Medical-Grade Acrylic Adhesives for Skin Contact

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SYNOPSIS

Pressure-sensitive acrylic adhesives for application to skin are made from 2-ethylhexyl acrylate, isooctyl acrylate or *n*-butyl acrylate copolymerized with polar functional monomers such as acrylic acid, methacrylic acid, vinyl acetate, methyl acrylate, *N*-vinylcaprolactam, or hydroxyethyl methacrylate. Functional comonomers increase cohesive strength, provide surface polarity, and enhance wear performance. Tack, adhesion to skin, adhesive transfer to skin, and wear performance of the adhesive are governed by the molecular weight, glass transition temperature, and the viscoelastic behavior of the adhesive. Viscoelastic properties of the adhesive as measured by the Williams plasticity number (WPN), dynamic storage modulus (G'), dynamic loss modulus (G''), and tan δ are important polymer properties for good wear performance. Sweating skin, a moist environment, and physical activity are the most important factors influencing the failure of an adhesive tape during wear. A medical-grade adhesive for application to human skin should be hypoallergenic. Medical-grade adhesives are utilized in making surgical tapes for holding dressings in place, adhesive bandages, adhesive dressings to cover wounds, and surgical operating drapes.

INTRODUCTION

Medical pressure-sensitive adhesives were made traditionally from natural rubber formulations. Today, pressure-sensitive adhesives used in skin contact applications are made more often from acrylic polymers because they are less irritating to skin. Although many adhesive compositions are known, very few of these are completely satisfactory for application to human skin. The requirements for an adhesive are stringent; it must adhere well to human skin during perspiration when the weather is hot, during showering, and physical activity, yet be removable without leaving adhesive residue on the skin's surface and causing skin damage. The adhesive should not irritate the skin.

Bulk properties of the adhesive and surface properties of the adhesive and skin determine the quality of performance on skin. The wear performance depends on adhesive viscoelastic properties and surface energy of the adhesive and skin. Viscoelastic properties dominate in tack, adhesion on, adhesion off, and adhesive transfer to skin on removal.

This article describes the properties of medical-grade acrylic pressure-sensitive adhesives that are intended for skin contact. The work was carried out to get a better understanding of adhesive properties that determine wear performance of adhesives on skin.

EXPERIMENTAL

Surface energy of skin and adhesives was determined from contact angles measured with a Ramé-Hart NRL contact angle goniometer at 23°C. Water and methylene iodide were used as probing liquids. The sessle drop method was used. The probing liquid droplet was deposited on the surface with a Pasteur pipette. The advancing contact angle was measured on both sides of the drop. Five drops were used for each contact angle value. Adhesive tape was conditioned for 24 h at a known relative humidity (RH) in closed jars containing a saturated solution of an appropriate inorganic salt. The Wu approach was used to determine the surface energy.[1]

Glass transition temperature (T_g) was determined with a differential scanning calorimeter at a heating rate of 10°C per minute.

Williams plasticity number (WPN) was mea-

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Table I Acrylic Monomers for Medical-Grade Adhesives

Hydrophobic		Hydrophilic	
2-ethylhexyl acrylate	2-EHA	Acrylic acid	AA
Isooctyl acrylate	IOA	Methacrylic acid	MAA
n-Butyl acrylate	BA	Vinyl acetate	VAc
		Methyl acrylate	MA
		N-Vinylcaprolactam	NVCL
		Hydroxyethyl methacrylate	HEMA

sured using a Williams Plastometer, manufactured by Scott Testers, Inc., following the procedures of ASTM Method D-926.

