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(54) Title: ADHESIVE COMPOSITION

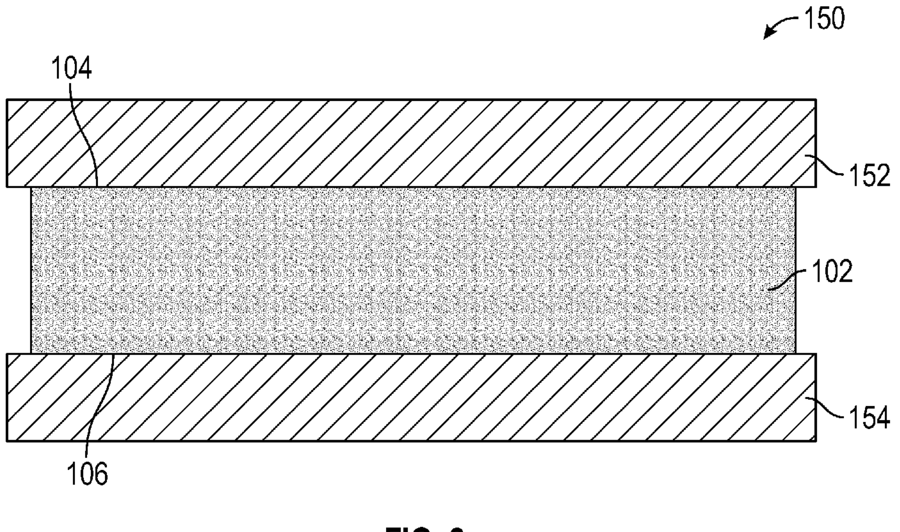

FIG. 2

(57) **Abstract:** Provided is an adhesive that includes a crosslinked network of polyvinyl acetal and acrylic copolymer obtained by reacting a functionalized polyvinyl acetal and acrylic monomers. The functionalized polyvinyl acetal is present in a weight fraction of from 1 percent to 20 percent of the overall weight of the adhesive and is comprised of a polyvinyl acetal backbone with pendent functional groups reactive with the acrylic monomers. The acrylic copolymer is present in a weight fraction of from 60 percent to 99 percent of the overall weight of the adhesive. Advantageously, the adhesive can provide both deformation resistance to prevent mechanical read-through of components from the backside of a polarizer-less display and a low coefficient of restitution for impact damping performance.

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ADHESIVE COMPOSITION

Field of the Invention

Provided are adhesive compositions and articles. The adhesive compositions and articles can be useful for bonding optical films in electronic display applications.

Background

Optically clear adhesives (OCAs) have diverse applications in consumer, industrial and automotive display technologies. These adhesives have become preferred bonding solutions for a number of reasons, including high adhesion and cohesion, protection, and enhanced performance of touchscreens as devices transitioned from resistive to capacitive touch technology. Desirable properties of OCAs can include optical clarity and high interfacial adhesion over a wide range of temperatures.

Conventional organic light-emitting diode (OLED) displays have required use of a circular polarizer to prevent total internal reflectance from disrupting display quality. Recent advancements in OLED display technology have enabled the reduction of total internal reflectance without the use of a circular polarizer, thus reducing or eliminating the need to include the polarizer in the OLED display assembly. Elimination of the polarizer in an OLED display can provide various technical benefits, including an overall reduction in device thickness as well as increases in efficiency. Improvements in efficiency, in turn, can improve display brightness, extend battery life, or both.

Summary

New technical and material challenges may arise upon eliminating the polarizer from the display. One of these challenges includes mechanical read-through of the components from the back of the display, such as the flexible printed circuit, the fingerprint sensor and texture from the cover panel. Where significant, these topological features can be visible to the viewer and are thus undesirable.

A technical need remains for an adhesive, and particularly an OCA, which is sufficiently stiff to resist deformation and prevent mechanical read-through of these backside components. This adhesive, however, must also be able to protect the display from a high impact event. Impact performance can be characterized by dropping a steel ball onto the display under precisely controlled conditions and checking for damage or loss of functionality. Moreover, an adhesive that provides good impact performance will also have a relatively low coefficient of restitution (COR). COR is a fundamental property of kinetic energy absorption for a given material and can be correlated to ball drop performance.

Provided herein are adhesives that achieve the beneficial properties of both deformation resistance to prevent mechanical read-through of components from the backside of a polarizer-less display and a low COR for impact damping performance. This is surprising because these performance attributes are typically inversely related, where an improvement for one often comes at a loss in performance for the other. Here, it was discovered that single layer OCAs that contain a blend of acrylic polymer and a polyvinyl acetal polymer such as polyvinyl butyral (PVB), or multilayered OCAs that contain at least one layer which is a blend of polyvinyl acetal polymer and acrylate, can enable both performance attributes to be achieved simultaneously.

In a first aspect, an adhesive is provided. The adhesive comprises: a crosslinked network of polyvinyl acetal and acrylic copolymer obtained by reacting a functionalized polyvinyl acetal and acrylic monomers, the functionalized polyvinyl acetal comprised of a polyvinyl acetal backbone with pendent acrylate groups that are reactive with the acrylic monomers, wherein the functionalized polyvinyl acetal is present in a weight fraction of from 1 percent to 20 percent of the overall weight of the adhesive, and further wherein the acrylic copolymer is present in a weight fraction of from 60 percent to 99 percent of the overall weight of the adhesive.

In a second aspect, a tape adhesive is provided that comprises a layer of the adhesive.

In a third aspect, a method of making an adhesive is provided, comprising: functionalizing polyvinyl acetal by reacting polyvinyl acetal with isocyanatoethyl (meth)acrylate and/or allyl isocyanate; and polymerizing acrylic monomers in the presence of the functionalized polyvinyl acetal to form a crosslinked network of polyvinyl acetal and acrylic copolymer.

Brief Description of the Drawings

FIGS. 1-3 are elevational side views of tape adhesives according to various exemplary embodiments.

Repeated use of reference characters in the specification and drawings is intended to represent the same or analogous features or elements of the disclosure. It should be understood that numerous other modifications and embodiments can be devised by those skilled in the art, which fall within the scope and spirit of the principles of the disclosure. The figures may not be drawn to scale.

DEFINITIONS

As used herein:

"alkyl" refers to a monovalent group that is a radical of an alkane and includes straight-chain, branched, cyclic, and bicyclic alkyl groups, and combinations thereof, including both unsubstituted and substituted alkyl groups. Unless otherwise indicated, the alkyl groups typically contain from 1 to 30 carbon atoms. In some embodiments, the alkyl groups contain 1 to 20 carbon atoms, 1 to 10 carbon atoms, 1 to 6 carbon atoms, 1 to 4 carbon atoms, or 1 to 3 carbon atoms. Cyclic groups can be monocyclic or polycyclic and typically have from 3 to 10 ring carbon atoms. Examples of "alkyl" groups include methyl, ethyl, n-propyl, n-butyl, n-pentyl, isobutyl, t-butyl, isopropyl, n-octyl, n-heptyl, ethylhexyl, cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, and norbornyl.

"allyl" refers a functional group having the formula CH_2=CH-CH_2-.

"cure" refers to the joining of polymer chains together by covalent chemical bonds, usually via crosslinking molecules or groups, to form a network polymer. Therefore, in this disclosure the terms "cured" and "crosslinked" may be used interchangeably. A cured or crosslinked polymer is generally characterized by insolubility but may be swellable in the presence of an appropriate solvent.

"curable" refers to a composition that can be cured.

"glass transition temperature" (or "T_g") refers to a temperature at which an amorphous polymer changes from a hard/glassy state to a more pliable rubbery state, or vice versa, and can be determined by performing a Dynamic Mechanical Analysis (or "DMA") temperature sweep at a given frequency. From this technique, the T_g can be defined as the temperature at which the tan(δ) peaks.

"(meth)acrylate" refers to a functional group that is either an acrylate group of the formula CH_2=CH-C(O)O- or a methacrylate group of the formula CH_2=C(CH_3)-C(O)O-.

