PRESSURE-SENSITIVE ADHESIVES

Introduction

A **pressure-sensitive adhesive** (PSA) is a viscoelastic material that adheres without the need of more than light pressure and requires no activation by water, solvent, or heat. The bond that is formed should be a permanent bond in the sense that the PSA remains bonded unless removal is desired and activated by the user. The Pressure Sensitive Tape Council suggests a number of other desirable features of many PSAs, including aggressive tack, the ability to adhere to a variety of surfaces, and to be removed cleanly without leaving residue. A common element to all PSAs is a polymeric network. This network may be uncross-linked or cross-linked, and it may also contain nonpolymeric additives that affect adhesive properties.

PSAs were first used commercially in medical applications in the late 1800s and entered commercial industrial use in the 1920s with the advent of masking tape and shortly thereafter, cellophane tape (1). The earliest PSAs used natural rubber and this elastomer remains one of the three main classes of polymers used in PSAs today. The other two are acrylics, which were introduced in the 1950s, and synthetic block copolymers, which were introduced in the 1960s. PSAs are used in a wide variety of industries today with the majority of PSAs delivered in the form of tapes or labels.

PSA Tape Construction

Because of their sticky nature, PSAs are not available as a bulk material for direct use. By far the most common method of using PSAs is as a tape, which is a thin
coating of PSA coated on a flexible backing material. Tapes are available as rolls (eg, box-sealing tape, transparent office tape), pads or sheets (eg, labels, stamps), and individual pieces (eg, medical bandages, decals). The simplest tape form is a single-sided tape in which one side of the backing is completely coated with a PSA. More complex variations are also available: double-sided tapes, strip coated single-sided tapes (eg, repositionable notes), pattern coated single-sided tapes (eg, some wound dressings), and transfer tapes (ie, where the adhesive layer can be applied to a surface without a backing). There are an extremely large number of variations of PSA tapes available, depending on the types of PSA used, backing materials used, and the overall construction.

A general tape construction includes a thin adhesive layer (10–750 µm) attached to a film or paper backing. It is important for the adhesive to remain attached to the backing, and in some cases it is necessary to provide a chemical primer coating or a surface treatment to the backing to ensure this. Flame and corona treatments are common methods to increase the surface energy of the film. In the case of a roll of tape, the side of the tape opposite from the adhesive is usually treated with a release coating to allow for unwinding of the tape (see Fig. 1a for schematic of laminate construction). Stacks or pads of tape may also be made using the same laminate structure with the exception that a release liner is placed under the bottom piece of tape in the pad. Individual pieces of tape (eg, adhesive bandages) can also be prepared by attaching a release liner to each piece of tape (see Fig. 1b). A transfer tape can be made by replacement of the backing with a second release liner. This allows for the user to apply a free film of PSA to a surface by removing one liner, applying the tape, and then removing the second liner. Alternatively, a single liner that is coated on both sides can be used to prepare a roll form of transfer tape.

![Fig. 1. (a) Linerless construction. (b) Liner constructions.](image-url)
Release Surfaces. Since PSAs will adhere to many surfaces with only light to moderate pressure, it is necessary to protect the surface of the PSA until just prior to use. This is done by keeping the PSA in contact with a release surface, that is, a surface that the PSA can be easily peeled from without damaging the PSA. The force needed to remove a PSA from the release surface can vary greatly, ranging from 5 g/25 mm width (premium release) to 2000 g/25 mm width (tight release). The primary requirements are that the force is low enough to avoid splitting the adhesive layer, avoid removing the adhesive from the backing, and avoid deforming the backing during removal. The force of removal should be high enough to avoid having the PSA accidentally come free from the release surface before the user intends to apply it.

Typical release surfaces are made using a release coating, a microscopically thin layer of a low surface energy material that is applied to a supporting substrate. In a roll of tape the release coating is applied to the side of the backing opposite the PSA, so that when rolled upon itself the PSA will be in contact with the release surface (often called a low adhesion backsize in this application). Alternatively, the release coating may be provided on a separate liner that is discarded after being removed from the PSA. The most common release coatings use silicones, long alkyl chain branched polymers, and fluorinated polymers. In addition to providing a low energy surface, many release coatings also contain low molecular weight material that can provide a weak boundary layer between the adhesive and the polymerized portion of the release coating. Although effective for release purposes, the transfer of low molecular weight compounds (particularly silicones) to the surface of the adhesive can sometimes have a negative effect on its subsequent adhesion properties.

Some smooth surfaces have a low enough surface energy that they can serve as a release surface without the addition of a special coating. Many plastics, such as polyethylene, polypropylene, and poly(vinyl chloride), can be release surfaces for some adhesives. Another approach for release without a special coating employs a rough surface, such as a fabric or specially microreplicated surface, that minimizes contact of the PSA with the surface. One should be careful about the tendency of a PSA to flow and fill in crevices when roughness is used to provide release, since this can lead to variations in release force with aging.

Additives. Many PSAs contain additives that, unlike tackifiers or plasticizers, are not intended to affect the inherent PSA properties. Pigments, such as titanium dioxide, are added to change a PSA’s appearance. Metal particles or carbon black can be added to provide electrical conductivity. Drugs such as nitroglycerin, nicotine, or estradiol are added for use in transdermal drug delivery.