Rheometrics Dynamic Spectrometer (RDS) was used to determine storage modulus (G'), loss modulus (G''), and tangent delta (tan δ) the ratio of G'' to G'. RDS is manufactured by Rheometrics, Inc. in Piscataway, New Jersey. The deformation (response) was printed by a Texas Instrument Model 700 terminal. G', G'', and tan δ were computed. Oscillation frequency was varied from 0.01 to 100 rad/s at 25% strain. Five temperatures, 25, 36, 60, 90 and 120°C were selected to run each frequency sweep separately. G' and G'' were plotted against frequency at one of the above temperatures on log-log graph paper. Time–temperature superposition principle was applied to cover the frequency range up to 1000 rad/s. A master graph was constructed by shifting the modulus curves of the above temperatures to the modulus curve of 36°C (skin surface temperature).

Wear performance test on normal skin was conducted utilizing a panel of 24 human subjects. Six to eight 1 × 3 in. strips of adhesive tape were applied to the upper arm and subjects allowed to engage in normal activities and bathing habits. At the end of 24 h, adhesion to skin and adhesive transfer on removal were evaluated utilizing a statistical method of ranking. Adhesion was rated from 0 (tape off) to 7 (perfect adhesion). Adhesive transfer was rated from 0 (no residue) to 2 (heavy residue).

Wear performance test on moist (perspiring) skin was conducted on a panel of 12 human subjects. Six to eight 1 × 3 in. strips of adhesive tape were applied to the back and subjects allowed to walk in a controlled room at 38°C and 50–60% RH. At the end of 1 h, adhesion and adhesive transfer to moist skin were determined as described above.

Table II Surface Energy of In Vivo Human Skin

Temp (°C)	RH (%)	γ^d (J/m^2)	γ^p (J/m^2)	γ_s (J/m^2)	d	p
23	34	0.033	0.005	0.038	0.87	0.13
23	50	0.032	0.010	0.042	0.76	0.24
28	60	0.035	0.019	0.054	0.65	0.35
32	56	0.034	0.017	0.051	0.67	0.33
33	51	0.035	0.022	0.057	0.61	0.39
36	50	0.035	0.022	0.057	0.61	0.39

γ_s = Total surface energy.
γ^d = Dispersive component of surface energy.
γ^p = Polar component of surface energy.
$d = \gamma^d/\gamma_s$ = dispersive fraction.
$p = \gamma^p/\gamma_s$ = polar fraction.

RESULTS AND DISCUSSION

Pressure-sensitive adhesives intended for use on skin have a glass transition temperature below room temperature. The adhesive polymer is made from two or more monomers to give it the T_g desired. The acrylic monomers used to make medical-grade pressure-sensitive acrylic adhesives are given in Table I. The hydrophobic monomer is copolymerized with one or more hydrophilic polar monomers. A larger amount of hydrophobic monomer is incorporated into the adhesive, which provides low T_g and pres-

Table III Surface Energy of Commercial Medical Adhesive

RH (%)	γ^d (J/m^2)	γ^p (J/m^2)	γ_s (J/m^2)
10	0.019	0.008	0.027
20	0.019	0.008	0.027
42	0.019	0.009	0.028
52	0.018	0.008	0.026
81	0.019	0.008	0.027
100	0.019	0.006	0.025

Table IV Surface Energy of Model BA/AA Copolymers, 23°C, 42% RH

BA/AA	γ^d (J/m^2)	γ^p (J/m^2)	γ_s (J/m^2)
100/0	0.027	0	0.027
95/5	0.026	0.002	0.028
90/10	0.033	0.001	0.034
70/30	0.034	0.005	0.039
40/60	0.038	0.003	0.041

Table V Surface Energy of BA/NVCL 95/5 Adhesive

RH (%)	γ^d (J/m^2)	γ^p (J/m^2)	γ_s (J/m^2
10	0.020	0.018	0.038
20	0.019	0.020	0.039
42	0.020	0.018	0.038
52	0.022	0.017	0.039
81	0.019	0.021	0.040
100	0.016	0.032	0.048

sure sensitivity, and smaller amounts of hydrophilic or polar monomers are present in the adhesive composition, which increases cohesive strength and provides surface polarity to the adhesive. The polar comonomers are incorporated into medical acrylic adhesives to enhance wear performance on skin. The polar comonomers contribute greater resistance to shear (cold flow) as well as provide greater tack and adhesion. The adhesion is enhanced by the improved interfacial interactions with skin due to the functional groups, e.g., carboxyl, hydroxyl, and amide.

