

Pressure-Sensitive Adhesive Joints

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Abstract

Self-adhesive materials are called, in the adhesive industry, pressure-sensitive adhesives (PSAs). PSAs are designed in the shapes of latex, solvent borne resin, rubber solution, or hot melt and are being used for foils and films, tapes, labels, and notepads which can make permanent, removable, or semi-removable adhesive joints for applications of general purpose product assembly by simple contact under light pressure. This special class of adhesives does not undergo any physical transformation or chemical reaction during the bonding process. The end-use properties of PSAs result from the nonlinear viscoelastic behavior of the adhesive material, and the elastomeric polymer basis of PSAs imparts them such a viscoelastic behavior caused by a carefully chosen polymer architecture and monomer composition with the proper addition of small molecules called tackifying resins. They are safe to use and easy to handle and thus are increasingly replacing more conventional types of adhesives. In this chapter, we review adhesion mechanism of PSAs, types of PSAs, adhesion properties and tests, mechanical behavior of joints, and especially different aspects of PSA applications.

Keywords: self-adhesives, pressure-sensitive adhesives, viscoelastic behavior, tackifying resins, adhesion mechanism

1. Introduction

Pressure-sensitive adhesives provide a quick and effective fastening method compared to most mechanical joining techniques. Adhesive bonding has become a preferred fastening technology in applications where dissimilar materials need to be joined. PSAs, with a viscoelastic nature, are composed of several key elements: a fluid, adhesive, tackifier and some kind of structured backing (**Figure 1**) [1].

PSAs have generally an elastomer basis, which can be of the following materials such as natural rubber, vinyl ethers, acrylics, butyl rubber, styrene block copolymers, silicones and nitriles. A tackifier, a low molecular weight resin, is added to the elastomer to increase adhesion and is generally one of the following common resins: terpenes, aromatic resins, hydrogenated hydrocarbon resins and terpene-phenol resins [2].

PSAs in the shapes of latex, solvent borne resin, rubber solution or hot melt are used for foils and films, tapes, labels and notepads which can make permanent, removable or semi-removable adhesive joints for applications of general purpose product assembly, display, tags, labels, and mailers, packaging tapes, masking and paper tapes, tapes for hygiene applications, double-sided tapes, cloth and duct tapes, heavy-duty and reinforced tapes and electrical tape as well as a wide variety of other products (**Figure 2**) [3].

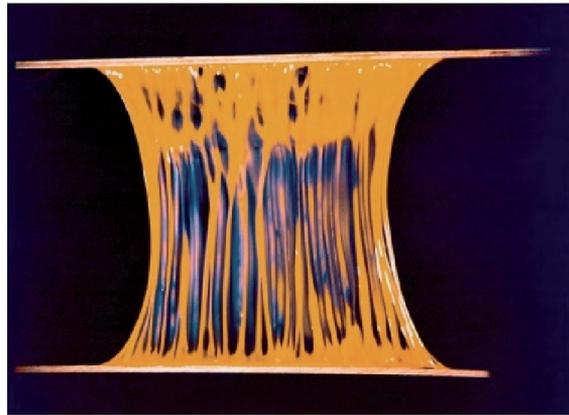


Figure 1.
Viscoelastic nature of pressure-sensitive adhesives.



Figure 2.
Various applications of different kinds of pressure-sensitive adhesives.

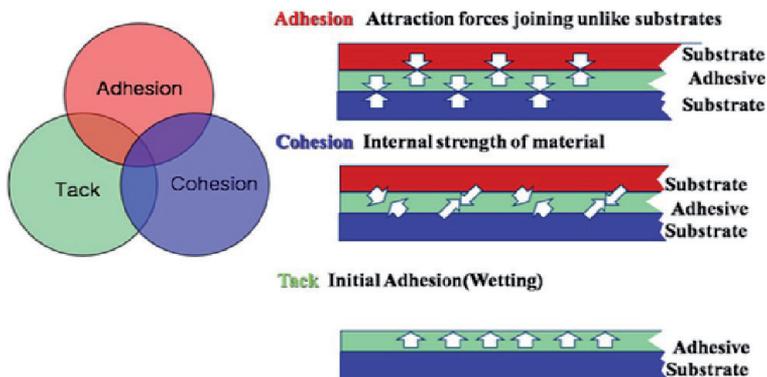


Figure 3.
Major elements of PSA's adhesion properties: tack, adhesion and cohesion.

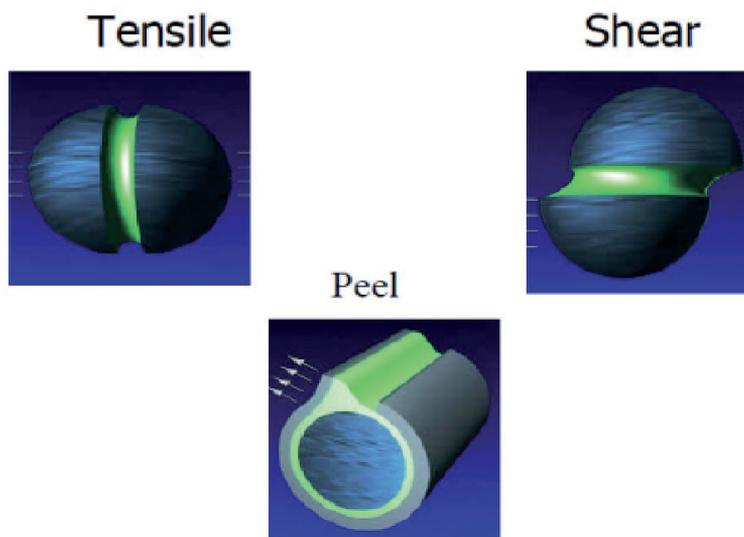


Figure 4.
Schematic of PSA main properties.

