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

TECHNICAL FIELD

[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

[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, 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] For arranging a front transparent menber such as a front transparent plate or a touch panel on a front surface of an image display panel, an "interlayer filling structure" is proposed in which 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. In the interlayer filling structure, a gap between the panel and the front transparent member is filled with a pressure sensitive adhesive to decrease a refractive index difference at the interface, and therefore deterioration of visibility due to reflection and scattering is suppressed. In addition, the interlayer filling structure has an advantage that 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 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 portion. By imparting a level difference absorbency using a pressure sensitive adhesive sheet having a large thickness, 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] For an interlayer filling pressure sensitive adhesive sheet, a solvent-free photocurable pressure sensitive adhesive is widely used because a pressure sensitive adhesive sheet having a large thickness can be formed with a uniform thickness (see, for example, Patent Documents 1 and 2). When a photocurable pressure sensitive adhesive is used, a pressure sensitive adhesive sheet in which a pressure sensitive adhesive composition is partially uncured (semi-cured) can be bonded to an adherend, and then photocured. In this method, an enhanced level difference absorbency can be attained during bonding since a semi-cured pressure sensitive adhesive sheet has high fluidity, and adhesion retaining force can be improved by subsequent photocuring.

PRIOR ART DOCUMENT

[0006] Patent Document 1: JP 2014-125524 A

Patent Document 2: WO2013/161666

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

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

[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. Due to narrowing of the frames of display devices or popularization of bezel-less display devices, the size of a display panel 10 is 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 an interlayer filling pressure sensitive adhesive sheet 5 alone (see FIG. 2). Accordingly, the interlayer filling 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 over a wide temperature range.

[0009] In addition, when the size of the display panel is comparable to or greater than the size of the front transparent member, sealing with a resin material may be performed for filling a gap 90 between the housing 9 and the front transparent member 7. For example, the molten resin material is poured into the gap 90, and then cooled to room temperature to solidify the resin, whereby sealing with the resin material is performed. When a high-temperature resin is poured into the gap 90, the front transparent member 7, the housing 9 and the pressure sensitive adhesive sheet 5 have a high temperature in the vicinity of the gap 90, and are cooled in solidification of the resin. Even when dimensional strain occurs in the front transparent member, the housing and the like due to such a temperature change, the pressure sensitive adhesive sheet 5 is required to have adhesive durability against strain stress so that peeling between adherends does not occur.

[0010] A conventional interlayer filling pressure sensitive adhesive sheet as disclosed in, for example, the aforementioned Patent Document 1 has a high glass transition temperature, and is therefore poor in adhesiveness and impact resistance at a low temperature. On the other hand, a pressure sensitive adhesive sheet having a low glass temperature as disclosed in the aforementioned Patent Document 2 has low adhesive durability against strain stress, so that it is difficult to have both impact resistance at a low temperature and durability against strain stress during heating or cooling in resin sealing or the like.

[0011] In view of the situations described above, an object of the present invention is to provide a pressure sensitive adhesive sheet that can impart a level difference absorbency and having excellent impact resistance and adhesive durability against strain stress over a wide temperature range.

MEANS FOR SOLVING THE PROBLEMS

[0012] The present invention relates to a pressure sensitive adhesive sheet in which a

pressure sensitive adhesive containing a base polymer is formed in a sheet shape. The haze of the pressure sensitive adhesive sheet is 1% or less.

[0013] In one embodiment, the pressure sensitive adhesive sheet is a photocurable pressure sensitive adhesive sheet in which a pressure sensitive adhesive composition containing a base polymer and a photocurable compound is formed in a layer shape. The photocurable pressure sensitive adhesive sheet has an adhesive strength of 1.5 N/10 mm or more to glass, and a shear storage elastic modulus of 0.15 MPa or less at a temperature of 25°C.

[0014] Preferably, the photocurable pressure sensitive adhesive composition is in a so-called semi-cured state, and has a polymerization ratio of 90 to 98%. The glass transition temperature of the semi-cured pressure sensitive adhesive sheet is preferably -5°C or lower. The loss tangent peak-top value of the semi-cured pressure sensitive adhesive sheet is preferably 1.6 or more.

[0015] In one embodiment of the pressure sensitive adhesive sheet of the present invention, the polymerization ratio of the pressure sensitive adhesive composition is about 99% or more. Such a fully cured pressure sensitive adhesive sheet is obtained by, for example, photocuring the semi-cured pressure sensitive adhesive sheet. A fully cured pressure sensitive adhesive sheet can be obtained by photocuring a photocurable pressure sensitive adhesive sheet having a polymerization ratio of less than 90%.

[0016] The glass transition temperature of the fully cured pressure sensitive adhesive sheet is preferably -3°C or lower. The shear storage elastic modulus of the fully cured pressure sensitive adhesive sheet at a temperature of 25°C ($G'_{25°C}$) is preferably 0.16 MPa or more. The peak-top value of loss tangent of the fully cured pressure sensitive adhesive sheet is preferably 1.5 or more. In the semi-cured pressure sensitive adhesive sheet, the glass transition temperature and $G'_{25°C}$ are each preferably within the above-mentioned range when the polymerization ratio is increased to 99% by curing, and the loss tangent peak-top value is preferably within the above-mentioned range.

[0017] As the base polymer contained in the pressure sensitive adhesive sheet, for example, a polymer is used in which an acryl-based polymer chain is crosslinked with a urethane-based segment. For satisfying the above-mentioned properties, the content of the urethane-based segment is preferably 3 to 30 parts by weight based on 100 parts by weight of the acryl-based polymer chain. The weight average molecular weight of the urethane-based segment is

preferably 4000 to 50000.

[0018] A base polymer in which an acryl-based polymer chain is crosslinked with a urethane-based segment is obtained by, for example, copolymerization of a monomer component forming the acryl-based polymer chain and a urethane (meth)acrylate having a (meth)acryloyl group at least at two terminals. The polyfunctional urethane (meth)acrylate is preferably a urethane di(meth)acrylate having a (meth)acryloyl group at both terminals.

[0019] The weight average molecular weight of the urethane di(meth)acrylate is preferably 4000 to 50000. The glass transition temperature of the urethane (meth)acrylate is preferably 0°C or lower.

[0020] A pressure sensitive adhesive sheet containing a base polymer in which an acryl-based polymer chain is crosslinked with a urethane-based segment is obtained by, for example, applying a composition, which contains an acryl-based monomer and/or a partially polymerized product thereof and a urethane meth)acrylate, onto a substrate in the form of a layer, and then irradiating the composition with an active ray to photocure the composition. In the pressure sensitive adhesive composition, the content of the urethane (meth)acrylate is preferably 3 to 30 parts by weight based on 100 parts by weight of the total of the acryl-based monomer and partially polymerized product thereof.

[0021] 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 disposed on a viewing-side surface. When a semi-cured pressure sensitive adhesive sheet is used, 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 sheet.

EFFECTS OF THE INVENTION

[0022] The pressure sensitive adhesive sheet of the present invention has a low glass transition temperature after full curing and has a high shear storage elastic modulus, so that it is possible to have both resistance to impacts of falling and the like and adhesive durability against strain stress over a wide temperature range. In addition, when being in a semi-cured state, the pressure sensitive adhesive sheet has a low shear storage elastic modulus, and is therefore excellent in level difference absorbency. 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

[0023] 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.

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.

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

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0024] FIG. 1 shows a pressure sensitive adhesive sheet with a release film in which 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.

[0025] [Physical Properties of Pressure Sensitive Adhesive Sheet]

The pressure sensitive adhesive sheet of the present invention is obtained by forming a pressure sensitive adhesive in a sheet shape. The pressure sensitive adhesive sheet is a transparent pressure sensitive adhesive sheet having a haze of 1.0% or less.

[0026] In one embodiment, the pressure sensitive adhesive that constitutes a pressure sensitive adhesive sheet is a photocurable pressure sensitive adhesive containing a monomer or oligomer (photocurable compound) having a photocurable functional group. The polymerization ratio of the photocurable pressure sensitive adhesive sheet is preferably 90 to

98%. In other words, it is preferable that the photocurable pressure sensitive adhesive sheet is in a semi-cured state, and contains 2 to 10% by weight of a photocurable compound. The polymerization ratio of the pressure sensitive adhesive sheet is calculated in accordance with the following expression from weights before and after the pressure sensitive adhesive sheet is heated at 130°C for 3 hours. The polymerization ratio of a prepolymer as described later is calculated by the same method as described above.

polymerization ratio (%) = weight after drying / weight before drying × 100

[0027] The shear storage elastic modulus of the semi-cured pressure sensitive adhesive sheet at 25°C ($G'_{25°C}$) is preferably 0.15 MPa or less from the viewpoint of imparting a level difference absorbency to the pressure sensitive adhesive sheet to prevent ingress of bubbles to the vicinity of a printing level difference. On the other hand, from the viewpoint of the moldability and handling property of the pressure sensitive adhesive sheet, the shear storage elastic modulus ($G'_{25°C}$) is preferably 0.03 MPa or more, more preferably 0.05 MPa or more, further preferably 0.07 MPa or more.

