature (Tg), and considerably contributes to enhancement of the storage elastic modulus by formation of intermolecular hydrogen bonds.

[0045] The amount of the hydroxy group-containing monomer based on the total amount of monomer components for forming the acryl-based base polymer is preferably 5 to 30% by weight, more preferably 8 to 25% by weight, further preferably 10 to 20% by weight. When the amount of the hydroxy group-containing monomer is increased, the amount of unreacted functional groups in the crosslinker decreases, so that with a small amount of the crosslinker, the degree of crosslinking (gel fraction) can be enhanced to secure both the processability and processing dimensional stability and the level difference absorbcency of

the pressure sensitive adhesive sheet before photocuring. Further, since unreacted hydroxy groups form intermolecular hydrogen bonds after crosslinking, a pressure sensitive adhesive sheet having a storage elastic modulus $G'_{25^{\circ}\text{C}}$ of 100 kPa or more can be obtained even with a gel fraction of 70% or less.

5 [0046] Examples of the carboxy group-containing monomer include acryl-based monomers such as (meth)acrylic acid, carboxyethyl (meth)acrylate and carboxypentyl (meth)acrylate, and unsaturated fatty acids such as itaconic acid, maleic acid, fumaric acid and crotonic acid.

[0047] When the pressure sensitive adhesive sheet is used for bonding a touch panel
10 sensor, it is preferable that a pressure sensitive adhesive sheet has a low acid content for preventing corrosion of the electrode by acid components. Further, when the pressure sensitive adhesive sheet is used for bonding a polarizing plate, it is preferable that the pressure sensitive adhesive sheet has a low acid content for inhibiting a polyvinyl alcohol
15 of the polarizer from being converted into polyene by acid components. The content of organic acid monomers, *e.g.*, (meth)acrylic acid, in such an acid-free pressure sensitive adhesive sheet is preferably 100 ppm or less, more preferably 70 ppm or less, further preferably 50 ppm or less. The organic acid monomer content of the pressure sensitive adhesive sheet can be determined by immersing the pressure sensitive adhesive sheet in
20 pure water, heating the pressure sensitive adhesive sheet at 100°C for 45 minutes, and determining the amount of acid monomers extracted in water by ion chromatography.

[0048] For reducing the content of acid monomers in the pressure sensitive adhesive sheet, the amount of organic acid monomer components such as (meth)acrylic acid in the monomer components that form the acryl-based base polymer is preferably small. Thus, for ensuring that the pressure sensitive adhesive sheet is free from acid, it is preferable
25 that the base polymer does not substantially contain an organic acid monomer (carboxy group-containing monomer) as a monomer component. In the acid-free pressure sensitive adhesive sheet, the amount of the carboxy group-containing monomer is preferably 0.5 parts by weight or less, more preferably 0.1 parts by weight or less, further preferably 0.05 parts by weight or less, ideally 0 parts by weight based on 100 parts by weight of the total
30 of monomer components in the base polymer.

[0049] The acryl-based base polymer may contain a nitrogen-containing monomer as the constituent monomer component. Examples of the nitrogen-containing monomer include vinyl-based monomer such as N-vinylpyrrolidone, methylvinylpyrrolidone, vinylpyridine,

vinylpiperidone, vinylpyrimidine, vinylpiperazine, vinylpyrazine, vinylpyrrole, vinylimidazole, vinyloxazole, vinylmorpholine, (meth)acryloylmorpholine, N-vinylcarboxylic acid amides and N-vinylcaprolactam; and cyano group-containing acryl-based monomers such as acrylonitrile and methacrylonitrile. Among them, N-vinylpyrrolidone is preferable because it considerably contribute to enhancement of adhesive strength by improvement of cohesive force.

[0050] When the acryl-based base polymer contains high-polarity monomers such as a hydroxyl group-containing monomer, a carboxy group-containing monomer and a nitrogen-containing monomer as constituent monomer components, the cohesive force of the pressure sensitive adhesive tends to be enhanced, leading to improvement of adhesion retainability at a high temperature. On the other hand, when the content of high-polarity monomers is excessively high, the glass transition temperature may be increased, leading to deterioration of adhesiveness and impact resistance at a low temperature. Thus, the amount of high-polarity monomers (total of a hydroxyl group-containing monomer, a carboxy group-containing monomer and a nitrogen-containing monomer) based on the total amount of monomer components for forming the acryl-based base polymer is preferably 10 to 45% by weight, more preferably 15 to 40% by weight, further preferably 18 to 35% by weight. In addition, the amount of the nitrogen-containing monomer based on the total amount of monomer components for forming the acryl-based base polymer is preferably 3 to 25% by weight, more preferably 5 to 20% by weight, further preferably 7 to 15% by weight.

[0051] Besides the above-described monomer components, the acryl-based base polymer may contain other monomer components. Examples of the monomer components include: vinyl-based monomers such as acid anhydride group-containing monomers, caprolactone adducts of acrylic acids, sulfonic acid group-containing monomers, phosphoric acid group-containing monomers, styrene and α -methylstyrene; cyano group-containing acryl-based monomers such as acrylonitrile and methacrylonitrile; epoxy group-containing monomers such as glycidyl (meth)acrylate; glycol-based acryl ester monomers such as polyethylene glycol (meth)acrylate, polypropylene glycol (meth)acrylate, methoxyethylene glycol (meth)acrylate and methoxypolypropylene glycol (meth)acrylate; and acrylic acid ester-based monomers such as tetrahydrofurfuryl (meth)acrylate, fluorine (meth)acrylate, silicone (meth)acrylate and 2-methoxyethyl (meth)acrylate.

[0052] Preferably, the acryl-based base polymer contains a (meth)acrylic acid alkyl ester

in the largest amount among the above-mentioned monomer components. The properties of the pressure sensitive adhesive sheet are apt to depend on the type of a monomer contained in the largest amount among the constituent monomers of the acryl-based base polymer (main monomer). For example, when the main monomer in the acryl-based base polymer is a (meth)acrylic acid alkyl ester having a linear or branched alkyl group having 6 or less carbon atoms, the $\tan \delta$ peak-top value tends to increase, leading to improvement of impact resistance. Particularly, when the main monomer is an acrylic acid C₄-alkyl ester such as butyl acrylate, the $\tan \delta$ peak-top value tends to increase. The amount of the (meth)acrylic acid alkyl ester having a linear or branched alkyl group having 6 or less carbon atoms is preferably 30 to 80% by weight, more preferably 35 to 75% by weight, further preferably 40 to 70% by weight based on the total amount of monomer components for forming the acryl-based base polymer. Particularly, the content of butyl acrylate as a constituent monomer component is preferably within the above-mentioned range.

[0053] The glass transition temperature (T_g) of the acryl-based base polymer is preferably -50°C or higher. The glass transition temperature of the acryl-based base polymer is preferably -5°C or lower, more preferably -10°C or lower, further preferably -15°C or lower. After introduction of a crosslinked structure into the acryl-based base polymer, the glass transition temperature may be calculated from the composition of the polymer on the basis of the theoretical glass transition temperature. The theoretical glass transition temperature (T_g) is calculated from the glass transition temperature (T_{g_i}) of a homopolymer of a constituent monomer component in the acryl-based base polymer and the weight fraction (W_i) of each monomer component in accordance with the following Fox equation:

$$1/T_g = \Sigma(W_i/T_{g_i}).$$

[0054] T_g represents a glass transition temperature (unit: K) of the base polymer, W_i represents a weight fraction (copolymerization ratio on a weight basis) of a monomer component i forming the segment, and T_{g_i} represents a glass transition temperature (unit: K) of a homopolymer of the monomer component i . As the glass transition temperature of the homopolymer, the value described in Polymer Handbook, 3rd edition (John Wiley & Sons, Inc., 1989) can be referred. As the glass transition temperature (T_g) of a homopolymer of a monomer which is not described in the document, a loss tangent ($\tan \delta$) peak-top temperature obtained by dynamic viscoelasticity measurement may be employed.

[0055] The acryl-based base polymer is obtained by polymerizing the monomer

components using various kinds of known methods such as solution polymerization, emulsification polymerization and mass polymerization. The solution polymerization method is suitable from the viewpoint of a balance of properties such as adhesive strength and retentive strength of the pressure sensitive adhesive, costs and so on. As a solvent for solution polymerization, ethyl acetate, toluene or the like is generally used. The solution concentration is normally about 20 to 80% by weight. As the polymerization initiator, an azo-based initiator, a peroxide-based initiator, a redox-based initiator obtained by combining a peroxide and a reducing agent (*e.g.*, combination of a persulfate and sodium hydrogen sulfite, combination of a peroxide and sodium ascorbate, or the like), or the like is preferably used. The usage amount of the polymerization initiator is not particularly limited, and is for example about 0.005 to 5 parts by weight, preferably about 0.02 to 3 part by weight based on 100 parts by weight of the total amount of monomer components that form the base polymer.