When considering pressure-sensitive adhesives and their applications, it's useful to keep in mind main adhesion properties such as shear strength, peel adhesion, tackiness and creep (**Figures 3 and 4**) determine the adhesion of PSA system and subsequently, the application it is used for needs a balance of mentioned properties which can be adjusted via polymerization or formulation process and its components.

In the following chapter, adhesion mechanism of PSAs, types of PSAs, adhesion properties and tests, mechanical and behavior of joints and especially different aspects of PSA applications in the industries will be thoroughly discussed.

2. Adhesion mechanism of PSAs

To understand how PSAs work, it is necessary to understand not only the properties of the individual components of the adhesive formulation and those of the formulation as a whole, but also the processes that take place upon contact of the PSAs with different types of substrates. Good interfacial interaction with a substrate is essential for PSA performance. Such interaction is caused by forces of different natures (van der Waals, H-bonding, acid–base, and donor–acceptor interactions) [2, 4].

At the macro level, this interaction between PSA and substrate results in a wetting–spreading process. Wetting of the substrate by the adhesive is crucial to establish good contact between them. Wetting is also important in the coating procedure (**Figure 5**) [5].

Generally PSAs are used as thin layers; therefore their flow is limited by the physico-mechanical interactions with the solid components of the laminate (liner and face) materials [6, 7]. The term “pressure-sensitive adhesive” itself presumes a definite pressure value necessary to form a strong adhesive joint. Upon converting to dimensionless variables, it would be logical to express pressure as a value relative to the elastic modulus. This is one possible approach to constructing the “dynamic” criterion of pressure sensitivity [4, 8, 9].

The phenomenon of tackiness features a high shear flow of an adhesive material under a compressive force, thus forming the adhesive joint. The flow of the adhesive

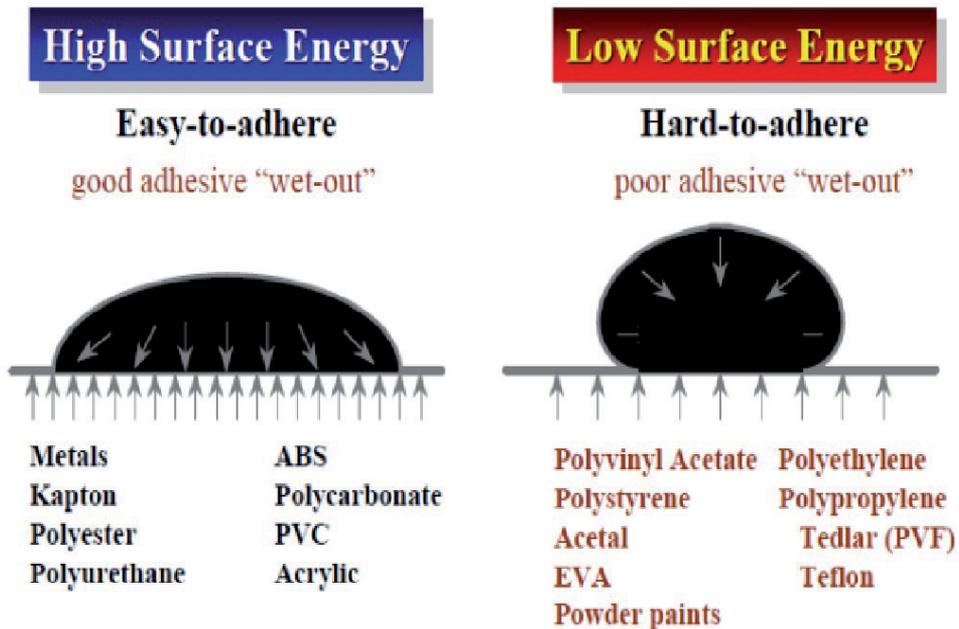


Figure 5. Wetting of the substrates as the crucial item in adhesion by PSAs.

is needed in the first several seconds to wet the surface of a substrate. Owing to the high viscosity of the PSA, proper wetting cannot be achieved in a reasonable time without compressive force [4].

The final adhesive properties of PSAs require a viscoelastic, non-Newtonian flow behavior which is located at rubbery plateau and related to the supramolecular properties of adhesive. For deeply understanding of viscoelastic behavior, there is the necessity of concluding the most important PSA properties. Totally, adhesives in a linkage have a behavior like a fluid or a solid. PSAs originate from a film-forming, elastomeric material, which combines a high degree of tack with an ability to quickly wet the surface to which it is applied, to provide instant bonding at low-to moderate pressure as a result of its flow characteristics. On the other hand, there is enough cohesion and elasticity in PSAs, in order that in spite of their high tackiness they can be applied with the fingers and easily removed without being left any residue. Furthermore, for achieving bond strength, PSAs must store energy and be elastic. Mainly, there should be a balance between viscous and elastic properties of PSAs. It should also be considered that PSAs have to pass contradictory requirements under different stress rates; at low shear rates, PSAs must flow (bonding) (Figure 6) and at high peeling rates there should be an elastic response (debonding) [6, 10–12].