[0028] When photocuring (post-curing) is performed after the semi-cured pressure sensitive adhesive sheet is bonded to an adherend, the polymerization ratio increases due to polymerization reaction of a photocurable compound, leading to an increase in shear storage elastic modulus of the pressure sensitive adhesive sheet. Preferably, the pressure sensitive adhesive sheet fully cured by post-curing (where the polymerization ratio of 99% or more) has a shear storage elastic modulus of 0.16 MPa or more at 25°C ($G'_{25°C}$). When the shear storage elastic modulus ($G'_{25°C}$) of the fully cured pressure sensitive adhesive sheet is 0.16 MPa or more, bonding reliability is improved. From the viewpoint of improving bonding reliability at a high temperature, the shear storage elastic modulus of the fully cured pressure sensitive adhesive sheet at 80°C ($G'_{80°C}$) is preferably 0.11 MPa or more.

[0029] On the other hand, from the viewpoint of imparting moderate viscidity to the pressure sensitive adhesive sheet to secure wettability, the shear storage elastic modulus ($G'_{25°C}$) of the fully cured pressure sensitive adhesive sheet is preferably 1 MPa or less, more preferably 0.5 MPa or less, further preferably 0.4 MPa or less. From the same viewpoint as described above, the shear storage elastic modulus ($G'_{80°C}$) of the fully cured pressure sensitive adhesive sheet is preferably 0.6 MPa or less, more preferably 0.4 MPa or less, further preferably 0.3 MPa or less.

[0030] The glass transition temperature of the semi-cured pressure sensitive adhesive sheet is preferably -5°C or lower. The glass transition temperature of the semi-cured pressure sensitive adhesive sheet is preferably -25°C or higher, more preferably -20°C or higher, further preferably -18°C or higher. The glass transition temperature of the fully cured pressure sensitive adhesive sheet is preferably -3°C or lower. The glass transition temperature of the fully cured 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 range, the pressure sensitive adhesive sheet tends to be excellent in impact resistance because it has appropriate viscidity even over a low-temperature range.

[0031] The loss tangent (tan δ) peak-top value (*i.e.*, tan δ at glass transition temperature) of the semi-cured pressure sensitive adhesive sheet is preferably 1.6 or more, more preferably 1.7 or more, further preferably 1.8 or more. The tan δ peak-top value of the fully cured pressure sensitive adhesive sheet is preferably 1.5 or more, more preferably 1.6 or more, further preferably 1.7 or more. A pressure sensitive adhesive sheet having a large tan δ peak-top value tends to exhibit a high viscous behavior, leading to excellent impact resistance.

[0032] The shear storage elastic modulus G', glass transition temperature and tan δ peak-top value of the pressure sensitive adhesive sheet are determined by measurement of viscoelasticity at a frequency of 1 Hz. The glass transition temperature is a temperature at which tan δ is maximum (peak-top temperature). The loss tangent (tan δ) 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 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 viscidity. As the loss tangent (tan δ) 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.

[0033] In each of the semi-cured pressure sensitive adhesive sheet and the fully cured pressure sensitive adhesive sheet, the upper limit of the tan δ peak-top value is not

particularly limited, but is generally 3.0 or less. From the viewpoint of the adhesion retaining force, the tan δ peak-top value is preferably 2.7 or less, more preferably 2.5 or less.

[0034] The adhesive strength of the semi-cured pressure sensitive adhesive sheet is preferably 3 N/10 mm or more, more preferably 4 N/10 mm or more, further preferably 5 N/10 mm or more. When the adhesive strength of the semi-cured pressure sensitive adhesive sheet is within the above-mentioned range, peeling at an interface between an adherend and a pressure sensitive adhesive sheet 5 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 5 after a release film 2 (lightly peelable film) temporarily attached to the other surface is peeled to bond the pressure sensitive adhesive sheet 5 to the adherend.

[0035] The adhesive strength of the fully cured pressure sensitive adhesive sheet is preferably 2 N/10 mm or more, more preferably 2.5 N/10 mm or more, further preferably 3 N/10 mm or more. When the adhesive strength of the fully cured 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.

[0036] The adhesive strength is determined by a peeling test conducted at a tension speed of 60 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.

[0037] The adhesive strength of the semi-cured pressure sensitive adhesive sheet at 65°C temperature is preferably 1 N/10 mm or more, more preferably 1.5 N/10 mm or more, further preferably 2 N/10 mm or more. The adhesive strength of the fully cured pressure sensitive adhesive sheet at 65°C is preferably 1 N/10 mm or more, more preferably 1.5 N/10 mm or more, further preferably 2 N/10 mm or more.

[0038] 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 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 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 sheet.

[0039] [Compositions of Pressure Sensitive Adhesive]

Composition of the pressure sensitive adhesive for the pressure sensitive adhesive sheet of the present invention is not particularly limited as long as the pressure sensitive adhesives satisfy the above mentioned requirements. 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 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.

[0040] An acryl-based pressure sensitive adhesive containing an acryl-based polymer can be preferably used as a base polymer because it is excellent in optical transparency, exhibits moderate wettability and adhesion characteristics such as cohesiveness and adhesiveness, and is also excellent in weather resistance, heat resistance and the like. In particular, an acryl-based base polymer having a structure in which an acryl-based polymer chain is crosslinked with a urethane-based segment is preferable.

[0041] [Base Polymer]

When the acryl-based polymer chain is crosslinked with a urethane-based segment, a high adhesion retaining force can be exhibited at a low glass transition temperature. In the base polymer, the content of the urethane-based segment is preferably 3 parts by weight or more based on 100 parts by weight of the acryl-based polymer chain.

[0042] When the amount of the urethane-based segment is excessively large, the viscidity of the pressure sensitive adhesive may be reduced due to an increase in crosslinking density, leading to deterioration of the level difference absorbency and impact resistance. In addition, when the amount of the urethane-based segment is excessively large, the transparency of the pressure sensitive adhesive sheet may be deteriorated, leading to an increase in haze. Thus, the amount of the urethane-based segment in the base polymer is preferably 30 parts by

weight or less, more preferably 25 parts by weight or less based on 100 parts by weight of the acryl-based polymer chain.

[0043] <Acryl-based Polymer Chain>

The acryl-based polymer chain contains a (meth)acrylic acid alkyl ester as a main constituent monomer component. In this specification, the "(meth)acryl" means acryl and/or methacryl.

[0044] 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.

[0045] 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 and nonadecyl (meth)acrylate.

[0046] 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.

[0047] The amount of the (meth)acrylic acid alkyl ester based on the total amount of monomer components for forming an acryl-based polymer chain 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 (Tg) of the polymer

chain 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 polymer chain is preferably 30% by weight or more, more preferably 40% by weight or more, further preferably 45% by weight or more. The monomer component forming an acryl-based polymer chain is a monomer component other than urethane (meth)acrylate or the like that is a constituent component of the urethane-based segment.

[0048] The acryl-based polymer chain may contain a hydroxyl group-containing monomer and a carboxy group-containing monomer as constituent monomer components. When the acryl-based polymer chain contains a hydroxyl group-containing monomer as a constituent monomer component, the transparency of the pressure sensitive adhesive sheet tends to be improved, and cloudiness under a high-temperature and high-humidity environment tends to be suppressed.

[0049] 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. From the viewpoint of high compatibility with the urethane-based segment and improvement of the transparency of the pressure sensitive adhesive sheet, it is preferable that the acryl-based polymer chain contains as a constituent monomer component a (meth)acrylic acid ester having a hydroxyalkyl group having 4 to 8 carbon atoms, among the above-mentioned (meth)acrylic acid esters.

[0050] The amount of the hydroxy group-containing monomer based on the total amount of monomer components for forming the acryl-based polymer chain is preferably 1 to 35% by weight, more preferably 3 to 30% by weight, further preferably 5 to 25% by weight.