[0056] For adjusting the molecular weight of the base polymer, a chain-transfer agent may be used. The chain-transfer agent can receive radicals from a growing polymer chain to stop extension of the polymer, and the chain-transfer agent having received the radicals can attack the monomer to start polymerization again. Accordingly, when a chain-transfer agent is used, an increase in molecular weight of the base polymer is inhibited without reducing the concentration of radicals in the reaction system. As the chain-transfer agent, for example, a thiol such as α -thioglycerol, lauryl mercaptan, glycidyl mercaptan, mercaptoacetic acid, 2-mercaptoethanol, thioglycolic acid, 2-ethylhexyl thioglycollate or 2,3-dimercapto-1-propanol is suitably used.

[0057] Although the amount of the chain-transfer agent is not particularly limited, using an excessively large amount of the chain-transfer agent may cause reduction of molecular weight of the base polymer, leading to deterioration of the processability and processing dimensional stability of the pressure sensitive adhesive sheet before photocuring. Thus, the amount of the chain-transfer agent is preferably 1 part by weight or less, more preferably 0.3 parts by weight or less, further preferably 0.15 parts by weight or less, especially preferably 0.1 parts by weight or less based on 100 parts by weight of the total of monomer components that form the base polymer.

[0058] The viscoelasticity of the pressure sensitive adhesive sheet before photocuring is influenced by the constituent components and the molecular weight of the base polymer. As the molecular weight of the base polymer increases, the storage elastic modulus $G'_{25^{\circ}\text{C}}$

tends to increase, and processability and processing dimensional stability tend to be improved. Thus, the weight average molecular weight of the acryl-based base polymer is preferably 300,000 or more, more preferably 350,000 or more, further preferably 400,000 or more. On the other hand, when the molecular weight of the base polymer is excessively large, the level difference absorbency tends to be deteriorated. Thus, the weight average molecular weight of the base polymer is preferably 1,500,000 or less, more preferably 1,000,000 or less, further preferably 800,000 or less, especially preferably 650,000 or less. The molecular weight of the base polymer refers to the molecular weight of the polymer before introduction of a crosslinked structure.

10 **[0059]** <Crosslinked Structure of Base Polymer>

In general, examples of the method for introducing a crosslinked structure into a base polymer include (1) a method in which a base polymer having a functional group capable of reacting with a crosslinker is prepared, and the crosslinker is then added to react the base polymer with the crosslinker; and (2) a method in which a photopolymerizable polyfunctional compound is incorporated in polymerization components of a base polymer to introduce a branched structure (crosslinked structure) into the polymer chain.

[0060] The pressure sensitive adhesive sheet of the present invention includes a base polymer having a crosslinked structure introduced by the method (1) above. Further, the pressure sensitive adhesive composition that forms the pressure sensitive adhesive sheet contains a photopolymerizable polyfunctional compound, and the crosslinked structure in the method (2) is introduced by performing photocuring after the pressure sensitive adhesive sheet is bonded to an adherend. That is, in the pressure sensitive adhesive sheet of the present invention, the base polymer has a crosslinked structure with a (thermal) crosslinker such as an isocyanate crosslinker. In the photocured pressure sensitive adhesive sheet, not only the crosslinked structure with an isocyanate crosslinker or the like but also a crosslinked structure with a photopolymerizable polyfunctional compound (photocrosslinker) such as polyfunctional (meth)acrylate is introduced into the base polymer.

30 **[0061]** <Crosslinker>

After polymerization of the base polymer, a crosslinker is added, and the mixture is optionally heated to introduce a crosslinked structure into the base polymer. Although crosslinking with an isocyanate crosslinker or the like may be described as “thermal

crosslinking” for discriminating the crosslinking from a crosslinking structure introduced by a photopolymerizable polyfunctional compound, the crosslinked structure by a crosslinker may be introduced without heating. By introducing a thermal-crosslinked structure into the acryl-based base polymer, the processability and processing dimensional stability of the pressure sensitive adhesive sheet before photocuring can be improved.

[0062] Examples of the crosslinker include compounds that react with functional groups such as a hydroxy group and a carboxy group contained in the base polymer. Specific examples of the crosslinker include isocyanate-based crosslinkers, epoxy-based crosslinkers, oxazoline-based crosslinkers, aziridine-based crosslinkers, carbodiimide-based crosslinkers and metal chelate-based crosslinkers.

[0063] In particular, isocyanate-based crosslinkers and epoxy-based crosslinkers are preferable because they have high reactivity with the hydroxy group and the carboxy group of the base polymer, so that introduction of a crosslinked structure is facilitated. Such a crosslinker forms a crosslinked structure by reacting with functional groups such as a hydroxy group and a carboxy group which are introduced into the base polymer. In an acid-free pressure sensitive adhesive in which the base polymer does not contain a carboxy group, it is preferable to form a crosslinked structure by use of an isocyanate-based crosslinker, *i.e.*, by reaction of a hydroxy group in the base polymer with the isocyanate crosslinker.

[0064] As an isocyanate-based crosslinker, a polyisocyanate having two or more isocyanate groups per molecule is used. Examples of the polyisocyanate-based crosslinker include lower aliphatic polyisocyanates such as butylene diisocyanate and hexamethylene diisocyanate; cycloaliphatic isocyanates such as cyclopentylene diisocyanate, cyclohexylene diisocyanate and isophorone diisocyanate; aromatic isocyanates such as 2,4-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate and xylylene diisocyanate; isocyanate adducts such as trimethylolpropane/tolylene diisocyanate trimer adducts (*e.g.* “CORONATE L” manufactured by Tosoh Corporation), trimethylolpropane/hexamethylene diisocyanate trimer adducts (*e.g.* “CORONATE HL” manufactured by Tosoh Corporation), trimethylolpropane adducts of xylylene diisocyanate (*e.g.* “TAKENATE D110N” manufactured by Mitsui Chemicals, Incorporated) and isocyanurate forms of hexamethylene diisocyanate (*e.g.* “CORONATE HX” manufactured by Tosoh Corporation).

[0065] The gel fraction of the pressure sensitive adhesive sheet can be adjusted within a

desired range by adjusting the amount of the crosslinker. For ensuring that the gel fraction of the pressure sensitive adhesive sheet before photocuring is 25 to 70%, the amount of the crosslinker is preferably 0.03 to 0.5 parts by weight, more preferably 0.05 to 0.3 parts by weight, further preferably 0.06 to 0.25 parts by weight, especially preferably 0.07 to 0.2 parts by weight based on 100 parts by weight of the base polymer. As the amount of the crosslinker increases, the gel fraction of the pressure sensitive adhesive sheet before photocuring tends to increase, and accordingly, the storage elastic modulus $G'_{25^{\circ}\text{C}}$ tends to increase.

[0066] <Photopolymerizable Polyfunctional Compound>

The photopolymerizable polyfunctional compound contained in the pressure sensitive adhesive sheet has two or more photopolymerizable functional groups per molecule. The photopolymerizable functional group may be any of radically polymerizable, cationically polymerizable and anionically polymerizable photopolymerizable functional groups, but a radical-polymerizable functional group having an unsaturated double bond (ethylenically unsaturated group) is preferable because it is excellent in reactivity. The photopolymerizable polyfunctional compound is preferably a polyfunctional (meth)acrylate because it has high compatibility with the acryl-based base polymer, and is especially preferably a polyfunctional acrylate because it has high photoradical reactivity.

[0067] Examples of the polyfunctional (meth)acrylate include difunctional (meth)acrylic acid esters such as hexanediol di(meth)acrylate, nonanediol di(meth)acrylate, polyethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, polytetramethylene glycol di(meth)acrylate, bisphenol A ethylene oxide-modified di(meth)acrylate, bisphenol A propylene oxide-modified di(meth)acrylate, alkanediol di(meth)acrylate, tricyclodecane dimethanol di(meth)acrylate, pentaerythritol di(meth)acrylate, neopentyl glycol di(meth)acrylate and glycerin di(meth)acrylate; trifunctional (meth)acrylic acid esters such as pentaerythritol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate and ethoxylated isocyanuric acid tri(meth)acrylate; tetrafunctional (meth)acrylic acid esters such as ditrimethylolpropane tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate and pentaerythritol tetra(meth)acrylate; and penta-or-more-functional (meth)acrylic acid esters such as dipentaerythritol penta(meth)acrylate etc. and dipentaerythritol hexa(meth)acrylate etc.