In practical point of view, the relation between adhesion properties and stress rates can be seen by applying peeling test on removable PSAs at different peel rates. The stress rate dependent stiffening is an increase in the elastic contribution to the rheology of the polymer. Major parts of the bond rupture energy are stored when the elastic parts are predominant, causing higher peel and tack properties [13].

Final properties of PSAs are dependent on the nonlinear viscoelastic behavior of the adhesive material being resulted from elastomeric polymer basis of PSAs as viscoelasticity. The same stiffening effect shall be seen by decrease in polymer temperature. This is because the polymer chains are encountered with a restriction in their ability to flow, and the modulus increases. As a result, the adhesive properties of PSAs are also temperature dependent [14].

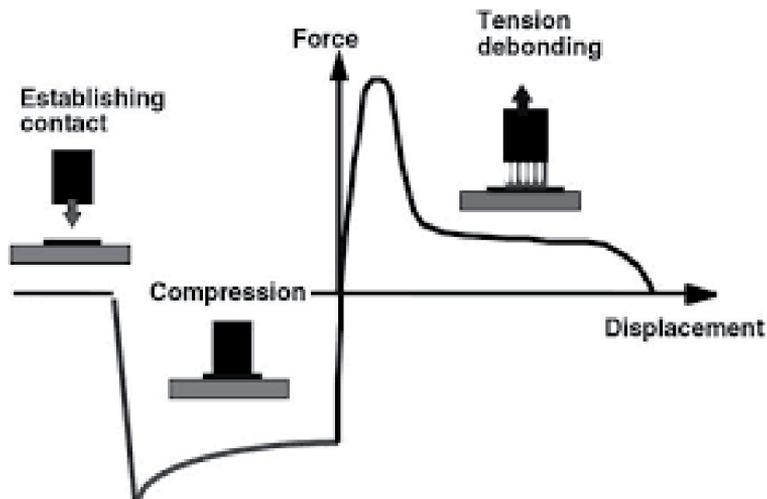


Figure 6.
Schematic of bonding and debonding process.

Pressure-sensitive adhesives must display irreversible work of deformation during bonding and reversible deformation work upon debonding. The ratio of both kinds of deformation work (i.e., of stored and dissipated energy) characterizes the behavior of PSAs.

About the temperature dependence of PSAs' mechanical properties, the storage modulus starts high at low temperatures where all motion within the polymer is frozen and the material behaves like a glass (**Figure 7**).

At higher temperatures it drops off and exhibits a plateau region which represents the elastomeric response generally encountered at normal end-use temperatures; the storage modulus then decreases further when softening begins. The temperature region through which the polymer changes from a glassy (hard) state into a liquid (rubber-like) state, this second order transition point is called the glass transition temperature (T_g), and is a very important parameter in the characterization of PSAs. In temperatures more than T_g , one can apply the time-temperature superposition principle. The side chain size and mobility of the polymer cause different viscoelasticity around T_g [4].

The essential performance characteristics when characterizing the nature of PSAs are tack, peel adhesion, and resistance to shear. The first property represents the adhesive's ability to adhere quickly (initial grab), and latter one evaluates its ability for not being peeled off, and the last one characterizes the resistance against not being flown when encountering with high shear forces. All in all, the first two characteristics are in direct relation with each other, but inversely related to the last one [15].

Tack is measured in two steps according to Zosel: the contact step and the separation one. At first step, in the surface points contact is made, increasing to a larger area while wetting out, viscous flow, and elastic deformation (**Figure 8**) [6].

To be wetted out high fluidity is implied according to the characterization by an appropriate viscosity of the adhesive. Wetting out, being covered the substrate surface by adhesive fluid, results in bonding formation because of the deformability of viscoelastic PSAs. Vice versa, debonding may be assumed the laminate's deformation, the creation and deformation of two new surfaces. Thus, it may be concluded that for bond-forming a high deformation with a medium elasticity is required, while debonding needs an average deformation with a high elasticity [16].

Viscosity and elastic moduli of PSAs as the properties depended on the experimental parameters used, such as the temperature and time, and the strain rate

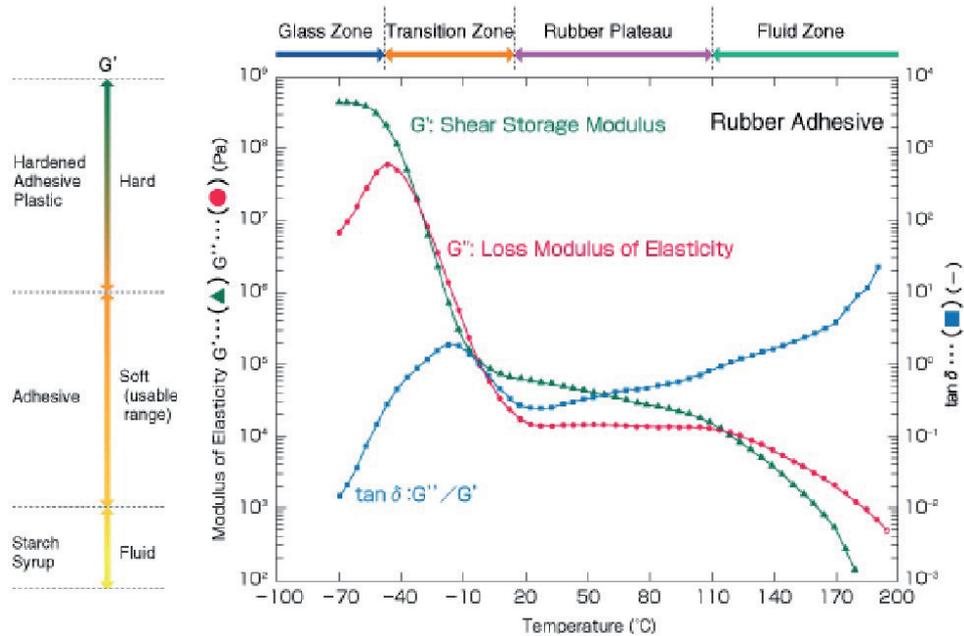


Figure 7.
Temperature dependence of PSAs' mechanical properties.

