(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
12 June 2008 (12.06.2008)

PCT

(10) **International Publication Number**
WO 2008/070386 A1

(51) **International Patent Classification:**
C09J 153/00 (2006.01) ***C09J 153/02*** (2006.01)

(21) **International Application Number:**
PCT/US2007/083741

(22) **International Filing Date:**
6 November 2007 (06.11.2007)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
60/868,975 7 December 2006 (07.12.2006) US

(71) **Applicant** *(for all designated States except US)*: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) **Inventors; and**

(75) **Inventors/Applicants** *(for US only)*: **WAID, Robert D.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **ZOLLER, Panu K.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **GADBOIS, Gregory B.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(74) **Agents: SPIELBAUER, Thomas M.** et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, St. Paul, Minnesota 55133-3427 (US).

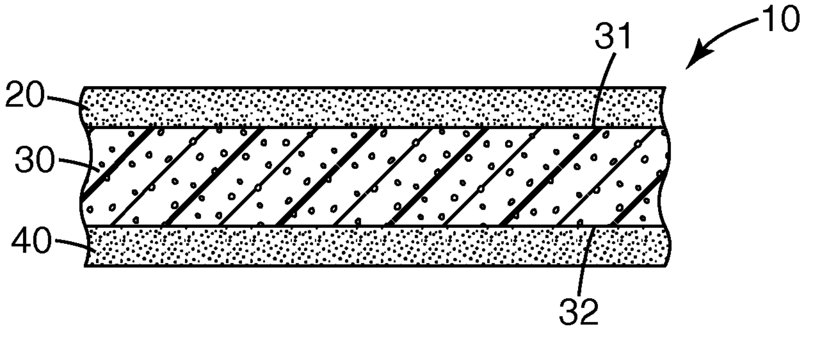
(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
— *with international search report*

(54) Title: BLENDS OF BLOCK COPOLYMER AND ACRYLIC ADHESIVES



(57) **Abstract:** Pressure sensitive adhesive compositions containing 92 to 99.9 parts of a block copolymer adhesive composition and 0.1 to less than 10 parts of an acrylic adhesive composition are described. Tapes including such adhesives, and methods of making such tapes are also described.

WO 2008/070386 A1

BLENDS OF BLOCK COPOLYMER AND ACRYLIC ADHESIVES

FIELD

[0001] The present disclosure relates to block copolymer-based adhesives. Particularly, acrylic modified, block copolymer pressure sensitive adhesives.

BACKGROUND

[0002] Adhesives and tapes are commonly used to bond two substrates together to form a bonded composite. While a vast array of adhesives and tapes are available, advances in substrates and end use requirements continues to drive a need for new adhesive formulations and tape constructions. In addition to performance properties, environmental regulations and processing costs also influence product formulation requirements. For example, in some applications it may be desirable to use a hot melt adhesive rather than a solvent-based adhesive.

[0003] While some efforts are directed at the identification and development of new materials for use in adhesive formulations, much progress can still be made by identifying, selecting, and combining the proper proportions of existing raw materials to arrive at useful adhesives and tapes.

SUMMARY

[0004] Briefly, in one aspect, the present disclosure provides a pressure sensitive adhesive composition comprising 92 to 99.9 parts of a block copolymer adhesive composition and 0.1 to less than 10 parts of an acrylic adhesive composition. The block copolymer adhesive composition comprises a first block copolymer comprising (i) at least one rubbery block comprising a first polymerized conjugated diene, a hydrogenated derivative thereof, or combinations thereof; and (ii) at least one glassy block comprising a first polymerized monovinyl aromatic monomer. The acrylic adhesive composition comprises 70 to 100 parts of at least one acrylic or methacrylic ester of a non-tertiary alkyl alcohol, wherein the non-tertiary alkyl alcohol contains 4 to 20 carbon atoms; and 0 to 30 parts of a copolymerized reinforcing monomer.

[0005] In some embodiments, the first block copolymer is a multi-arm block copolymer of the formula Q_n-Y, wherein Q represents an arm of the multi-arm block copolymer, n represents the number of arms and is a whole number of at least 3; and Y is the residue of a multifunctional coupling agent. Each arm, Q, independently has the formula R-G wherein R represents the rubbery block; and G represents the glassy block. In some embodiments, the first block copolymer is a polymodal, asymmetric star block copolymer.

[0006] In some embodiments, the pressure sensitive adhesive further comprises a second block copolymer comprising at least one rubbery block comprising a polymerized second conjugated diene, a hydrogenated derivative thereof, or combinations thereof; and at least one glassy block comprising a second polymerized monovinyl aromatic monomer. In some embodiments, the second block copolymer is a linear block copolymer.

[0007] In some embodiments, the pressure sensitive adhesive further comprises a first high Tg tackifier having a Tg of at least 60 degrees C, wherein the first high Tg tackifier is compatible with at least one rubbery block. In some embodiments, the block copolymer adhesive composition further comprises a second high Tg tackifier having a Tg of at least 60 degrees C, wherein the second high Tg tackifier is compatible with the at least one glassy block.

[0008] In some embodiments, the pressure sensitive adhesive is a hot melt adhesive. In some embodiments, the pressure sensitive adhesive is a solvent-based adhesive.

[0009] In another aspect, the present disclosure provides a tape comprising a foam backing having a first major surface and a second major surface; and a first adhesive skin bonded to the first major surface, wherein the first adhesive skin comprises a first pressure sensitive adhesive according to any one of the preceding claims. In some embodiments, the tape further comprises a second adhesive skin bonded to the second major surface.

[0010] In some embodiments, the backing is a foam backing. In some embodiments, the foam comprises a thermoplastic foam. In some embodiments, the foam comprises a thermoset foam.

[0011] In yet another aspect, the present disclosure provides a method of making a tape. In some embodiments, the method comprises extruding a foam backing and coextruding a first pressure sensitive adhesive to form the first adhesive skin bonded to the first major surface of the foam backing. In some embodiments, the method further comprises extruding a second adhesive to form a second adhesive skin bonded to the second major surface of the foam backing.

[0012] In some embodiments, the method comprises providing a foam backing, and applying a first adhesive composition comprising the first pressure sensitive adhesive to the first surface of the foam backing. In some embodiments, applying the first adhesive composition comprises laminating.

[0013] In some embodiments, applying the first adhesive composition comprises coating, optionally wherein the method further comprises crosslinking the first adhesive composition, optionally wherein crosslinking the first adhesive composition comprises radiation crosslinking.

[0014] In another aspect, the present disclosure provides a bonded composite comprising a first substrate having a first surface; a second substrate having a second surface; and a bonding interface between the first surface of the first substrate and the second surface of the second substrate, wherein the bonding interface comprises a pressure sensitive adhesive according to the present disclosure. In some embodiments, the first surface has a surface energy of less than 35 dyne per centimeter.

[0015] The above summary of the present disclosure is not intended to describe each embodiment of the present invention. The details of one or more embodiments of the invention are also set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. 1 illustrates a tape according to some embodiments of the present disclosure.

[0017] FIG. 2 illustrates a bonded composite according to some embodiments of the present disclosure.

DETAILED DESCRIPTION

[0018] In one aspect, the present disclosure provides a pressure sensitive adhesive composition comprising both a block copolymer adhesive composition and an acrylic adhesive composition. In some embodiments, the pressure sensitive adhesive further comprises one or more additional block copolymers, one or more tackifiers, other additives, and combinations thereof.

[0019] In some embodiments, the pressure sensitive adhesive composition comprises at least about 90 parts, and in some embodiments, at least about 92 parts, and in some embodiments, at least about 96 parts of a block copolymer adhesive composition. In some embodiments, the pressure sensitive adhesive composition comprises no greater than about 99.9 parts, and in some embodiments, no greater than about 99 parts, or even no greater than about 98 parts of a block copolymer adhesive composition. In some embodiments, the pressure sensitive adhesive composition comprises 92 to 99.9 parts and, in some embodiments, 96 to 99 parts of a block copolymer adhesive composition.

[0020] The first block copolymer comprises a rubbery block, R, and at least one glassy block, G. In some embodiments, the first block copolymer comprises at least three glassy blocks. In some embodiments, the first block copolymer comprises between three and five glassy blocks, inclusive. In some embodiments, the first block copolymer comprises four glassy blocks.

[0021] In some embodiments, the first block copolymer is a multi-arm block copolymer having the general formula Q_n-Y, wherein Q represents an arm of the multi-arm block copolymer; n represents the number of arms and is a whole number of at least 3; and Y is the residue of a multifunctional coupling agent. Each arm, Q, independently has the formula R-G, wherein G represents the glassy block; and R represents the rubbery block.