[0051] 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.

[0052] The acryl-based polymer chain 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.

0053] When the acryl-based polymer chain contains high-polarity monomers such as a hydroxyl group-containing monomer and a carboxy group-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 polymer chain is preferably 3 to 40% by weight, more preferably 5 to 35% by weight, further preferably 10 to 30% by weight. In addition, the amount of the nitrogen-containing monomer based on the total amount of monomer components for forming the acryl-based polymer chain is preferably 1 to 25% by weight, more preferably 2 to 20% by weight, further preferably 3 to 15% by weight.

[0054] Besides the above-described monomer components, the acryl-based polymer chain 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.

[0055] The acryl-based polymer chain may contain polyfunctional compound (monomer or oligomer). The polyfunctional compound includes at least two polymerizable functional

groups each having an unsaturated double bond, such as (meth)acryloyl group and vinyl group, per molecule. Examples of the polyfunctional compound include 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 (meth)acrylate, alkanediol di(meth)acrylate, tricyclodecane dimethanol di(meth)acrylate, ethoxylated isocyanuric acid triacrylate, pentaerythritol tri(meth)acrylate, pentaerythritol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol poly(meth)acrylate, dipentaerythritol hexa(meth)acrylate, neopentyl glycol di(meth)acrylate, glycerin di(meth)acrylate, epoxy (meth)acrylate, butadiene (meth)acrylate and isoprene (meth)acrylate.

[0056] When the acryl-based polymer chain contains a polyfunctional monomer as a constituent monomer component, a branched structure (crosslinked structure) is introduced into the polymer chain. As described later, a crosslinked structure is introduced into the acryl-based polymer chain by the urethane-based segment in the pressure sensitive adhesive according to the present invention. When the amount of the crosslinked structure introduced by polyfunctional monomer components other than the urethane-based segment, the adhesive strength of the pressure sensitive adhesive at a low temperature may be reduced. Thus, the amount of polyfunctional compounds (other than urethane acrylate) based on the total amount of monomer components for forming the acryl-based polymer chain is preferably 3% by weight or less, more preferably 1% by weight or less, further preferably 0.5% by weight or less, especially preferably 0.3% by weight or less.

[0057] Preferably, the acryl-based polymer chain 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 polymer chain (main monomer). For example, when the main monomer in the acryl-based polymer chain is a (meth)acrylic acid alkyl ester having a linear or branched alkyl group having 6 or less carbon atoms, the tan δ peak-top value tends to increase, leading to improvement of impact resistance. Particularly, when the main monomer is an acrylic acid C_4-alkyl ester such as butyl acrylate, the tan δ 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 polymer chain. Particularly, the content of butyl acrylate as a constituent monomer component is preferably within the above-mentioned range.

[0058] The theoretical glass transition temperature (Tg) of the acryl-based polymer chain is preferably -50°C or higher. The theoretical glass transition temperature (Tg) of the acryl-based polymer chain is preferably -10°C or lower, more preferably -20°C or lower, further preferably -25°C or lower. The theoretical glass transition temperature (Tg) is calculated from the glass transition temperature (Tg_i) of a homopolymer of a constituent monomer component in the acryl-based polymer chain and the weight fraction (W_i) of each monomer component in accordance with the following Fox equation:

$$1/Tg = \Sigma(W_i/Tg_i).$$

[0059] Tg represents a glass transition temperature (unit: K) of the polymer chain, W_i represents a weight fraction (copolymerization ratio on a weight basis) of a monomer component i forming the segment, and Tg_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 (Tg) of a homopolymer of a monomer which is not described in the document, a loss tangent (tan δ) peak-top temperature obtained by dynamic viscoelasticity measurement may be employed.

[0060] <Urethane-based Segment>

The urethane-based segment is a molecular chain having a urethane bond, and both terminals of the urethane-based segment are covalently bonded to the acryl-based polymer chain, so that a crosslinked structure is introduced into the acryl-based polymer chain.

[0061] (Structure of Urethane-based Segment)

The urethane-based segment typically includes a polyurethane chain obtained by reacting diol and diisocyanate. From the viewpoint of obtaining a pressure sensitive adhesive that can have both adhesiveness at a low temperature and a retaining force at a high temperature, the molecular weight of the polyurethane chain in the urethane-based segment is preferably 4000 to 50000, more preferably 4500 to 40000, further preferably 5000 to 30000.

[0062] The larger the molecular weight of the polyurethane chain in the urethane-based segment increases, the longer the distance between crosslinking points of the acryl-based polymer chain. When the molecular weight of the polyurethane chain is excessively small, and thus the distance between crosslinking points is short, the storage elastic modulus increases due to an increase in cohesive force. Since the viscidity of the pressure sensitive adhesive sheet is accordingly reduced, and thus the loss tangent (tan δ) decreases, the level difference absorbency and impact resistance tend to be deteriorated. When the molecular weight of the polyurethane chain is excessively large, and thus the distance between crosslinking points is long, the storage elastic modulus may be low, leading to an insufficient adhesion retaining force. When the molecular weight of the polyurethane chain is within the above-mentioned range, the pressure sensitive adhesive has moderate cohesiveness, and therefore it is possible to have both impact resistance and an adhesion retaining force.

[0063] Examples of the diol to be used for formation of the polyurethane chain include low-molecular-weight diols such as ethylene glycol, diethylene glycol, propylene glycol, butylene glycol and hexamethylene glycol; and high-molecular-weight polyols such as polyester polyol, polyether polyol, polycarbonate polyol, acryl polyol, epoxy polyol and caprolactone polyol.

[0064] The polyether polyol is obtained by ring-opening and addition polymerization of an alkylene oxide with a polyhydric alcohol. Examples of the alkylene oxide include ethylene oxide, propylene oxide, butylene oxide, styrene oxide and tetrahydrofuran. Examples of the polyhydric alcohol include the above-described diols, glycerin and trimethylolpropane.

[0065] The polyester polyol is polyester having a hydroxyl group at the terminal, and is obtained by reacting a polybasic acid with a polyhydric alcohol in such a manner that the alcohol equivalent is in surplus over the carboxylic acid equivalent. As a polybasic acid component and a polyhydric alcohol component which form the polyester polyol, a combination of a dibasic acid a diol is preferable.

[0066] Examples of the dibasic acid component include aromatic dicarboxylic acids such as orthophthalic acid, isophthalic acid and terephthalic acid; cycloaliphatic dicarboxylic acids such as hexahydrophthalic acid, tetrahydrophthalic acid, 1,3-cyclohexanedicarboxylic acid and 1,4-cyclohexanedicarboxylic acid; aliphatic dicarboxylic acids such as oxalic acid, succinic acid, malonic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, dodecanedicarboxylic acid and octadecanedicarboxylic acid; and

acid anhydrides and lower alcohol esters of these dicarboxylic acids.

[0067] Examples of the diol component include ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, diethylene glycol, triethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, 1,4-cyclohexanedimethanol, 1,4-cyclohexanediol, bisphenol A, bisphenol F, hydrogenated bisphenol A and hydrogenated bisphenol F.

[0068] Examples of the polycarbonate polyol include polycarbonate polyols obtained by subjecting a diol component and phosgene to polycondensation reaction; polycarbonate polyols obtained by subjecting a diol component and a carbonic acid diester such as dimethyl carbonate, diethyl carbonate, dipropyl carbonate, diisopropyl carbonate, dibutyl carbonate, ethylbutyl carbonate, ethylene carbonate, propylene carbonate, diphenyl carbonate or dibenzyl carbonate to transesterification condensation; copolymerized polycarbonate polyols obtained using two or more polyol components; polycarbonate polyols obtained by subjecting the above-mentioned various polycarbonate polyols and a carboxy group-containing compound to esterification reaction; polycarbonate polyols obtained by subjecting the above-mentioned various polycarbonate polyols and a hydroxyl group-containing compound to etherification reaction; polycarbonate polyols obtained by subjecting the above-mentioned various polycarbonate polyols and an ester compound to transesterification reaction; polycarbonate polyols obtained by subjecting the above-mentioned various polycarbonate polyols and a hydroxyl group containing compound to transesterification reaction; polyester-based polycarbonate polyols obtained by polycondensation of the above-mentioned various polycarbonate polyols and a dicarboxylic acid compound; and copolymerized polyether-based polycarbonate polyols obtained by copolymerizing the above-mentioned various polycarbonate polyols and an alkylene oxide.