The most commonly used additives, however, are stabilizers. These are usually added to protect the PSA from thermal-oxidative degradation or from photodegradation, and are generally present at low levels in a formulation (e.g., about 0.5–2 wt%). Hindered phenols (e.g., Irganox available from Ciba Specialty Chemicals) are most commonly used to prevent thermally induced oxidation, although phosphites and thioethers are also used, sometimes in combination with each other. Ultraviolet absorbers, hindered amines, or simple pigments are most commonly added for protection from photodegradation.
Types of Tape

**Industrial Tape.** Packaging tapes represent the largest volume of PSA tapes and typically use stiff, oriented polypropylene or polyester film backings to provide low extensibility and high shear strength. Addition of glass or plastic fibers in the lengthwise direction is used in filament tape to provide extremely high tensile strength. Masking tape, the earliest example of industrial tape, typically has a crepe paper backing saturated with rubber. The creping allows for conformability when uneven surfaces are masked, paper allows for easy hand tearability, and the rubber saturation provides resistance to paints and solvents. A number of electrical tapes use plasticized PVC or other similar soft backings to provide conformability for wire wrapping applications.

**Consumer and Office Tape.** Clear, cellulose acetate tape is widely used as a general-purpose office tape. Paper tapes of all types provide hand tearability and ease of printing, but are generally not used for applications where high strength is required. Strip coated labels are used as repositionable notes.

**Medical.** Medical tapes often have cloth or cloth-like backings for comfort and breathability. Numerous synthetic breathable, conformable nonwovens (eg, spunlaced polyester such as Sontara, a trademark of DuPont; creped polypropylene) have been developed for such purposes. In some instances, film tapes are preferred to provide a barrier for wound coverage or to increase hydration to speed transdermal drug delivery. Electrically conductive adhesives are used for electrode applications.

**Labels.** Labels typically have a paper backing, but film backed labels are becoming more common. Labels can be both permanent or repositionable, and water dispersible PSAs are used for compatibility with recycling operations.

**Other.** Specialized PSA tapes with virtually any possible backing are also available: hook-and-loop (eg, Velcro, a trademark of Velcro USA, Inc.) backing, reflective tapes, magnetic backing, furniture pads, wall hooks, carpet tiles, etc.

**Specialty Constructions.** Although not solely pressure-sensitive, there are a number of materials which are responsive to other stimuli to either activate, deactivate, or modify PSA-type behavior. Medical adhesives that are not tacky at room temperature, but which undergo a phase transition leading to PSA properties at body temperature, can be used for ease of handling and positioning (2). In a reverse mode, PSAs for medical use that lose their adhesive properties on demand have been developed to make tapes that can be removed with little or no trauma. This transition can be achieved by exposure to light which causes cross-linking and a subsequent stiffening of the PSA (3) or alternatively by swelling with water to effect a phase separation of a water soluble tackifier that disrupts the skin/PSA interface (4,5). Other removal approaches have included application of heating or cooling (2) to effect a phase change of part of the adhesive or application of various solvents or oils to disrupt the interface between PSA and adherend (6). Stretch release tapes allow for a clean and easy removal by using a large stretching deformation in the backing to cause a low removal force at the interface between substrate and PSA (7).
Three main types of test methods are used to determine the physical properties of PSAs: peel, tack, and shear (8) (see also Adhesion). Standard test methods are available for all three properties, and numerous additional variations of tests measuring these properties have also been used (9). Environmental conditions are an extremely important factor in all PSA testing. PSAs are almost always very sensitive to temperature. Many PSAs are also sensitive to humidity, particularly if stored in environments where they can either absorb or lose moisture.

**Peel Adhesion.** In a peel adhesion test a length of tape is adhered to a surface and then the tape is removed by lifting away from the surface in a specified manner. The results are reported as the force required for a given width of tape. It is important to note whether the mode of failure is adhesive (ie, between adhesive and substrate), transfer (ie, between adhesive and film backing), or cohesive (ie, splitting of the adhesive layer). The standard ASTM method (10) involves adhering the tape to a carefully controlled stainless steel test plate and then peeling the tape from the plate at a controlled rate of 15 cm/min and 180° angle (see Fig. 2).

Substrates other than steel (eg, polyethylene, phenolic resin, skin) may be used to try to better model actual use conditions. Similarly, the rate and angle of peel may be modified where appropriate to better match actual usage conditions. Other important factors to control in a peel test include the type of rolldown with which the tape is applied (eg, hardness and diameter of roller, load applied, rate of rolldown, number of passes of roller) and the amount of time the tape is allowed to dwell prior to removal.

It should be understood that, strictly speaking, peel is a tape property rather than a PSA property. That is, the backing or other construction of the tape can often have a strong influence on the peel adhesion. The primary backing effects are the influence on actual peel angle, which can differ from the nominal angle if the backing is sufficiently stiff, and backing deformation, which can occur if the adhesive force is sufficiently large to exceed the strength of the backing.

The peel tests described above are applied rate tests, but peel tests may also be performed as applied load tests. The easiest applied load test to perform is to adhere a tape to a substrate and attach a weight to one end of the tape such that the weight hangs freely below the substrate. The rate at which the load peels the tape from the substrate is then recorded. A low load, low rate variation on this test is a so-called flagging test, in which a tape is wound around a cylinder and

![Fig. 2. 180° peel adhesion.](image-url)
then the rate at which the tape unwinds is measured. In this case, the only load present is due to the weight of the tape and any stress put into the tape during application.