[0022] Generally, a rubbery block exhibits a glass transition temperature (Tg) of less than room temperature. In some embodiments, the Tg of the rubbery block is less than about 0 °C, or even less than about -10 °C. In some embodiments, the Tg of the rubbery block is less than about -40 °C, or even less than about -60 °C.

[0023] Generally, a glassy block exhibits a Tg of greater than room temperature. In some embodiments, the Tg of the glassy block is at least about 40 °C, at least about 60 °C, at least about 80 °C, or even at least about 100 °C.

[0024] In some embodiments, the rubbery block comprises a polymerized conjugated diene, a hydrogenated derivative of a polymerized conjugated diene, or combinations thereof. In some embodiments, the conjugated dienes comprise 4 to 12 carbon atoms. Exemplary conjugated dienes include butadiene, isoprene, ethylbutadiene, phenylbutadiene, piperylene, pentadiene, hexadiene, ethylhexadiene, and dimethylbutadiene. The polymerized conjugated dienes may be used individually or as copolymers with each other. In some embodiments, the conjugated diene is selected from the group consisting of isoprene, butadiene, ethylene butadiene copolymers, and combinations thereof.

[0025] In some embodiments, at least one glassy block comprises a polymerized monovinyl aromatic monomer. In some embodiments, both glassy blocks of a triblock copolymer comprise a polymerized monovinyl aromatic monomer. In some embodiments, the monovinyl aromatic monomers comprise 8 to 18 carbon atoms. Exemplary monovinyl aromatic monomers include styrene, vinylpyridine, vinyl toluene, alpha-methyl styrene, methyl styrene, dimethylstyrene, ethylstyrene, diethyl styrene, t-butylstyrene, di-n-butylstyrene, isopropylstyrene, other alkylated-styrenes, styrene analogs, and styrene homologs. In some embodiments, the monovinyl aromatic monomer is selected from the group consisting of styrene, styrene-compatible monomers or monomer blends, and combinations thereof.

[0026] As used herein, “styrene-compatible monomers or monomer blends” refers to a monomer or blend of monomers, which may be polymerized or copolymerized, that preferentially associate with polystyrene or with the polystyrene endblocks of a block copolymer. The compatibility can arise from actual copolymerization with monomeric styrene; solubility of the compatible monomer or blend, or polymerized monomer or blend in the polystyrene phase during hot melt or solvent processing; or association of the monomer or blend with the styrene-rich phase domain on standing after processing.

[0027] In the general formula for some multi-arm block copolymers of the present disclosure, Q_n-Y, n represents the number of arms and is a whole number of at least 3, i.e., the multi-arm block copolymer is a star block copolymer. In some embodiments, n is ranges from 3-10. In some embodiments, n ranges from 3-5. In some embodiments, n is 4. In some embodiments, n is equal to 6 or more.

[0028] In some embodiments, the first block copolymer is a polymodal block copolymer. As used herein, the term “polymodal” means that the copolymer comprises glassy blocks having at least two different molecular weights. Such a block copolymer may also be characterized as having at least one “high” molecular weight glassy block, and at least one “low” molecular weight glassy block, wherein the terms high and low are used relative to each other. In some embodiments the ratio of the number average molecular weight of the high molecular weight glassy block, $(Mn)_H$, relative to the number average molecular weight of the low molecular weight glassy block,$(Mn)_L$, is at least about 1.25.

[0029] In some embodiments, $(Mn)_H$ ranges from about 5,000 to about 50,000. In some embodiments, $(Mn)_H$ is at least about 8,000, and in some embodiments at least about 10,000. In some embodiments, $(Mn)_H$ is no greater than about 35,000. In some embodiments, $(Mn)_L$ ranges from about 1,000 to about 10,000. In some embodiments, $(Mn)_L$ is at least about 2,000, and, in some embodiments, at least about 4,000. In some embodiments, $(Mn)_L$ is less than about 9,000, and, in some embodiments, less than about 8,000.

[0030] In some embodiments, the first block copolymer is an asymmetric block copolymer. As used herein, the term “asymmetric” means that the arms of the block copolymer are not all identical. Generally, a polymodal block copolymer is an asymmetric block copolymer (i.e., a polymodal asymmetric block copolymer) as not all arms of a polymodal block copolymer are identical since the molecular weights of the glassy blocks are not all the same. In some embodiments, the block copolymers of the present disclosure are polymodal, asymmetric block copolymers. Methods of making asymmetric, polymodal block copolymers are described in, e.g., U.S. Patent No. 5,296,547.

[0031] Generally, the multifunctional coupling agent may be any polyalkenyl coupling agent or other material known to have functional groups that can react with carbanions of the living polymer to form linked polymers. The polyalkenyl coupling agent may be aliphatic, aromatic, or heterocyclic. Exemplary aliphatic polyalkenyl coupling agents include polyvinyl and polyalkyl acetylenes, diacetylenes, phosphates, phosphites, and dimethacrylates (e.g., ethylene dimethacrylate). Exemplary aromatic polyalkenyl coupling agents include polyvinyl benzene, polyvinyl toluene, polyvinyl xylene, polyvinyl anthracene, polyvinyl naphthalene, and divinyldurene. Exemplary polyvinyl groups include divinyl, trivinyl, and tetravinyl groups. In some embodiments, divinylbenzene (DVB) may be used, and may include o- divinyl benzene, m-divinyl benzene, p-divinyl benzene, and mixtures thereof. Exemplary heterocyclic polyalkenyl coupling agents include divinyl pyridine, and divinyl thiophene. Other exemplary multifunctional coupling agents include silicon halides, polyepoxides, polyisocyanates, polyketones, polyanhydrides, and dicarboxylic acid esters.

[0032] In some embodiments, the pressure sensitive adhesive compositions of the present disclosure comprise at least about 0.1 parts, in some embodiments, at least about 0.5 parts, at least about 1 part, or even at least about 2 parts of an acrylic adhesive composition. In some embodiments, the pressure sensitive adhesive compositions of the present disclosure comprise no greater than about 10 parts, in some embodiments, no greater than about 8 parts, no greater than about 5 parts, or even no greater than about 4 parts an acrylic adhesive composition.

[0033] In some embodiments, the non-tertiary alkyl alcohol contains 4 to 20 carbon atoms. Exemplary acrylic acid esters include isooctyl acrylate, 2-ethylhexyl acrylate, butyl acrylate, isobornyl acrylate, and combinations thereof. Exemplary methacrylic acid esters include the methacrylate analogues of these acrylic acid esters.

[0034] In some embodiments, the acrylic adhesive composition comprises the reaction product of at least one acrylic or methacrylic ester of a non-tertiary alkyl alcohol and, optionally, at least one copolymerized reinforcing monomer. In some embodiments, the acrylic adhesive composition comprises at least about 70 parts, in some embodiments, at least about 80 parts, at least about 90 parts, at least about 95 parts, or even about 100 parts of at least one acrylic or methacrylic ester of a non-tertiary alkyl alcohol. In some embodiments, acrylic adhesive composition comprises no greater than about 30 parts, in some embodiments, no greater than about 20 parts, no greater than about 10 parts, no greater than about 5 parts, and even no greater than 1 part of at least one copolymerized reinforcing monomer. In some embodiments, the acrylic adhesive composition does not include a copolymerized reinforcing monomer.

[0035] In some embodiments, the copolymerized reinforcing monomer is selected from the group consisting of acrylic acid, methacrylic acid, 2-carboxyethyl acrylate, N,N' dimethyl acrylamide, N,N' diethyl acrylamide, butyl carbamoyl ethyl acrylate, and combinations thereof.

[0036] In some embodiments, the block copolymer adhesive composition comprises a second block copolymer. In some embodiments, the second block copolymer may be a linear block copolymer. A linear block copolymer can be described by the formula

$$R - (G)_m$$

wherein R represents a rubbery block, G represents a glassy block, and m, the number of glassy blocks, is 1 or 2. In some embodiments, m is one, and the linear block copolymer is a diblock copolymer comprising one rubbery block and one glassy block. In some embodiments, m is two, and the linear block copolymer comprises two glassy endblocks and one rubbery midblock, i.e., the linear block copolymer is a triblock copolymer.

[0037] In some embodiments, the rubbery block of the second block copolymer comprises a polymerized conjugated diene, a hydrogenated derivative thereof, or combinations thereof. In some embodiments, the conjugated dienes comprise 4 to 12 carbon atoms. Exemplary conjugated dienes useful in the second block copolymer include any of the exemplary conjugated dienes described above.