[0068] From the viewpoint of appropriately adjusting the viscoelasticity such as G' and $\tan \delta$ of the photocured pressure sensitive adhesive sheet, the molecular weight of the

photopolymerizable polyfunctional compound is preferably 1500 or less, more preferably 1000 or less. The functional group equivalent (g/eq) of the polyfunctional compound is preferably 50 to 500, more preferably 70 to 300, further preferably 80 to 200. The photopolymerizable polyfunctional compound is preferably liquid at normal temperature
5 because it has moderate compatibility with the base polymer.

[0069] The content of the photopolymerizable polyfunctional compound in the photocurable pressure sensitive adhesive sheet is preferably 1 to 6 parts by weight, more preferably 2 to 5 parts by weight, further preferably 2.5 to 4 parts by weight based on 100 parts by weight of the acryl-based base polymer. When the content of the
10 photopolymerizable polyfunctional compound is small, the gel fraction and the storage elastic modulus $G'_{25^{\circ}\text{C}}$ of the photocured pressure sensitive adhesive sheet tend to be small, and the adhesion retention tends to be insufficient. On the other hand, when the content of the photocurable polyfunctional compound is large, the photocured pressure sensitive adhesive sheet may be excessively hard, leading to insufficient impact resistance. Further,
15 as the content of the photocurable polyfunctional compound increases, the ratio of the base polymer in the pressure sensitive adhesive sheet (pressure sensitive adhesive composition) before photocuring tends to decrease, leading to deterioration of processability and processing dimensional stability.

[0070] From the viewpoint of enhancing cohesiveness of the polymer in the photocured pressure sensitive adhesive sheet, and enhancing the adhesion retaining force, it is preferable to use a compound having three or more photopolymerizable functional groups per molecule as a photopolymerizable polyfunctional compound. In particular, a tri-or-more-functional acrylate is preferable. A difunctional photopolymerizable compound and a tri-or-more-functional photopolymerizable compound may be used in combination. The
20 content of the tri-or-more-functional photopolymerizable polyfunctional compound in the photocurable pressure sensitive adhesive sheet is preferably 0.5 to 5 parts by weight, more preferably 1 to 4.5 parts by weight, further preferably 2 to 4 parts by weight based on 100 parts by weight of the acryl-based base polymer.

[0071] Even with only a difunctional photopolymerizable compound, it is possible to
30 enhance the adhesion retaining force after photocuring by increasing the amount of the compound. However, when the amount of the photopolymerizable compound is increased for enhancing the adhesion retention of the photocured pressure sensitive adhesive sheet, the storage elastic modulus $G'_{25^{\circ}\text{C}}$ of the pressure sensitive adhesive sheet before

photocuring tends to decrease, leading to deterioration of processability and processing dimensional stability.

[0072] <Pressure Sensitive Adhesive Composition>

A pressure sensitive adhesive composition is prepared by mixing a crosslinker, a
5 photopolymerizable polyfunctional compound, a photopolymerization initiator, and
optionally an oligomer, various additives and the like with the base polymer. Preferably,
the pressure sensitive adhesive composition has a viscosity (*e.g.*, about 0.5 to 20 Pa·s)
suitable for application of the composition onto a substrate. The viscosity of the pressure
sensitive adhesive composition can be set within an appropriate range by adjusting the
10 molecular weight of the base polymer, the amount of the photopolymerizable
polyfunctional compound, and composition, molecular weight and amount of other
components (*e.g.*, oligomer), and so on. Additives such as thickener may be used for the
purpose of, for example, adjusting the viscosity.

[0073] <Photopolymerization initiator>

15 The photocurable pressure sensitive adhesive composition contains a
photopolymerization initiator. Examples of the photopolymerization initiator include
benzoin ether-based photopolymerization initiators, acetophenone-based
photopolymerization initiators, α -ketol-based photopolymerization initiators, aromatic
sulfonyl chloride-based photopolymerization initiators, photoactive oxime-based
20 photopolymerization initiators, benzoin-based photopolymerization initiators, benzyl-
based photopolymerization initiators, benzophenone-based photopolymerization initiators,
ketal-based photopolymerization initiators, thioxanthone-based photopolymerization
initiators and acylphosphine oxide-based photopolymerization initiators. The content of
the photopolymerization initiator in the pressure sensitive adhesive composition is
25 preferably 0.01 to 5 parts by weight, more preferably from 0.05 to 3 parts by weight based
on 100 parts by weight of the base polymer.

[0074] (Oligomer)

The pressure sensitive adhesive composition may contain oligomers for the
purpose of, for example, adjusting the adhesive strength and the viscosity of the pressure
sensitive adhesive sheet. As the oligomer, one having a weight average molecular weight
30 of, for example, about 1000 to 30000 is used. The oligomer is preferably an acryl-based
oligomer because it is excellent in compatibility with the acryl-based base polymer.

[0075] The acryl-based oligomer contains a (meth)acrylic acid alkyl ester as a main

constituent monomer component. In particular, the acryl-based oligomer is preferably one containing as a constituent monomer component a (meth)acrylic acid alkyl ester having a linear or branched alkyl group (linear or branched alkyl (meth)acrylate) and a (meth)acrylic acid alkyl ester having a cycloaliphatic alkyl group (cycloaliphatic alkyl (meth)acrylate). Specific examples of the linear or branched alkyl (meth)acrylate and the cycloaliphatic alkyl (meth)acrylate are as shown above as constituent monomers of the acryl-based base polymer.

[0076] The glass transition temperature of the acryl-based oligomer is preferably 20°C or higher, more preferably 50°C or higher, further preferably 80°C or higher, especially preferably 100°C or higher. When a base polymer which has a low glass transition temperature (T_g) and in which a crosslinked structure is introduced by a urethane-based segment, and an acryl-based oligomer having a high glass transition temperature (T_g) are used in combination, the adhesion retaining force of the pressure sensitive adhesive sheet tends to be improved. The upper limit of the glass transition temperature of the acryl-based oligomer is not particularly limited, but is generally 200°C or lower, preferably 180°C or lower, more preferably 160°C or lower. The glass transition temperature of the acryl-based oligomer is calculated in accordance with the Fox equation.

[0077] Among the shown (meth)acrylic acid alkyl esters, the linear or branched alkyl (meth)acrylate is preferably methyl methacrylate because it has a high glass transition temperature, and is excellent in compatibility with the base polymer. As the cycloaliphatic alkyl (meth)acrylate, dicyclopentanyl acrylate, dicyclopentanyl methacrylate, cyclohexyl acrylate and cyclohexyl methacrylate are preferable. That is, the acryl-based oligomer is preferably one containing as constituent monomer components at least one selected from the group consisting of dicyclopentanyl acrylate, dicyclopentanyl methacrylate, cyclohexyl acrylate and cyclohexyl methacrylate, and methyl methacrylate.

[0078] The amount of the cycloaliphatic alkyl (meth)acrylate based on the total amount of monomer components for forming the acryl-based oligomer is preferably 10 to 90% by weight, more preferably 20 to 80% by weight, further preferably 30 to 70% by weight. The amount of the linear or branched alkyl (meth)acrylate based on the total amount of monomer components for forming the acryl-based oligomer is preferably 10 to 90% by weight, more preferably 20 to 80% by weight, further preferably 30 to 70% by weight.

[0079] The weight average molecular weight of the acryl-based oligomer is preferably 1000 to 30000, more preferably 1500 to 10000, further preferably 2000 to 8000. When an

acryl-based oligomer having a molecular weight falling within the above-mentioned range is used, the adhesive strength and the adhesion retaining force of the pressure sensitive adhesive sheet tend to be improved.

5 [0080] The acryl-based oligomer is obtained by polymerizing the above-mentioned monomer components by various polymerization methods. In polymerization of the acryl-based oligomer, various polymerization initiators may be used. In addition, a chain-transfer agent may be used for the purpose of adjusting the molecular weight.

10 [0081] When the pressure sensitive adhesive composition contains an oligomer component such as an acryl-based oligomer, the content of the oligomer component is preferably 0.1 to 10 parts by weight, more preferably 0.2 to 5 parts by weight based on 100 part by weight of the above base polymer. When the content of the oligomer in the pressure sensitive adhesive composition is within the above-described range, it is possible to improve adhesiveness without deteriorating the processability and processing dimensional stability of the pressure sensitive adhesive sheet before curing, and in
15 particular, the adhesive strength of the photocured pressure sensitive adhesive sheet tends to be enhanced.