"oligomer" refers to a molecule that comprises at least two repeat units and that has a molecular weight less than its entanglement molecular weight; such a molecule, unlike a polymer, exhibits a significant change in properties upon the removal or addition of a single repeat unit.

Detailed Description

As used herein, the terms "preferred" and "preferably" refer to embodiments described herein that can afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful and is not intended to exclude other embodiments from the scope of the invention.

As used herein and in the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a" or "the" component may include one or more of the components and equivalents thereof known to those skilled in the art. Further, the term "and/or" means one or all of the listed elements or a combination of any two or more of the listed elements.

It is noted that the term “comprises,” and variations thereof do not have a limiting meaning where these terms appear in the accompanying description. Moreover, “a,” “an,” “the,” “at least one,” and “one or more” are used interchangeably herein. Relative terms such as left, right, forward, rearward, top, bottom, side, upper, lower, horizontal, vertical, and the like may be used herein and, if so, are from the perspective observed in the particular drawing. These terms are used only to simplify the description, however, and not to limit the scope of the invention in any way.

Reference throughout this specification to “one embodiment,” “certain embodiments,” “one or more embodiments” or “an embodiment” means that a particular feature, structure, material, or characteristic described relating to the embodiment is included in at least one embodiment of the invention. Thus, the appearances of the phrases such as “in one or more embodiments,” “in certain embodiments,” “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily referring to the same embodiment of the invention.

The provided adhesives are generally based on a crosslinked network of polyvinyl acetal and acrylic copolymer obtained by reacting a functionalized polyvinyl acetal and an acrylic monomer. In some embodiments, the functionalized polyvinyl acetal can be reacted with a mixture of two or more different acrylic monomers.

Polyvinyl acetal is a useful class of polymers derived from the condensation reaction between polyvinyl alcohol and an aldehyde, typically formaldehyde. The resulting material exhibits excellent chemical resistance, good mechanical properties, and exceptional thermal stability, making it applicable for different technical purposes.

Polyvinyl acetal is known for use in production of various engineering plastics. Its excellent thermal stability allows it to withstand high temperatures without significant degradation, making it suitable for applications where heat resistance is essential. Additionally, it exhibits good mechanical strength and dimensional stability, making it valuable in the production of components and parts for various industries, including automotive, electrical, and consumer goods.

The polyvinyl acetal can be prepared by saponifying polyvinyl acetate to prepare polyvinyl alcohol and then acetalizing the polyvinyl alcohol with an aldehyde in the presence of a catalyst. The degree of saponification of the polyvinyl alcohol is not particularly limited, and is commonly within a range of 70 to 99.9 mol%. The degree of saponification is preferably 70 to 99.9 mol%, more preferably 80 to 99.8 mol%.

The average degree of polymerization of the polyvinyl alcohol is also not particularly limited. Preferably, the polyvinyl alcohol used has a high average degree of polymerization for improved strength and toughness. The lower limit of the average degree of polymerization of the polyvinyl alcohol is preferably 200 repeat units and the upper limit thereof is preferably 4,000 repeat units. With the average degree of polymerization of the polyvinyl alcohol falling within this range, the reaction upon acetalization of the polyvinyl alcohol is facilitated and the resulting polyvinyl acetal can exhibit high mechanical strength. The lower limit of the average degree of polymerization of the polyvinyl alcohol is more preferably 300 repeat units and the upper limit thereof is more preferably 3,000 repeat units. The lower limit is more preferably 400 repeat units with the upper limit being preferably 2,000 repeat units.

The average degree of polymerization of the polyvinyl alcohol as used herein refers to a viscosity average degree of polymerization obtained based on JIS K6726:1994. In the case where the polyvinyl alcohol resin used is a mixture of two or more types of polyvinyl alcohol resins, the average degree of polymerization of the polyvinyl alcohol refers to an apparent viscosity average degree of polymerization of the whole polyvinyl alcohol resin mixture.

For acetalization of the polyvinyl alcohol with an aldehyde in the presence of a catalyst, a solution containing the polyvinyl alcohol may be used. An exemplary solvent used for the solution containing the polyvinyl alcohol is water.

The aldehyde is not particularly limited. Commonly, a C1-C10 aldehyde is favorably used. The C1-C10 aldehyde is not particularly limited, and may be either a linear aldehyde or a branched aldehyde. Examples thereof can include n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, 2-ethylbutyraldehyde, n-hexylaldehyde, n-octylaldehyde, n-nonylaldehyde, n-decylaldehyde, formaldehyde, acetaldehyde, and benzaldehyde. Aldehydes may be used alone or in combination of two or more thereof. Preferred among these are n-butyraldehyde, n-hexylaldehyde, and n-valeraldehyde, and more preferred is n-butyraldehyde.

In some embodiments, the polyvinyl acetal is comprised of polyvinyl butyral (where the aldehyde is n-butyraldehyde, the polyvinyl acetal is referred to as polyvinyl butyral). The use of the polyvinyl butyral allows appropriate adhesion force to glass, leading to better light resistance and weather resistance. Two or more types of polyvinyl acetals may be optionally used in combination.

In some embodiments, the polyvinyl acetal can be functionalized by reacting the polyvinyl acetal with isocyanatoethyl (meth)acrylate or allyl isocyanate in the presence of a suitable catalyst and an acrylic monomer. This reaction provides a polyvinyl acetal backbone with pendent (meth)acrylate or allyl groups. These pendent functional groups, in turn, are copolymerizable with any number of other acrylic monomers. The isocyanatoethyl (meth)acrylate or allyl isocyanate can be present in any wt% based on the total weight of the polyvinyl acetal as appropriate to create the desired degree of functionality. For example, the isocyanatoethyl (meth)acrylate or allyl isocyanate can be present in an amount of from 0.1 percent to 15 percent, from 0.3 percent to 13 percent, from 0.5 percent to 10 percent, or in some embodiments, less than, equal to, or greater than 0.1 percent, 0.3, 0.5, 1, 3, 6, 10, 13, or 15 percent by weight, relative to that of the polyvinyl acetal.

If the degree of reactive functionalization of the polyvinyl acetal is too great, the adhesive may become highly crosslinked leading to a loss of adhesion performance. Contrarily, adhesive compositions in which the polyvinyl acetal is too low may decrease compatibility between the acrylic and PVA polymers which may create unwanted haze. Additional hydroxyl reactive compounds that also contain co-polymerizable or crosslinkable functional groups may be used. Pendent crosslinkable functionality of a sufficient degree can enable the functionalized polyvinyl acetal to function as a crosslinking agent to form a crosslinked network even when reacted with acrylic monomers that are monofunctional.

Once functionalized, the polyvinyl acetal can then be reacted with one or more acrylic monomers to form a crosslinked network comprised of the functionalized polyvinyl acetal and acrylic copolymer. The acrylic copolymer is generally a random copolymer, but suitable copolymers can also include acrylic block copolymers and tapered block copolymers.

Useful acrylic monomers include both alkyl and polar monomers. Such polar monomers are inclusive of acid-functional monomers, hydroxy-functional monomers, nitrogen-containing monomers, and combinations thereof. Hydroxy-functional monomers include, for example,. 2-hydroxyethyl (meth)acrylate, and 2-hydroxy-propyl (meth)acrylate, 4-hydroxybutyl(meth)acrylate. Advantageously, polar monomers can help compatibilize the polyvinyl acetal (e.g. butyral) polymer with high glass transition temperature (high-T_g) and low glass transition temperature (low-T_g) alkyl (meth)acrylate monomers to produce an adhesive with relatively lower haze. In some embodiments, these polar monomers can have a glass transition temperature (T_g) greater than 0°C, while the T_g can be less than that of the high-T_g monofunctional alkyl (meth)acrylate monomer. In a preferred embodiment, the adhesive is derived from precursors comprising from 40 wt% to 90 wt% of alkyl (meth)acrylate monomers having a homopolymer T_g of less than 0°C. When characterized using DMA, the adhesive preferably displays at least one glass transition temperature (T_g) less than 10°C.