**Tack.** Tack is in many ways similar to peel adhesion in that a bond is formed and then broken in a lifting manner. When dealing with theoretical descriptions of tack, all of the same considerations that are involved with peel adhesion mechanics are employed. In a practical sense, however, the bond formed in a tack test typically exists for only a short time and is formed with a relatively light amount of force when compared to a peel test. In addition, the test is typically performed with the tape held fixed and a probe or ball being used to contact the tape.

The most common ASTM standard method is a probe tack method (11), in which a cylindrical probe is raised into contact with the adhesive surface of the tape and then pulled back (see Fig. 3). The maximum force attained during removal is reported as the tack value. Typical conditions involve an application pressure of 100 g/cm², a contact time of 1 s, and a removal rate of 1 cm/s, but all of these parameters may be varied with most test equipment.

Another ASTM standard method, rolling ball tack (12), involves placing a piece of tape, adhesive side up, at the base of an inclined surface. A steel ball is allowed to roll down the incline from a fixed height, and the distance that the ball travels across the adhesive surface of the tape is taken as a tack value. Longer distances of travel indicate that the tape is less tacky. Other tests involving drums, rollers, or loops of tape have also been used, but are not as common.

Although it can be influenced by backing properties, rolling ball tack is generally considered to be fairly independent of the backing. Probe tack can be more dependent on backing properties, but very flexible backings may be reinforced with more rigid backings in order to reduce the influence of backing on the tack value. More sophisticated tack tests have been developed that measure force throughout the entire debonding process in conjunction with video observation of the bond (13) or using atomic force microscopy as a probe (14).
Shear Holding Power. Shear represents an entirely different property from peel and tack, and is more related to bulk material properties rather than interfacial properties. The most common ASTM standard method is a holding-power test (15), in which a fixed area of a piece of tape is applied to a vertical test panel and a weight is hung from the free end of the tape (see Fig. 4). The length of time until the load of the weight pulls the tape from the test panel is recorded as the shear holding time. Of particular importance in this test is the mass of the weight used and the area of tape applied to the test panel. Typical contact areas are 0.5 × 0.5 in. (1.27 × 1.27 cm) and 1.0 × 1.0 in. (2.54 × 2.54 cm). Typical weights are 500–1000 g.

As with other pressure-sensitive adhesive tests, the temperature is an important variable and tests are typically carried out at room temperature. A variation on this method is the SAFT test (shear-adhesion-failure temperature) in which the test apparatus is placed in an oven where the temperature is set to rise at 4.5°C/min. The temperature at which the tape fails is recorded as the SAFT value.

In theory, shear is strictly a bulk property of the adhesive that is not affected by surface interactions or the backing in a tape construction. In practice, however, the shear holding power can be affected both by backing and by surface interactions. The force in the shear holding test appears to be entirely in the direction of the hanging tape, but since it is a single-overlap shear joint there are forces generated normal to the plate that can lift the tape from the plate in a peel mode (16). This can be significant for very firm adhesives that have very little tendency to slip in a shear mode, but may be easier to peel from the steel surface. A clear indication that this is occurring is when the mode of failure is described as “pop-off” (i.e., the tape falls cleanly from the plate instead of slipping down the face of the plate). Another potentially interfering factor is backing deformation. This is particularly true for tapes with easily deformable backings, but can also be seen for tapes with relatively stiff backings that have adhesives that are extremely resistant to shear.
deformation. The backing deformation can cause curling or buckling of the tape that can also lead to the introduction of additional peel forces.

**Rheological Tests.** Other rheological tests that measure viscoelastic properties are available. Dynamic mechanical rheometry (DMA or DMTA when temperature is included) involves a parallel plate rheometer that can deform a disk of material in a shearing motion. This is done as a function of frequency of shearing and often with varying temperature. The shear storage and loss moduli, $G'$ and $G''$, or the dynamic viscosity can be obtained with this test. These rheological properties can be related to tack, peel, and shear, and have found much use in development and analysis of PSAs (17). Another way to obtain shear modulus is to use a double-overlap shear apparatus in which the load is applied to a slip plate instead of directly to the tape. This configuration removes both the peel forces associated with single-overlap shear and the potential deformation that may occur in the standard shear holding test.

**Materials**

There are three major classes of polymers used in PSAs today: block copolymer, natural rubber, and acrylic. A number of other polymers used in smaller, specialty applications include silicones, polyisobutylenes, polyolefins, styrene-butadiene, poly(vinyl alkyl ether)s, and polyurethanes.

**Block-Copolymer Rubbers.** Block copolymer rubbers are thermoplastic elastomers that are the most widely used class of PSAs (see ELASTOMERS, THERMOPLASTIC). The most commonly used are ABA block copolymers, where A is polystyrene and B is a polydiene. Polyisoprene ($R = \text{CH}_3$) and polybutadiene ($R = \text{H}$) are the most common B polymers, giving SIS and SBS copolymers, respectively (see BUTADIENE POLYMERS; ISOPRENE POLYMERS).

The mechanism by which these perform is based on phase separation of the polystyrene and the polydiene. The polystyrene is generally present in an amount from 10 to 20% of the rubber, and as the minor component it phase separates into microscopic spherical domains that act as cross-links at each end of a polydiene polymer chain. Molecular weights of the entire block copolymer are typically of the order of 100,000–200,000 g/mol. At room temperature the polystyrene is glassy ($T_g \sim 100^\circ\text{C}$) and the polydiene is rubbery ($T_g \sim -70^\circ\text{C}$). Each SIS (or SBS) polymer chain will have each chain end anchored in a glassy polystyrene domain, with a rubbery polyisoprene link connecting them. Thus the material acts as a cross-linked rubber. When the temperature is increased to above the polystyrene $T_g$, the microscopic polystyrene domains can be melted, allowing the individual polymer chains to flow and this allows the material to be hot-melt processed. Upon cooling
the domain, structure is reformed. A tackifier is always needed, and plasticizers are often added as well to increase tack and reduce cost.