Surface Energy of Skin

Satisfactory adhesion is expected only when the adhesive wets the skin. A knowledge of the surface energy of skin and adhesive is of interest. In Table II the surface energy of in vivo human skin is given as a function of temperature and RH. At higher temperatures and RH the skin surface exhibits pin point sweating. The surface energy of in vivo human skin increases with temperature and RH. The total surface energy (γ_s) increases from about 0.038 J/m^2 at 23°C and 34% RH to 0.057 J/m^2 at 28°C and 50–60% RH. The dispersive component (nonpolar) (γ^d) of the surface energy remains unchanged at 0.032–0.035 J/m^2 over the temperature and RH range of 23–36°C and 34–60% RH, respectively. The polar component (γ^p) of the surface energy of skin increases from 0.005 to 0.022 J/m^2 over the temperature and RH ranges. During sweating, skin is a high energy surface. The surface of skin and its interaction with the adhesive will have an effect on adhesion.

Surface Properties of Adhesives

The adhesive must properly wet the skin surface in order to bond to skin. The surface energy of the adhesive has to be lower than that of skin in order to obtain good adhesion. The surface energy of a commercial medical-grade acrylic adhesive is not affected by a humid environment, as shown in Table III. Over the range of 10 to 100% RH γ^d is 0.019 J/m^2 and γ^p is 0.008 J/m^2, and γ_s remains 0.027 J/m^2. The adhesive exhibits low surface polarity.

The surface properties of solvent based BA/AA copolymers were studied as a function of copolymer composition. In Table IV γ^p of the model adhesive composition BA/AA was found to be zero for 100% BA as expected; however, γ^p increased only slightly with AA content reaching a plateau at 30% AA. The surface polarity was found to be low for all BA/AA copolymers. The low surface polarity suggests that a large proportion of the carboxyl groups is oriented away from the air–adhesive interface. Other polar groups may behave differently compared to carboxyl groups. γ_s of the BA/AA copolymers increased with AA content reaching a plateau around 30 wt %. As the AA content increases from 0 to 60%, γ^d increases from 0.027 to 0.038 J/m^2, γ^p increases only slightly from 0 to 0.005 J/m^2, and γ_s increases from 0.027 to 0.041 J/m^2. The values found for γ_s suggest that no more than 5% AA should be present in the BA/AA copolymer if good adhesion is to be achieved on substrates possessing surface energies over 0.030 J/m^2. This is relevant since the surface energy of normal human skin is about 0.038–0.042 J/m^2.

The surface polarity of the BA/NVCL 95/5 ad-

G″ = loss modulus, loss energy, energy dissipation, viscous component, plastic component of shear modulus.

G′ = storage modulus, stored energy, elastic component of shear modulus.

$$\tan \delta = G''/G'$$

Figure 1 Definition of loss and storage components of shear modulus.

Table VI Properties of Commercial Medical-Grade Acrylic Adhesives

Glass transition temperature (T_g), °C	−35 to −50
Williams plasticity number (WPN), mm	1.6 to 2.3
Shear modulus, 36°C, 1 rad/s, 25% strain, kPa	
G′ (storage modulus)	10 to 18
G″ (loss modulus)	6 to 9
Tangent δ	0.5 to 0.6

hesive composition with amide functionality is shown in Table V. Over the range 10–100% RH γ^d is about 0.019 J/m^2. γ^p increases from about 0.019 J/m^2 at 10–81% RH to 0.032 J/m^2 at 100% RH. γ_s increases from about 0.039 J/m^2 at 10–81% RH to 0.048 J/m^2 at 100% RH. NVCL enhances surface polarity to a greater extent than AA. The surface polarity of BA/NVCL 95/5 is high. It increases at a high rate in the first 2–4 h of conditioning and increases significantly with RH. It seems that the polymer amide functionality promotes high surface polarity and the substantial increase in surface polarity with increasing humidity. The high polar character perhaps can be associated with the tape's excellent wear performance under severe humidity conditions.