Acid-functional monomers include, but are not limited to, those selected from ethylenically unsaturated carboxylic acids, ethylenically unsaturated sulfonic acids, ethylenically unsaturated phosphonic acids, and mixtures thereof. Examples of such compounds include those selected from acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, citraconic acid, maleic acid, oleic acid, β-carboxyethyl (meth)acrylate, 2-sulfoethyl methacrylate, styrene sulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, vinylphosphonic acid, and mixtures thereof.

In some embodiments, the (meth)acrylate copolymer is substantially free of polymerized acid-functional monomers. In this context, the term “substantially free” means that the (meth)acrylate polymer contains less than 1 weight percent, less than 0.5 weight percent, less than 0.2 weight percent, or less than 0.1 weight percent of these monomers. In some embodiments, the crosslinkable composition may be substantially free of acid-functional monomers in order to eliminate indium tin oxide ("ITO") and metal trace corrosion that otherwise could damage touch sensors and their integrating circuits or connectors.

Nitrogen-containing monomers include, but are not limited to, N-vinylpyrrolidone; N-vinylcaprolactam; acrylamide; mono- or di-N-alkyl substituted acrylamide such as N, N-dimethylacrylamide; t-butyl acrylamide; dimethylaminoethyl acrylamide; acryloylmorpholine, and N-octyl acrylamide. In some embodiments, the crosslinked network of polyvinyl acetal and acrylic copolymer comprises from 0 percent to 20 percent, 0.5 percent to 10 percent, from 1 percent to 5 percent, or in some embodiments equal to or greater than 0 percent, or less than, equal to, or greater than 0.1, 0.5, 1, 2, 3, 4, 5, 7, 10, 12, 15, or 20 percent polymerized units of nitrogen-containing monomers by weight, relative to the overall weight of the adhesive composition.

Other polar monomers include alkoxy-functional (meth)acrylate monomers. Representative examples 2-(2-ethoxyethoxy)ethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-(methoxyethoxy)ethyl, 2-methoxyethyl methacrylate, and polyethylene glycol mono(meth)acrylates.

In some embodiments, the crosslinked network of polyvinyl acetal and acrylic copolymer includes from 0.5 percent to 45 percent, from 1 percent to 30 percent, or in some embodiments, less than, equal to, or greater than 0.5, 1, 2, 3, 4, 5, 7, 10, 12, 15, 17, 20, 25, 30, 35, 40 and 45 percent polymerized units of alkoxy-functional (meth)acrylate monomers by weight, relative to the overall weight of the crosslinked network. In other embodiments, the crosslinked network comprises polymerized units of less than 20 percent, less than 15 percent, or less than 10 percent of alkoxy-functional (meth)acrylate monomers by weight or is free of polymerized units of alkoxy-functional (meth)acrylate monomers. When the polyvinyl acetal (e.g. butyral) polymer displays a lower crosslinkable functionality, then higher amounts of polar monomer may be necessary to provide a compatibilized mixture. Conversely, when the polyvinyl acetal possesses a relatively higher degree of functionality, then less polar monomer may be needed for compatibilization.

In certain embodiments, the crosslinked network includes polymerized units of one or more polar monomers of 2-hydroxyethyl (meth)acrylate or N,N-dimethyl acrylamide. The adhesive can include polymerized units of one or more of these monomers in an amount of from 5 percent to 55 percent, from 7 percent to 45 percent, from 10 percent to 35 percent, or in some embodiments, less than, equal to, or greater than 5 percent, 7, 10, 15, 20, 25, 30, 35, 40, 45, 50, or 55 percent relative to the overall weight of the adhesive composition.

In some embodiments, the crosslinked network includes polymerized units of one or more low-T_g (meth)acrylate monomers, i.e., a (meth)acrylate monomer that, when reacted to form a homopolymer, has a T_g no greater than 0°C. In some embodiments, the low-T_g monomer has a

homopolymer T_g of from -80°C to -5°C, from -70°C to -10°C, or in some embodiments, less than, equal to, or greater than -80°C, -70, -60, -50, -40, -30,
-20, -10, or 5°C.

The low-T_g monomer can, for example, have the formula:

$$H_2C{=}CR^1C(O)OR^8$$

, wherein R^1 is H or methyl and R^8 is an alkyl with 1 to 22 carbons or a heteroalkyl with 2 to 20 carbons and 1 to 6 heteroatoms selected from oxygen or sulfur. The alkyl or heteroalkyl group can be linear, branched, cyclic, or a combination thereof.

Examples of low-T_g monomers include but are not limited to ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, n-pentyl acrylate, isoamyl acrylate, n-hexyl acrylate, 2-methylbutyl acrylate, 2-ethylhexyl acrylate, 4-methyl-2-pentyl acrylate, n-octyl acrylate, 2-octyl acrylate, isooctyl acrylate, isononyl acrylate, decyl acrylate, isodecyl acrylate, lauryl acrylate, isotridecyl acrylate, octadecyl acrylate, and dodecyl acrylate.

In some embodiments, the crosslinked network comprises polymerized units of at least one low-T_g monomer(s) having an alkyl group with 6 to 24 carbon atoms. In some embodiments, the low-T_g monomer has an alkyl group with 7 or 8 carbon atoms. Exemplary monomers include, but are not limited to, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, 2-octyl (meth)acrylate, isodecyl (meth)acrylate, and lauryl (meth)acrylate. In some embodiments, the monomer is an ester of (meth)acrylic acid with an alcohol derived from a renewable source, such as 2-octyl (meth)acrylate. Other suitable monomers include branched long chain acrylates such as those described in U.S. Patent No. 8,137,807, hereby incorporated by reference. Additional suitable alkyl monomers include secondary alkyl acrylates such as those described in U.S. Patent No. 9,102,774, hereby incorporated by reference.

The adhesive can comprise at least 20, 30, 40, 50, 60, 70 or 80 percent by weight of polymerized units of monofunctional alkyl (meth)acrylate low-T_g monomer (i.e., having a homopolymer T_g of less than 0°C), based on the total weight of the adhesive. The adhesive typically comprises no greater than 60, 70, 80 or 90 percent by weight of polymerized units of monofunctional alkyl (meth)acrylate monomer having a T_g of less than 0°C, based on the total weight of the adhesive composition.

The T_g of the homopolymer of various monomers is known and is reported in various handbooks. The T_g of some illustrative monomers is also reported in International Patent Application No. WO 2016/094277 (Janoski et al.).

The polyvinyl acetal can be present in an amount of from 85.0 wt% to 99.9 wt%, from 87.0 wt% to 99.7 wt%, from 90.0 wt% to 99.5 wt%, or in some embodiments less than, equal to, or greater than 85.0 wt%, 87.0, 90.0, 91.0, 92.0, 94.0, 96.0, 97.0, 98.0, 99.0, 99.5, 99.7 or 99.9 wt% relative to the overall weight of the functionalized polyvinyl acetal.

Relative to the overall weight of the adhesive, the functionalized polyvinyl acetal can represent a weight fraction of from 1 percent to 20 percent, from 2 percent to 15 percent, from 3 percent to 12 percent, or in some embodiments, less than, equal to, or greater than 1 percent, 2, 3, 4, 5, 8, 10, 12, 15 or 20 percent.

The acrylic copolymer can be present in a weight fraction of from 60 percent to 99 percent, from 70 percent to 98 percent, from 80 percent to 97 percent, or in some embodiments, less than, equal to, or greater than 60 percent, 70, 80, 85, 90, 93, 95, 97, 98, or 99 percent, relative to the overall weight of the adhesive.

The functionalized polyvinyl acetal and acrylic monomers can be combined with any number of additional additives, including catalysts, crosslinkers, ultraviolet light absorbers, dyes and pigments.