[0082] (silane coupling agent)

A silane coupling agent can also be added in the pressure sensitive adhesive composition for the purpose of adjusting the adhesive strength. When the pressure
20 sensitive adhesive composition includes a silane coupling agent, the content thereof is normally about 0.01 to 5.0 parts by weight, preferably 0.03 to 2.0 parts by weight based on 100 parts by weight of the base polymer.

[0083] (Other additives)

In addition to the components exemplified above, additives such as a tackifier, a
25 plasticizer, a softener, a degradation inhibitor, a filler, a colorant, an ultraviolet ray absorber, an antioxidant, a surfactant and an antistatic agent maybe contained in the pressure sensitive adhesive composition.

[0084] [Pressure Sensitive Adhesive Sheet]

A pressure sensitive adhesive composition is applied onto a substrate, and a
30 solvent is optionally removed by drying to form a pressure sensitive adhesive sheet on the substrate. For the substrate to be used for formation of the pressure sensitive adhesive sheet, any suitable material is used. The substrate may be a release film having a release layer on a contact surface with the pressure sensitive adhesive sheet.

[0085] As the base film of the release film, films composed of various resin materials are used. Examples of the resin material include polyester-based resins such as polyethylene terephthalate and polyethylene naphthalate, acetate-based resins, polyether sulfone-based resins, polycarbonate-based resins, polyamide-based resins, polyimide-based resins, 5 polyolefin-based resins, (meth)acryl-based resins, polyvinyl chloride-based resins, polyvinylidene chloride-based resins, polystyrene-based resins, polyvinyl alcohol-based resins, polyacrylate-based resins and polyphenylene sulfide-based resins. Among them, polyester-based resins such as polyethylene terephthalate are especially preferable. The thickness of the base film is preferably 10 to 200 μm , more preferably 25 to 150 μm .

10 Examples of the material of the release layer include silicone-based release agents, fluorine-based release agents, long-chain alkyl-based release agents and aliphatic amide-based release agents. The thickness of the release layer is generally about 10 to 2000 nm.

[0086] For applying the pressure sensitive adhesive composition on the substrate, various kinds of coating methods such as roll coating, kiss roll coating, gravure coating, 15 reverse coating, roll brushing, spray coating, dip roll coating, bar coating, knife coating, air knife coating, curtain coating, lip coating, and extrusion coating may be employed.

[0087] When the pressure sensitive adhesive composition includes a solvent, the solvent is preferably dried after application of the pressure sensitive adhesive composition on the substrate. As a method for drying, a suitable method can be appropriately employed 20 according to a purpose. The heating/drying temperature is preferably 40°C to 200°C, more preferably 50°C to 180°C, further preferably 70°C to 170°C. Drying time can be appropriately set. The drying time is preferably 5 seconds to 20 minutes, more preferably 5 seconds to 15 minutes, further preferably 10 seconds to 10 minutes.

[0088] After the solvent is removed by drying, it is preferable to dispose a cover sheet for 25 protecting the surface of the pressure sensitive adhesive sheet. Preferably, a release film having a release layer on the contact surface with the pressure sensitive adhesive sheet, like the base film, is used as the cover sheet.

[0089] After the pressure sensitive adhesive composition is applied onto the substrate, heating is optionally performed to introduce a crosslinked structure into the base polymer. 30 The heating temperature and the heating time may be appropriately set according to the type of crosslinker to be used, and normally, the heating is performed at 20°C to 160°C for about 1 minute to 7 days. The heating for removing the solvent by drying may also serve as heating for crosslinking. As described above, the introduction of the crosslinked

structure does not necessarily require heating.

[0090] A crosslinking catalyst may be used for accelerating formation of a crosslinked structure. Examples of the crosslinking catalyst of the isocyanate-based crosslinker include metal-based crosslinking catalysts (particularly tin-based crosslinking catalysts) such as tetra-n-butyl titanate, tetraisopropyl titanate, NACEM ferric, butyl tin oxide, dioctyl tin dilaurate and dibutyl tin dilaurate.

[0091] Release films 1 and 2 are bonded, respectively, to surfaces of the pressure sensitive adhesive sheet 5 to obtain a pressure sensitive adhesive sheet in which a release film is temporarily attached to each of both surfaces as shown in FIG. 1. The substrate and the cover sheet used for formation of the pressure sensitive adhesive sheet may be remain attached to the pressure sensitive adhesive to be used as release films 1 and 2.

[0092] When release films 1 and 2 are disposed on both surfaces of the pressure sensitive adhesive sheet 5, the thickness of one release film 1 and the thickness of the other release film 2 may be the same, or different. The peeling strength in peeling of the release film temporarily attached to one surface from the pressure sensitive adhesive sheet 5 and the peeling strength in peeling of the release film temporarily attached to the other surface from the pressure sensitive adhesive sheet 5 may be the same or different. When the peeling strength of the release film on one surface is different from the peeling strength of the release film on the other surface, excellent workability can be attained by performing the bonding of adherends in the following procedure: the release film 2 with relatively small peeling strength (lightly peelable film) is first peeled from the pressure sensitive adhesive sheet 5, and bonded to a first adherend, and the release film 1 with relatively large peeling strength (heavily peelable film) is peeled, and bonded to a second adherend.

[0093] [Image Display Device]

The pressure sensitive adhesive sheet of the present invention can be used for bonding various transparent members and opaque members. The type of the adherend is not particularly limited, and examples thereof include various resin materials, glass and metals. The pressure sensitive adhesive sheet of the present invention has high transparency, and is therefore suitable for bonding optical members of an image display device etc. In particular, the pressure sensitive adhesive sheet of the present invention can impart level difference absorbency and impact resistance, and is therefore suitably used for bonding a transparent member such as a front transparent plate or a touch panel onto a viewing-side surface of an image display device.

[0094] FIG. 2 is a sectional view showing an example of a stacking configuration of an image display device in which the front transparent plate 7 is bonded to a viewing-side surface of an image display panel 10 with the pressure sensitive adhesive sheet 5 interposed therebetween. The image display panel 10 includes an image display cell 6 such as a liquid crystal cell or an organic EL cell, and a polarizing plate 3 bonded to the viewing-side surface of the image display cell 6 with a pressure sensitive adhesive sheet 4 interposed therebetween. The front transparent plate 7 includes a transparent flat plate 71 and a printed layer 76 disposed on the peripheral edge of one principal surface of the transparent flat plate 71. As the transparent plate 71, for example, a transparent resin plate such as that of an acryl-based resin or a polycarbonate-based resin, or a glass plate is used. The transparent plate 71 may have a touch panel function. As the touch panel, a touch panel of any type such as resistive film type, capacitance type, optical type or ultrasonic type is used.

[0095] The polarizing plate 3 disposed on a surface of the image display panel 10 and the printed layer 76-formed surface of the front transparent plate 7 are bonded to each other with the pressure sensitive adhesive sheet 5. The order of bonding is not particularly limited, bonding of the image display panel 10 to the pressure sensitive adhesive sheet 5 may precede, or bonding of the front transparent plate 7 to the pressure sensitive adhesive sheet 5 may precede. The former bonding and the latter bonding may be performed simultaneously. For improving workability in bonding, it is preferred that one release film (lightly peelable film) 2 is first peeled off to expose the first principal surface of the pressure sensitive adhesive sheet followed by bonding the image display panel 10, and then the other release film (heavily peelable film) 1 is peeled off to expose the second principal surface of the pressure sensitive adhesive sheet 5 followed by bonding the front transparent plate 7.

[0096] It is preferred to perform degassing for removing bubbles at the interface between the pressure sensitive adhesive sheet 5 and the flat plate 71 of the front transparent plate 7, and in the vicinity of a non-flat portion such as the printed layer 76 after pressure sensitive adhesive sheet 5 and the front transparent plate 7 are bonded to each other. As a degassing method, an appropriate method such as heating, pressurization or pressure reduction can be employed. For example, it is preferred that bonding is performed while ingress of bubbles is suppressed under reduced pressure and heating, and pressurization is then performed in parallel with heating through autoclave or the like for the purpose of,

for example, suppressing delay bubbles. When degassing is performed by heating, the heating temperature is generally in a range of 40°C to 150°C. When pressurization is performed, the pressure is generally in a range of generally about 0.05 MPa to 2 MPa.