[0038] In some embodiments, at least one glassy block, and in some embodiments, each glassy block of the second block copolymer comprises a polymerized monovinyl aromatic monomer. In some embodiments, the monovinyl aromatic monomers comprise 8 to 18 carbon atoms. Exemplary polymerized monovinyl aromatic monomers useful in the second block copolymer include any of the exemplary polymerized monovinyl aromatic monomer, as described above.

[0039] In some embodiments, block copolymer adhesive compositions of the present disclosure comprise a first high Tg tackifier having a glass transition temperature (Tg) of at least 60 degrees Celsius (° C). As used herein, the terms “high glass transition temperature tackifier” and “high Tg tackifier” refers to a tackifier having a glass transition temperature of at least 60 °C. In some embodiments, the first high Tg tackifier has a Tg of at least 65 °C, or even at least 70°C. In some embodiments, the first high Tg tackifier has a softening point of at least about 115 °C, and, in some embodiments, at least about 120 °C.

[0040] The first high Tg tackifier is primarily compatible with the rubbery block of the first block copolymer. In some embodiments, the first high Tg tackifier is also compatible with the rubbery block of the second block copolymer. In some embodiments, the first high Tg tackifier is primarily compatible with the rubbery block of the first and, optionally, the second block copolymer.

[0041] As used herein, a tackifier is "compatible" with a block if it is miscible with that block. Generally, the miscibility of a tackifier with a block can be determined by measuring the effect of the tackifier on the Tg of that block. If a tackifier is miscible with a block it will alter (e.g., increase) the Tg of that block.

[0042] A tackifier is "primarily compatible" with a block if it is at least miscible with that block, although it may also be miscible with other blocks. For example, a tackifier that is primarily compatible with a rubbery block will be miscible with the rubbery block, but may also be miscible with a glassy block.

[0043] Generally, resins having relatively low solubility parameters tend to associate with the rubbery blocks; however, their solubility in the glassy blocks tends to increase as the molecular weights or softening points of these resins are lowered. Exemplary tackifiers that are primarily compatible with the rubbery blocks include polymeric terpenes, hetero-functional terpenes, coumarone-indene resins, esters of rosin acids, disproportionated rosin acid esters, hydrogenated rosin acids, C5 aliphatic resins, C9 hydrogenated aromatic resins, C5/C9 aliphatic/aromatic resins, dicyclopentadiene resins, hydrogenated hydrocarbon resins arising from C5/C9 and dicyclopentadiene precursors, hydrogenated styrene monomer resins, and blends thereof.

[0044] In some embodiments, the block copolymer adhesive compositions include a second high Tg tackifier that is primarily compatible with the glassy block(s) of the first block copolymer and, optionally, with the glassy block(s) of the second block copolymer. Generally, a tackifier that is primarily compatible with a glassy block is miscible with the glassy block and may be miscible with a rubbery block.

[0045] Generally, resins having relatively high solubility parameters tend to associate with the glassy blocks; however, their solubility in the rubbery blocks tends to increase as the molecular weights or softening points of these resins are lowered. Exemplary tackifiers that are primarily compatible with the glassy blocks include coumarone-indene resins, rosin acids, esters of rosin acids, disproportionated rosin acid esters, C9 aromatics, alpha-methyl styrene, C9/C5 aromatic-modified aliphatic hydrocarbons, and blends thereof.

[0046] In some embodiments, the pressure sensitive adhesives of the present disclosure further comprise at least one component selected from the group consisting of a low Tg tackifier, a plasticizer, and combinations thereof. As used herein, the term "low glass transition temperature tackifier" refers to a tackifier having a glass transition temperature of less than 60 °C. Exemplary low Tg tackifiers include polybutenes.

[0047] Generally, a plasticizer is compatible with one or more blocks of the linear block copolymer, and/or one or more blocks of the multi-arm block copolymer. Generally, a plasticizer that is compatible with a block will be miscible with that block and will lower the Tg of that block. Exemplary plasticizers include naphthenic oils, liquid polybutene resins, polyisobutylene resins, and liquid isoprene polymers.

[0048] In some embodiments, the ratio of multi-arm block copolymers to linear block copolymers ranges from 1.5:1 to 9:1. In some embodiments, the ratio of multi-arm block copolymers to linear block copolymer is at least 1.85:1, or even at least 3:1. In some embodiments, the ratio of multi-arm block copolymers to linear block copolymers is no greater than 5.7:1, or even no greater than 4:1.

[0049] In some embodiments, the ratio of the total amount of high glass transition temperature tackifiers to block copolymers ranges from 0.8:1 to 1.25:1. In some embodiments, the ratio of the total amount of high Tg tackifiers to block copolymers is at least 0.85:1, or even at least 0.9:1. In some embodiments, the ratio of the total amount of high Tg tackifiers to block copolymers is no greater than 1.15:1, or even no greater that 1.1 to 1.

[0050] In some embodiments, the ratio of the rubbery block compatible high Tg tackifier to the glassy block compatible high Tg tackifier is ranges from 1:1 to 9:1. In some embodiments, the ratio of the rubbery block compatible high Tg tackifier to the glassy block compatible high Tg tackifier is at least 1.25:1, or even at least 1.5:1. In some embodiments the ratio of the rubbery block compatible high Tg tackifier to the glassy block compatible high Tg tackifier is no greater than 4:1, or even no greater than 3:1.

[0051] In some embodiments, the ratio of the combination of the block copolymers and high Tg tackifiers to the acrylate component is at least 8.3:1. In some embodiments, the ratio of the combination of the block copolymers and high Tg tackifiers to the acrylate component is at least 12.5:1, at least 22:1, at least 90:1, or even at least 180:1. In some embodiments, the pressure sensitive adhesive comprises no greater than 10% by weight of the acrylate component, in some embodiments, no greater than 8%, no greater than 4%, no greater than 1% or even no greater than 0.5% by weight.

[0052] In some embodiments, the ratio of the combination of the block copolymers, high Tg tackifiers, and acrylate component to the liquid plasticizer ranges from 32:1 to 10:1. In some embodiments, the ratio of the combination of the block copolymers, high Tg tackifiers, and acrylate component to the liquid plasticizer is no great than 25:1, or even no greater than 20:1. In some embodiments, the ratio of the combination of the block copolymers, high Tg tackifiers, and acrylate component to the liquid plasticizer is at least 12.5:1.

[0053] In some embodiments, the pressure sensitive adhesive of the present disclosure is a hot melt adhesive. As used herein, a hot melt adhesive is a polymer or blended polymeric material with a melt viscosity profile such that it can be coated on a substrate or carrier in a thin layer at a process temperature significantly above normal room temperature, but retains useful pressure-sensitive adhesive characteristics at room temperature.

[0054] The pressure-sensitive adhesive compositions of the present invention can be made using methods known in the art. For example, they can be made by dissolving the block copolymers, suitable tackifiers, any plasticizer(s), and any other additives in a suitable solvent, and coating onto a substrate (e.g., release liner, tape backing, core, or panel) using conventional means (e.g., knife coating, roll coating, gravure coating, rod coating, curtain coating, spray coating, air knife coating). In some embodiments, the pressure-sensitive adhesive is prepared in a substantially solvent-free process (i.e., the adhesive contain no greater than about 20 wt. % solvent, in some embodiments, no greater than about 10 wt. % solvent and, in some embodiments, no greater than about 5 wt. % solvent, in some embodiments, no greater than 1 wt. % solvent, or even no greater than trace amounts of solvent (i.e., essentially no solvent). Such substantially solvent-free processes are known and include, e.g., compounding by calendaring or roll milling, and extruding (e.g., single. screw, twin screw, disk screw, reciprocating single screw, pin barrel single screw, etc.). Commercially available equipment such as BRABENDER or BANBURY internal mixers are also available to batch mix the adhesive compositions. After compounding, the adhesive may be coated through a die into a desired form, such as a layer of adhesive, or it may be collected for forming at a later time.

[0055] In another aspect, the present disclosure provides a tape comprising a backing and a pressure sensitive skin adhesive bonded to at least one major surface of the backing. In some embodiments, the tape comprises a core and a skin adhesive bonded to both major surfaces of the core, wherein at least one skin adhesive is a pressure sensitive adhesive. In some embodiments, both skin adhesives are pressure sensitive adhesives. In some embodiments, both skin adhesives are the same adhesive. In some embodiments, the skin adhesives are different adhesives.