Block copolymers are synthesized by an organic solution anionic polymerization that can lead to high purity, fairly monodisperse, and relatively low cost polymers. The solvent is then removed from the polymer which is available commercially in the form of rubber pellets or crumb. Adhesives can be prepared by dissolving the rubber in solvent, formulating with tackifier and/or plasticizer, and subsequently coating from the same solvent. This is typically used for small volume products or for small-scale laboratory experiments.

More typical, though, is hot-melt processing of these adhesives. The rubber is blended with tackifier and/or plasticizer in a bulk mixer or extruder at elevated temperature (e.g., 150–200 °C), coated as a molten liquid, and cooled. The lack of need for post-curing is a significant advantage over natural rubber PSAs. The high purity and consistency of the input rubber is also an advantage when compared to natural rubber.

The high degree of cross-linking gives adhesives with high cohesive strength, but can be a disadvantage in situations where stress relaxation of the adhesive is beneficial. A number of variations on the basic SIS or SBS copolymers are available. Differing amounts of di-block, SI or SB, polymer may be included which causes incomplete cross-linking, and will typically lead to higher adhesion, better stress relaxation, and lower shear strength.

Typical formulations are shown in Table 1 (18). The rolling ball tack is clearly dependent on the amount of tackifier with lower levels of tackifier giving superior rolling ball tack. The probe tack also shows a decrease in force with increasing tackifier. Shear holding strength shows an increase with increasing coupling efficiency because of the formation of a stronger cross-link network. Interesting differences between shear holding power to steel and to kraft paper illustrate the importance of the substrate selection when testing a PSA. The peel adhesion behavior is somewhat more complicated, since it is strongly influenced both by

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<th>Formulation</th>
<th>1</th>
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<td>50</td>
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<td>206</td>
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<td>&gt;1500</td>
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$^a$ All formulations contain 100 parts block copolymer (S–I + S–I–S) and 2 parts Butazate stabilizer. Except where indicated the test methods are ASTM standards noted above.

$^b$ Wingtack 95 (trademark to Goodyear Chemical).

$^c$ % S–I–S is the number of S–I–S molecules divided by the number of S–I–S + S–I molecules.

$^d$ To convert N/cm to ppi, divide by 1.75.

$^e$ Cohesive failure.

$^f$ Shocky peel.

$^g$ Holding power to steel and kraft paper, PSTC-7 (see Ref. 9).
initial adhesion and by the ability of the adhesive to deform and absorb energy upon removal. Increasing tackifier levels will generally increase adhesion because of the dilution of the polymer network, which increases molecular mobility and reduces the PSA storage modulus. However, increasing tackifier will also increase the $T_g$ of the PSA, and if the $T_g$ reaches or exceeds the use temperature then the material will entirely lose PSA properties.

Antioxidants are usually employed to prevent oxidation of the double bond in either of the polydienes. Specialty grades are available where the polydiene has been hydrogenated, which gives much better chemical stability and uv resistance. Multiarm and star-block copolymers are some examples of specialty copolymers that can be used to modify the performance of block copolymer adhesives (19).

These PSAs are still commonly referred to in much of industry as Kraton (a trademark of Shell Chemical) adhesives, although block-copolymer rubbers are also available worldwide from several other major sources: Dexco, Enichem, and Nippon-Zeon. The most common uses of block-copolymer PSAs are in packaging tapes, although they find use in nearly all types of PSA applications.

**Natural Rubber.** Natural rubber is obtained from the *Hevea brasiliensis* tree as a latex. It is primarily cis-1,4-polyisoprene with small amounts of bound proteins and other contaminants (see Rubber, Natural).

\[
\begin{array}{c}
\text{CH}_2 \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \quad \text{CH}_3 \\
\end{array}
\]

The latex is ammoniated, coagulated, and air dried or smoked to obtain gum rubber. As with most other rubbers, a tackifier must be blended with natural rubber in order to produce a PSA, since the rubber itself has a very low glass-transition temperature ($T_g \sim -70^\circ C$) and a high shear storage plateau modulus. The molecular weight of the input rubber is quite high, greater than 1,000,000 g/mol, and so the rubber is usually milled between steel rolls to break the rubber chains and reduce the molecular weight to make subsequent processing easier (20).

When coated from solvent, natural rubber can be used to make a PSA with a combination of good cohesive shear strength and the ability to dissipate stress within a bond. This is due to the ability of the high molecular weight of the polyisoprene to establish good shear strength without the need for cross-linking. The lack of cross-linking aids in stress relaxation. Because of the double bond in polyisoprene, natural rubber is subject to oxidation, and antioxidants are typically added to the adhesive formulations.

Natural rubber can also be formulated and coated directly from latex, although the costs are typically higher than compounding of gum rubber and coating from solvent. Hot-melt processing of natural rubber is a newer technology that offers the possibility of efficient, solvent-free production (21). Because the high molecular weights of the natural rubber will not survive a hot-melt extrusion or mixing process, it is necessary to post-cure hot-melt natural rubber adhesives with, for example, electron beam radiation curing if high cohesive strength is necessary.
The most common uses of natural rubber PSAs are in masking tapes, packaging tapes, duct tapes, and other cloth tapes.