5 [0097] Since the pressure sensitive adhesive sheet of the present invention has a storage elastic modulus $G'_{25^{\circ}\text{C}}$ of 100 to 250 kPa and a gel fraction of 25 to 70% at 25°C before photocuring, the pressure sensitive adhesive sheet easily follows a level difference shape of a printing layer 76 or the like, so that generation of voids can be suppressed, and glue missing during processing, and positional displacement between members in conveyance and processing hardly occur, so that excellent processability and processing dimensional
10 stability are exhibited.

[0098] The pressure sensitive adhesive sheet before photocuring is bonded to an adherend such as a front transparent plate, and the pressure sensitive adhesive composition that forms the pressure sensitive adhesive sheet is then photocured. Photoirradiation causes polymerization reaction of the photopolymerizable polyfunctional
15 compound to proceed, and accordingly, the storage elastic modulus of the pressure sensitive adhesive sheet increases, so that bonding reliability between the pressure sensitive adhesive sheet 5 and the front transparent member 70 is enhanced.

[0099] The light irradiation amount during photocuring is not particularly limited as long as the pressure sensitive adhesive sheet can be photocured, and the light irradiation
20 amount is, for example, about 50 to 10000 mJ/cm² in terms of an accumulated light amount. Preferably, the light irradiation amount is set in such a manner that the amount of residual C=C bonds is 15% or less. The amount of residual C=C bonds is determined by infrared spectroscopy. The amount of C=C bonds amount in the pressure sensitive adhesive sheet before photocuring is set to 100%, and the amount of C=C bonds in the
25 pressure sensitive adhesive sheet completely cured by irradiating the sheet with an active energy ray at 10000 mJ/cm² is set to 0%. When the amount of residual C=C bonds is 15% or less, the physical properties of the pressure sensitive adhesive sheet are almost identical to those when the amount of residual C=C bonds is 0%.

[0100] When the gap 90 exists between the housing 9 and the front transparent plate 7,
30 it is preferable that the gap 90 is filled with a resin material or the like to perform sealing. As described above, the post-cured pressure sensitive adhesive sheet has a high shear storage elastic modulus, and is therefore excellent in bonding reliability over a wide temperature range. Thus, even when stress strain occurs at a bonding interface of the

pressure sensitive adhesive sheet due to a temperature change in sealing with the resin material or the like, peeling at the bonding interface can be suppressed. In addition, the photocured pressure sensitive adhesive sheet has a low glass transition temperature and a large $\tan \delta$ peak-top value, and is therefore excellent in impact resistance, so that peeling by impacts of falling and the like hardly occurs.

[0101] [Optical Film with Pressure Sensitive Adhesive Sheet]

The pressure sensitive adhesive sheet of the present invention can be used not only in a form in which a release film is temporarily attached to each of both surfaces as shown in FIG. 1, but also as a film with a pressure sensitive adhesive in which a pressure sensitive adhesive sheet is bonded to an optical film or the like. For example, in the form shown in FIG. 3, the release film 1 is temporarily attached to one surface of the pressure sensitive adhesive sheet 5, and a polarizing plate 3 is bonded to the other surface of the pressure sensitive adhesive sheet 5. In the form shown in FIG. 4, a pressure sensitive adhesive sheet 4 is further provided on the polarizing plate 3, and the release film 2 is temporarily attached on the pressure sensitive adhesive sheet 4.

[0102] In a form in which an optical film such as a polarizing plate is bonded to a pressure sensitive adhesive sheet beforehand as described above, the release film 1 temporarily attached to a surface of the pressure sensitive adhesive sheet 5 may be peeled to bond the pressure sensitive adhesive sheet 5 to a front transparent member, followed by post-curing the pressure sensitive adhesive sheet 5 as necessary.

EXAMPLES

[0103] The present invention will be described more specifically below by showing examples and comparative examples, but the present invention is not limited to these examples.

[0104] [Preparation of Acrylic Oligomer]

60 parts by weight of dicyclopentanyl methacrylate (DCPMA), 40 parts by weight of methyl methacrylate (MMA), 3.5 parts by weight of α -thioglycerol as a chain-transfer agent, and 100 parts by weight of toluene as a polymerization solvent were mixed, and stirred in a nitrogen atmosphere at 70°C for 1 hour. 0.2 parts by weight of 2,2'-azobisisobutyronitrile (AIBN) is added as a thermopolymerization initiator, and the mixture was reacted at 70°C for 2 hours, then heated to 80°C, and reacted for 2 hours. Thereafter, the reaction liquid was heated to 130°C, and toluene, the chain-transfer agent

and unreacted monomers were removed by drying to obtain a solid acrylic oligomer. The weight average molecular weight of the acrylic oligomer was 5100.

[0105] [Example 1]

<Polymerization of Base Polymer>

5 In a reaction vessel equipped with a thermometer, a stirrer, a cooler and a nitrogen gas introduction pipe, 64.5 parts by weight of butyl acrylate (BA), 6.0 parts by weight of cyclohexyl acrylate (CHA), 9.6 parts by weight of N-vinylpyrrolidone (NVP), 10 parts by weight of 4-hydroxybutyl acrylate (4HBA) and 5.0 parts by weight of isostearyl acrylate as monomer components, 0.2 parts by weight of azoisobutyronitrile (AIBN) as a thermopolymerization initiator and 0.065 parts by weight of α -thioglycerol (TGR) as a chain-transfer agent were added along with 233 parts by weight of ethyl acetate,. The mixture was stirred in a nitrogen atmosphere at 23°C for 1 hour, and purged with nitrogen. Thereafter, the mixture was reacted at 56°C for 5 hours, and subsequently reacted at 70°C for 3 hours to prepare an acryl-based base polymer solution.

15 **[0106]** <Preparation of Photocurable Pressure Sensitive Adhesive Composition>

To the obtained acryl-based base polymer solution were added the following post-addition components in the following amounts based on 100 parts by weight of the base polymer, and the mixture was then uniformly mixed to prepare a photocurable pressure sensitive adhesive composition.

20 (Post-Addition Components)

Trimethylolpropane adduct of xylylene diisocyanate ("TAKENATE D 110N" manufactured by Mitsui Chemicals, Inc.) as isocyanate-based crosslinker: 0.1 parts by weight;

Dipentaerythritol hexaacrylate (DPHA) as photopolymerizable polyfunctional monomer: 3.0 parts by weight;

Acrylic oligomer described above: 5 parts by weight;

1-Hydroxy-cyclohexyl-phenyl-ketone ("IRGACURE 184" manufactured by BASF) as photopolymerization initiator: 0.2 parts by weight; and

3-Glycidoxypropyltrimethoxysilane ("KBM-403" manufactured by Shin-Etsu Chemical Co., Ltd.) as silane coupling agent: 0.3 parts by weight.

[0107] <Preparation of Pressure Sensitive Adhesive Sheet>

A 75 μ m-thick polyethylene terephthalate (PET) film ("DIAFOIL MRF75" manufactured by Mitsubishi Chemical Corporation) having a silicone-based release layer

on a surface thereof was provided as a substrate (also serving as heavily peelable film), and the photocurable pressure sensitive adhesive composition was applied onto the substrate, and heated at 100°C for 3 minutes to remove the solvent, followed by bonding a 75 μm-thick PET film (“DIAFOIL MRE75” manufactured by Mitsubishi Chemical Corporation) having a silicone-based release layer on a surface thereof. The laminate was aged in an atmosphere of 25°C for 3 days to promote crosslinking, thereby obtaining a pressure sensitive adhesive sheet with a release film temporarily attached on each of both sides.

[0108] [Example 2 and Comparative Examples 1 to 5]

The type and the amount of the photopolymerizable polyfunctional monomer in the post-addition components were changed as shown in Tables 1 and 2. A pressure sensitive adhesive sheet was prepared in the same manner as in Example 1 except for the above.

[0109] [Example 3 and Comparative Examples 6 and 7]

The amount of the crosslinker (TAKENATE D110N) in the post-addition components was changed as shown in Tables 1 and 2. A pressure sensitive adhesive sheet was prepared in the same manner as in Example 1 except for the above.

[0110] [Examples 4 and 5 and Comparative Examples 8 and 9]

The amount of chain-transfer agent (TGR) in polymerization of the base polymer was changed as shown in Tables 1 and 2. A pressure sensitive adhesive sheet was prepared in the same manner as in Example 1 except for the above.

[0111] [Example 6]

The charge-in monomers in polymerization of the base polymer were changed to 62.9 parts by weight of 2-ethylhexyl acrylate (2HEA), 14.5 parts by weight of NVP, 9.7 parts by weight of 4HBA and 12.9 parts by weight of 2-hydroxyethyl acrylate (2HEA). A pressure sensitive adhesive sheet was prepared in the same manner as in Example 1 except for the above.