[0056] As used herein, the term “core” may be used interchangeably with the term “backing” when referring to a double-sided tape construction, i.e., a tape construction having an adhesive layer on both major surfaces of the backing or core.

[0057] At least one skin adhesive of the tapes of the present disclosure is a pressure sensitive adhesive comprising a blend of a block copolymer adhesive composition and an acrylic adhesive composition, as described herein. In some embodiments, the second skin adhesive may be a heat-activated adhesive. In some embodiments, both skin adhesives are pressure sensitive adhesives comprising a blend of a block copolymer adhesive composition and an acrylic adhesive composition, as described herein.

[0058] In some embodiments, one or more of the skin adhesive may be directly bonded to a major surface of a backing or core. In some embodiments, one or more of the skin adhesives may be indirectly bonded to a major surface of a backing or core. In some embodiments, e.g., a primer layer may be interposed between the skin adhesive and the major surface. Useful primers are generally known and include, e.g., the primers described in U.S. Patent No. 5,677,376 (Groves) and U.S. Patent No. 5,605,964 (Groves).

[0059] Any known backing or core may be used. Exemplary backings include papers and polymeric films (e.g., polyethylene, polyurethane, polyester, and polypropylene), metal foils, and woven and non-woven webs. In some embodiments, a backing or core comprising a foam may be used, e.g., open cell foams or closed cell foams. In some embodiments, the foam may comprise thermoplastic foam. In some embodiments, the foam may comprise a thermoset foam. Exemplary foams include acrylic foams, polyethylene foams, and polyurethane foams. Exemplary foams are also described in, e.g., the Handbook of Polymer Foams, David Eaves, editor, published by Shawbury, Shrewsbury, Shropshire, UK : Rapra Technology, 2004.

[0060] Referring to **FIG. 1**, exemplary tape **10**, according to some embodiments of the present disclosure, comprises backing (or core) **30** and two adhesive layers. First adhesive layer **20** is bonded to first major surface **31** of backing **30**, while second adhesive layer **40** is bonded to second major surface **32** of backing **30**. As shown in **FIG. 1**, both first adhesive layer **20** and second adhesive layer **40** are directly bonded a major surface of backing **30**. In some embodiments, one or both adhesive layer may be indirectly bonded to backing **30**. For example, in some embodiments, one or more additional layers (e.g., primers, adhesion promoting layers, films, webs, scrims, and the like) may be interposed between the backing and an adhesive layer.

[0061] In another aspect, the present disclosure provides a bonded composite. As used herein, a bonded composite comprises a first substrate having a first major surface and a second substrate having a first major surface, wherein the first major surface of the first substrate is bonded to the first major surface of the second substrate via a bonding interface. In the bonded composites of the present disclosure, the bonding interface comprises a core having a first skin adhesive bonded to the first major surface of the core and a second skin adhesive bonded to the second major surface of the core. At least one skin adhesive of the bonding interface of the present disclosure is a pressure sensitive adhesive comprising a blend of a block copolymer adhesive composition and an acrylic adhesive composition, as described herein. In some embodiments, both skin adhesives are pressure sensitive adhesives comprising a blend of a block copolymer adhesive composition and an acrylic adhesive composition, as described herein.

[0062] In some embodiments, the first substrate comprises metal, glass, ceramic, or polymeric materials, and combinations thereof. In some embodiments, the first substrate includes a primed, painted, or polymeric surface. In some embodiments, the painted surface may comprise an automotive paint or clearcoat.

[0063] In some embodiments, the first major surface of the first substrate is a low surface energy surface. As used herein, a low surface energy surface means a surface with a measured surface energy below approximately 35 dyne per centimeter. The surface energy of a surface may be tested according to ASTM Standard D2578. Suitable test kits include, e.g., the ACCU-DYNE surface wetability kit, available from Diversified Enterprises, Claremont, New Hampshire.

[0064] In some embodiments, the second substrate comprises metal, glass, ceramic, or polymeric materials, and combinations thereof. In some embodiments, the second substrate includes a primed, painted, or polymeric surface. In some embodiments, the painted surface may comprise an automotive paint or clearcoat. In some embodiments, the first major surface of the second substrate is a low surface energy surface.

[0065] In some embodiments, the core of the bonding interface comprises a foam, e.g., an open cell foams or a closed cell foams. In some embodiments, the foam comprises a thermoplastic foam. In some embodiments, the foam comprises a thermoset foam. In some embodiments, the foam comprises an acrylic foam. In some embodiments, the foam is a flexible foam. Generally, a flexible foam is a foam which, when in sheet form, can be bent back upon itself with out fracturing. Exemplary foams are described in, e.g., the Handbook of Polymer Foams, David Eaves, editor, published by Shawbury, Shrewsbury, Shropshire, UK : Rapra Technology, 2004.

[0066] Referring to **FIG. 2**, exemplary bonded composite **50**, according to some embodiments of the present disclosure, comprises first substrate **60** bonded to second substrate **70** via bonding interface **110**. Bonding interface **110** comprises a tape comprising backing (or core) **130** and two adhesive layers. First adhesive layer **120** is bonded to a first major surface of backing **130**, while second adhesive layer **140** is bonded to a second major surface of backing **130**. As shown in **FIG. 2**, both first adhesive layer **120** and second adhesive layer **140** are directly bonded a major surface of backing **130**. In some embodiments, one or both adhesive layer may be indirectly bonded to backing **130**.

[0067] As shown in **FIG. 2**, in some embodiments, first adhesive layer **120** is bonded directly to major surface **61** of first substrate **60**. Similarly, in some embodiments, second adhesive layer **140** is directly bonded to major surface **71** of second substrate **70**. In some embodiments, one or both adhesive layers may be indirectly bonded to a major surface of a substrate. For example, in some embodiments, one or more additional layers (e.g., primers, adhesion promoting layers, films, webs, scrims, and the like) may be interposed between an adhesive layer and a substrate.

[0068] In another aspect, the present disclosure provides methods of making a tape comprising a backing or a core, wherein the backing or the core comprises a foam, such as those described above. The tape comprises at least one skin adhesive, wherein at least one skin adhesive is a pressure sensitive adhesive comprising a blend of a block copolymer adhesive composition and an acrylic adhesive composition, as described herein.

[0069] In some embodiments, the method comprises extruding a foam. In some embodiments, the method further comprises extruding at least one skin adhesive. In some embodiments, the foam and at least one skin adhesive are co-extruded. Methods of extruding polymeric foams and methods of coextruding polymer foams and skin adhesives are described, e.g., in U.S. Patent No. 6,103,152 (Gehlsen et al.) and U.S. Patent No. 6,630,531 (Khandpur et al.), both of which are assigned to the present assignee, and are herein incorporated by reference in their entireties.

[0070] In some embodiments, the method of making foam core tapes comprises extruding a foam core and coextruding a first pressure sensitive adhesive as described herein to form a first adhesive skin bonded to the first major surface of the foam core. In some embodiments, the method further comprises extruding a second adhesive to form a second adhesive skin bonded to the second major surface of the foam core.

[0071] In some embodiments, the method of making foam core tapes comprises providing the foam core, which may have been produced by extrusion or any other known means, and applying a first adhesive composition comprising a first pressure sensitive adhesive as described herein to the first surface of the foam core. The first adhesive composition may be applied by, e.g., laminating or coating (e.g., knife coating, roll coating, gravure coating, rod coating, curtain coating, spray coating, or air knife coating).

[0072] In some embodiments, the second adhesive may be independently extruded or co-extruded with the foam and/or the first adhesive. In some embodiments, the second adhesive may be applied to the foam core by, e.g., laminating or coating.

[0073] In some embodiments, the first and/or second adhesive may be cured. Any known curing processes may be used, e.g., thermal curing and radiation curing. In some embodiments, one or both adhesives may crosslinked via exposure to actinic radiation, e.g., electron beam radiation or ultraviolet radiation.

[0074] The following specific, but non-limiting, examples will serve to illustrate the invention. In these examples, all percentages are parts by weight unless otherwise indicated.