Viscoelastic Behavior

The functional characteristics of a pressure-sensitive adhesive are governed by the viscoelastic behavior of the adhesive. The viscous or flow character determines the adhesive wet-out on skin and apparent tack on touch. The elastic property determines the strength and integrity of the adhesive. A good pressure-sensitive adhesive must have a balance of viscoelastic properties. This balance would include sufficient flow to enable the adhesive to form a bond with skin. Also, it must have internal integrity to maintain the bond. T_g and molecular weight determine the viscoelastic properties. T_g is inherent to the adhesive composition. Molecular weight can be controlled by degree of polymerization. Low molecular weight adhesives will have the viscous property dominate the elastic property. An adhesive with balanced viscoelastic properties can be synthesized by proper selection of monomers and controlling the degree of polymerization. It has been found that polarity of the adhesive enhances the bond the adhesive makes with skin. Therefore, a viscoelastic adhesive with built-in polar functionality will have the necessary polarity for adhesion to skin. Often, copolymerizing a number of selected monomers will give desirable adhesive performance.[2-4] Adhesive polymer molecular structure controls its performance. To characterize the adhesive, Williams plasticity number (WPN) and polymer dynamic modulus (*G*) were determined regularly. *G* indicates the viscoelastic property of the adhesive.[5] Figure 1 defines *G*′, *G*″ and tan δ. Dynamic testing of adhesives is a useful method of analysis of pressure-sensitive adhesives.[6] Viscoelastic properties of the adhesive play an important role in tack and wear performance.

The properties of commercial adhesives are

Table VII Properties of Experimental Adhesives

	BA/NVCL	2-EHA/NVCL/HEMA/AA
	95/5	78.5/15/5/1.5
Glass transition temperature (T_g), °C	−45	−40
Williams plasticity number (WPN), mm	2.1	2.3
Shear modulus, kPa		
36°C, 1 rad/s, 25% strain		
G′ (storage modulus)	13	23
G″ (loss modulus)	8	14
Tangent δ	0.6	0.6

Table VIII Moduli and tan δ as Function of Frequency for BA/NVCL 95/5 Adhesive, 36°C, 25% Strain

Frequency (rad/s)	G'' (kPa)	G' (kPa)	Tan δ
0.01	1.2–2.1	3.5–4.7	0.5–0.6
0.1	2.5–4.2	4.6–8.2	0.5–0.6
1	6.5–8.8	10–18	0.5–0.6
10	12–20	21–30	0.5–0.6
100	28–44	44–62	0.5–0.8
1000	70–110	90–130	0.6–0.9

Table IX Tape Wear Performance of BA/NVCL 95/5 Adhesive

	Backing Material		
	Rayon Cloth	Paper	Vinyl
Adhesion to skin at 24 h	6.4	6.4	6.4
Adhesive transfer at 24 h	0.5	0.5	0.7

shown in Table VI. Commercial medical-grade pressure-sensitive adhesives are viscoelastic materials that exhibit a characteristic shear modulus at skin surface temperature of 36°C. At 36°C, 1 rad/s and 25% strain G' and G'' are in the range shown in Table VI. The shear moduli of the adhesives are in a narrow range near 10 kPa. T_g is low, in the range −35 to −50°C. WPN is a measure of resistance to cold flow and is in the range 1.6–2.3 mm. A WPN above 2.0 mm is more desirable since the adhesive in use leaves only negligible amounts of adhesive on the skin on removal.