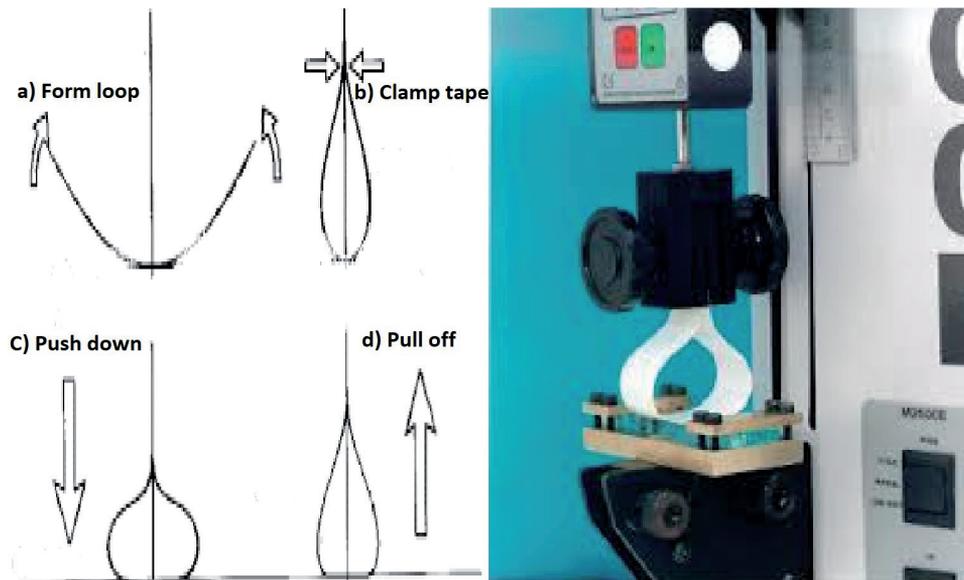


Figure 8.
Contact and separation step schematics in tack test: (a) Form loop (b) Clamp tape (c) Push down (d) Pull off.

cannot be assumed intrinsic material characteristics. So, when speaking of tack, a similar dependence on time, temperature, and the strain rate has to be taken into account which is illustrated by the quite different values of the tack obtained using different experimental techniques namely, quick stick, rolling ball, or loop tack, being evaluated by different time and strain rates, and by the dependence of the adhesive properties to environmental conditions [17].

Peel and peel strength are measured by separating an adhesive applied to a substrate at some angle with respect to the substrate, usually at an angle of 90° or

180°. Similar to tack, the measurement of the peel adhesion involves a bonding step before the debonding or peeling step (**Figure 9**) [7, 15].

Tack as one of the adhesive properties of PSAs is the resistance of the adhesive to being separated after a short time of contact, or by light pressure. Peel is evaluated after an approximately long time of contact after being applied onto the surface of the substrate via a light or medium pressure. The time available for bond forming which means wetting of the surface and then penetration during the first contact step is longer for peeling tests than for tack. After that, flow properties of the adhesive during bonding are less critical for the tack measurement compared to peeling evaluation. Moreover, that how resistant is the PSA in debonding stage is depended on the viscosity/elasticity balance for achieving peelability (removability or repositionability) and on the strain rate influencing the separation resistance substantially than during the measurement of the tack [18–21].

The liquid adhesive must be coated onto a release liner or face material. Good coatability implies adequate machinability or processing properties on the coater (metering roll, drying tunnel) (**Figure 10**) [22].

During production, transport, and coating process, the adhesive fluid is subjected to shear forces resulting in changes of the viscosity. The coated shear-thinned adhesive firstly must wet the web, and the wetting out stage depends on the viscosity of PSA. Except for hot-melt PSAs, the coated fluid adhesive film must go through evaporation of the carrier liquid or solvents (drying) which will result in formation of a solid film. Evaporation of the solvents depends on the fact that how it is diffused into the adhesive layer namely, on the adhesive viscosity. As a conclusion, the viscosity of the adhesive, i.e., the time (shear rate)/temperature dependence of the viscosity, influences the coating process of PSAs [23, 24].

Conventional PSAs can be classified as either nonpermanent (2.7–9.0 N/25 mm for 180° peel adhesion) or permanent (above 9 N/25 mm for 180° peel adhesion) (**Figure 11**) [4, 14, 17, 24].