Often for these blended systems, two or more T_g values (as defined by peak tan delta values observed when performing a DMA temperature sweep at 1 Hz) can be detectable for respective phases or domains within the adhesive. The lowest T_g will typically be associated with the acrylic copolymer phase of the crosslinked network. To achieve a low COR, it is generally preferred to maintain a low T_g in the acrylate phase, typically at least -60°C and up to 10°C, up to 0°C, or up to -10°C.

To provide resistance to deformation, the adhesive should have a relatively high storage modulus at 25°C for an adhesive material, which can be measured by performing a dynamic mechanical analysis (DMA) using a temperature sweep at a frequency of 1 Hz. A storage modulus greater than 200,000 pascals, greater than 400,000 pascals, greater than 600,000 pascals, greater than 800,000 pascals, or even greater than 1 megapascal at 25°C can be preferred. To enable good topographical feature coverage (e.g., inkstep coverage) and/or good compliance and bonding to the substrate, additional heat from a heat-assisted lamination and/or autoclave process (for instance, at temperatures exceeding 60°C, or even exceeding 65°C) can be helpful.

In some embodiments the adhesive is considered optically transparent with low haze (less than 4%, 3%, or 2%).

FIGS. 1-3 show exemplary transfer adhesives incorporating the provided adhesive compositions. A tape adhesive according to one exemplary embodiment is illustrated in FIG. 1 and hereafter denoted by the numeral 100. The tape adhesive 100 is comprised of a primary layer 102 composed of a polyvinyl acetal-based adhesive composition as described herein and having opposed first and second major surfaces 104, 106. Advantageously, the primary layer 102 provides mechanical resistance to deformation while preserving high impact performance.

FIG. 2 shows a tape adhesive assembly 150 representing a bonded assembly. The assembly 150 includes the tape adhesive 100 comprised of the primary layer 102, whose characteristics are described above. The assembly 150 further includes a pair of release substrates 152, 154 disposed on each of the respective opposing major surfaces 104, 106 of the primary layer 102. In some embodiments, the primary layer 102 directly contacts both of the release substrates 152, 154 thereby acting to adhesively couple these release substrates 152, 154 to each other. Useful release substrates are known in the art, and can include for example liners constructed of silicone-coated polyester or silicone-coated paper.

FIG. 3 shows a tape adhesive 200 according to yet another embodiment, bearing similarities to the construction of tape adhesive 100 except a pair of secondary layers 252, 254 are interposed between a primary layer 202 and the release substrates 252, 254, as shown. The secondary layers 210, 210' can function as skin layers made from acrylic OCAs that contain a lower weight fraction of polyvinyl acetal relative to that of the primary layer 202.

In a preferred embodiment, one or both of the secondary layers 210, 210' contain a zero or essentially zero amount of polyvinyl acetal. A potential advantage of this embodiment is the retention of high room temperature tack, which can be beneficial for certain applications. Another potential advantage is the possibility of introducing greater flowability at the surface, which can improve adhesive wetting of the substrate or topological features such as an inkstep, where present. Further advantages can include the possibility of isolating certain functionalities, such as UV blocking, to a particular layer.

Adhesives and adhesive layers described herein can be made using a batch or continuous process. In exemplary embodiments, the adhesive includes a plurality of contiguous layers which cannot be delaminated. Each of the layers includes a photopolymerized matrix of polymeric chains, and at least one of the outer layers is photopolymerized to a pressure-sensitive adhesive state. Details of this process are described, for example, in European Patent No. EP 0 305 161 (Zimmerman, et al.).

Uncured compositions can be coated on an unstructured or structured release liner using conventional coating techniques. For example, these compositions can be applied by methods such as roller coating, flow coating, dip coating, spin coating, spray coating knife coating, and die coating. Coating thicknesses may vary. The composition may be of any desirable concentration for subsequent coating based on the desired viscosity. Optionally, the coated release liner may be brought in contact with a second backing prior to curing.

In some embodiments, curing takes place by activating a photoinitiator. Useful photoinitiators include benzoin ethers such as benzoin methyl ether and benzoin isopropyl ether; substituted acetophenones such as 2,2-dimethoxy-2-phenylacetophenone photoinitiator, available the trade name IRGACURE 651, available from Merck KGaA, Darmstadt, Germany or ESACURE KB-1 photoinitiator, available from LEHVOSS Group, Hamburg, Germany, and dimethylhydroxyacetophenone; substituted α-ketols such as 2-methyl-2-hydroxy propiophenone; aromatic sulfonyl chlorides such as 2-naphthalene-sulfonyl chloride; photoactive oximes such as 1-phenyl-1,2-propanedione-2-(O-ethoxy-carbonyl)oxime; mono- or bis-acrylphosphine oxides such as IRGANOX 819 from BASF SE, Ludwigshafen, Germany or LUCIRIN TPO from Merck KGaA.

Preferred photoinitiators are photoactive compounds that undergo a Norrish I cleavage to generate free radicals that can initiate by addition to the acrylic double bonds. The photoinitiator can be added to the mixture to be coated after the polymer (e.g. syrup) has been formed, i.e., photoinitiator can be added. Such polymerizable photoinitiators are described, for example, in U.S. Patent Nos. 5,902,836 and 5,506,279 (Gaddam et al.).

Photoinitiators can be present in an amount of from 0.1 to 5 percent by weight, based on the overall weight of the uncured composition. Relatively thick coatings can be achieved when the extinction coefficient of the photoinitiator is low.

Polymerization can be conducted in the absence of non-polymerizable organic solvents such as ethyl acetate, toluene and tetrahydrofuran, which are non-reactive with the functional groups of the monomers. Solvents influence the rate of incorporation of different monomers in the polymer chain and generally lead to lower molecular weights as the polymers gel or precipitate from solution. It can thus be beneficial for the crosslinked network composition can be free of non-polymerizable organic solvent.

The uncured composition with the photoinitiator can be cured by irradiation with actinic radiation. Actinic radiation can be, for instance, ultraviolet (UV) radiation having a UVA maximum at a wavelength range of 280 to 425 nanometers to polymerize the monomer components. UV light sources are not particularly restricted. Low light intensity sources, such as blacklights, generally provide intensities ranging from 0.1 or 0.5 mW/cm^2 (milliwatts per square centimeter) to 10 mW/cm^2 (as measured in accordance with procedures approved by the United States National Institute of Standards and Technology as, for example, with a UVIMAP UM 365 L-S radiometer manufactured by Electronic Instrumentation & Technology, Inc., in Sterling, VA). High light intensity sources generally provide intensities greater than 10, 15, or 20 mW/cm^2 and up to 450 mW/cm^2. High intensity light sources provide intensities up to 500, 600, 700, 800, 900 or 1000 mW/cm^2. UV light used to polymerize the monomer components can be provided by various light sources such as light emitting diodes (LEDs), blacklights, medium pressure mercury lamps, or any combination thereof.

UV exposure time for polymerization and curing generally varies depending on the intensity of the light source(s) used. For example, complete curing with a low intensity light course can be accomplished with an exposure time ranging from about 30 to 300 seconds; whereas complete curing with a high intensity light source can be accomplished with shorter exposure time ranging from about 5 to 20 seconds. Partial curing with a high intensity light source can typically be accomplished with exposure times of from 2 to 10 seconds, or from 2 to 5 seconds.

The uncured composition optionally contains one or more additives. While not all are suitable for OCA applications, additives can include antioxidants, plasticizers, tackifiers, stabilizers, ultraviolet absorbers, lubricants, processing aids, antistatic agents, colorants, impact resistance aids, fillers, matting agents, flame retardants (e.g., zinc borate) and the like. Some examples of fillers or pigments include inorganic oxide materials such as zinc oxide, titanium dioxide, silica, carbon black, calcium carbonate, antimony trioxide, metal powders, mica, graphite, talc, ceramic microspheres, glass or polymeric beads or bubbles, fibers, starch and the like.