**Acrylics.** Acrylic adhesives are copolymers produced from esters of acrylic acid (see ACRYLIC ESTER POLYMERS). An acrylic copolymer suitable for use in a PSA must contain a significant fraction of a monomer that gives a homopolymer with a low glass-transition temperature \( T_g \). This monomer will typically give a homopolymer with a \( T_g \) less than \(-20^\circ C\) and usually in the range of \(-40\) to \(-80^\circ C\). It is this low \( T_g \) monomer that gives the PSA its soft, tacky properties. The most common monomers used to give low \( T_g \) polymers are 2-ethylhexyl acrylate, isooctyl acrylate (3M Company manufactures isooctyl acrylate for internal consumption), and butyl acrylate.

The tacky characteristic of an acrylic copolymer was described as early as 1933 (22). On their own, these low \( T_g \) homopolymers are tacky, but they lack the cohesive strength needed to make suitable PSAs, and therefore need reinforcement to prevent the PSA from splitting and oozing during use. There are a number of methods for providing this reinforcement, including the addition of high \( T_g \) monomers to the copolymer; addition of monomers that cause intermolecular interactions between individual copolymers; covalent cross-linking of the copolymer; and physical cross-linking of the copolymer via graft or block copolymers.

The first useful acrylic PSAs were introduced in the 1950s with the incorporation of high \( T_g \) functional monomers (23), such as acrylic acid and acrylamide, used for reinforcement. This continues to be a widely used approach for acrylic PSA reinforcement. Typical acrylic PSAs contain up to 10% of these reinforcing monomers. Additional high \( T_g \), but nonfunctional, monomers may also be added to the copolymer, with some typical examples being vinyl acetate, ethyl acrylate, methyl acrylate, and methyl methacrylate.

Graft copolymers that provide reinforcement may be prepared in a manner somewhat similar to that of the rubber block copolymers. The graft copolymers are prepared by adding macromonomers (ie, polymers with a reactive functional group on one end) during copolymerization. Typical macromonomer examples are polystyrene or poly(methyl methacrylate)s, with molecular weights between 2000 and 50,000 g/mol, that are terminated with a reactive acrylate group. The block structure that forms differs from the A–B–A rubber copolymers, since the macromonomers are incorporated into the polymer at random. The combination of polydispersity in the length of the acrylic backbone, polydispersity in the number of grafts per backbone, and polydispersity in the length of each graft generally leads to adhesives that do not possess as much elastic strength as the A–B–A rubber copolymers.
Acrylic adhesives tend to be more stable than rubber-based adhesives since they have a saturated backbone. They are also generally designed so that they function as PSAs without the need for any tackification or plasticization, although tackifiers can be added to modify adhesion or reduce cost. Both of these features help to differentiate them from rubber-based PSAs. The ability to avoid use of tackifiers and antioxidants makes acrylics a good choice for medical applications where minimal skin irritation is desired.

Acrylic PSAs can be prepared by a number of synthetic routes and the subsequent processing into a PSA tape naturally varies. The earliest synthetic method was free-radical polymerization in an organic solvent. The resulting solution is usually directly coated to make a tape or mixed with other components (e.g., additional solvent, tackifier) prior to coating, but it may also be dried of solvent to provide bulk adhesive for later compounding steps.

Acrylics can also be prepared in water by either emulsion or suspension polymerization. Both of these water-based polymerizations rely on the insolubility of the acrylate monomers in a continuous aqueous phase which leads to the creation of small polymeric particles dispersed in water. Although superficially similar, there are important differences between the two types of polymerization, with the most significant being that suspension particles are typically 50–500 µm in diameter, whereas emulsion particles are typically 50–200 nm in diameter (24). Emulsions are widely used since the small particle size can lead to well-stabilized dispersions and also help to effect good film forming properties. Emulsions have an advantage over solution polymers, since the molecular weight of the polymer can be controlled independently of the rate of reaction, allowing for very high molecular weights to be obtained. Suspensions are less common, but in some cases the large particle size can be used to control tape properties. One prominent example is in repositionable notes (e.g., Post-It, a trademark of 3M) which take advantage of the low surface contact area of the large particles to keep adhesion at a controlled, low level.

Acrylics can also be bulk polymerized. One method for bulk polymerization involves coating a mixture of acrylic monomers along with a photoinitiator onto a film and UV curing to form the adhesive in place. Also being solventless, this can be an attractive method for making thick coatings. In addition, novel phase structure can be imparted by in place curing in some instances [e.g., bicontinuous microemulsions (25)].

Acrylic PSAs find wide use in office tapes, medical tapes, packaging tapes, automotive tapes, and specialty applications where good stability is desired.

Specialty Materials.

Silicones. Most silicone PSAs are based on a poly(dimethylsiloxane) network that is chemically cross-linked during a curing process.

\[
\begin{align*}
\text{CH}_3 & \\
\overline{\text{O}} & \overline{\text{Si}} \cdots \\
\text{CH}_3
\end{align*}
\]
This cross-linked network is generally prepared by addition of a multifunctional, reactive silicate resin to a long chain poly(dimethylsiloxane). They can be prepared to have very high temperature performance, good solvent resistance, and low irritation in medical applications (see SILICONES). Among their disadvantages, however, is that they tend to be expensive, are usually applied from solvent, and usually need a specialty release liner, since they will not release well from most silicone-based release liners (26).