Table 1: Summary of materials

AA	acrylic acid	
BA	butyl acrylate	
EA	ethyl acrylate	
IOA	isooctyl acrylate	
2-EHA	2-ethylhexyl acrylate	
IRGACURE 651	2,2 dimethoxy-2-phenylacetophenone	Ciba Specialty Chemicals Corp. (Tarrytown, NY)
IOTG	isooctyl thioglycolate	
KRATON 1161-D	SIS linear block copolymer (15% S, 19% diblock)	Kraton Polymers, Inc. (Houston, Texas)
SANTICIZER 141	2-ethylhexyl diphenyl phosphate	Ferro Co. (Bridgeport, New Jersey)
ESCOREZ 1310LC	aliphatic C-5 tackifying resin	ExxonMobil Chemical LTD. (Southampton, Hampshire, GB)
4900 CMB	Black pigment having a 50/50 blend of carbon black in ethylene vinyl acetate copolymer resin having a melt index of about 150	MA Hanna Color (Suwanee, Georgia)
SUPERESTER W-115	stabilized rosin acid ester	Arakawa Chemical USA (Chicago, IL)
IRGANOX 1010	Pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)proprionate	Ciba Specialty Chemical Co. (Tarrytown, NY)
TINUVIN 328	2-(2-hydroxy-3,5-di-(tert)-amylphenyl)benzotriazole	Ciba Special Chemicals Co. (Tarrytown, NY)
REGALITE R1125	Hydrogenated hydrocarbon resin	Eastman Chemical Co.

		(Kingsport, TN)
CUMAR 130	Aromatic thermoplastic resin	Neville Chemical Co. (Pittsburgh, PA)
NYPLAST 222B	Naphthenic oil plasticizer	Nynas Naphthenics AB (Stockholm, Sweden)
INDOPOL H-8	Polybutene plasticizer	BP Amoco Chemicals (Naperville, IL)

[0075] Preparation of Acrylic Polymers

[0076] Acrylic Polymer 1 (AP-1) was prepared by mixing 45 parts of IOA; 45 parts of BA; 10 parts of AA; 0.15 part IRGACURE 651; and 0.06 part of IOTG. Discreet film packages were formed from a packaging film (0.0635 mm thick ethylene vinyl acetate copolymer film sold as VA-24 Film from CT Film, Dallas, Texas). The AP-1 composition was sealed into the film packages, which measured approximately 10 centimeters (cm) by 5 cm by 0.5 cm thick. While immersed in a water bath maintained between about 21°C and about 32°C, the packages were exposed to ultraviolet (UV) radiation having an intensity of about 3.5 milliWatts per square centimeter (mW/sq cm), and a total energy of about 1680 milliJoules per square centimeter (mJ/sq cm) as measured in NIST units. The method of forming the packages and curing are described in Example 1 of U. S. Patent No. 5,804,610, the subject matter of which is incorporated herein by reference in its entirety.

[0077] Acrylic Polymer 2 (AP-2) was prepared according to the procedure for AP-1, except that 85 parts of 2-EHA; 15 parts of AA; 0.15 parts of IRGACURE 651; and 0.8 part IOTG were used. Similarly, Acrylic Polymer 3 (AP-3) was prepared according to the procedure for Acrylic Polymer 1 except that the composition was 95 parts of 2-EHA; 5 parts of AA; 0.15 part IRGACURE 651; and 0.03 part of IOTG. AP-2 and AP-3 were placed in packages and exposed to UV energy, according to the procedure for AP-1.

[0078] First skin adhesive

[0079] Pressure-sensitive adhesives according to the compositions shown in Table 2 were compounded using a 60 mm, co-rotating twin screw extruder (available from Berstorff), (the "first adhesive extruder"). A polymodal, asymmetric star block copolymer ("PASBC") was prepared according to U.S. Patent No. 5,393,373, the subject matter of which is hereby incorporated by reference in its entirety. The polymer had number average molecular weights of about 4,000 Dalton and about 21,500 Dalton for the two endblocks, 127,000 – 147,000 Dalton for the arm, and about 1,100,000 Dalton for the star measured by SEC (size exclusion chromatography) calibrated using polystyrene standards. The polystyrene content was between 9.5 and 11.5 percent by weight. The mole percentage of high molecular weight arms was estimated to be about 30 %.

[0080] The polymodal asymmetric block copolymer and a linear styrene-isoprene-styrene (SIS) block copolymer (KRATON 1161-D) were dry fed into the first zone of the first adhesive extruder. Using a roll-feed extruder (available from Berstorff), either acrylic polymer AP-1 and AP-2 was heated and fed into the third zone of the first adhesive extruder. Antioxidant (IRGANOX 1010), ultraviolet light absorber (TINUVIN 328), pigmented EVA (4900 CMB) were dry fed; and (REGALITE R1125); (CUMAR 130); and (NYPLAST 222B) were melt fed in to various zones of the first adhesive extruder.

Table 2 – First skin adhesive compositions (Weight Percent).

	First skin adhesive					
	Adh-1	Adh-2	Adh-3	Adh-4	Adh-5	Adh-6
PASBC*	31.44	30.52	31.16	32.19	30.85	30.85
KRATON 1161D	13.47	13.08	13.35	13.80	13.22	13.22
REGALITE R1125	24.92	25.90	26.44	31.90	26.17	26.17
CUMAR 130	16.62	17.26	17.63	10.64	17.45	17.45
NYPLAST 222B	6.50	6.24	6.37	5.34	0	0
INDOPOL H-8	0	0	0	0	6.31	6.31
IRGANOX 1010	1.34	1.31	1.34	1.38	1.32	1.32
TINUVIN 328	1.34	1.31	1.34	1.38	1.32	1.32
4900 CMB	0.38	0.38	0.38	0.37	0.37	0.37
AP-1	4.00	4.00	2.00	0	0	0
AP-2	0	0	0	3.00	3.00	3.00

* Polymodal, asymmetric star block copolymer

Table 2 (cont.) – Pressure sensitive adhesive compositions (Weight Percent).

	First skin adhesive				
	Adh-7	Adh-8	Adh-9	Adh-10	Adh-11
PASBC*	29.59	31.30	31.93	32.23	31.93
Kraton 1161-D	12.62	13.34	13.63	13.77	13.63
REGALITE R1125	29.32	30.85	31.51	31.85	31.51
CUMAR 130	9.77	10.28	10.50	10.61	10.50
NYPLAST 222B	7.90	7.19	7.34	7.42	7.34
INDOPOL H-8	0	0	0	0	0
IRGANOX 1010	1.26	1.32	1.35	1.37	1.35
TINUVIN 328	1.26	1.32	1.35	1.37	1.35
CMB 4900	0.37	0.38	0.38	0.37	0.38
AP-1	0	0	0	0	0
AP-2	7.92	4.00	2.00	1.00	2.00

* Polymodal, asymmetric star block copolymer

[0081] Comparative first skin adhesives CE 1-3

[0082] Pressure-sensitive adhesives according to the compositions shown in Table 3 were compounded in the first adhesive extruder, as described above for first skin adhesive Adh-1, with the following exception. These adhesives of these comparative examples did not contain an acrylic polymer; therefore, no acrylic polymer was fed in to the second zone of the extruder.

Table 3 – Comparative first skin adhesive compositions (Weight Percent).

	Comparative first skin adhesive		
	CE-1	CE-2	CE-3
PASBC*	31.80	33.19	31.80
Kraton 1161-D	13.63	14.23	13.63
Regalite R1125	26.98	32.89	26.98
Cumar 130	17.99	10.97	17.99
Nyplast 222B	6.50	5.50	0
Indopol H-8	0	0	6.50
IRGANOX 1010	1.36	1.42	1.36
TINUVIN 328	1.36	1.42	1.36
CMB 4900	0.38	0.38	0.38

* Polymodal, asymmetric star block copolymer

[0083] Second skin adhesive.

[0084] A pressure sensitive adhesive was compounded in a 60 mm, co-rotating twin screw extruder (available from Berstorff) (the “second adhesive extruder”) in a similar manner as described for the first skin adhesives, except that the composition was as follows: 12.70% of the polymodal, asymmetric star block copolymer (PASBC); 53.10% (by weight) AP-1; 23.30% tackifying resin (ESCOREZ 1310LC); 3.80% tackifying resin (SUPERESTER W115; 6.20% plasticizer (SANTICIZER 141); 0.26% antioxidant (IRGANOX 1010); and 0.25% ultraviolet light absorber (TINUVIN 328).

[0085] Double-sided foam tape samples.

[0086] Foam cores (FC1 – FC-5) having the compositions shown in Table 4 were compounded according to the following procedure. Black pigmented EVA (4900 CMB) was dry fed in to the first zone of a 90 mm, co-rotating twin screw extruder (the "core extruder") (available from Berstorff, Hannover, Germany). Using a roll-feed extruder (available from Berstorff), both acrylic polymers AP-2 and AP-3 were heated and fed into the second zone of the core extruder. DUALITE U010-185D expandable microspheres (expandable microspheres having a shell composition containing acrylonitrile and methacrylonitrile and a core of isopentane, available from Henkel Corporation (Gulph Mills, Pennsylvania)) were fed into the ninth zone of the core extruder.