[0069] The polyacryl polyol is obtained by copolymerizing a (meth)acrylic acid ester and a monomer component having a hydroxyl group. Examples of the monomer having a hydroxyl group include (meth)acrylic acid hydroxyalkyl esters such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate and 2-hydroxypentyl (meth)acrylate; polyhydric alcohol (meth)acrylic acid monoesters such as glycerin and trimethylolpropane; and N-methylol (meth)acrylamide. Examples of the (meth)acrylic acid ester include methyl

(meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and cyclohexyl (meth)acrylate.

[0070] The polyacryl polyol may contain as a copolymerizable component a monomer component other than the components described above. Examples of the copolymerizable monomer component other than the components described above include unsaturated monocarboxylic acids such as (meth)acrylic acid; unsaturated dicarboxylic acids such as maleic acid, and anhydrides and mono- or diesters thereof; unsaturated nitriles such as (meth)acrylonitrile; unsaturated amides such as (meth)acrylamide and N-methylol (meth)acrylamide; vinyl esters such as vinyl acetate and vinyl propionate; vinyl ethers such as methylvinyl ether; α-olefins such as ethylene and propylene; halogenated α,β-unsaturated aliphatic monomers such as vinyl chloride and vinylidene chloride; and α,β-unsaturated aromatic monomers such as styrene and α-methylstyrene.

[0071] The diisocyanate to be used for formation of the polyurethane chain may be either an aromatic or aliphatic diisocyanate. Examples of the aromatic diisocyanate include 1,5-naphthalene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), 4,4'-diphenyldimethylmethane diisocyanate, tetramethyldiphenylmethane diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2-chloro-1,4-phenyl diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, xylylene diisocyanate, 4,4'-diphenyl ether diisocyanate, 4,4'-diphenylsulfoxide diisocyanate, 4,4'-diphenylsulfone diisocyanate and 4,4'-biphenyl diisocyanate. Examples of the aliphatic diisocyanate include butane-1,4-diisocyanate, hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, 2,4,4-trimethylhexamethylene diisocyanate, cyclohexane-1,4-diisocyanate, isophorone diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 1,3-bis(isocyanatemethyl)cyclohexane and methylcyclohexane diisocyanate.

[0072] As the diisocyanate, a derivative of an isocyanate compound can also be used. Examples of the derivative of an isocyanate compound include dimers of polyisocyanate, trimers of isocyanate (isocyanurates), polymeric MDI, adducts with trimethylolpropane, biuret modified products, allophanate modified products and urea modified products. As the diisocyanate component, a urethane prepolymer having an isocyanate group at the terminal may be used.

[0073] (Introduction of Crosslinked Structure into Acryl-based Polymer Chain by Urethane-

based Segment)

When a compound having at the terminal of a polyurethane chain a polyfunctional group copolymerizable with a monomer component for forming an acryl-based polymer chain, or a compound having at the terminal of a polyurethane chain a functional group capable of reacting with a carboxy group, a hydroxyl group or the like contained in an acryl-based polymer chain is used, a crosslinked structure can be introduced into the acryl-based polymer chain by a urethane-based segment. It is preferable that a crosslinked structure is introduced by a urethane-based segment using a urethane di(meth)acrylate having a (meth)acryloyl group at both terminals of a polyurethane chain because crosslinking points are easily introduced uniformly into the acryl-based polymer chain, and excellent compatibility between the acryl-based polymer chain and the urethane-based segment is exhibited. For example, when a monomer component for forming an acryl-based polymer chain is copolymerized with a urethane di(meth)acrylate, a crosslinked structure can be introduced into the acryl-based polymer chain by a urethane-based segment.

[0074] The urethane di(meth)acrylate having a (meth)acryloyl group at both terminals is obtained by, for example, using a (meth)acrylic compound having a hydroxyl group, in addition to a diol component, in polymerization of polyurethane. From the viewpoint of controlling the chain length (molecular weight) of the urethane-based segment, it is preferable that an isocyanate-terminated polyurethane is synthesized by reacting a diol with a diisocyanate in such a manner that the isocyanate is in surplus, and a (meth)acrylic compound having a hydroxyl group is then added to react the isocyanate group at the terminal of the polyurethane with a hydroxyl group of the (meth)acrylic compound.

[0075] By reacting a polyhydric alcohol with a polyisocyanate compound in such a manner that the polyisocyanate compound is in surplus, a polyurethane chain having an isocyanate group at the terminal is obtained. For obtaining an isocyanate-terminated polyurethane, a diol component and a diisocyanate component may be used in such a manner that the NCO/OH ratio (equivalent ratio) is preferably 1.1 to 2.0, more preferably 1.15 to 1.5. A diol component and a diisocyanate component may be mixed in substantially equal amounts and reacted, followed by adding a diisocyanate component.

[0076] Examples of the (meth)acrylic compound having a hydroxyl group include hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate,

hydroxyhexyl (meth)acrylate, hydroxymethyl acrylamide and hydroxyethyl acrylamide.

[0077] As the urethane (meth)acrylate, a commercially available product from a company such as Arakawa Chemical Industries, Ltd., Shin-Nakamura Chemical Co., Ltd., Toagosei Co., Ltd., Kyoeisha Chemical Co., Ltd., Nippon Kayaku Co., Ltd., The Nippon Synthetic Chemical Industry Co., Ltd., Negami Chemical Industrial Co., Ltd., Daicel-Allnex Ltd may be used. The weight average molecular weight of the urethane (meth)acrylate is preferably 4000 to 50000, more preferably 4500 to 40000, further preferably 5000 to 30000.

[0078] The glass transition temperature of the urethane (meth)acrylate is preferably 0°C or lower, more preferably -10°C or lower, further preferably -20°C or lower. By using a urethane (meth)acrylate having a low glass transition temperature (Tg), a pressure sensitive adhesive excellent in adhesive strength at a low temperature even when a crosslinked structure is introduced by a urethane-based segment to enhance the cohesive force of the base polymer. The lower limit of the glass transition temperature of the urethane (meth)acrylate is not particularly limited, but is preferably -100°C or higher, more preferably -90°C or higher, further preferably -80°C or higher from the viewpoint of obtaining a pressure sensitive adhesive excellent in retaining force at a high temperature.

[0079] When a crosslinked structure is introduced into the acryl-based polymer chain by a urethane-based segment using a urethane (meth)acrylate, the glass transition temperature of the urethane-based segment of the base polymer is substantially equal to the glass transition temperature of the urethane (meth)acrylate.

[0080] <Preparation of Base Polymer>

A polymer with a crosslinked structure introduced into an acryl-based polymer chain by a urethane-based segment can be polymerized by various known methods. When a urethane (meth)acrylate is used as a constituent component of the urethane-based segment, a monomer component for forming the acryl-based polymer chain may be copolymerized with the urethane (meth)acrylate.

[0081] The amount of the urethane (meth)acrylate is preferably 3 to 30 parts by weight, more preferably 4 to 25 parts by weight based on 100 parts by weight of the monomer component for forming the acryl-based polymer chain. When the amount of the urethane (meth)acrylate is adjusted, it is possible to prepare a base polymer in which the content of a urethane-based segment is within the above-mentioned range. When the content of the

urethane-based segment is excessively low, the adhesion retaining force of the pressure sensitive adhesive sheet tends to be reduced due to reduction of cohesiveness of the base polymer. When the content of the urethane-based segment is excessively high, the viscidity of the pressure sensitive adhesive sheet tends to be reduced due to an increase in cohesiveness of the base polymer, leading to deterioration of impact resistance.

[0082] Photopolymerization is preferable as a method for polymerization of the base polymer. In photopolymerization, a polymer can be prepared without use of a solvent, so that it is not necessary to dry and remove the solvent during formation of the pressure sensitive adhesive sheet, and a pressure sensitive adhesive sheet having a large thickness can be uniformly formed. In addition, photopolymerization is suitable for formation of a semi-cured pressure sensitive adhesive sheet because the polymerization ratio is easily adjusted, and polymerization can be resumed by performing photoirradiation again.

[0083] In preparation of the base polymer, the total amount of a monomer component for forming the acryl-based polymer chain and the urethane (meth)acrylate for introducing a crosslinked structure may be reacted at once, or polymerization may be performed in a multiple stages. For performing polymerization in multiple stages, a method is preferable in which a monofunctional monomer for forming an acryl-based polymer chain are polymerized to form a prepolymer composition (prepolymerization), and a polyfunctional compound such as a urethane di(meth)acrylate is added in a syrup of the prepolymer composition to polymerize the prepolymer composition and the polyfunctional monomer (main polymerization). The prepolymer composition is a partially polymerized product containing a polymerized product with a low polymerization ratio and an unreacted monomer.