**Polyisobutylene.** Polyisobutylene (PIB) is an all hydrocarbon elastomer prepared by cationic polymerization of isobutylene.

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CH₃
[-CH₂-C-]ₙ
CH₃
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The lack of double bonds gives it good chemical stability. PIB varies from a liquid to a rubber as the molecular weight is shifted from low (<5000 g/mol) to high (>100,000 g/mol). PIB PSAs are usually prepared as a mixture of PIB rubber with a tackifier or oil in a manner similar to other rubber-based PSAs. Low molecular weight PIB can also be used as a tackifier in blends with high molecular weight PIB or in blends with other rubbers as well. One advantage of a high and low molecular weight blend of PIBs is that this takes full advantage of the inherent chemical stability. These adhesives are typically used in applications where good aging or chemical resistance is needed (e.g., pipe wrap, electrical tapes) or in medical applications where low skin irritation potential is beneficial. Among their disadvantages is that they are difficult to cross-link, so that they usually have low cohesive strength, and very high molecular weight PIBs need to be solvent processed since they become difficult to hot-melt process (27).

**Polyolefins.** A variety of amorphous poly(α-olefins) have been used as the base elastomer in PSAs.

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[-CH₂-CH-]ₙ
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Polypropylene, \( R = \text{CH}_3 \) \hspace{1cm} Polyhexene, \( R = \text{C}_6\text{H}_{13} \)

Typical polypropylene and polyethylene materials are highly crystalline and thus have little applicability in PSAs. The key to using a polyolefin in a PSA is to select one with a high degree of amorphous character. These range from amorphous polypropylene or propylene–ethylene copolymers to poly(α-olefins) with longer side chains that disrupt crystallinity (28,29). Polyolefins are usually either tackified or cross-linked to produce suitable PSA properties. The lack of double bonds provides stability benefits similar to those in PIB. The raw materials are generally low cost and can be hot-melt processed. Among their disadvantages is that they
do not yet have the wide range of formulation flexibility that can be achieved with block-copolymer or acrylic PSAs.

**Tackifiers/Plasticizers**

As mentioned above, tackifiers and/or plasticizers are often used as part of many PSA formulations, most particularly in synthetic and natural rubber PSAs. Tackifiers and plasticizers are low molecular weight compounds that are compatible with the base polymer of the PSA. They act as a diluent in the base polymer because they are not part of the polymeric network made up by the base polymer (30). They must be compatible with the base polymer to avoid problems of phase separation. In particular, if the tackifier/plasticizer has a lower surface energy than the base polymer, then phase separation can create a layer of pure tackifier/plasticizer on the surface of the PSA and destroy the tack of the formulation. The most common tackifiers are based on rosin acids, small-chain hydrocarbons, and terpenes.

A typical rosin acid is abietic acid, although the acids used for most rosin-based tackifiers are chemically modified, often by hydrogenation and/or esterification to form more stable products.

![Abietic acid](image)

The small chain hydrocarbon tackifiers are oligomers with molecular weights in the range of several hundred to 2000 g/mol. They are typically obtained from petroleum feed streams and fall into three general classes. The most common C-5 aliphatic hydrocarbons are *cis-* and *trans-*piperylene and isoprene.

![cis-Piperylene, trans-Piperylene, Isoprene](image)

The similarity in chemical structure to isoprene explains why these are quite compatible with natural rubber and synthetic isoprene-based polymers (or block copolymers). The C-9 aromatic hydrocarbon resins include indene- and styrene-based oligomers. Because of the difference in chemical structure these will associate with the end-blocks in S–I–S copolymers, and thus have a reinforcing effect and improve high temperature performance. Finally, mixtures of aliphatic and aromatic hydrocarbon resins are commonly used as a way to tailor compatibility and physical properties of the resultant PSAs.

Terpenes are similar to the aliphatic hydrocarbon resins in that the most common, α- and β-pinene, can be considered to be dimers of isoprene.
Like rosins, terpenes are derived from pine trees (via turpentine) or other natural sources, such as citrus peels.

The difference between plasticizers and tackifiers is somewhat arbitrary and the effect of this difference is described below in the section on Physical Properties. Plasticizers are typically lower in molecular weight and melting or softening point than are tackifiers. Hydrocarbon oils including aromatic, naphthenic, and paraffinic are commonly used with rubber-based adhesives. Phthalates, such as dioctyl phthalate or dibutyl phthalate, are more typically used in small amounts with acrylics. Since plasticizers are usually low molecular weight compounds, there is often more latitude in the chemical types that will be compatible with the base polymer because of the contribution from entropy of mixing.

**Physical Properties**

By definition a PSA must have physical properties that differ from most ordinarily encountered materials. It should behave like a liquid when it is forming a bond with a substrate, but after application it should behave like a solid in order to retain the bond. This dual liquid–solid behavior should be present without the need to make any chemical or physical modifications to the PSA, but should rather be an intrinsic material property.

When acting as a liquid it must have an appropriate surface energy that will allow it to wet a substrate. Liquids with appropriate surface energy have the capability to easily wet a substrate because of the high degree of molecular mobility that they possess. Except in very limited circumstances though, (eg, two smooth glass plates “bonded” together by a thin layer of liquid), they do not have enough strength to keep two surfaces bonded together. So in order to have the needed strength to be a PSA, a material must be a solid, but it must be capable of behaving like a liquid during the time it takes to form a bond (of the order of 1 s).