Repositionable PSPs are a special class of removable pressure-sensitive products (labels and tapes) that stick to various surfaces but remove cleanly and can be reapplied. The final adhesion builds up over a few hours. Non-permanent adhesives are

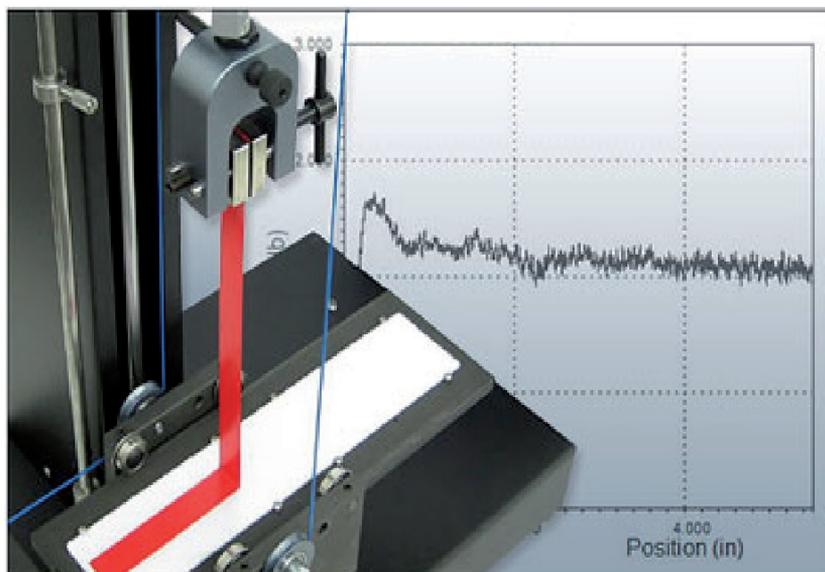


Figure 9.
Peeling test in PSAs.

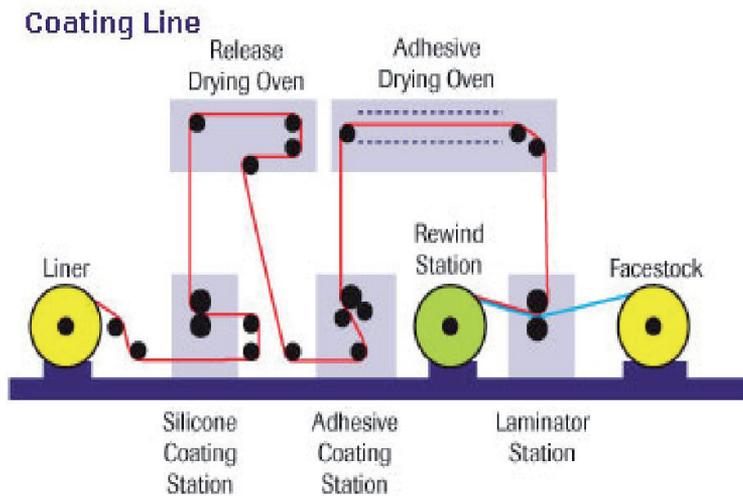


Figure 10. Coating line of PSAs.

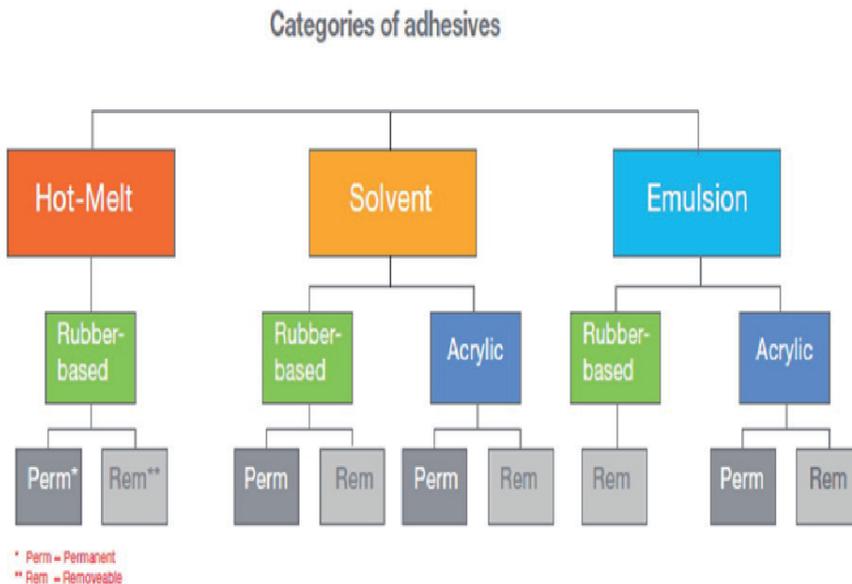


Figure 11. Categories of adhesives according to the permanency property.

generally used in the manufacturing process of removable tapes and labels, protective laminates, and other less durable products [25].

For so-called removable adhesives (non-permanent adhesives), the flow properties (viscosity), cohesion of the adhesive and the harbor of the adhesive to the face stock are crucial. Ideally, should the bond to the substrate be nonpermanent, a clean separation from the substrate will be expected and the adhesive remains on the face material. One other requirement for good removability is the low peel value with a permanent character. A clean release from the substrate and no build-up of the peel with time are the minimal requirements for removable PSAs. Based on the adhesive properties, it is possible to formulate the rheological properties required for removable and permanent adhesives [1, 6, 14, 18].

3. Types of pressure-sensitive adhesives and applications

Self-adhesive materials are called, in the adhesives trade, pressure-sensitive adhesives. PSAs are designed to stick on almost any surface by simple contact under light pressure. Among the different classes of adhesives, pressure-sensitive adhesives (PSAs) are perhaps the most common type found in consumer products. Self-adhesive tapes and labels of all kinds are ubiquitous in everyday life. Despite the fact that PSAs are supposed to adhere to substrates, they are different from other adhesives in many ways. First, PSAs are mainly nonstructural adhesives; they cannot be compared with epoxies for structural applications. Moreover, PSAs mainly adhere to a surface upon contact without any chemical reaction [6, 15, 23, 26].