[0084] By performing prepolymerization of a constituent component of the acryl-based polymer, branch points (crosslinking points) with a polyfunctional compound such as a urethane di(meth)acrylate can be uniformly introduced into the acryl-based polymer chain. In addition, the pressure sensitive adhesive sheet can also be formed by applying a mixture of a low-molecular-weight polymer or a partially polymerized product and an unpolymerized monomer component (pressure sensitive adhesive composition) onto a substrate, and then performing main polymerization on the substrate.

[0085] A low-polymerization composition such as a prepolymer composition has a low viscosity, and is thus excellent in application property, and therefore by using a method in

which a pressure sensitive adhesive composition that is a mixture of a prepolymer composition and a polyfunctional compound is applied, and then main polymerization is performed on a substrate, productivity of the pressure sensitive adhesive sheet can be improved, and the thickness of the pressure sensitive adhesive sheet can be made uniform. In addition, by adjusting the polymerization ratio in main polymerization, a semi-cured pressure sensitive adhesive sheet excellent in level difference absorbency can be obtained.

[0086] [Pressure Sensitive Adhesive Sheet]

As described above, a prepolymer composition with a low polymerization ratio is prepared by prepolymerization, a pressure sensitive adhesive composition obtained by adding a polyfunctional compound etc. to the prepolymer composition is applied in the form of a layer onto a substrate, and the pressure sensitive adhesive composition on the substrate is polymerized (main polymerization) to obtain a semi-cured pressure sensitive adhesive sheet.

[0087] <Prepolymerization>

The prepolymer composition can be prepared by, for example, polymerizing a composition obtained by mixing a monomer component for forming the acryl-based polymer chain and a polymerization initiator. The prepolymer forming composition may contain a polyfunctional compound (polyfunctional monomer or polyfunctional oligomer). For example, a part of the polyfunctional compound as a raw material for the polymer is included in the prepolymer forming composition, and after polymerization of the prepolymer, the remainder of the polyfunctional compound is added, and subjected to main polymerization.

[0088] Preferably, the prepolymer forming 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 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.

[0089] In polymerization, a chain-transfer agent, a polymerization inhibitor (polymerization-delaying agent) or the like may be used for the purpose of, for example, adjusting the

molecular weight. Examples of the chain-transfer agent include thiols such as α-thioglycerol, lauryl mercaptan, glycidyl mercaptan, mercaptoacetic acid, 2-mercaptoethanol, thioglycolic acid, 2-ethylhexyl thioglycolate and 2,3-dimercapto-1-propanol, and α-methylstyrene dimers.

[0090] The prepolymer forming composition may contain a chain-transfer agent etc. as necessary in addition to the monomer and the polymerization initiator. The polymerization initiator and the chain-transfer agent which are used in prepolymerization are not particularly limited, and the above-mentioned photopolymerization initiators and chain-transfer agents can be used.

[0091] Although the polymerization ratio of the prepolymer is not particularly limited, the polymerization ratio is preferably 3 to 50% by weight, more preferably 5 to 40% by weight from the viewpoint of obtaining a viscosity suitable for application of the prepolymer onto a substrate. The polymerization ratio of the prepolymer can be adjusted to fall within a desired range by adjusting the type and amount of the photopolymerization initiator, the irradiation intensity and irradiation time of an active ray such as UV light, and so on.

[0092] <Preparation of Pressure Sensitive Adhesive Composition>

The urethane (meth)acrylate, and the remainder of a monomer component for forming the acryl-based polymer chain, a polymerization initiator and a chain-transfer agent, and other additives as necessary are mixed with the prepolymer composition to prepare a pressure sensitive adhesive composition. 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 polymerization ratio of the prepolymer, the amount of the urethane (meth)acrylate, the compositions, molecular weights and amounts 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.

[0093] The polymerization initiator and the chain-transfer agent to be used for main polymerization are not particularly limited, and for example, the above-mentioned photopolymerization initiators and chain-transfer agents may be used. When the polymerization initiator in prepolymerization is not deactivated and remains in the prepolymer composition, addition of the polymerization initiator for main polymerization may be omitted.

[0094] (Oligomer)

The pressure sensitive adhesive composition may contain oligomers for the purpose of, for example, adjusting the adhesive strength and the viscidity of the pressure sensitive adhesive sheet. As the oligomer, one having a weight average molecular weight 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.

[0095] 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 polymer chain.

[0096] The glass transition temperature of the acryl-based oligomer is preferably 20°C or higher, more preferably 30°C or higher, further preferably 40°C or higher. When a base polymer which has a low glass transition temperature (Tg) and in which a crosslinked structure is introduced by a urethane-based segment, and an acryl-based oligomer having a high glass transition temperature (Tg) 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.

[0097] 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.

[0098] 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.

[0099] 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 tend to be improved.

[0100] 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.

[0101] When the pressure sensitive adhesive composition contains an oligomer component such as an acryl-based oligomer, the content of the oligomer component is preferably 0.5 to 20 parts by weight, more preferably 1 to 15 parts by weight, further preferably 2 to 10 parts by weight based on 100 parts by weight of the base polymer. When the content of the oligomer in the pressure sensitive adhesive composition is within the above-mentioned range, adhesiveness at a high temperature and the retaining force at a high temperature tend to be improved.

[0102] (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 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.

[0103] (Crosslinker)

The base polymer may have a crosslinked structure formed by other than that of the above-mentioned polyfunctional compound as necessary. The crosslinked structure can be

introduced in the base polymer by adding a crosslinker into the pressure sensitive adhesive composition. The crosslinker can form a crosslinked structure by reacting with a functional group, such as a hydroxyl group and a carboxy group introduced into 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.

[0104] When the amount of the crosslinked structure introduced by components other than the urethane-based segment is increased, the viscidity may be reduced, leading to deterioration of impact resistance. Thus, the amount of the crosslinker is preferably 3 parts by weight or less, more preferably 2 parts by weight or less, further preferably 1 part by weight or less based on 100 parts by weight of the base polymer.

[0105] (Other additives)

In addition to the components exemplified above, additives such as a tackifier, a 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.

[0106] <Application and Main Polymerization of Pressure Sensitive Adhesive Composition>

The pressure sensitive adhesive composition is applied in the form of a layer onto a substrate, and irradiated with an active ray to perform photocuring. At the time of performing photocuring, it is preferable that a cover sheet is disposed over the surface of the coating layer, and the pressure sensitive adhesive composition is irradiated with an active ray while being held between two sheets, so that hindrance of polymerization by oxygen is prevented.

[0107] For each of the substrate and cover sheet to be used for formation of the pressure sensitive adhesive sheet, any suitable material is used. Each of the substrate and the cover sheet may be a release film having a release layer on a contact surface with the pressure sensitive adhesive sheet.

[0108] 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,

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. 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.

[0109] For applying the pressure sensitive adhesive composition on the substrate, various kinds of coating methods such as roll coating, kiss roll coating, gravure coating, 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.

[0110] The pressure sensitive adhesive composition applied in the form of a layer onto the substrate is irradiated with an active ray to perform main polymerization. In main polymerization, unreacted monomer components in the prepolymer composition react with the urethane (meth)acrylate to obtain a base polymer in which a crosslinked structure is introduced into an acryl-based polymer chain by a urethane-based segment. A semi-cured pressure sensitive adhesive sheet is obtained by adjusting the polymerization ratio in main polymerization so that a part of the polymerizable compound remains in an unreacted state.

[0111] The active ray may be selected according to the type of a polymerizable component such as a monomer or urethane (meth)acrylate, the type of a photopolymerization initiator or the like, and in general, an ultraviolet ray and/or visible light having a short wavelength are used. The accumulated amount of irradiation light is preferably about 100 to 5000 mJ/cm^2. The light source for photoirradiation is not particularly limited as long as it can emit light in a wavelength range over which the photopolymerization initiator contained in the pressure sensitive adhesive composition is sensitive to light, and a LED light source, a high-pressure mercury lamp, an ultra-high mercury lamp, a metal halide lamp, a xenon lamp or the like is preferably used. The polymerization ratio can be adjusted to fall within a predetermined range by stopping photoirradiation after reaching a predetermined polymerization ratio. As described above, the polymerization ratio of the semi-cured pressure sensitive adhesive is preferably 90 to 98%.