Where present, additives can represent from 0.1 percent to 15 percent, from 0.3 percent to 10 percent, from 0.5 percent to 5 percent, or in some embodiments less than, equal to, or greater than 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1, 2, 5, 7, or 10, 11, 12, 13, 14, or 15 percent of the weight of the uncured adhesive composition.

EXAMPLES

Objects and advantages of this disclosure are further illustrated by the following non-limiting examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure. Unless otherwise noted, all parts, percentages, and ratios in the Examples and the rest of the specification are by weight.

Materials

Table 1 lists components used in preparing the Examples and Comparatives described herein.

Table 1.

Name	Description	Source
2EHA	2-Ethylhexyl acrylate	BASF SE, Ludwigshafen, Germany
2HEA	2-hydroxyethyl acrylate	Osaka Organic Chemical, Osaka City, Japan
ACM	Acrylamide	Zibo Zhangdian Oriental Chemical Co., Ltd., Zibo City, P. R. China
BA	Butyl acrylate	BASF SE
BD1	Karenz BD1, 1,4-Bis (3-mercaptobutyroyloxy) butane	Resonac Corporation, Japan
BL1B	EVERSORB BL1B ultraviolet light absorber	Everlight USA
CN983	Multi-functional urethane acrylate oligomer	Merck KGaA
D1173	DAROCUR 1173, 2-Hydroxy-2-methylpropiophenone	Merck KGaA
EB230	EBECRYL 230 crosslinker	Allnex USA
GPTMS	Glycidoxypropyl trimethoxysilane adhesion promoter	Shin-Etsu Chemical, Tokyo, Japan
HBA	Hydroxybutyl acrylate	BASF SE
I819	OMNIRAD 819, or phenyl bis(2,4,6-trimethylbenzoyl)phosphine oxide photoinitiator	IGM Resins BV, Waalwijk, The Netherlands
IEM	Isocyanatoethyl methacrylate copolymer-pendent crosslinker	Merck KGaA, Darmstadt, Germany
OTP	OMNIPOL TP photoinitiator, polymeric version of Ethyl(2,4,6-Trimethylbenzoyl)-phenyl phosphinate (CAS# 1834525-17-5)	IGM Resins BV, Waalwijk, The Netherlands
PVB	Grade 30HH polyvinylbutyral	Kuraray Co., Ltd., Osaka, Japan
TMPTA	Trimethylolpropane triacrylate	Merck KGaA
TPO	2,4,6-trimethylbenzoyl) diphenylphosphine oxide photoinitiator	Merck KGaA

Test methods

For each of the tests listed below, examples were coated between release-coated carrier liners (RF02N and RF22N, SKC Haas, Korea) and were cut to approximately 5 cm width by 10 cm length and their thickness was measured.

Impact Test

For the purpose of impact test performance improvement in the target application, adhesives which absorb and dissipate more of the impact energy will display a lower Coefficient of Restitution (herein referred to as the COR). OCAs that absorb relatively less impact energy will possess a higher COR.

COR was obtained using known methods, as disclosed for example in Skórski et al., Experimental Determination of the Coefficient of Restitution for Selected Modern Hybrid Composites. *Materials*. 2021; 14(19):5638. Samples were tested using a ram equipped with an acceleration sensor, and a mounting plate which can be monitored for deflection by means of the distance sensors. Assuming that the ram's energy during the test dissipated only at the moment it hit the plate, it is possible, on the basis of the time between individual impacts, to determine the height that the ram reached after an impact. The calculated height of the ram after impact, and the known initial drop height can then be used to calculate the coefficient of restitution for a given material. This method is described with more detail by Skórski et al.

Each example was prepared for testing of the COR by removing a carrier layer and laminating the adhesive to a piece of 51-micrometer (2-mil) polyethylene terephthalate (PET) and then autoclaving at 65°C with 5 kg force for 5 minutes. The purpose of this step was to prevent adhesion to dynamic testing components of the test system. The adhesive-PET construction was dwelled overnight in a controlled environment held at 23 ± 2°C and 50 ± 10% relative humidity, then laminated directly to the mounting plate of the test system. Accordingly, reported COR values were not a direct measurement of the adhesive in isolation, but rather a comparative measurement of an adhesive-PET laminate. Three replicates were tested and their average was reported.

Deformation Resistance Test

To measure resistance to deformation, a test coupon is prepared by removing a carrier liner and laminating the adhesive to 51-micrometer (2-mil) PET, then to 0.7 millimeter LCD glass. Samples are allowed to dwell overnight in a controlled environment held at 23 ± 2°C and 50 ± 10% relative humidity prior to testing. The sample is then tested using a TA XT Plus Texture Analyzer with a 7-mm rounded probe. The test coupon is placed on the base stage of the instrument with the PET side up, and the probe is applied to the PET surface of the test coupon with a force of 50 g for 60 seconds. The relative penetration depth in millimeters is measured as a function of time. The maximum penetration depth, referred to as the Average (Avg) Peak Positive (Pos) Distance from this test, is then recorded.

OCAs which resist mechanical deformation that leads to mechanical read-through of components from the backside of a polarizer-less display perform better in this test, with a lower penetration depth result. OCAs which allow more mechanical deformation will perform worse as evidenced by a higher penetration depth result. Note that for this test, performance trends with 1 h testing were found to closely match those that were observed with 60 second testing. Therefore, the faster test time was selected for reasonable timing of data gathering with multiple concepts and replicates. Twelve replicates were tested and their average was reported.

Haze Test

Haze measurements were made using a HunterLab (Reston, VA) UltrascanPro Spectrophotometer in transmission mode. One of the carrier liners was removed and the sample was laminated to a clear piece of 0.7 mm thick LCD glass (Swift Glass, Elmira Heights, New York). The remaining carrier liner was removed, and the sample was placed in the UltrascanPro Spectrophotometer to measure transmission and %Haze through the OCA/glass assembly.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was used to determine the shear storage modulus (G’) as a function of temperature as well as the one or more T_g values of the material. An 8-mm diameter by 1-mm thick disk of laminated assembly layers was placed between the upper and lower geometries of a DHR parallel plate rheometer (TA Instruments, New Castle, DE). A temperature scan was performed by ramping from -45°C to 150°C at 3°C/minute. During this ramp, the samples was oscillated at a frequency of 1 Hz and a strain of approximately 0.4%. G’, loss modulus (G”), and tan delta were recorded at 25°C during this scan. The one or more T_g values of the material were also determined as the temperatures at which the tan delta peak values were observed.

Preparatory Examples (PEs)

Preparatory Example PVB0

430 g of 30HH grade PVB was mixed with 2050 g of 2EHA in a vessel utilizing a mixing blade and applied heat. This solution was mixed for 90 minutes at a temperature of approximately 50°C until the PVB was well solvated by the 2EHA.

Preparatory Example PVB0.6-IEM

430 g of 30HH grade PVB was mixed with 2050 g of 2EHA in a vessel utilizing a mixing blade and applied heat. This solution was mixed for 90 minutes at a temperature of approximately 50°C until the PVB was well solvated by the 2EHA. 2.5 g of Bismuth catalyst (BICAT 8108) was

added and allowed to mix for 10 minutes. 2.57 g of IEM was added to the vessel and the solution was mixed for 20 hours at a temperature of approximately 60°C.

Preparatory Example PVB5.7-IEM

430 g of 30HH grade PVB was mixed with 2050 g of 2EHA in a vessel utilizing a mixing blade and applied heat. This solution was mixed for 90 minutes at a temperature of approximately 50°C until the PVB was well solvated by the 2EHA. 2.5 g of Bismuth catalyst (BICAT 8108) was added and allowed to mix for 10 minutes. 25.8 g of IEM was added to the vessel and the solution was mixed for 20 hours at a temperature of approximately 60°C.