[0112] [Example 7]

A pressure sensitive adhesive sheet was prepared in the same manner as in Example 6 except that the post-addition components did not include an acrylic oligomer.

[0113] [Example 8]

The photopolymerizable polyfunctional monomer in the post-addition components was changed as shown in Table 1. A pressure sensitive adhesive sheet was prepared in

the same manner as in Example 6 except for the above.

[0114] [Evaluation]

<Weight average molecular weight>

The weight average molecular weights (M_w) of the base polymer and acrylic oligomer were measured by a GPC (gel permeation chromatography) apparatus (product name “HLC-8120GPC”) manufactured by TOSOH CORPORATION. The base polymer was dissolved in tetrahydrofuran to prepare a 0.1 wt% solution, this solution was filtered with a 0.45 μm membrane filter, and the resulting filtrate was used as a measurement sample. GPC measurement conditions are as follows.

10 (Measurement conditions)

Column: G7000HXL + GMHXL + GMHXL manufactured by TOSOH CORPORATION

Column size: each 7.8 mm ϕ $\times$ 30 cm (total column length: 90 cm)

Column temperature: 40°C, Flow rate: 0.8 mL/min

15 Injection amount: 100 μL

Eluent: tetrahydrofuran

Detector: differential refractometer (RI)

Standard sample: polystyrene

20 **[0115]** <Storage elastic modulus, glass transition temperature and $\tan \delta$ peak-top of pressure sensitive adhesive sheet>

Ten pressure sensitive adhesive sheets were laminated to a thickness of about 1.5 mm, and the laminate thus obtained was used as a sample for measurement. The dynamic viscoelasticity was measured under the following conditions using “Advanced Rheometric Expansion System (ARES)” manufactured by Rheometric Scientific, Inc.

25 (Measurement Conditions)

Deformation mode: torsion

Measurement Frequency: 1 Hz or 1×10^{-7} Hz

Temperature elevation rate: 5°C/minute

Shape: parallel plate (7.9 mm ϕ)

30 **[0116]** The shear storage elastic modulus was determined by reading a storage elastic modulus G' at 25°C from the measurement result. The temperature at which the loss tangent ($\tan \delta$) was maximum (peak-top temperature) was defined as a glass transition temperature of the pressure sensitive adhesive sheet. In addition, the value of $\tan \delta$ at the

glass transition temperature (peak-top value) was read.

[0117] <Gel fraction>

0.2 g of the pressure sensitive adhesive is collected from the pressure sensitive adhesive sheet, and was used as a sample for measuring gel fraction. For measurement of the gel fraction of the photocured pressure sensitive adhesive, the sample was collected from the sample for measurement of adhesive strength. The sample was wrapped in a porous polytetrafluoroethylene film having pore diameter of 0.2 μm (manufactured by Nitto Denko Corporation; trade name: "NTF-1122") cut to a size of 100 mm $\times$ 100 mm, and the wrapped opening was tied with a kite string. The total weight (A) of the porous polytetrafluoroethylene film and the kite string measured beforehand was subtracted from the weight of this sample to calculate the weight (B) of the pressure sensitive adhesive sample. The pressure sensitive adhesive sample wrapped in the porous polytetrafluoroethylene film was immersed in approximately 50 mL of ethyl acetate at 23°C for 7 days to elute sol components of the pressure sensitive adhesive to the outside of the polytetrafluoroethylene film. After immersion, the pressure sensitive adhesive wrapped in the porous polytetrafluoroethylene film was taken out, dried at 130°C for 2 hours, and allowed to cool for about 20 minutes, and the dry weight (C) was measured. The gel fraction of the pressure sensitive adhesive was calculated from the following formula.

$$\text{gel fraction (\%)} = 100 \times (C - A) / B$$

[0118] <Adhesive Strength>

The lightly peelable film was peeled from the pressure sensitive adhesive sheet, the pressure sensitive adhesive sheet was bonded to a 50 μm -thick PET film, and cut to a width of 10 mm and a length of 100 mm, the heavily peelable film was then peeled, and the pressure sensitive adhesive sheet was press-bonded to a glass plate with a 5 kg roller to prepare a sample for measuring adhesive strength. Further, from the glass plate side, an ultraviolet ray was applied with an accumulated light amount of 3000 mJ/cm^2 by a metal halide lamp (300 mW/cm^2) to prepare a sample for measurement of an adhesive strength of a photocured pressure sensitive adhesive sheet. The sample was held under an environment at 25°C or 65°C for 30 minutes, and thereafter, using a tensile tester, a test piece was peeled from the glass plate under the condition of a tension speed of 300 mm/minute and a peeling angle of 180° to measure the peeling strength.

[0119] <Level difference absorbcency>

The pressure sensitive adhesive sheet was cut to a size of 75 mm × 45 mm, the lightly peelable film was peeled from the pressure sensitive adhesive sheet, and by a roll laminator (inter-roll pressure: 0.2 MPa and feeding speed: 100 mm/minute), the pressure sensitive adhesive sheet was bonded to the center of a 125 μm-thick PET film cut to a size of 100 mm × 50 mm. Thereafter, the heavily peelable film was peeled, and a 500 μm-thick glass plate (100 mm × 50 mm) printed with a 20 μm-thick black ink in a frame pattern on the peripheral edge portion was bonded to the pressure sensitive adhesive sheet by a roll laminator (inter-roll pressure: 0.2 MPa and feeding speed: 100 mm/minute). The ink-printed region of the glass plate extended over 5 mm from both ends in the short side direction and 15 mm from the both ends in the long side direction, and the black ink layer was in contact with the region of 5 mm from the ends of the four sides of the pressure sensitive adhesive sheet. The sample was treated in an autoclave (50°C, 0.5 MPa) for 30 minutes, and then observed with a digital microscope at a magnification of 20 times to examine presence or absence of bubbles in the vicinity of the boundary of the black ink printed-region. A sample having no bubbles was rated “OK”, and a sample having bubbles was rated “NG”.

[0120] <Processability>

The lightly peelable film was peeled from the pressure sensitive adhesive sheet, bonded to a 100 μm-thick PET film (“COSMOSHINE A4100” manufactured by Toyobo Co., Ltd.), and punched from the PET film side with a press machine to prepare a sample for evaluation of processability. The sample was left standing in an atmosphere at a temperature of 23°C and a relative humidity of 50% for 1 week, the heavily peelable film was then peeled, and whether or not glue missing occurred was visually checked. A sample without glue missing was rated “OK”, and a sample with glue missing was rated “NG”.

[0121] <Interlayer Adhesiveness>

(Preparation of Test Sample)

The pressure sensitive adhesive sheet was cut to a size of 75 mm × 45 mm, the lightly peelable film was peeled from the pressure sensitive adhesive sheet, and the pressure sensitive adhesive sheet was bonded to the center of an ink-printed layer-free 500 μm-thick flat glass plate (100 mm × 50 mm) by a roll laminator (inter-roll pressure: 0.2 MPa and feeding speed: 100 mm/minute). The heavily peelable film was peeled from the pressure sensitive adhesive sheet, and a 500 μm-thick glass plate printed with a 30 μm-

thick black ink in a frame pattern on the peripheral edge portion (50 mm × 100 mm, the ink-printed region is identical to that used in the level difference absorbency test) was bonded to the pressure sensitive adhesive sheet by vacuum pressure-bonding (surface pressure: 0.3 MPa, pressure: 100 Pa). The sample was treated in an autoclave (50°C, 0.5 MPa) for 30 minutes, and then irradiated with an ultraviolet ray with an accumulated light amount of 3000 mJ/cm² by a metal halide lamp (300 mW/cm²) from the glass plate side having a black ink-printed layer, so that the pressure sensitive adhesive layer was photocured.

[0122] The sample was held under an environment at 60°C for 30 minutes, and a 200 μm-thick polystyrene sheet was then inserted between two glass plates to a distance of 1 mm from the end portion of the pressure sensitive adhesive sheet as shown in FIG. 5A, and was held for 10 seconds. The end portion of the pressure sensitive adhesive sheet was observed with a digital microscope at a magnification of 20 times. A sample suffering from generation of streaky bubbles (see FIG. 5B) or delamination between the glass plate and the pressure sensitive adhesive sheet was rated “NG”, and a sample which did not suffer from either generation of bubbles or delamination was rated “OK”.