[0112] Release films 1 and 2 are bonded, respectively, to surfaces of the semi-cured 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 release films used as a substrate and a cover sheet during 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.

[0113] 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.

[0114] [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.

[0115] 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 an 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.

[0116] 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.

[0117] 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.

[0118] The pressure sensitive adhesive sheet of the present invention has a shear storage elastic modulus of 0.15 MPa or less in a semi-cured state, and therefore easily follows the level difference shape of a printed layer 76 or the like, so that generation of air gaps can be suppressed.

[0119] The semi-cured pressure sensitive adhesive sheet is bonded to an adherend such as a front transparent plate, and photocuring (post-curing) of the pressure sensitive adhesive sheet is then performed. The polymerization ratio is increased by post-curing, and the storage elastic modulus of the pressure sensitive adhesive sheet accordingly increases, so that bonding reliability between the pressure sensitive adhesive sheet 5 and a front transparent member 7 is improved. The polymerization ratio of the post-cured pressure sensitive adhesive sheet is preferably 99% or more.

[0120] When the gap 90 exists between the housing 9 and the front transparent plate 7, 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 post-cured pressure sensitive adhesive sheet has a low glass transition temperature and a large tan δ peak-top value, and is therefore excellent in impact resistance over a wide temperature range, so that peeling by impacts of falling and the like hardly occurs.

[0121] As described above, semi-cured pressure sensitive adhesive sheet containing an unreacted photocurable compound has a low shear storage elastic modulus, and is excellent in level difference absorbency. Thus, the pressure sensitive adhesive sheet is suitably used for bonding an adherend to a surface of an image display panel such as a front transparent plate or touch panel having a printing level difference.

[0122] Although mainly described above is a method in which a front transparent plate having a printing level difference of a printed layer is bonded to a semi-cured pressure sensitive adhesive sheet and then post-curing is performed, a fully cured pressure sensitive adhesive sheet may be bonded to the adherend when a level difference absorbency is not required. For example, the pressure sensitive adhesive composition is applied in the form of a

layer onto a substrate, and main polymerization is then performed to a polymerization ratio of 99% or more to obtain a fully cured pressure sensitive adhesive sheet. Even when a fully cured pressure sensitive adhesive sheet is used, peeling due to stress strain and impacts of falling and the like hardly occurs, so that bonding with excellent reliability can be performed as in the case of using a semi-cured pressure sensitive adhesive sheet and performing post-curing after the bonding.

[0123] [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.

[0124] 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

[0125] 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.

[0126] [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.

[0127] [Example 1]

(Polymerization of Prepolymer)

52.8 parts by weight of butyl acrylate (BA), 10.9 parts by weight of cyclohexyl acrylate (CHA), 9.7 parts by weight of N-vinyl-2-pyrrolidone (NVP), 14.8 parts by weight of 4-hydroxybutyl acrylate (4HBA) and 11.8 parts by weight of isostearyl acrylate (ISTA) as prepolymer forming monomer components, and photopolymerization initiators (0.035 parts by weight of "IRGACURE 184" manufactured by BASF SE and 0.035 parts by weight of "IRGACURE 651" manufactured by BASF SE) were blended, and the mixture was irradiated with an ultraviolet ray to a viscosity of about 20 Pa·s (BH viscometer No. 5 Rotor, 10 rpm, measurement temperature: 30°C), so that the mixture was polymerized to obtain a prepolymer composition (polymerization ratio: about 9%).

[0128] <Preparation of Photocurable Pressure Sensitive Adhesive Composition>

The following materials are added to the prepolymer composition: 7 parts by weight of a terminally acrylic-modified polyether urethane ("UV-3300B" manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.) and 3 parts by weight of a terminally acrylic-modified polyether urethane ("UV-3010B" manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.) as urethane (meth)acrylates; 5 parts by weight of the acrylic oligomer; 0.05 parts by weight of IRGACURE 184 and 0.57 parts by weight of IRGACURE 651 as photopolymerization initiators; 0.1 parts by weight of an α-methylstyrene dimer ("NOFMER MSD" manufactured by NOF CORPORATION) as a chain-transfer agent; and 0.3 parts by weight of "KBM 403" manufactured by Shin-Etsu Chemical Co., Ltd. as a silane coupling agent. The mixture was then heterogeneously mixed to prepare a pressure sensitive adhesive composition.

[0129] (Preparation of Pressure Sensitive Adhesive Sheet)

A 75 μm-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 in a thickness of 150 μm to form a coating layer on the substrate. To the coating layer, a 75 μm-thick PET film ("DIAFOIL MRE75" manufactured by Mitsubishi Chemical Corporation) with one surface subjected to silicone release treatment was bonded as a cover sheet (also serving as lightly peelable film). By a black light, which was position-adjusted so that the irradiation intensity at an irradiation surface just below the lamp was 5 mW/cm^2, the laminate was irradiated with an ultraviolet ray from the cover sheet-side for 130 seconds to be photocured, thereby obtaining a pressure sensitive adhesive sheet having a thickness of 150 μm and a polymerization ratio of 94%.

[0130] [Examples 2 to 7 and Comparative Examples 1 to 10]

The compositions of charged monomers in polymerization of the prepolymer, and the types and added amounts of the polyfunctional compound (urethane acrylate and/or polyfunctional acrylate), acrylic oligomer, photopolymerization initiator and chain-transfer agent added to the pressure sensitive adhesive composition were changed as shown in Tables 1-1 and 1-2. In the same manner as in Example 1 except for the above, the photocurable pressure sensitive adhesive composition was prepared, applied onto the substrate, and photocured to obtain a pressure sensitive adhesive sheet. In Example 4 and Comparative Examples 4 and 5, a pressure sensitive adhesive composition identical to that in Example 3 was used, and the ultraviolet ray irradiation time was changed to obtain a pressure sensitive adhesive sheet having a polymerization ratio as shown in Table 1-1.

[0131] [Evaluation]

<Weight average molecular weight>

The weight average molecular weights (Mw) of the acrylic oligomer and urethane (meth)acrylate 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.

(Measurement conditions)

Column: G7000HXL + GMHXL + GMHXL manufactured by TOSOH CORPORATION

Column size: each 7.8 mmφ × 30 cm (total column length: 90 cm)

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

Injection amount: 100 μL

Eluent: tetrahydrofuran

Detector: differential refractometer (RI)

Standard sample: polystyrene

[0132] <Storage elastic modulus, glass transition temperature and tan δ 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.

(Measurement Conditions)

Deformation mode: torsion

Measurement Frequency: 1 Hz

Temperature elevation rate: 5°C/minute

Shape: parallel plate (7.9 mmφ)

[0133] The shear storage elastic modulus was determined by reading a storage elastic modulus G' at each temperature from the measurement result. The temperature at which the loss tangent (tan δ) was maximum (peak-top temperature) was defined as a glass transition temperature of the pressure sensitive adhesive sheet. In addition, the value of tan δ at the glass transition temperature (peak-top value) was read.

[0134] <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. 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.

[0135] <Haze>

Using a test piece with the pressure sensitive adhesive sheet bonded to a 800 μm-thick non-alkali glass (total light transmittance: 92%; haze: 0.4%), the haze was measured with a haze meter (manufactured by MURAKAMI COLOR RESEARCH LABORATORY CO., Ltd.; device name "HM-150"). A value obtained by subtracting the haze of the non-alkali glass (0.4%) from the measured value was defined as the haze of the pressure sensitive adhesive sheet.

[0136] <Level difference absorbency>

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.

[0137] <Peelability from Release Film>

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 a 500 μm-thick glass film (100 mm × 50 mm) was bonded to the pressure sensitive adhesive sheet by a roll laminator (inter-roll pressure: 0.2 MPa and feeding speed: 100 mm/minute). A pickup tape was bonded to the end portion of the heavily peelable film temporarily attached to the pressure sensitive adhesive sheet, and peeling was performed at a peeling angle of 90°. A sample delaminated at an interface between the pressure sensitive adhesive sheet and the heavily peelable film was rated "OK", and a sample delaminated at an interface between the glass plate and the heavily peelable film was rated "NG".

[0138] <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 by a metal halide lamp (300 mW/cm^2) from the glass plate side having a black ink-printed layer, so that the sample was cured to increase the polymerization ratio to 99%.

[0139] 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".