Preparatory Example PVB9.1-allyl

420 g of 30HH grade PVB was mixed with 2000 g of 2EHA in a vessel utilizing a mixing blade and applied heat. This solution was mixed for 90 minutes at a temperature of approximately 50°C until the PVB was well solvated by the 2EHA. 2.5 g of Bismuth catalyst (BICAT 8108) was added and allowed to mix for 10 minutes. 41.9 g of Allyl isocyanate was added to the vessel and the solution was mixed for 20 hours at a temperature of approximately 60°C.

The final compositions for preparatory examples PVB0, PVB0.6-IEM, PVB6-IEM and PVB9.1-allyl are summarized in Table 2 below.

Table 2.

	PVB0	**PVB0.6-IEM**	**PVB5.7-IEM**	**PVB9.1 -allyl**
30HH, g	430	430	430	420
IEM, g	0	2.57	25.8	0
Allyl, g	0	0	0	41.9
EHA, g	2050	2050	2050	2000
IEM, wt% relative to functionalized PVB	0.0%	0.6%	5.7%	0.0%
Allyl isocyanate, wt% relative to functionalized PVB	0.0%	0.0%	0.0%	9.1%
Functionalized PVB, wt% relative to full composition of preparatory example	17.3%	17.4%	18.2%	18.8%
2EHA, wt% relative to the full composition of the preparatory example	82.7%	82.6%	81.8%	81.2%

Preparatory Examples PE1-PE3 were prepared according to the formulations listed in Table 3. Functionalized PVB (PVB0-IEM, PVB0.6-IEM, PVB6-IEM) and Acrylate monomers were charged in a vessel to provide a 2000 g mixture at the wt% ratios that are shown. Values of wt% are relative to the overall composition of the preparatory example. HDDA, I819, and BL1B were then added. The vessel was sealed and mixed on a jar roller for 16 hours.

Table 3.

	PE1	**PE2**	**PE3**
PVB0-IEM, wt%	0	0	61.46
PVB0.6-IEM, wt%	58.22	0	0
PVB6-IEM, wt%	0	61.08	0
Additional 2EHA, wt%	14.70	17.73	14.87
(Functionalized PVB wt% relative to the overall composition of PE)	10.71	10.59	10.59
(2EHA wt% relative to the overall composition of PE)	65.45	65.36	65.36
nnDMA, wt%	1.77	1.78	1.78
IBOA, wt%	7.08	7.07	7.07
2HEA, wt%	14.15	14.17	14.17
HDDA, wt%	0.05	0.05	0.05
I819, wt%	0.30	0.49	0.49
BL1B, wt%	0.50	0.49	0.49

Preparatory Examples PE4-PE6 were prepared according to the formulations listed in Table 4. Functionalized PVB (PVB0.6-IEM), if present, and acrylate monomers were charged in a vessel to provide a 2000 g mixture at the wt% ratios that are shown. Note that PE5 and PE6 do not contain PVB. D1173 was then added to the vessel. Values of wt% are relative to the overall composition of the preparatory example. The mixture was then irradiated with 365 nm UVLEDs with an intensity of 0.3 mW/cm^2 until the mixture (herein referred to as the pre-polymer) reached a viscosity of about 100-1500 cp as measured by a Brookfield viscometer. EB230 or HDDA, I819, BL1B and KBM403 were then added. The vessel was sealed and mixed on a jar roller for 16 hours.

Table 4.

	PE4	PE5	PE6
PVB0.6-IEM, wt%	21.02	0	0
Additional 2EHA, wt%	53.05	72.81	46.52
(Functionalized PVB wt% relative to the overall composition of PE)	*3.66*	*0.00*	*0.00*
(2EHA wt% relative to the overall composition of PE)	*70.41*	*72.81*	*46.52*
nnDMA, wt%	1.90	1.97	2.97
IBOA, wt%	7.61	7.87	32.66
2HEA, wt%	15.22	15.74	16.83
D1173	0.10	0.04	0.04
EB230, wt%	0.20	0.69	0.00
HDDA, wt%	0.00	0.00	0.10
I819, wt%	0.30	0.30	0.30
BL1B, wt%	0.49	0.49	0.49
KBM403, wt%	0.10	0.10	0.10

Examples and Comparatives

Examples EX1-EX5 and Comparative CE1 were prepared according to Table 5, and consisted of single layer adhesives prepared by blending the preparatory adhesive compositions listed in Tables 2-3 to provide the overall compositions shown. DMA test results, including T_g values and 25°C shear storage modulus, and Impact and Deformation Resistance Test results, including average COR and average peak positive distance (50 g for 60 seconds), are also reported in Table 5. Final composition wt% are relative to the overall weight of the adhesive composition unless otherwise indicated.

The examples were coated onto 51-micrometer carrier release liners (RF02N/RF22N from SKC Haas) using a roll-to-roll coating method and subsequently polymerized and cured with a 3380 mJ dose of UVV light irradiation from a 405-nm UVLED light source. All adhesive layers had a caliper (i.e., thickness) of approximately 150 micrometers.

Table 5.

	CE1	EX1	EX2	EX3	EX4	EX5
Blend ratios of preparatory examples:						
PE1, wt%	0	32.4	0	37	39.4	43.1
PE4, wt%	0	0	100	0	0	0
PE5, wt%	100	67.6	0	63	60.6	56.9
Final composition of each, relative to the overall adhesive composition:						
Functionalized PVB, wt%	0.00	3.47	3.66	3.96	4.22	4.62
2EHA, wt%	72.81	70.43	70.41	70.09	69.91	69.64
nnDMA, wt%	1.97	1.91	1.90	1.90	1.89	1.88
IBOA, wt%	7.87	7.61	7.61	7.58	7.56	7.53
2HEA, wt%	15.74	15.22	15.22	15.15	15.11	15.05
D1173, wt%	0.04	0.03	0.10	0.03	0.02	0.02
EB230, wt%	0.69	0.47	0.20	0.43	0.42	0.39
HDDA, wt%	0.00	0.02	0.00	0.02	0.02	0.02
I819, wt%	0.30	0.30	0.30	0.30	0.30	0.30
BL1B, wt%	0.49	0.49	0.49	0.49	0.49	0.49
KBM403, wt%	0.10	0.07	0.10	0.06	0.06	0.06
T_g1 (°C)	-25	-23	-26	-24	-23	-32
T_g2 (°C)	n/a	65	60	63	65	64
G'(kPa), 25°C	53	196	159	248	219	791
Avg. Impact Test COR	0.29	0.31	0.31	0.32	0.33	0.32
Avg. peak positive distance (50 g for 60 s)	0.057	0.045	0.044	0.029	0.031	0.019

Reported in Table 6 are the overall compositions of Examples EX6-EX8 and Comparatives CE2-CE3, consisting of single layer adhesives. Table 6 also reports corresponding DMA test results (T_g values and 25°C shear storage modulus), Impact and Deformation Resistance Test results, including average COR and average peak positive distance (50 g for 60 seconds), and Haze Test results. These examples were prepared by charging functionalized PVB (preparatory example PVB0-IEM, PVB0.6-IEM, or PVB6-IEM) and acrylate monomers into a vessel to provide a 100 g mixture at the wt% ratios that are shown. D1173 was then added to the vessel. Values of wt% are relative to the overall composition of the example. The mixture was then irradiated with 365nm UVLEDs with an intensity of 0.3 mW/cm^2 until the pre-polymer reached a viscosity of about 100-1500 cp as measured by a Brookfield viscometer. HDDA, I819, BL1B, and KBM403 were then added. The vessel was sealed and mixed on a jar roller for 16 hours. The examples were coated onto 51-micrometer carrier release liners (RF02N/RF22N from SKC Haas) using a roll-to-roll coating method, and subsequently polymerized and cured with 3380 mJ of UVV light from a 405-nm UVLED light source. Adhesive layers had a caliper of approximately 150 micrometers.

Table 6.