The properties of two experimental adhesive compositions BA/NVCL 95/5 and 2-EHA/NVCL/HEMA/AA 78.5/15/5/1.5 synthesized in this work that exhibited good wear performance on normal skin as well as moist (perspiring) skin are given in Table VII. The adhesive is pressure sensitive at that temperature at which G'' is 10 kPa. For good wear on skin, G'' must be a narrow range near 10 kPa at 36°C and 1 rad/s. Moduli and tan δ throughout the frequency range 0.1–1000 rad/s for the BA/NVCL 95/5 adhesive composition are shown in Table VIII. G', G'', and tan δ increase with frequency.

Table IX shows tape wear performance of adhesive BA/NVCL 95/5 coated on rayon cloth, nonwoven paper, and vinyl film tape backing materials. The BA/NVCL 95/5 adhesive composition exhibited high adhesion to skin and low adhesive transfer. Table X gives tape wear performance of experimental adhesive compositions on rayon cloth backing material. It is seen that the adhesive compositions give high adhesion to normal skin as well as moist skin and low adhesive transfer.

Figure 2 defines the viscoelastic behavior of adhesive compositions that show the necessary G' and G'' that result in a balance of tack, adhesion to skin, and adhesive transfer on removal. A good acrylic adhesive for skin contact should have a moduli-frequency relationship shown in Figure 2. Adhesives with moduli higher than the acceptable range will not flow well and will adhere poorly to human skin.

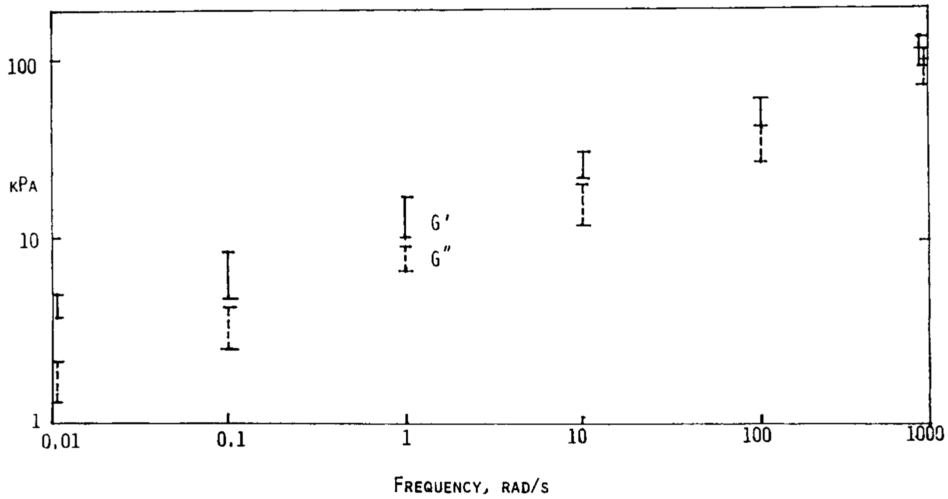

Figure 2 Storage modulus (G') and loss modulus (G'') as a function of frequency for high-performance skin contact acrylic adhesive.

Table X Tape Wear Performance of Adhesive Compositions on Rayon Cloth Backing

	Normal Skin		Moist Skin	
Adhesive Composition	Adhesion at 24 h	Adhesive Transfer at 24 h	Adhesion at 1 h	Adhesive Transfer at 1 h
BA/NVCL 95/5	6.4	0.5	6.3	0.2
2-EHA/BA/IBMA/NVCL 45/20/20/15	6.8	0.6	6.3	0.3
2-EHA/NVCL/HEMA/AA 78.5/15/5/1.5	6.6	0.8	6.4	0
Commercial A	5.9	0.9	5.5	0.3
Commercial B	6.8	0.5	6.3	0.4

Table XI Properties of High-Performance Medical-Grade Acrylic Adhesive 36°C, 25% Strain