Polymers are the only class of materials that possess this combination of properties. Because of their extended, chain-like molecular structure they form networks (which may or may not be cross-linked) that resist large-scale molecular motion, and therefore provide solid-like behavior. The portions of the polymer molecule in between network junctions, however, can undergo small-scale motion that is similar to that of a liquid when viewed on a short time scale. An important feature of all PSAs is the glass transition temperature $T_g$ of its polymeric components. If the PSA is cooled below its $T_g$, then it will behave like a glassy solid, since even the small-scale, between-network motions will be frozen. Above its $T_g$, though, the
small-scale, between-network motion provides the liquid-like behavior needed for bonding.

The ability to form an initial bond is most generally referred to as the “tack” of a PSA. It is necessary for the glass transition of the PSA to be below the application temperature. It is also necessary, however, for the plateau storage modulus $G'$ of the PSA to be low enough to allow the PSA to deform sufficiently to make good intermolecular contact with the adherend. The Dahlquist criterion for bonding states that $G'$ needs to be less than 100 kPa on a 1-s time scale. This is a good general rule of thumb, although the amount of intermolecular contact will also be influenced by PSA thickness, surface roughness, and application pressure.

In Figure 5, the storage modulus of a typical cross-linked rubber is compared to that of a PSA made from a mixture of the rubber and tackifier. The rubber has a low $T_g$, which is why it is soft and rubbery at room (or use) temperature, but its modulus is too high for it to be a PSA. Addition of tackifier decreases the modulus below the Dahlquist criterion and allows for the mixture to be a PSA. The effect of dilution of the rubber network with a tackifier can be predicted by rubber elasticity theory using the equation below (31,32). The effect of fillers can also be predicted.

$$G_e \equiv v^2 (\rho/M_e) RT (1 + 2.5c + 14.1c^2)$$

where $G_e$ is the plateau modulus, $v$ the volume fraction of network molecules
in the continuous phase, $\rho$ the density, $M_e$ the entanglement spacing molecular weight, $R$ the gas constant, $T$ the temperature, and $c$ the filler volume fraction. In the common case of an S–I–S block copolymer, the continuous phase comprises the polyisoprene and mid-block tackifiers and the filler volume comprises the polystyrene and end-block tackifiers.

Although the $T_g$ of the mixture increases with additional tackifier, it is still below room temperature. Addition of more tackifier will continue to reduce the plateau storage modulus, but will eventually raise the $T_g$ above the use temperature and the subsequent mixture would have no tack.

As described above, the distinction between plasticizers and tackifiers is somewhat arbitrary, but the important difference between the two is that addition of a plasticizer will not affect or will lower the $T_g$ of the PSA formulation. The effect of lowering the modulus is the same as for a tackifier.

The glass-transition temperature of the mixture can be approximately calculated using the Fox equation (33):

$$\frac{1}{CT_g} = \frac{x_1}{T_{g1}} + \frac{x_2}{T_{g2}} + \cdots + \frac{x_n}{T_{gn}}$$

where $CT_g$ is the calculated glass-transition temperature; $x_1, x_2, \ldots, x_n$ are the weight fractions of the adhesive components; and $T_{g1}, T_{g2}, \ldots, T_{gn}$ are the $T_g$’s for the individual components. More complex approximations for the glass-transition temperatures are also available (33,34).

Once a bond is created, the PSA should resist removal (unless controlled or easy removal is a desired feature for a particular product). Adhesion can be looked at as being controlled by two primary components. The intrinsic adhesion (also called the work of adhesion) between the adhesive and substrate is caused by intermolecular interactions. These can be van der Waals interactions for nonfunctional adhesives (e.g., rubbers, polyolefins) or can also include hydrogen bonding, acid–base interactions, or actual covalent chemical bonding (35). The intrinsic adhesion, however, is generally small when compared to the practical strength of the adhesive bond, which is the force of adhesion that is actually measured (36). This is due to the second contribution to the force of adhesive removal, which is the ability of the adhesive to viscoelastically deform and absorb energy prior to debonding. The adhesive force for PSA bonds has been extensively analyzed using the theory of fracture mechanics (37–44). In a general sense, one can say that debonding occurs when the adhesive has been deformed sufficiently to store enough elastic stress to overcome the intrinsic work of adhesion.

In Figure 6, a generalized peel force vs peel rate curve is shown. At very low peel rate the dotted line indicates that the adhesive is undergoing cohesive failure. As the tape is slowly lifted away from the substrate the adhesive is able to undergo viscous deformation and absorb all of the energy being imparted by the peel before it can be transferred to the surface. Put another way, the viscous dissipation is rapid enough at slow peel rates to prevent the adhesive from building up enough stored elastic energy to overcome the intrinsic adhesion at the surface. The modulus of the adhesive increases with increasing rate leading to
increasing peel adhesion force. A transition will occur at a sufficiently high peel rate where the adhesive can now build up enough stored elastic energy to cleanly and smoothly remove from the substrate. Beyond this transition rate the peel force again increases with increasing peel rate (shown by the solid line) until another transition occurs to “shocky” peel. This “shocky” peel is related to the increased stiffening and glass-like behavior of the adhesive at increasing peel rate. In a roll unwind case, the unwinding tape will accelerate as it passes this shocky peel transition since the peel force will now begin to decrease with increasing rate. Since most peel is performed by pulling the tab end of a tape at a constant rate, the tape unwinding from the roll will move faster than the tab being pulled until slack accumulates in the tape, causing the effective peel rate at the roll to drop to near zero. As the tab end continues to be pulled the slack is taken up and this process is repeated to give a jerky or shocky peel. The peel force shown in Figure 3 for the shocky region (dashed line) is an average peel force, since the instantaneous peel forces measured will vary greatly.