	CE2	**CE3**	**EX6**	**EX7**	**EX8**
PVB0-IEM, wt%	0.00	0.00	25.90	24.64	23.58
PVB0.6-IEM, wt%	25.91	25.91	0.00	0.00	0.00
PVB9.1 -allyl, wt%	0.00	0.00	0.00	0.00	0.00
Additional 2EHA, wt%	26.43	1.73	38.82	30.12	21.56
(Functionalized PVB wt% relative to the overall adhesive composition)	4.51	4.51	4.48	4.26	4.08
(2EHA wt% relative to the overall adhesive composition)	47.83	23.13	60.24	50.50	41.06
nnDMA, wt%	1.89	1.89	1.89	1.89	1.90
IBOA, wt%	29.64	54.35	7.47	7.46	7.50
HEA, wt%	14.94	14.94	24.69	34.66	44.23
D1173, wt%	0.05	0.05	0.05	0.05	0.05
HDDA, wt%	0.05	0.05	0.10	0.10	0.10
I819, wt%	0.49	0.49	0.49	0.49	0.49
OTP, wt%	0.00	0.00	0.00	0.00	0.00
BL1B, wt%	0.49	0.49	0.49	0.49	0.49
KBM403, wt%	0.10	0.10	0.10	0.10	0.10
BD1, wt%	0.00	0.00	0.00	0.00	0.00
% Haze	-	-	1.25	0.44	0.88
T_g1 (°C)	-6.0	23.0	-24.0	-11.5	-5.0
T_g2 (°C)	61.0	55.0	60.0	61.0	60.0
G', 25°C (kPa)	3419	11540	1080	730	443
Avg. Impact Test COR	0.42	0.63	0.35	0.36	0.37
Avg. peak positive distance (50 g for 60 s)	0.018	0.019	0.023	0.028	0.024

Reported in Table 7 is the overall composition of Example EX9, consisting of a single layer adhesive. Table 7 also reports corresponding 25°C shear storage modulus, Impact and Deformation Resistance Test results, including average COR and average peak positive distance (50 g for 60 seconds). This example was prepared by charging functionalized PVB (preparatory example PVB9.1-Allyl) and acrylate monomers into a vessel to provide a 100 g mixture at the wt% ratios that are shown. BL1B, OMNIPOL TP and BD1 were then added. The vessel was sealed and mixed on a jar roller for 16 hours. The example was coated onto 51-micrometer carrier release liners

(RF02N/RF22N from SKC Haas) using a roll-to-roll coating method, and subsequently polymerized and cured with 2400 mJ of UVV light from a 405-nm UVLED light source. The adhesive had a caliper of approximately 150 micrometers.

Table 7.

	EX9
PVB9.1 -allyl, wt%	70.63
Additional 2EHA, wt%	0.00
(Functionalized PVB wt% relative to the overall adhesive composition)	13.28
(2EHA wt% relative to the overall adhesive composition)	57.35
nnDMA, wt%	1.78
IBOA, wt%	7.12
HEA, wt%	14.15
OTP, wt%	5.62
BL1B, wt%	0.47
BD1, wt%	0.19
G', 25°C (kPa)	1240
Avg. Impact Test COR	0.36
Avg. peak positive distance (50 g for 60 s)	0.032

Compositions of Examples EX10-EX22 and Comparative CE4 are reported in Table 8. These were multilayer adhesives prepared using the preparatory example compositions shown in Tables 3 and 4 with corresponding Impact and Deformation Resistance Test results also reported in Table 8. The adhesives were coated onto 51um carrier release liners (RF02N/RF22N from SKC) using a multilayer coating die according to the methods as described in European Patent No. EP 0 305 161 (Zimmerman, et al.), and subsequently polymerized and cured with 2480 mJ of UVV light from a 405-nm UVLED light source.

Combined adhesive layers had a caliper of approximately 150 micrometers. Layer numbers were defined as follows: “L1” is a layer disposed against the 1st release liner; “L2” is a layer disposed between L1 and L3; and “L3” is a layer disposed against the 2nd release liner.

Table 8.

Layer #		EX10	EX11	EX12	EX13	EX14	EX15	EX16	EX17	EX18	EX19	EX20	EX21	EX22	CE4
L1	PE#	5	5	4	4	4	4	6	6	5	5	5	5	5	5
	Caliper	50	25	50	25	12	42	25	12	25	12	60	50	25	12
L2	PE#	1	1	1	1	1	1	1	1	2	2	3	3	3	3
	Caliper	50	100	50	100	126	96	100	126	100	126	30	50	100	126
L3	PE#	5	5	5	5	5	5	5	5	5	5	5	5	5	5
	Caliper	50	25	50	25	12	12	25	12	25	12	50	50	25	12
	% Haze	-	-	-	-	-	-	-	-	-	0.29	-	-	2.63	3.05
	Avg. Impact Test COR	0.29	0.33	0.31	0.33	0.37	0.34	0.34	0.36	0.34	0.38	0.3	0.3	0.35	0.37
	Avg. peak positive distance (50 g for 60 s)	0.033	0.024	0.030	0.017	0.017	0.020	0.020	0.020	0.03	0.027	0.028	0.028	0.02	0.021

All cited references, patents, and patent applications in the above application for letters patent are herein incorporated by reference in their entirety in a consistent manner. In the event of inconsistencies or contradictions between portions of the incorporated references and this application, the information in the preceding description shall control. The preceding description, given in order to enable one of ordinary skill in the art to practice the claimed disclosure, is not to be construed as limiting the scope of the disclosure, which is defined by the claims and all equivalents thereto.

CLAIMS:

What is claimed is:

1. An adhesive comprising:

a crosslinked network of polyvinyl acetal and acrylic copolymer obtained by reacting a functionalized polyvinyl acetal and acrylic monomers,

wherein the functionalized polyvinyl acetal is present in a weight fraction of from 1 percent to 20 percent of the overall weight of the adhesive and is comprised of a polyvinyl acetal backbone with pendent functional groups reactive with the acrylic monomers; and

further wherein the acrylic copolymer is present in a weight fraction of from 60 percent to 99 percent of the overall weight of the adhesive.

2. The adhesive of claim 1, wherein the polyvinyl acetal backbone is a polyvinyl butyral backbone.

3. The adhesive of claim 1 or 2, wherein the polyvinyl acetal backbone with pendent functional groups is obtained by reacting polyvinyl acetal with isocyanatoethyl (meth)acrylate or allyl isocyanate.

4. The adhesive of any one of claim 1-3, wherein the acrylic copolymer is a reaction product comprising polymerized units of one or more of hydroxy-functional monomers, nitrogen-containing monomers, and combinations thereof.

5. The adhesive of claim 4, wherein polymerized units of the one or more hydroxy-functional monomers, nitrogen-containing monomers, and combinations thereof are present in a weight fraction of from 5 percent to 55 percent relative to the overall weight of the adhesive.

6. The adhesive of any one of claims 1-5, wherein the functionalized polyvinyl acetal is obtained at least in part by reacting polyvinyl acetal and isocyanatoethyl (meth)acrylate with each other.

7. The adhesive of any one of claims 1-6, wherein the functionalized polyvinyl acetal is obtained at least in part by reacting polyvinyl acetal and allyl isocyanate with each other.

8. The adhesive of claim 6 or 7, wherein polyvinyl acetal is present in an amount of from 85.0 wt% to 99.9 wt%, relative to the overall weight of the functionalized polyvinyl acetal.

9. The adhesive of any one of claims 1-8, wherein the adhesive is optically transparent.

10. The adhesive of any one of claims 1-9, wherein the adhesive displays a T_g of less than 0°C and a shear storage modulus at 25°C greater than 200 kPa, as measured by a dynamic mechanical analysis temperature sweep at 1 Hz.

11. The adhesive of any one of claims 1-10, wherein the adhesive is derived from precursors comprising from 40 wt% to 90 wt% of alkyl (meth)acrylate monomers having a homopolymer T_g of less than 0°C.

12. The adhesive of any one of claims 1-11, wherein the adhesive is substantially free of acid-functional repeat units.

13. A tape adhesive comprising a layer of the adhesive of any one of claims 1-12.

14. The tape adhesive of claim 13, wherein the layer is a first layer having a pair of opposing major surfaces and further comprising a second layer disposed on one of the opposing major surfaces, wherein the second layer contains a lower weight fraction of polyvinyl acetal relative to that of the first layer.