Pressure-sensitive adhesives can be classified by the type of ingredients used to make them (e.g., rubber-based, acrylic and silicone) and by their state (e.g., organic solvent solution, emulsion, solid (hot melt) and aqueous solution) (Figure 12).

Emulsions are dispersion of particles containing acrylic polymer in water (latexes). Labels and Packaging Materials (LPM) has manufacturing infrastructures in USA and Europe and wide manufacturing companies to provide latexes around the world. There are also acrylic polymers in petroleum-based solvents—usually of low to moderate solids content. End users prefer the performance of solvent based acrylic polymers although they are more expensive than their water borne counterparts (latexes) [7, 15]. Hot melt PSAs are based on block copolymers. Oils, plasticizers and tackifiers are the necessary components of the formulation needed to obtain appropriate performance. Most hot melts (HM) are dependent on C5/C9 streams from petroleum distilleries. The other PSA acrylic grade UV compositions, which are solventless, produce films with higher thickness, including foam-like adhesives. The two-stage process creating performance advantages in the second stage of curing gives the opportunity of very high molecular weight reactions which can't be cast from solvent. Warm melts (100% solids materials) are either made in solvent and stripped (AC resin) or polymerized to near 100% and coated. They use hot-melt equipment (high coating speeds) and give performance of solvent benefits—high coating speed and solvent-like performance simultaneously.

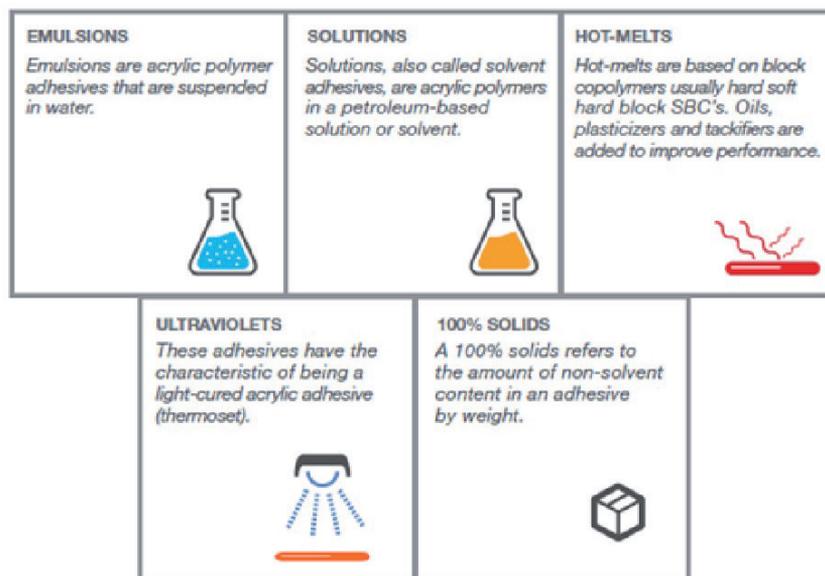


Figure 12.
Different types of PSAs by their state.

PSA are constructed based on these elements as follows:

- **Adhesive:** Typical adhesives are acrylic, natural rubber, or synthetic rubber. Special adhesives with a smaller application base are silicone, butyl, or EVA (ethylene-vinyl-acetate).
- **Backings:** A backing or carrier is a relatively thin, flexible, web based film. Backings can be a paper, film, foil, foam, fabrics, nonwovens, or laminates which are surely chosen based on the application—such as cushioning, dampening, maintaining a barrier, etc.
- **Primer:** A primer is used to increase adhesion of the adhesive to the backing and can be a liquid substance coated onto the backing surface, or a physical treatment, such as corona or flame treatment. This stage is of high importance if the tape needs to be removed cleanly, or if the tape is subjected to stress permanently with a load.
- **Release Coating:** Release coating is a treatment process which should be applied on the backing of a single-sided tape, and the release liner for a double-sided tape. This process ensures stable unwinding of the tape during the application especially for automatic applications in which the tape can be unwound at high speeds. Different release forces can be used for either easy unwinding or harder unwinding, depending on the customer's needs.

Common structure of different tapes and labels are presented in **Figure 13**.

For commercially used PSA systems with excellent performance levels, synthetic polymers based on acrylics, silicones, polyurethanes, and polyesters are preferred (**Figure 14**) [27].

From historical point of view, the first PSAs were rubber based. They are still the cheapest to produce and also the simplest to formulate for they are typically compounds of natural rubber and tackifier which is miscible with the rubber in approximately equal proportions. First versions of rubber based PSAs were not cross-linked, but today a cross-linking step is added to avoid flow [1, 6, 22, 23, 26].

Types of rubber based PSAs are as follows:

- **Natural rubber:** They must be cross-linked for increasing cohesive strength.
- **Reclaimed rubber:** This rubber is used to coat the calender surfaces considering its vulcanized properties.
- **SBR:** This grade must be combined with natural rubber and a small volume of tackifier for enhancement of the adhesion strength.
- **Block copolymer:** It should be plasticized by heating process via the formation of styrene domains such as SIS and SBS.
- **Polyisobutylene:** This rubber is a blend of high and low molecular weight resins made by partial crosslinking of butyl rubber and addition of fillers.