Table 4: Foam core compositions and properties.

	Component Parts By Weight Percent (%)				Foam Density	Thickness
Composition	AP-3	AP-2	Microspheres	Pigment	g/cm^3	mm
FC-1	91.82	4.8	3	0.38	0.53	0.99
FC-2	90.22	6.6	2.8	0.38	0.55	0.99
FC-3	86.33	9.59	3.7	0.38	0.55	0.98
FC-4	84.73	9.59	5.3	0.38	0.51	0.99
FC-5	94.32	0	5.3	0.38	0.51	0.99

[0087] Three-layer co-extruded tape samples were prepared by coextruding a first skin adhesive layer, a foam core layer as the middle layer, and a second skin adhesive layer. Examples 1-11 use exemplary adhesives according to some embodiments of the present disclosure (Adh-1 through Adh-11). Reference examples 1-3 use comparative adhesive CE-1 through CE-3. The tape constructions are described in Table 5.

[0088] The second skin adhesive was compounded in the second adhesive extruder, as described above, and fed through an outer layer of a three-layer, multi-manifold film die obtained from Cloeren Inc. (Orange, Texas). A foam core layer was compounded in the core extruder, as described above, and fed to the center layer of the three-layer die. A first skin adhesive was compounded in the first adhesive extruder, as described above, and fed to the outer layer of the three-layer die, opposite the second skin adhesive.

[0089] Upon exiting the die, the co-extruded layers were cast onto a silicone release coated casting roll. The roll was cooled with water having a temperature of about 12°C. The cooled extrudate was transferred from the casting roll to a 0.117 mm thick two-side silicone coated polyethylene release liner that was transported at the same speed as the casting roll to the end of the web transport line. The first skin adhesive was in contact with the liner after the transfer whereas the second skin adhesive was open to the air. The liner had differential release properties which allow the tape to be unrolled after winding without liner confusion. Release liners are well-known in the art, and any known release liner may be used. Typically, the release liner comprises a film or paper substrate coated with a release material. Commercially available release liners include, but are not limited to, silicone coated papers, and silicone coated films, such as polyester films. Suitable release liners are also disclosed in U.S. Patents Nos. 6,835,422; 6,805,933; 6,780,484; and 6,204,350 assigned to 3M Innovative Properties Company.

[0090] The foam core and both adhesive skins were crosslinked on-web using electron beam curing while supported on the liner. Two sequential irradiation steps acting on opposite faces of the tape were employed. The first skin adhesive was irradiated through the polyethylene liner, whereas the second skin adhesive was irradiated in an open-face condition. The electron beam units were BROADBAND curtain-type electron beam processors (PCT Engineered Systems, LLC., Davenport, IA), operated according the acceleration voltage and dose conditions provided in Table 5.

Table 5: Compositions of three-layer tape samples.

				First skin adhesive		Second skin adhesive	
Ex.	First skin adhesive	Acrylic Polymer (wt. %)	Foam Core	Acceleration voltage (keV)	Dose (Mrad)	Acceleration voltage (keV)	Dose (Mrad)
1	Adh-1	4	FC-1	247	11.5	235	10
2	Adh-2	4	FC-2	247	11.5	235	10
3	Adh-3	2	FC-2	247	11.5	235	10
4	Adh-4	3	FC-3	250	10	230	10
5	Adh-5	3	FC-3	250	10	230	10
6	Adh-6	3	FC-3	275	7	230	10
7	Adh-7	7.9	FC-4	250	9	230	10
8	Adh-8	4	FC-4	250	9	230	10
9	Adh-9	2	FC-4	250	9	230	10
10	Adh-10	1	FC-4	250	9	230	10
11	Adh-11	2	FC-5	250	9	230	10
RE-1	CE-1	0	FC-2	247	11.5	235	10
RE-2	CE-2	0	FC-3	245	11.5	230	10
RE-3	CE-3	0	FC-3	245	11.5	230	10

[0091] The cured adhesive tapes were tested for adhesion to low surface energy automotive paints according to the “Breakaway and Continuous Peel Adhesion” (BACP) , METHOD described in Ford Motor Co. Specification WSB-M3G138-B. Tensile testing was carried out using an MTS Model 1122 tensile tester (MTS Systems Corp., Eden Prairie, MN) equipped with TestWorks 4 software programmed to calculate the breakaway load value, averaged continuous peel value, and total energy.

[0092] The test surfaces were steel panels painted with automotive paint systems comprising a base electrocoat, pigmented basecoat, and a low surface energy, carbamate-crosslinked unpigmented acrylic-based clearcoat. The experimental tapes were adhered to the clearcoat for testing. Test Surface 1 had a measured surface energy (Accu-Dyne solutions) of 33 dynes/cm, and Test Surface 2 had a measured surface energy of 32 dynes/cm.

[0093] After applying the test tape to the test surface, the samples were conditioned prior to testing. First, the samples were conditioned at room temperature for three days. Next, the samples were conditioned at 38 °C and 100% relative humidity for six days. Four samples were tested for each tape, and the average result is reported in Table 6. The observed failure mode(s) for each set of samples is also reported in Table 6.

Number	Failure mode
1	Foam split
2	Combination of foam split and clean removal
3	Pop-off

Table 6: Compositions of three-layer tape samples.

Ex.	First skin adhesive	Acrylic Polymer (wt. %)	Test surface	Breakaway Load (Newtons)	Peel (N/cm)	Peel Failure Mode	Total Energy (N·cm)
1	Adh-1	4	1	122.1	48.4	1	764
2	Adh-2	4	1	126.7	51.2	1	803
3	Adh-3	2	1	130.9	49.7	1	787
RE-1	CE-1	0	1	120.4	31.2	1,2	503
4	Adh-4	3	1	99.2	45.7	1	693
5	Adh-5	3	1	109.3	49.0	1	797
6	Adh-6	3	1	98.4	43.4	1	662
RE-2	CE-2	0	1	88.0	18.5	N/A	N/A
RE-3	CE-3	0	1	75.7	17.5	3	285
7	Adh-7	7.9	1	102.5	51.7	1,3	770
8	Adh-8	4	1	105.1	50.6	1	760
9	Adh-9	2	1	104.4	53.4	1,3	796
10	Adh-10	1	1	103.0	54.1	1	801

11	Adh-11	2	1	93.0	37.8	1	588
12	Adh-1	4	2	126.6	49.1	1	780
13	Adh-2	4	2	131.6	51.4	1	812
14	Adh-3	2	2	127.8	53.2	1	830
RE-4	CE-1	0	2	127.5	50.7	1	796

[0094] Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

What is Claimed is:

1. A pressure sensitive adhesive composition comprising:

   (A) 92 to 99.9 parts of a block copolymer adhesive composition comprising:

      (a) a first block copolymer comprising

         (i) at least one rubbery block comprising a first polymerized conjugated diene, a hydrogenated derivative thereof, or combinations thereof; and

         (ii) at least one glassy block comprising a first polymerized monovinyl aromatic monomer; and

   (B) 0.1 to less than 10 parts, optionally less than 9 parts, optionally less than 8 parts, optionally less than 5 parts, optionally less than 3 parts, of an acrylic adhesive composition comprising:

      (i) 70 to 100 parts of at least one acrylic or methacrylic ester of a non-tertiary alkyl alcohol, wherein the non-tertiary alkyl alcohol contains 4 to 20 carbon atoms; and

      (ii) 0 to 30 parts of a copolymerized reinforcing monomer.

2. The pressure sensitive adhesive according to claim 1, wherein the first block copolymer is a multi-arm block copolymer of the formula Q_n-Y, wherein:

   (a) Q represents an arm of the multi-arm block copolymer and each arm independently has the formula R-G, wherein:

      (i) R represents the rubbery block; and

      (ii) G represents the glassy block;

   (b) n represents the number of arms and is a whole number of at least 3; and

   (c) Y is the residue of a multifunctional coupling agent.

3. The pressure sensitive adhesive according to claim 2, further comprising a second block copolymer comprising at least one rubbery block comprising a polymerized second conjugated diene, a hydrogenated derivative thereof, or combinations thereof; and at least one glassy block comprising a second polymerized monovinyl aromatic monomer.