[0140] <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 5 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.

[0141] 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 "NG".

[0142] <Physical Properties of Cured Pressure Sensitive Adhesive Sheet>

In preparation of the pressure sensitive adhesive sheet in each of examples and comparative examples, the ultraviolet ray irradiation time was changed to prepare a pressure sensitive adhesive sheet having a polymerization ratio of 99%, and the viscoelasticity (storage elastic modulus, glass transition temperature and tan δ peak), the haze and the adhesive strength were measured in the same manner as described above. In Example 4 and Comparative Examples 4 and 5, the physical properties of the cured pressure sensitive adhesive sheet were not measured because the composition of the pressure sensitive adhesive was identical to that in Example 6.

[0143] <Evaluation Results>

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

<Acryl-based Monomer>

BA: butyl acrylate

2HEA: 2-ethylhexyl acrylate

CHA: cyclohexyl acrylate

NVP : N-vinyl-2-pyrrolidone

4HBA : 4-hydroxybutyl acrylate

2HEA : 2-hydroxyethyl acrylate

ISTA: isostearyl acrylate

[0144] <Urethane Acrylate>

UV-3300B: "UV-3300B" manufactured by The Nippon Synthetic Chemical Industry Co., Ltd. (polyether urethane diacrylate having a weight average molecular weight of about 12000 and a glass transition temperature of -30°C)

3400: polyether urethane diacrylate having a weight average molecular weight of about 3400

UV-4200: "UA-4200" manufactured by Shin-Nakamura Chemical Co., Ltd. (polyether urethane diacrylate having a weight average molecular weight of about 1000)

UN-350: "ART RESIN UN-350" manufactured by Negami Chemical Industrial Co., Ltd. (polyester urethane diacrylate having a weight average molecular weight of about 12500 and a glass transition temperature of -57°C)

UV-3000B: "UV-3000B" manufactured by The Nippon Synthetic Chemical Industry Co., Ltd. (polyester urethane diacrylate having a weight average molecular weight of about 18000 and a glass transition temperature of -39°C)

UV-3010B: "UV-3010B" manufactured by The Nippon Synthetic Chemical Industry Co., Ltd. (polyester urethane diacrylate having a weight average molecular weight of about 11000)

Urethane monoacrylate: polyether urethane monoacrylate having a weight average molecular weight of about 1300)

<Polyfunctional Acrylate>

HDDA: hexanediol diacrylate

<Photopolymerization Initiator>

Irg651: IRGACURE 651 (2,2-dimethoxy-1,2-diphenylethane-1-one)

Irg184: IRGACURE 184 (1-hydroxy-cyclohexyl-phenyl-ketone)

[0145] Table 1-1

			Example 1	Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3	Example 3	Example 4	Comparative Example 4	Comparative Example 5	Example 5
Composition	prepolymer composition	BA	52.8	52.8	52.8	52.8	52.8	60.5	60.5	60.5	60.5	60.5
		2EHA	-	-	-	-	-	-	-	-	-	-
		CHA	10.9	10.9	10.9	10.9	10.9	12.4	12.4	12.4	12.4	12.4
		NVP	9.7	9.7	9.7	9.7	9.7	10.2	10.2	10.2	10.2	10.2
		4HBA	14.8	14.8	14.8	14.8	14.8	16.9	16.9	16.9	16.9	16.9
		2HEA	-	-	-	-	-	-	-	-	-	-
		ISTA	11.8	11.8	11.8	11.8	11.8	-	-	-	-	-
	urethane diacrylate	UV-3300B	7	10	-	15	-	5	5	5	5	7
		3400	-	-	10	-	-	-	-	-	-	-
		UA-4200	-	-	-	-	-	-	-	-	-	-
		UN-350	-	-	-	-	-	5	5	5	5	-
		UV-3000B	-	-	-	-	-	-	-	-	-	-
		UV-3010B	3	10	-	15	-	-	-	-	-	3
	urethane monoacrylate		-	-	-	-	5	-	-	-	-	-
	polyfunctional acrylate	HDDA	-	0.2	-	0.2	-	-	-	-	-	-
	acrylic oligomer		5	5	5	5	5	5	5	5	5	5
	photo-polymerization initiator	Irg651	0.57	0.57	0.55	0.57	0.55	0.55	0.55	0.55	0.55	0.55
		Irg184	0.07	0.07	0.05	0.07	0.05	0.05	0.05	0.05	0.05	0.05
	chain-transfer agent	NOFMER MSD	0.1	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	silane coupling agent	KBM-403	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

[0146] Table 1-2

			Example 6	Example 7	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10
Composition	prepolymer composition	BA	68.7	68.7	57.0	54.0	—	—	—
		2EHA	—	—	—	—	56.0	56.0	52.0
		CHA	—	—	12.0	11.0	—	—	—
		NVP	16.9	16.9	—	15.0	13.0	13.0	29.0
		4HBA	14.4	14.4	23.0	20.0	20.0	20.0	8.0
		2HEA	—	—	8.0	—	11.0	11.0	11.0
		ISTA	—	—	—	—	—	—	—
	urethane diacrylate	UV-3300B	—	—	—	—	—	—	—
		3400	—	—	—	—	—	—	—
		UA-4200	—	—	—	—	—	15	—
		UN-350	3.5	5	—	—	—	—	—
		UV-3000B	—	—	—	—	—	—	—
		UV-3010B	—	—	—	—	—	—	—
	urethane monoacrylate			—	—	—	—	—	—
	polyfunctional acrylate	HDDA	—	—	0.12	0.12	2	0.12	0.3
	acrylic oligomer		5	5	—	—	5	5	—
	photo-polymerization initiator	Irg651	0.55	0.55	0.05	0.05	0.55	0.55	0.55
		Irg184	0.05	0.05	0.05	0.05	0.05	0.05	0.05
	chain-transfer agent	NOFMER MSD	0.2	0.2	—	—	0.2	0.2	0.2
	silane coupling agent	KBM-403	0.3	0.3	0.3	0.3	0.3	0.3	0.3

[0147] Table 2-1

		Example 1	Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3	Example 3	Example 4	Comparative Example 4	Comparative Example 5	Example 5
Evaluation before post-curing	polymerization ratio	94	94	95	94	95	95	92	88	99	95
	Tg (℃)	-10	-10	-9	-11	-10	-9	-11	-12	-5	-10
	tanδ	2.0	1.9	1.8	1.8	1.8	2.0	2.0	2.1	2.0	2.0
	$G'_{25℃}$ (MPa)	0.15	0.14	0.15	0.18	0.11	0.15	0.12	0.08	0.20	0.15
	$G'_{80℃}$ (MPa)	0.15	0.12	0.14	0.14	0.06	0.11	0.09	0.07	0.15	0.13
	adhesive strength at 25℃ (N/10mm)	7	7	2	3	12	11	6	1	10	8
	adhesive strength at 65℃ (N/10mm)	3	3	0.6	1	5	4	2	0.5	2	3
	haze (%)	0.4	0.4	0.4	2.0	0.3	0.4	0.4	0.4	0.4	0.4
	level difference absorbency	OK	OK	OK	NG	OK	OK	OK	OK	NG	OK
	adhesive deposit	OK	OK	OK	OK	OK	OK	OK	NG	OK	OK
Evaluation after post-curing	polymerization ratio	99	99	99	99	99	99				99
	Tg (℃)	-5	-6	-5	-7	-5	-5				-5
	tanδ	2.0	1.9	1.8	1.8	1.8	2.0				2.0
	$G'_{25℃}$ (MPa)	0.23	0.22	0.19	0.25	0.14	0.20				0.21
	$G'_{80℃}$ (MPa)	0.18	0.15	0.16	0.18	0.08	0.15				0.14
	adhesive strength at 25℃ (N/10mm)	4	5	1	3	13	10				6
	adhesive strength at 65℃ (N/10mm)	2	2	0.3	1	8	2				2
	haze (%)	0.4	0.4	0.4	2.0	0.3	0.4				0.4
	Interlayer adhesiveness	OK	OK	NG	OK	NG	OK				OK
	falling impact durability	OK	OK	NG	OK	OK	OK				OK