Acrylic PSAs are the best choice for optimization and formulation using copolymerization of a long side-chain acrylic such as *n*-butyl acrylate (BA) or 2 ethylhexyl acrylate (2-EHA) with a low glass transition temperature T_g (soft monomers), a short side-chain acrylic such as methyl methacrylate (MMA) (hard monomer) to

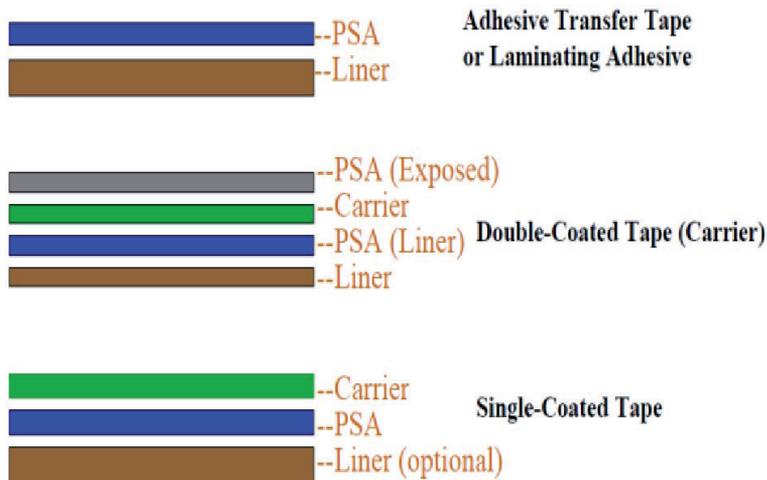


Figure 13.
 Common structure of different tapes and labels.

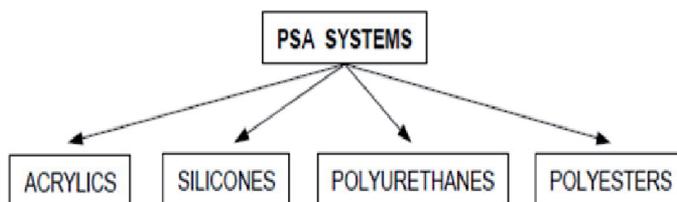


Figure 14.
 Commercially used PSA systems.

adjust the T_g , and acrylic acid to improve adhesion, optimize elongational properties (their mechanical response to deformation in uniaxial extension) and control colloidal stability [28].

Acrylates and other suitable monomers such as vinyl acetate, acryl amide, and acrylonitrile are copolymerized to synthesize an acrylic copolymer with optimized adhesion properties. Crosslinking agents are also added for cohesion improvement. Acrylics can be synthesized in organic solvents in which no further formulation happens except for the time it is needed to modify their properties. Acrylics can also be synthesized in water (water borne) but here it is needed to add materials called emulsifiers to make the polymer dispersible in water. The third group of acrylics is solvent-free acrylic PSA (**Figure 15**) [7, 15, 27].

Acrylic latex based PSAs are used primarily in the production of different kinds of tapes such as industrial single-sided, double-sided, and transfer adhesive tapes. Another important application of emulsion pressure-sensitive adhesives resides in the manufacture of water-soluble labels. The newest application of them is in the medical products in which neutral electrodes and adhesive tapes are of high importance for securing operating theatre sheets [27, 29–31].

An issue in the field of PSAs is to give them some water solubility depending on the hydrophilic properties of the groups incorporated into the polymer chain. The T_g of the water-soluble monomers (**Figure 16**) is the main property for the water solubility and also adhesive properties of the synthesized copolymers [28].

In spite of advantages of water borne acrylic PSAs, the solvent-borne counterparts have been marginally preferred in high-performance applications because of their superior adhesive performance at high temperatures (**Figure 17**). The latter

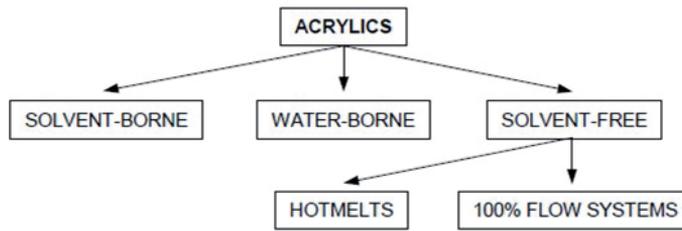


Figure 15.
Acrylic PSAs different types.

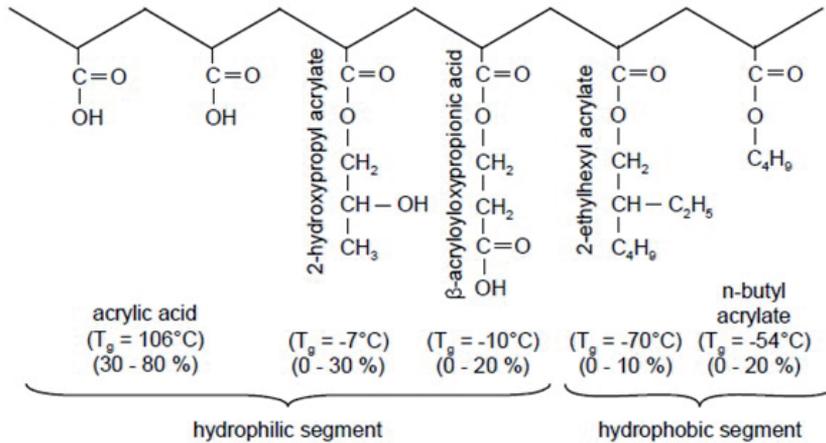


Figure 16.
Structure of emulsion acrylic based PSAs.

one have much higher shear strength, together with higher peel and tack properties, for the aforementioned applications considering the continuous network morphology made by physical entanglements of acrylic chains in the solvent-borne adhesives when the solvent has evaporated [32]. In comparison, the microgels in the latex particles retain their discrete morphology in the adhesive film [33]. This morphology decreases the shear strength of the latex based PSAs because of the poor interconnections between the microgels and the linear polymers in the structure of the film [34, 35].