A specific type of adhesive failure is “lift” which is a very slow low-angle peel of a tape at its edges. The optimal physical properties to resist lift often differ from those necessary to provide high short-term peel adhesion. Longer time (low frequency) material properties become important, and the ability of the adhesive or backing to relax stress over time also becomes important, since stresses imparted to the tape during application can lead to long-term failure if they cannot be dissipated.

**Fig. 6.** Peel force vs peel rate schematic showing cohesive failure (dotted line), adhesive failure (solid line), and shocky peel (dashed line).
Another undesirable feature of a PSA tape is creep or oozing. This is most often seen with uncross-linked adhesives that undergo viscous flow over long times. This is governed by properties similar to those that govern lift, except that the ability of the adhesive to relax stress through flow (which helps reduce lift) can lead to increased creep. It is usually necessary to strike a balance between lift, creep, and the short-term tack and adhesion properties needed in a PSA tape.

General Manufacture

A wide variety of methods have been used to make PSAs and PSA tapes, ranging from multistep processes to completely integrated manufacturing methods. Synthesis of the PSA (or PSA-component-like rubber) can be a solvent-based process (eg, organic solution, emulsion, or suspension polymerization) or a solventless process (eg, reactive extrusion, bulk polymerization).

A common thread through nearly all PSA tape manufacture is a processing step where the PSA is present as part or all of a liquid phase (distinguished from the “liquid-like” behavior it shows during use) that may be applied to a surface in a thin coating. This liquid phase is obtained in three primary ways. The PSA is dissolved as a solution in organic solvent or water and the solvent or water is removed by drying after the coating step. The PSA is heated to a temperature at which it becomes molten (ie, hot-melt processing) and the PSA is cooled after the coating step. The PSA is formed by coating low molecular weight liquid compounds that may be polymerized in place after coating. General industry trends are toward solventless processes since these eliminate the use of hazardous organic solvents and the high energy usage due to drying.

The PSA is usually coated directly onto the backing film, although it may also be coated onto the release liner and subsequently laminated to the backing film. Coating on liner is usually done with soft or stretchy backings that can deform during oven drying or with cure-in-place systems where the backing may absorb the liquid prepolymer mixture before polymerization can occur.

Economic Aspects

Of the three major classes of polymers in use today, acrylics make up the largest volume of material at 33% of the total PSA market. Synthetic block-copolymer elastomer represents 25% of the total PSA market. Since these are almost universally compounded with tackifying resins, the amount of PSA produced using block copolymers could be twice as large as the amount of elastomer used. Natural rubber represents 22% of the total PSA market, but is also compounded with resin to produce a PSA, and so the total amount of PSA produced is also larger (45). This represents a shift toward acrylics from 10 years ago when the relative
amounts of acrylic, block copolymer, and natural rubber elastomer was 23, 29, and 28%, respectively (46).

Estimated production (47) volumes (by area coated) of tapes and labels in 1997 were $7.5 \times 10^9$ m$^2$ in the United States, $7.7 \times 10^9$ m$^2$ in Europe, and $(6–8) \times 10^9$ m$^2$ in Asia. Estimated use of PSAs (by mass) in 1998 was 250,000 t in the United States and 295,000 t in Europe. Estimated sales volumes of pressure-sensitive products in 1999 were $11 \times 10^9$ m$^2$ in the United States, $8.4 \times 10^9$ m$^2$ in Europe, and $1.9 \times 10^9$ m$^2$ in Japan, with global growth rates for these markets estimated at between 4 and 6% annually for tapes and between 7 and 11% annually for labels (47,48).

BIBLIOGRAPHY

2. U.S. Pat. 5412035 (May 2, 1995), E. E. Schmitt and co-workers (to Landec Co.).
3. WO 0061692 (Oct. 19, 2000), C. Ansell (to Smith & Nephew, Plc.).
5. U.S. Pat. 5352516 (Oct. 4, 1994), D. J. Therriault and M. J. Zajaczkowski (to Adhesives Research, Inc.).
18. U.S. Pat. 4096203 (June 20, 1978), D. J. St. Clair (to Shell Oil Co.).
25. U.S. Pat. 5670557 (Sept. 23, 1997), T. M. Dietz and co-workers (to Minnesota Mining and Manufacturing Co.).
29. U.S. Pat. 5112882 (May 12, 1992), G. N. Babu and co-workers (to Minnesota Mining and Manufacturing Co.).
36. Ref. 16, p. 140.
45. D. Satas, in Ref. 1, p. 6.
46. D. Satas, in Ref. 17, p. 4.

**GENERAL REFERENCES**


ADAM S. CANTOR
3M Healthcare Markets

**PSA.** See Pressure Sensitive Adhesives.

**PULTRUSION.** See Composites, Fabrication.

**PVC.** See Vinyl Chloride Polymers.

**PVDC.** See Vinylidene Chloride Polymers.

**PVDF.** See Vinylidene Fluoride Polymers.

**PVF.** See Vinyl Fluoride Polymers.

**PVK.** See Vinylcarbazole Polymers.

**PVP.** See Vinyl Amide Polymers.