15. The tape adhesive of claim 14, wherein the second layer contains a zero amount of polyvinyl acetal.

16. A method of making an adhesive, comprising:

functionalizing polyvinyl acetal by reacting polyvinyl acetal with isocyanatoethyl methacrylate and/or allyl isocyanate; and

polymerizing acrylic monomers in the presence of the functionalized polyvinyl acetal to form a crosslinked network of polyvinyl acetal and acrylic copolymer.

17. The method of claim 16, wherein the polyvinyl acetal comprises polyvinyl butyral.

18. The method of claim 16 or 17, wherein the acrylic copolymer is the reaction product of one or more of hydroxy-functional monomers, nitrogen-containing monomers, and combinations thereof.

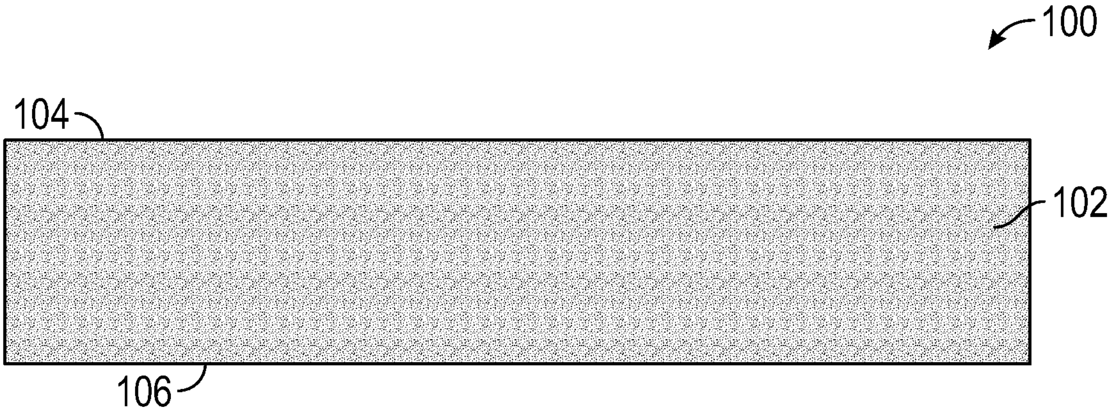

FIG. 1

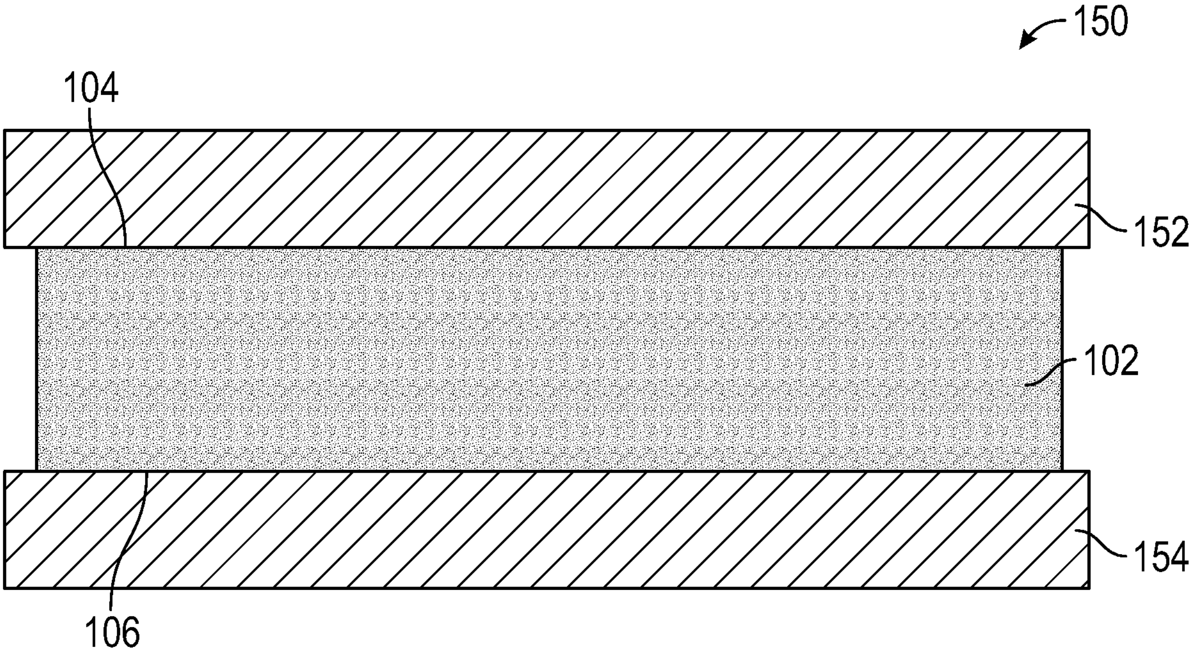

FIG. 2

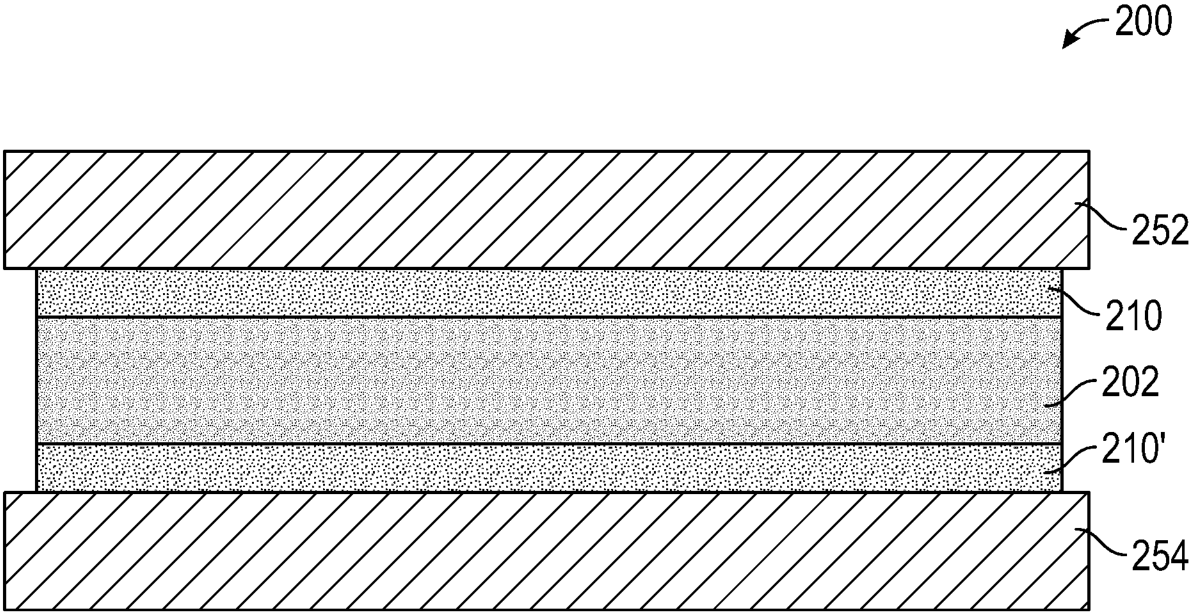

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2024/057508

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F8/30 C08F261/12 C09J4/06
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C09J

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2018/304576 A1 (JANOSKI JONATHAN E [US] ET AL) 25 October 2018 (2018-10-25) the whole document -----	1-18
A	WO 2016/094277 A1 (3M INNOVATIVE PROPERTIES CO [US]) 16 June 2016 (2016-06-16) cited in the application the whole document -----	1-18
A	US 2007/092733 A1 (YANG JIE [US] ET AL) 26 April 2007 (2007-04-26) the whole document -----	1-18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 November 2024	28/11/2024

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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