[0148] Table 2-2

		Example 6	Example 7	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10
Evaluation before post-curing	polymerization ratio	97	95	95	95	95	94	95
	Tg (℃)	-7	-9	-23	-4	-9	-9	-5
	tanδ	1.8	1.9	2.4	2.0	1.5	1.6	1.6
	$G'_{25℃}$ (MPa)	0.15	0.14	0.09	0.14	0.15	0.17	0.13
	$G'_{80℃}$ (MPa)	0.09	0.09	0.07	0.11	0.13	0.15	0.09
	adhesive strength at 25℃ (N/10mm)	11	10	6	8	1	1	7
	adhesive strength at 65℃ (N/10mm)	3	4	1	2	0.3	0.4	2
	haze (%)	0.4	0.4	0.2	0.2	0.4	0.4	0.5
	level difference absorbency	OK	OK	OK	OK	OK	NG	OK
	adhesive deposit	OK	OK	OK	OK	NG	NG	OK
Evaluation after post-curing	polymerization ratio	99	99	99	99	99	99	99
	Tg (℃)	-5	-5	-20	1	-6	-4	-1
	tanδ	1.8	1.8	2.4	2.1	1.2	1.6	1.6
	$G'_{25℃}$ (MPa)	0.19	0.21	0.12	0.21	0.21	0.24	0.17
	$G'_{80℃}$ (MPa)	0.11	0.12	0.10	0.14	0.18	0.20	0.13
	adhesive strength at 25℃ (N/10mm)	10	8	6	5	0.4	0.3	6
	adhesive strength at 65℃ (N/10mm)	3	3	2	2	0.1	0.1	2
	haze (%)	0.4	0.4	0.2	0.2	0.4	0.6	0.5
	Interlayer adhesiveness	OK	OK	NG	OK	NG	NG	OK
	falling impact durability	OK	OK	OK	NG	NG	NG	NG

[0149] In Examples 1 and 2 using a pressure sensitive adhesive composition obtained by adding a urethane diacrylate etc. to a prepolymer composition obtained by prepolymerization of an acryl-based monomer having butyl acrylate as a main monomer, the semi-cured pressure sensitive adhesive sheet was excellent in level difference absorbency, had no adhesive deposit, and had favorable interlayer adhesiveness and falling impact durability in evaluation using the fully cured pressure sensitive adhesive sheet.

[0150] In Comparative Example 1 using a low-molecular-weight urethane diacrylate, the pressure sensitive adhesive sheet had low adhesive strength to an adherend either before or after photocuring (post-curing), and was poor in interlayer adhesiveness and falling impact durability. In Comparative Example 2 where the added amount of the urethane diacrylate was increased, the pressure sensitive adhesive sheet had a high haze, and hence reduced transparency. In addition, the pressure sensitive adhesive sheet before post-curing had a high storage elastic modulus $G'_{25°C}$, and was therefore poor in level difference absorbency. In Comparative Example 3 using a urethane monoacrylate, the pressure sensitive adhesive sheet after post-curing had a low shear storage elastic modulus, and was poor in adhesive durability.

[0151] In Examples 3, 5, 6 and 7 where the composition of the acryl-based monomer in the prepolymer forming composition was changed, a favorable adhesive property was exhibited as in Examples 1 and 2.

[0152] In Example 4 where a pressure sensitive adhesive composition identical to that in Example 3 was used, and the polymerization ratio was reduced to 92%, the glass transition temperature of the semi-cured pressure sensitive adhesive sheet was reduced as compared to Example 3, and accordingly, the storage elastic moduli $G'_{25°C}$ and $G'_{80°C}$ were reduced. In Comparative Example 4 where the polymerization ratio was further reduced, the glass transition temperature of the semi-cured pressure sensitive adhesive sheet and the storage elastic moduli $G'_{25°C}$ and $G'_{80°C}$ were further reduced, and adhesive strength was insufficient. On the other hand, in Comparative Example 5 where the polymerization ratio was 99%, the level difference absorbency was insufficient due to an increase in storage elastic modulus $G'_{25°C}$.

[0153] In Comparative Example 6 where a urethane-based material was not used, and the glass transition temperature was reduced by adjustment of the composition of the acryl-based

monomer, the photocured pressure sensitive adhesive sheet had low storage elastic moduli $G'_{25°C}$ and $G'_{80°C}$, and was poor in bonding reliability. In Comparative Example 7 where cohesiveness was enhanced by increasing the ratio of polar monomers (NVB and 4HBA) in the acryl-based monomer component, the pressure sensitive adhesive sheet had favorable adhesiveness, but had a high glass transition temperature, and hence poor in impact resistance. Comparative Example 10 showed the same tendency.

[0154] In Comparative Example 8 where the ratio of the polyfunctional acrylate in the pressure sensitive adhesive composition was increased, the pressure sensitive adhesive sheet had a small tan δ peak-top value and low viscidity, and therefore had insufficient adhesive strength, and poor impact resistance. Comparative Example 9 where a crosslinked structure was introduced by a low-molecular-weight urethane diacrylate showed the same tendency. In these Comparative Examples, one of the reasons why the loss tangent (tan δ) is smaller as compared to Examples 1 to 7 etc. where the main monomer in the acryl-based polymer chain is an acrylic acid C_4-alkyl ester (butyl acrylate) may be that the main monomer in the acryl-based polymer chain is an acrylic acid C_8-alkyl ester (2-hydroxyethyl acrylate).

[0155] These results show that a pressure sensitive adhesive sheet containing a base polymer in which a crosslinked structure is introduced into an acryl-based polymer chain using a urethane diacrylate having a specific molecular weight exhibits a high shear storage elastic modulus even at a low glass transition temperature, has a large loss tangent (tan δ), and is therefore able to have both adhesive durability and impact resistance.

DESCRIPTION OF REFERENCE CHARACTERS

[0156]

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
100	image display device

CLAIMS

1. A photocurable pressure sensitive adhesive sheet in which a pressure sensitive adhesive composition containing a base polymer and a photocurable compound is formed in a layer shape,

the pressure sensitive adhesive sheet having a haze of 1% or less,

the pressure sensitive adhesive sheet having an adhesive strength of 1.5 N/10 mm or more to glass,

the pressure sensitive adhesive sheet having a shear storage elastic modulus of 0.15 MPa or less at a temperature of 25°C,

pressure sensitive adhesive sheet having a glass transition temperature of -3°C or lower, and a shear storage elastic modulus of 0.16 MPa or more at 25°C when the pressure sensitive adhesive composition is cured to a polymerization ratio of 99%.

2. The pressure sensitive adhesive sheet according to claim 1, wherein a polymerization ratio of the pressure sensitive adhesive composition is 90 to 98%.

3. The pressure sensitive adhesive sheet according to claim 1 or 2, having a glass transition temperature of -5°C or lower.

4. The pressure sensitive adhesive sheet according to any one of claims 1 to 3, having a loss tangent peak-top value of 1.6 or more.

5. The pressure sensitive adhesive sheet according to any one of claims 1 to 4, wherein the loss tangent peak-top value is 1.5 or more when the pressure sensitive adhesive composition is cured to a polymerization ratio of 99%.

6. The pressure sensitive adhesive sheet according to any one of claims 1 to 5, wherein the base polymer includes an acryl-based polymer chain crosslinked with a urethane-based segment, and a contain of the urethane-based segment is 3 to 30 parts by weight based on 100 parts by weight of the acryl-based polymer chain.

7. The pressure sensitive adhesive sheet according to claim 6, wherein an average molecular weight of the urethane-based segment is 4000 to 50000.

8. The pressure sensitive adhesive sheet according to claim 6 or 7, wherein in the base polymer, a monomer component for forming the acryl-based polymer chain and a urethane (meth)acrylate having a (meth)acryloyl group at the terminal are copolymerized to introduce a crosslinked structure into the acryl-based polymer chain by the urethane-based segment.

9. A method for manufacturing an image display device in which a transparent member having a level difference portion disposed on a viewing-side surface,

the method comprising

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

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

10. A method for manufacturing the pressure sensitive adhesive sheet according to any one of claims 1 to 8,

the method comprising:

applying a composition containing an acryl-based monomer and/or a partially polymerized product thereof and a urethane (meth)acrylate onto a substrate in a layer shape; and

thereafter irradiating the composition with an active ray to photocure the composition.

11. The method according to claim 10, wherein the composition contains 3 to 30 parts by weight of the urethane (meth)acrylate based on 100 parts by weight of the total of the acryl-based monomer and partially polymerized product thereof.

12. The method according to claim 10 or 11, wherein an average molecular weight of the

urethane (meth)acrylate is 4000 to 50000.

13. The method according to any one of claims 10 to 12, wherein a glass transition temperature of the urethane (meth)acrylate is 0°C or lower.