[0123] <Impact Resistance>

A test sample was prepared in the same manner as in the above-described preparation of an interlayer adhesiveness test sample except that the size of the ink-printed layer-free flat glass plate was changed to 100 mm × 70 mm. The glass plate was bonded to both surfaces of the pressure sensitive adhesive sheet, treatment was performed in an autoclave, and the pressure sensitive adhesive was cured. As shown in FIG. 6, both ends of the test sample 95 in the short side direction were placed on tables 93 disposed with a distance of 60 mm therebetween in such a manner that the ink-printed layer 76-formed glass plate 7 was situated on the lower side, and the upper surface of the end portion of the ink-printed layer-free glass plate 8 was fixed on a table 80 with a pressure sensitive adhesive tape (not shown). The test sample 95 fixed on the tables 93 with the pressure sensitive adhesive tape was held under an environment at -5°C for 24 hours, and then taken out into an environment at room temperature, and after 40 seconds or less, a metal ball 97 having a mass of 11 g was dropped from a height of 300 mm to the glass plate 7 to conduct an impact resistance test.

[0124] In the impact resistance test, a cylindrical guide 99 was used for maintaining consistency of the drop position of the metal ball, and the metal ball 97 was dropped to a

position at a distance of 10 mm in each of the short side direction and the long side direction from the inner edge corners of the frame of the printed region of the printed layer 76. Two tests were conducted. A sample in which the glass plate was not peeled in any of the tests was rated “OK”, and a sample in which the glass plate was peeled in one or both of the two tests was rated “G”.

[0125] [Evaluation Results]

The combination of pressure sensitive adhesive compositions used for preparation of each pressure sensitive adhesive sheet and evaluation results are shown in Tables 1 and 2. In Tables 1 and 2, the components are represented by the following abbreviations.

10 <Acryl-based Monomer>

BA: butyl acrylate

2HEA: 2-ethylhexyl acrylate

CHA: cyclohexyl acrylate

NVP: N-vinyl-2-pyrrolidone

15 4HBA: 4-hydroxybutyl acrylate

2HEA: 2-hydroxyethyl acrylate

ISTA: isostearyl acrylate

<Photopolymerizable Polyfunctional Monomer>

20 HDDA: hexanediol diacrylate (“NK Ester A-HD-N” manufactured by Shin-Nakamura Chemical Co., Ltd., functional group equivalent: 113 g/eq)

APG 400: polypropylene glycol #400 (n = 7) diacrylate (“NK Ester APG 400” manufactured by Shin-Nakamura Chemical Co., Ltd., functional group equivalent: 268 g/eq)

25 TMPTA: trimethylpropane triacrylate (“NK Ester A-TMPT” manufactured by Shin-Nakamura Chemical Co., Ltd., functional group equivalent 99 g/eq)

DPHA: dipentaerythritol hexaacrylate (“NK Ester A-DPH” manufactured by Shin-Nakamura Chemical Co., Ltd., functional group equivalent: 96 g/eq)

[0126] Table 1

base polymer	monomer composition	Example1	Example2	Example3	Example4	Example5	Example6	Example7	Example8
		64.5	64.5	64.5	64.5	64.5	-	-	-
post-addition components	2EHA	-	-	-	-	-	62.9	62.9	62.9
	CHA	6.0	6.0	6.0	6.0	6.0	-	-	-
	NVP	9.6	9.6	9.6	9.6	9.6	14.5	14.5	14.5
	4HBA	14.9	14.9	14.9	14.9	14.9	9.7	9.7	9.7
	2HEA	-	-	-	-	-	12.9	12.9	12.9
	ISTA	5.0	5.0	5.0	5.0	5.0	-	-	-
	AIBN	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	TGR	0.065	0.065	0.065	0.08	0.10	0.065	0.065	0.065
properties before photocuring	Mw ($\times 10^4$)	54	54	54	36	31	53	53	53
	TAKENATE DI10N	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1
	HDDA	-	-	-	-	-	-	-	-
	APG400	-	3.0	-	-	-	-	-	-
	TMPTA	-	-	-	-	-	-	-	4.0
	DPHA	3.0	2.4	3.0	3.0	3.0	3.0	3.0	-
	acrylic oligomer	0.4	0.4	0.4	0.4	0.4	0.4	0	0.4
	photo-polymerization initiator	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
properties after photocuring	silane coupling agent	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	G' _{25°C} (kPa)	140	120	150	120	120	120	120	130
	1Hz	7.5	7.1	8.0	6.9	6.3	6.7	6.2	6.4
	10 ⁷ Hz	45	44	52	43	41	41	42	40
	Gel fraction (%)	11.1	10.2	9.7	11.1	11.1	8.7	8.7	8.3
	adhesive strength (N/10mm)	OK	OK	OK	OK	OK	OK	OK	OK
	level difference absorbency	OK	OK	OK	OK	OK	OK	OK	OK
	Processability	OK	OK	OK	OK	OK	OK	OK	OK
properties after photocuring	G' _{25°C} (kPa)	230	220	230	230	230	240	210	260
	Tg (°C)	-8	-9	-8	-9	-9	-4	-5	-5
	tanδ peak top	1.86	1.90	1.87	1.70	1.73	1.70	1.72	1.72
	Gel fraction (%)	84	80	83	82	85	90	82	88
	adhesive strength (N/10mm)	6.0	8.0	6.0	6.0	5.0	6.7	5.0	7.5
	Interlayer adhesiveness	OK	OK	OK	OK	OK	OK	OK	OK
	falling impact durability	OK	OK	OK	OK	OK	OK	OK	OK

[0127] Table 2

		Comparative Example1	Comparative Example2	Comparative Example3	Comparative Example4	Comparative Example5	Comparative Example6	Comparative Example7	Comparative Example 8	Comparative Example 9
base polymer	BA	64.5	64.5	64.5	64.5	64.5	64.5	64.5	64.5	64.5
	2EHA	-	-	-	-	-	-	-	-	-
	CHA	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
	NVP	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6
	4HBA	14.9	14.9	14.9	14.9	14.9	14.9	14.9	14.9	14.9
	2HEA	-	-	-	-	-	-	-	-	-
	ISTA	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
post- addition components	AIBN	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	TGR	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.14	0.17
	Mw (×10 ⁴)	54	54	54	54	54	54	54	21	17
	TAKENATE DI10N	0.1	0.1	0.1	0.1	0.1	0.05	0.5	0.1	0.1
	HDHA	-	-	-	-	7.0	-	-	-	-
	APG400	-	-	-	7.0	-	-	-	-	-
	TMPA	-	-	-	-	-	-	-	-	-
properties before photocuring	DPHA	0.5	4.0	7.0	-	-	3.0	3.0	3.0	3.0
	acrylic oligomer	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
	photo-polymerization initiator	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	silane coupling agent	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	1Hz	140	120	90	70	80	50	160	80	70
	10 ⁷ Hz	7.6	6.9	4.5	3.7	4.1	3.1	8.1	3.6	3.1
	Gel fraction (%)	47	44	41	41	43	32	72	41	43
properties after photocuring	adhesive strength (N/10mm)	10.2	9.1	8.7	7.2	8.1	13.3	6.4	9.8	8.7
	level difference absorbcency	OK	OK	OK	OK	OK	OK	NG	OK	OK
	Processability	OK	OK	OK	NG	NG	NG	OK	NG	NG
	G' _{25°C} (kPa)	150	480	1000	110	160	140	200	200	200
	Tg (°C)	-10	-3	-2	-6	-4	-9	-4	-5	-5
	tand peak top	1.89	1.56	0.90	1.70	1.65	1.87	1.91	1.56	1.58
	Gel fraction (%)	72	94	95	80	93	70	84	82	84
properties after photocuring	adhesive strength (N/10mm)	8.0	4.7	3.0	14.6	2.8	8.4	3.5	4.0	4.0
	Interlayer adhesiveness	NG	OK	NG	NG	NG	NG	NG	OK	OK
properties after photocuring	falling impact durability	OK	NG	NG	OK	OK	NG	NG	NG	NG

[0128] All of the pressure sensitive adhesive sheets of Examples 1 to 8 were excellent in level difference absorbency and processability before photocuring, and excellent in both of interlayer adhesiveness and falling impact durability.

[0129] Comparison of Example 1 with Comparative Examples 1 to 3 reveals that as the
5 amount of the polyfunctional monomer increases, the gel fraction of the photocured pressure sensitive adhesive sheet tends to increase, and accordingly, the storage elastic modulus $G'_{25^{\circ}\text{C}}$ tends to increase, and the peak top value of $\tan \delta$ tends to decrease. In Comparative Example 1 where the amount of the polyfunctional monomer was small, adhesive strength after photocuring was higher than that in Example 1, but the adhesion
10 retaining force was low, and peeling occurred in the interlayer adhesion test. In Comparative Examples 2 and 3 where the amount of the polyfunctional monomer was large, the viscosity of the pressure sensitive adhesive sheet was low, and impact resistance was insufficient. Further, in Comparative Example 3, interlayer adhesiveness was deteriorated due to reduction of adhesive strength. Comparison of Example 1 with
15 Comparative Examples 1 to 3 reveals that as the amount of the polyfunctional monomer increases, the ratio of the base polymer in the pressure sensitive adhesive composition decreases, and therefore the gel fraction and the storage elastic modulus of the pressure sensitive adhesive sheet before photocuring decrease.