4. The pressure sensitive adhesive according to claim 3, wherein the second block copolymer is a linear block copolymer, optionally wherein the linear block copolymer is a triblock copolymer.

5. The pressure sensitive adhesive according to claim 4, wherein the second block copolymer is a triblock copolymer selected from the group consisting of styrene-isoprene-styrene, styrene-butadiene-styrene, styrene-ethylene-butadiene-styrene, and combinations thereof.

6. The pressure sensitive adhesive of any one of the preceding claims, wherein the block copolymer adhesive composition further comprises a first high Tg tackifier having a Tg of at least 60 degrees C, wherein the first high Tg tackifier is compatible with at least one rubbery block.

7. The pressure sensitive adhesive according to claim 6, wherein the block copolymer adhesive composition further comprises a second high Tg tackifier having a Tg of at least 60 degrees C, wherein the second high Tg tackifier is compatible with the at least one glassy block.

8. The pressure sensitive adhesive according to any one of the preceding claims further comprising at least one component selected from the group consisting of a low Tg tackifier, a plasticizer, and combinations thereof.

9. The pressure sensitive adhesive according to any one of the preceding claims, wherein the first conjugated diene is selected from the group consisting of isoprene, butadiene, ethylene butadiene copolymers, and combinations thereof.

10. The pressure sensitive adhesive according to any one of claims 3-9, wherein the second conjugated diene is selected from the group consisting of isoprene, butadiene, ethylene butadiene copolymers, and combinations thereof.

11. The pressure sensitive adhesive according to any one of the preceding claims, wherein the first monovinyl aromatic monomer is selected from the group consisting of styrene, styrene-compatible blends, and combinations thereof.

12. The pressure sensitive adhesive according to any one of claims 3-11, wherein the second monovinyl aromatic monomer is selected from the group consisting of styrene, styrene-compatible blends, and combinations thereof.

13. The pressure sensitive adhesive according to any one of the preceding claims, wherein the first block copolymer is a polymodal, asymmetric star block copolymer.

14. The pressure sensitive adhesive according to any one of claims 2-13, wherein n is a whole number ranging from 3 to 5, inclusive, optionally wherein n is 4.

15. The pressure sensitive adhesive according to any one of the preceding claims, wherein the acrylic or methacrylic acid ester is selected from the group consisting of isooctyl acrylate, 2-ethylhexyl acrylate, butyl acrylate, isobornyl acrylate, and combinations thereof.

16. The pressure sensitive adhesive according to any one of the preceding claims, wherein the copolymerized reinforcing monomer is selected from the group consisting of acrylic acid, methacrylic acid, 2-carboxyethyl acrylate, N,N' dimethyl acrylamide, N,N' diethyl acrylamide, butyl carbamoyl ethyl acrylate, and combinations thereof.

17. The pressure sensitive adhesive according to any one of claims 6-16, wherein the Tg of the first high Tg tackifier is at least 65 degrees C.

18. The pressure sensitive adhesive according to any one of claims 6-17, wherein the Tg of the second high Tg tackifier is at least 65 degrees C.

19. The pressure sensitive adhesive according to any one claim 6-18, wherein the first high Tg tackifier has a softening point of at least about 115 degrees C, optionally, at least about 120 degrees C.

20. The pressure sensitive adhesive according to any one of claims 6-19, wherein the first high Tg tackifier has a softening point of at least about 115 degrees C, optionally, at least about 120 degrees C.

21. The pressure sensitive adhesive according any one claims 6-20, wherein the first high Tg tackifier is selected from the group consisting of polymeric terpenes, hetero-functional

terpenes, coumarone-indene resins, esters of rosin acids, disproportionated rosin acid esters, hydrogenated rosin acids, C5 aliphatic resins, C9 hydrogenated aromatic resins, C5/C9 aliphatic/aromatic resins, dicyclopentadiene resins, hydrogenated hydrocarbon resins arising from C5/C9 and dicyclopentadiene precursors, hydrogenated styrene monomer resins, and blends thereof.

22. The pressure sensitive adhesive according to any one of claims 8-21, wherein the low Tg tackifier is selected from the group consisting of polybutene resins.

23. The pressure sensitive adhesive according to any one of claims 8-22, wherein the plasticizer is selected from the group consisting of naphthenic oils, liquid polybutene resins, polyisobutylene resins, and liquid isoprene polymers.

24. The pressure sensitive adhesive according to any one of the preceding claims, wherein the pressure sensitive adhesive is a hot melt adhesive.

25. The pressure sensitive adhesive according to any one of claims 1-23, wherein the pressure sensitive adhesive is a solvent-based adhesive.

26. The pressure sensitive adhesive according to any one of claims 4-25, wherein the ratio of multi-arm block copolymers to linear block copolymers ranges from 1.5:1 to 9:1, optionally wherein the ratio of multi-arm block copolymers to linear block copolymer is at least 1.85:1, and optionally wherein the ratio of multi-arm block copolymers to linear block copolymers is no greater than 5.7:1.

27. The pressure sensitive adhesive according to any one of claims 7-26, wherein the ratio of the total amount of high Tg tackifiers to block copolymers ranges from 0.8:1 to 1.25:1, optionally wherein the ratio of the total amount of high Tg tackifiers to block copolymers is at least 0.85:1, and optionally wherein, the ratio of the total amount of high Tg tackifiers to block copolymers is no greater than 1.15:1.

28. The pressure sensitive adhesive according to any one of claims 7-27, wherein the ratio of the rubbery block compatible high Tg tackifier to the glassy block compatible high Tg tackifier is ranges from 1:1 to 9:1, optionally wherein the ratio of the rubbery block compatible high Tg tackifier to the glassy block compatible high Tg tackifier is at least

1.25:1, optionally the ratio of the rubbery block compatible high Tg tackifier to the glassy block compatible high Tg tackifier is no greater than 4:1.

29. The pressure sensitive adhesive according to any one of claims 7-28, the ratio of the combination of the block copolymers and high Tg tackifiers to the acrylate component is at least 8.3:1; optionally wherein the ratio of the combination of the block copolymers and high Tg tackifiers to the acrylate component is at least 12.5:1.

30. The pressure sensitive adhesive according to any one of claims 8-28, wherein the ratio of the combination of the block copolymers, high Tg tackifiers, and acrylate component to the liquid plasticizer ranges from 32:1 to 10:1, optionally wherein, the ratio of the combination of the block copolymers, high Tg tackifiers, and acrylate component to the liquid plasticizer is no great than 25:1, and optionally wherein, the ratio of the combination of the block copolymers, high Tg tackifiers, and acrylate component to the liquid plasticizer is at least 12.5:1.

31. A tape comprising a foam backing having a first major surface and a second major surface; and a first adhesive skin bonded to the first major surface, wherein the first adhesive skin comprises a first pressure sensitive adhesive according to any one of the preceding claims.

32. The tape according to claim 31 further comprising a second adhesive skin bonded to the second major surface.

33. The tape according to claim 32, wherein the first pressure sensitive adhesive and the second adhesive are the same adhesive.

34. A tape comprising a foam backing having a first major surface and a second major surface, a first adhesive skin comprising a first pressure sensitive adhesive bonded to the first major surface, and a second adhesive skin comprising a second pressure sensitive adhesive bonded to the second major surface, wherein the first pressure sensitive adhesive and the second pressure sensitive adhesive each independently comprise a pressure sensitive adhesive according to any one of claims 1-30.

35. The tape according to anyone of claims 31-34, wherein the foam comprises a thermoplastic foam.

36. The tape according to anyone of claims 31-34, wherein the foam comprises a thermoset foam.

37. The tape according to anyone of claims 31-34, wherein the foam comprises an acrylic foam.

38. A method of making the tape according to any one of claims 31-37, comprising extruding the foam backing and coextruding the first pressure sensitive adhesive to form the first adhesive skin bonded to the first major surface of the foam backing.

39. The method of claim 38, further comprising extruding the second adhesive to form a second adhesive skin bonded to the second major surface of the foam backing.

40. The method of claim 39, wherein extruding the second adhesive comprises coextruding the second adhesive with the first pressure sensitive adhesive and the foam backing.

41. The method according to claims 38 and 39, wherein the second adhesive is a pressure sensitive adhesive according to any one of claims 1-30.

42. A method of making the tape according to any one of claims 31-37, comprising providing the foam backing, and applying a first adhesive composition comprising the first pressure sensitive adhesive to the first surface of the foam backing.

43. The method of claim 42, wherein applying the first adhesive composition comprises laminating.

44. The method of claim 43 wherein applying first adhesive composition comprises coating, optionally wherein the method further comprises crosslinking the first adhesive composition, optionally wherein crosslinking the first adhesive composition comprises radiation crosslinking.