Performance Property	Time (s)	Frequency (rad/s)	G'' (kPa)	G' (kPa)	Tan δ
Wear/adhesion/flow	100	0.01	1–3	2–5	0.5–0.6
Wear/adhesion/flow	10	0.1	2–5	4–8	0.5–0.6
Wear/adhesion/flow	1	1	10–18	20–27	0.5–0.7
Tack/peel/transfer	0.01	100	28–42	45–62	0.6–0.7
Tack/peel/transfer	0.002	500	55–80	70–100	0.8
Tack/peel/transfer	0.001	1000	70–110	90–110	0.8–1

Adhesives with moduli below the acceptable range will exhibit poor cohesive strength and will transfer large amounts of adhesive to the skin on removal. Not only must the moduli be within the acceptable range, tan δ must be within the acceptable range as well.

Adhesive wear on skin, tack, and adhesive removal from skin can be related to frequency, long-time phenomena and short-time phenomena as shown in Figure 3. The low frequency (0.01 rad/s) area in Figure 2 is related to long-time phenomena such as adhesive flow behavior, adhesion, and wear performance on skin. The viscous component of the modulus controls adhesive flow and wet-out on skin. The elastic component of the modulus controls the cohesive strength of the adhesive. The adhesive must have flow character as well as cohesive integrity. In the low-frequency area, tan δ should be 0.4–0.7. As tan δ increases above 0.7, the adhesive will exhibit poor cohesive strength and G' and G'' will be below the acceptable range. As tan δ decreases below 0.4, the adhesive will adhere to skin poorly and G' and G'' will be higher than the acceptable range.

The high-frequency area (100–1000 rad/s) is related to short-time phenomena such as tack. An adhesive with good tack exhibits tan δ greater than 0.6 in the high-frequency area.

Table XI gives the moduli required for an acrylic adhesive that will exhibit high wear performance, high tack, low peel force, and low adhesive transfer to skin. The quality of the adhesive can be judged from tan δ in the temperature range or frequency range where it is intended to be used. The ideal situation would involve an adhesive having a relatively high elastic G' and a high plastic G'' in the frequency range of use. For the adhesives synthesized in this work, tan δ is 0.5 in the frequency range 0.01 to 1 rad/s and at higher frequencies tan δ increases to 0.6–1.0.

$t_s = 1/\omega$
t = time in seconds
ω = frequency in rad/s

Figure 3 Relationship of frequency and time.

Table XII Hypoallergenic Clinical Tests for Tape

Cumulative irritation
Maximization
Modified draize

Table XII shows the clinical tests carried out to determine if an adhesive-coated product that is applied to human skin is hypoallergenic. The Cumulative Irritation Test is used to determine the level of dermal irritation. The Maximization Test is carried out to determine sensitization potential. The Modified Draize Test is carried out to determine irritation/sensitization potential of the adhesive coated product. All of the tests are conducted on a panel of human subjects.

CONCLUSION

The wear performance behavior of acrylic adhesive tapes on skin is governed by the surface energy of skin, surface energy of the adhesive, and the viscoelastic behavior of the adhesive. Polar comonomers incorporated into the adhesive composition enhance interfacial interactions with the dynamic skin surface resulting in improved adhesion during sweating when the skin surface energy is higher.

Viscoelastic properties of the adhesive, G' and G'', are related to adhesive tack, wear adhesion to skin, and adhesive transfer to skin on removal. A master graph of G' and G'' against frequency characterizes the adhesive viscoelastic behavior. Adhesive performance is related to low-frequency and high-frequency areas of the master graph. The low-frequency area is related to long-time phenomena such as adhesive flow behavior, adhesive wet-out on skin, and wear adhesion on skin. The high-frequency area is related to short-time phenomena such as adhesive tack, peel force from skin, and adhesive transfer to skin. A high-performance medical-grade acrylic pressure-sensitive adhesive exhibits characteristic shear moduli in a narrow range at skin surface temperature. The results are interpreted in a manner to provide a rational basis for the synthesis and selection of high performance acrylic pressure-sensitive adhesives for skin contact.

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