[0130] In Comparative Examples 4 and 5, the amount of the polyfunctional monomer
20 was large, so that the pressure sensitive adhesive sheet before photocuring had a small gel fraction and storage elastic modulus, and the processability of the pressure sensitive adhesive sheet was deteriorated. Further, in Comparative Examples 4 and 5, the polyfunctional monomer was added in an amount equivalent to that in Comparative Example 3 (7 parts by weight based on 100 parts by weight of the base polymer), but the
25 photocured pressure sensitive adhesive sheet had a small storage elastic modulus $G'_{25^{\circ}\text{C}}$ and insufficient interlayer adhesiveness.

[0131] In Example 2 where APG 400 which is a difunctional acrylate was used in combination with DPHA which is a hexafunctional acrylate, the same properties as in Example 1 were exhibited. Further, in Example 8 where TMPTA which is a trifunctional
30 acrylate was used as the polyfunctional monomer, the same properties as in Example 6 were exhibited. It is apparent from these results that use of a polyfunctional monomer having three or more polymerizable functional groups per molecule ensures that in contrast with a case where a difunctional monomer is used, the interlayer adhesive

strength of the photocured pressure sensitive adhesive sheet can be enhanced even with a small amount of the polyfunctional monomer, and therefore both of the processability of the pressure sensitive adhesive sheet before photocuring and the interlayer adhesive strength of the photocured pressure sensitive adhesive sheet can be secured.

5 **[0132]** Comparison of Examples 1 and 3 and Comparative Examples 6 and 7 reveals that as the amount of the crosslinker increases, the gel fraction and the storage elastic modulus of the pressure sensitive adhesive sheet before photocuring tend to increase, and the glass transition temperature of the pressure sensitive adhesive sheet tends to rise. In Comparative Example 6 where the amount of the crosslinker was small, the pressure sensitive adhesive sheet before photocuring was excessively soft, and therefore had poor processability. On the other hand, in Comparative Example 7 where the amount of the crosslinker was large, the pressure sensitive adhesive sheet before photocuring was hard, and adhesiveness and the level difference absorbency were insufficient. Further, in both of Comparative Examples 6 and 7, the photocured pressure sensitive adhesive sheet had
10 insufficient interlayer adhesive strength and impact resistance.
15

[0133] Comparison of Examples 1 and 4 and Comparative Examples 8 and 9 reveals that as the amount of the chain-transfer agent during polymerization of the base polymer increased, the molecular weight of the base polymer tended to decrease. In Comparative Examples 8 and 9, the pressure sensitive adhesive sheet before photocuring had a small storage elastic modulus and poor processability because the base polymer had a small molecular weight. Further, in Comparative Examples 8 and 9, the photocured pressure sensitive adhesive sheet had a small $\tan \delta$ peak top value, and insufficient impact resistance.
20

[0134] Comparison between Examples 6 and 7 reveals that by adding an oligomer to the pressure sensitive adhesive composition, the adhesive strength of the photocured pressure sensitive adhesive sheet can be enhanced without significantly changing other properties.
25

[0135] Comparison of the Examples with the Comparative Examples reveals that a photocurable pressure sensitive adhesive sheet in which properties before photocuring and after photocuring fall within specific ranges has both a level difference absorbency and processability before photocuring and is excellent in impact resistance and adhesive durability after photocuring.
30

DESCRIPTION OF REFERENCE CHARACTERS

5	[0136]	5	pressure sensitive adhesive sheet
		1,2	release film
		3	polarizing plate
		4	pressure sensitive adhesive sheet
		6	image display cell
		10	image display panel
		7	front transparent plate
		9	housing
10		100	image display device

CLAIMS

1. A pressure sensitive adhesive sheet in which a pressure sensitive adhesive composition is formed in a sheet shape,

5 the pressure sensitive adhesive composition being photocurable and comprising:

an acryl-based base polymer having a crosslinked structure;

a photopolymerizable polyfunctional compound having two or more photopolymerizable functional groups per molecule; and

a photopolymerization initiator,

10 wherein the acryl-based base polymer having a crosslinked structure is prepared by introducing 0.03 to 0.5 parts by weight of polyisocyanate crosslinker into 100 parts by weight of an acryl-based base polymer having a weight average molecular weight of 300,000 or more,

15 wherein a content of the photopolymerizable polyfunctional compound in the pressure sensitive adhesive composition is 1 to 6 parts by weight based on 100 parts by weight of the acryl-based base polymer, wherein of the 1 to 6 parts by weight of the photopolymerizable polyfunctional compound, 0.5 to 4 parts by weight thereof is a compound having three or more photopolymerizable functional groups per molecule,

wherein

20 the pressure sensitive adhesive sheet has a storage elastic modulus of 100 to 250 kPa at 25°C and 1 Hz, and has a gel fraction of 25 to 70%, and

after the pressure sensitive adhesive composition is photocured, the pressure sensitive adhesive sheet has a storage elastic modulus of 180 to 400 kPa at 25°C and 1 Hz.

25 2. The pressure sensitive adhesive sheet according to claim 1, wherein a storage elastic modulus at 25°C and 10^{-7} Hz is 4.5 kPa or more.

3. The pressure sensitive adhesive sheet according to claim 1 or 2, wherein after the pressure sensitive adhesive composition is photocured, a glass transition temperature of the
30 photocured pressure sensitive adhesive sheet is -3°C or lower.

4. The pressure sensitive adhesive sheet according to any one of claims 1 to 3, wherein after the pressure sensitive adhesive composition is photocured, a gel fraction of the photocured

pressure sensitive adhesive sheet is 65 to 95%.

5. The pressure sensitive adhesive sheet according to any one of claims 1 to 4, wherein after the pressure sensitive adhesive composition is photocured, a loss tangent peak-top value of the photocured pressure sensitive adhesive sheet is 1.5 or more.

6. The pressure sensitive adhesive sheet according to any one of claims 1 to 5, wherein an adhesive strength to glass is 4 N/10 mm or more, and after the pressure sensitive adhesive composition is photocured, an adhesive strength to glass of 4 N/10 mm or more.

7. The pressure sensitive adhesive sheet according to any one of claims 1 to 6, wherein the acryl-based base polymer contains 5 to 30 parts by weight of a hydroxy group-containing monomer based on 100 parts by weight of the total of monomer components.

8. The pressure sensitive adhesive sheet according to any one of claims 1 to 7, wherein the pressure sensitive adhesive composition includes an acryl-based oligomer having a weight average molecular weight of 1000 to 30000.

9. A method for manufacturing the pressure sensitive adhesive sheet set forth in any one of claims 1 to 8, the method comprising:

applying a pressure sensitive adhesive composition onto a substrate in a sheet shape, the pressure sensitive adhesive composition comprising an acryl-based base polymer, a crosslinker, and a photopolymerizable polyfunctional compound having two or more photopolymerizable functional groups per molecule; and

introducing into the acryl-based base polymer a crosslinked structure with the crosslinker.

10. A pressure sensitive adhesive sheet with a release film, comprising:

the pressure sensitive adhesive sheet according to any one of claims 1 to 8;

a first release film temporarily attached to a first principal surface of the pressure sensitive adhesive sheet; and

a second release film temporarily attached to a second principal surface of the pressure

sensitive adhesive sheet.

11. An optical film with a pressure sensitive adhesive layer, comprising:

an optical film;

5 a first pressure sensitive adhesive sheet stacked on a first principal surface of the optical film;

and a second pressure sensitive adhesive sheet stacked on a second principal surface of the optical film, wherein

the first pressure sensitive adhesive sheet is the pressure sensitive adhesive sheet

10 according to any one of claims 1 to 8.

12. A method for manufacturing an image display device including a transparent member having a level difference portion arranged on a viewing-side surface,

the method comprising

15 bonding the pressure sensitive adhesive sheet according to any one of claims 1 to 8 and the transparent member, and then

irradiating the pressure sensitive adhesive sheet with an active ray to photocure the pressure sensitive adhesive composition in the pressure sensitive adhesive sheet.