45. The method according to any one of claims 42-44, wherein the first adhesive composition is a solvent-based adhesive, and the method further comprises drying the first adhesive composition.

46. The method according to any one of claims 42-45, further comprising applying a second adhesive composition to the second surface of the foam.

47. The method according to claim 46, wherein the second adhesive composition comprises a pressure sensitive adhesive according to any one of claims 1-30.

48. The method of claim 46 or 47, wherein applying the second adhesive composition comprises laminating.

49. The method of claim 46 or 47 wherein applying second adhesive composition comprises coating, optionally wherein the method further comprises crosslinking the second adhesive composition, optionally wherein crosslinking the second adhesive composition comprises radiation crosslinking.

50. The method according to any one of claims 46-49, wherein the second adhesive composition is a solvent-based adhesive, and the method further comprises drying the second adhesive composition.

51. A bonded composite comprising:
a first substrate having a first surface;
a second substrate having a second surface; and
a bonding interface between the first surface of the first substrate and the second surface of the second substrate, wherein the bonding interface comprises a pressure sensitive adhesive according to any of claims 1-30.

52. A bonded composite comprising:
a first substrate having a first surface;
a second substrate having a second surface; and
a bonding interface between the first surface of the first substrate and the second surface of the second substrate, wherein the bonding interface comprises a tape according to any of claims 31-37.

53. The bonded composite according to claim 51 or 52, wherein the first surface has a surface energy of less than 35 dyne per centimeter.

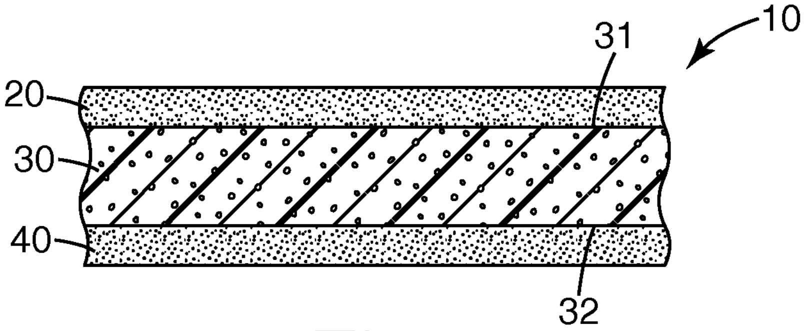


Fig. 1

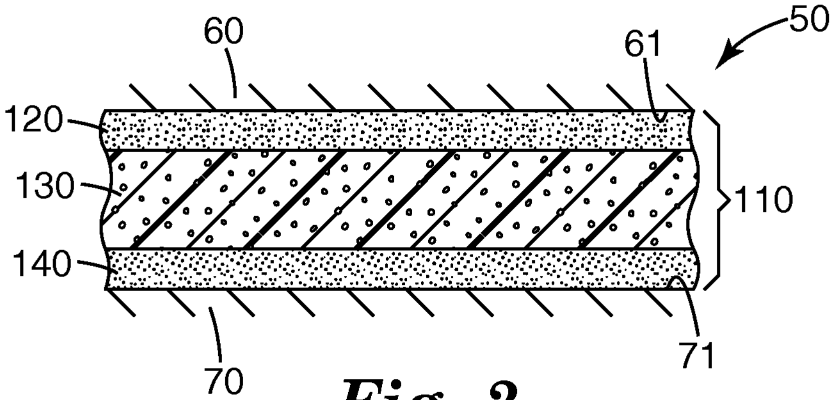


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2007/083741

A. CLASSIFICATION OF SUBJECT MATTER

C09J 153/00(2006.01)i, C09J 153/02(2006.01)i

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)

IPC 8: C09J, C08F, A61K, B32B

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

Korean Utility models and applications for Utility models since 1975
Japanese Utility models and applications for Utility models since 1975

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

eKIPASS (KIPO internal), PAJ, USAPP, USP

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,503,621 B1 (MA, J. et al.) 07 January 2003 See abstract, and column 3, line 17 ~ column 9, line2, and table 2.	1 - 6
Y	See all examples.	7
Y	KR 10-0235818 B1 (DOW CHEM. CO., LTD. et al.) 15 December 1999 See abstract and page 3 ~ 4.	7
A	US 7,084,209 B2 (EVERAERTS, A. I. et al.) 01 August 2006 See the whole document.	1 - 7
A	US 6,579,941 B1 (SASAKI, Y. et al.) 17 June 2003 See the whole document.	1 - 7
A	US 6,632,522 B1 (HYDE, P. D. et al.) 14 October 2003 See the whole document.	1 - 7
A	JP 09-053059 A (NIPPON JEON CO., LTD.) 25 February 1997 See the whole document.	1 - 7

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"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
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 10 MARCH 2008 (10.03.2008)	Date of mailing of the international search report **10 MARCH 2008 (10.03.2008)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer CHO Han Sol Telephone No. 82-42-481-5580

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2007/083741

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 8 ~ 53
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2007/083741

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6503621 B1	07.01.2003	AT 327296 E	15.06.2006
		AU 200054921 A1	20.08.2001
		AU 200054921 A5	20.08.2001
		BR 200017096 A	14.01.2003
		CA 2398498 A1	16.08.2001
		CN 1311045 C	18.04.2007
		CN 1433452 A	30.07.2003
		DE 60028256 C0	29.06.2006
		DE 60028256 T2	29.03.2007
		EP 1263913 A1	11.12.2002
		EP 1263913 B1	24.05.2006
		JP 15522275	22.07.2003
		KR 10-2002-0075911 A	07.10.2002
		KR 10-0732927 B1	29.06.2007
		MX PA02007618 A	28.01.2003
		WO 01-59025 A1	16.08.2001
KR 10-0235818 B1	15.12.1999	AU 2145092 A1	30.12.1992
		CA 2109826 C	07.10.2003
		CA 2109826 C	26.11.1992
		DE 69223783 C0	05.02.1998
		DE 69223783 T3	24.07.2003
		EP 588923 A1	30.03.1994
		EP 588923 B2	16.10.2002
		EP 588923 B1	29.12.1997
		ES 2110502 T3	16.02.1998
		ES 2110502 T5	01.05.2003
		JP 65-09595 A	27.10.1994
		KR 10-1994-0701833 A	28.06.1994
		US 5292819 A	08.03.1994
		US 5372870 A	13.12.1994
		US 5399627 A	21.03.1995
		WO 92-20725 A1	26.11.1992
US 7084209 B2	01.08.2006	US 2004-0202881 A1	14.10.2004

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2007/083741

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6579941 B1	17.06.2003	AT 286100 E	15.01.2005
		AU 2001267072 B2	24.12.2001
		AU 200167072 A1	24.12.2001
		AU 200167072 A5	24.12.2001
		BR 200111620 A	16.09.2003
		CA 2412527 AA	20.12.2001
		CA 2412527 A1	20.12.2001
		CN 1561377 A	05.01.2005
		DE 60108123 C0	03.02.2005
		DE 60108123 T2	19.01.2006
		EP 1290099 A2	12.03.2003
		EP 1290099 B1	29.12.2004
		MX PA02012286 A	06.06.2003
		PL 360871 A1	20.09.2004
		US 2004-0058171 A1	25.03.2004
		US 6841257 B2	11.01.2005
		WO 01-96488 A2	20.12.2001
		WO 01-96488 A3	04.07.2002
US 6632522 B1	14.10.2003	AT 231539 E	15.02.2003
		AU 6898596 A1	17.07.1997
		AU 705376 B2	20.05.1999
		BR 9612254 A	13.07.1999
		CA 2241032 AA	03.07.1997
		CA 2241032 C	28.10.2003
		DE 69625931 C0	27.02.2003
		DE 69625931 T2	05.02.2004
		EP 868498 A1	07.10.1998
		EP 868498 B1	22.01.2003
		JP 2000-502385 A	29.02.2000
		KR 10-1999-0076634 A	15.10.1999
		KR 10-0413983 B1	17.06.2005
		NZ 316689 A	29.04.1999
		US 6063838 A	16.05.2000
		WO 97-23577 A1	03.07.1997
JP 09-053059 A	25.02.1997	JP 2000119619 A2	25.04.2000
		JP 2000303049 A2	31.10.2000
		JP 3464772 B2	10.11.2003
		JP 3465833 B2	10.11.2003
		JP 3609321 B2	12.01.2005