UV PSAs have the characteristic of being a light-cured acrylic adhesive (thermoset). UV PSAs are nonflammable and solvent free. UV adhesives offer advantages of lower VOCs and better environmental compliance. In the case of saturated acrylic pressure-sensitive adhesives, the photogeneration of initiator radicals by α -cleavage photoinitiators or H-abstraction photoinitiators is followed by a reaction with the acrylic chain that produces a new radical reacting with a neighboring acrylic chain (**Figure 18**) [27].

Totally, acrylic PSA categories are as follows:

Water-soluble

In this grade, monomers having carboxyl groups are copolymerized.

Non-cross-linked

In this one, monomers having low and high T_g are copolymerized to produce a PSA.

Cross-linked

Here, a low T_g monomer is cross-linked by blending with a crosslinking agent.



Figure 17. Applications of solvent based PSAs such as examples of custom applications for sealing, gasketing, shielding and sound insulation, and foam tapes and adhesives are used in automotive or other industrial applications where strength, heat, or moisture resistance is required (close-up application of heated mirror).

Structural bonding tape (Structural PSAs) is an acrylic pressure-sensitive tape impregnated with an epoxy resin being cured under heat. This adhesive is cured in an oven at about 145°C for 20 min. The composition of structural PSA in which we have inherently pressure-sensitive before the curing process is a combination of soft monomers of acrylate with low T_g and hard monomers of epoxy with high T_g in the polymer chain (**Figure 19**) [36].

Pressure-sensitive thermosetting adhesive based on acrylic ester/epoxy resin is an initially tacky and conformable thermosetting adhesive produced by blending comprising epoxy resin or a mixture of about 20–60 wt. % epoxy resin and 0, 5–10 wt. % hardener being activated by heating for hardening of the epoxy resins [36].

The other PSA grade which is currently available for industrial application is cross-linkable acrylic hot melt PSAs (HMPSAs) designed to be cross-linked by a UV-lamp or UV-laser light. HMPSAs propose advantages such as relatively low application viscosity at higher temperatures, high processing speeds, aggressive tack, high resistance to plasticizers and solvents, and too high heat resistance after curing process. There are chemically built-in photoreactive functional groups on acrylic chains in UV-acrylic hot melts. UV grades are solvent free and are processed as hot melts. The adhesive film is cross-linked with UV radiation after the acrylic film has been coated with the UV-acrylic hot melt for self-adhesive material production [28, 33].

It is easy to coat heavy depositions of UV grades of acrylic PSA at a good speed since these are 100% solid adhesives. Using photoreactive diluents viscosity can be modified within certain limits and also, the UV dose can be controlled by adjusting the power of UV lamps and the speed at which the substrate is passed under the lamps in the production line.

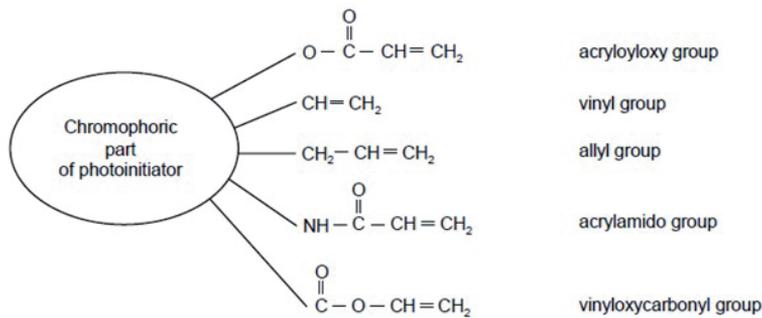


Figure 18. General examples of the chemical structure of unsaturated photoinitiators [27].

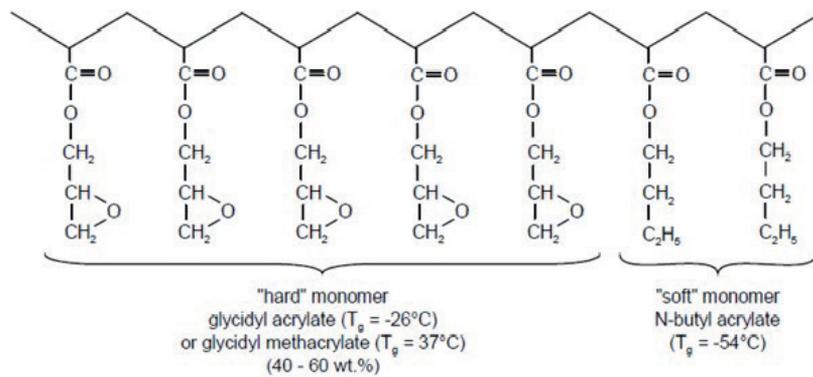


Figure 19. The polymer morphology of a structural acrylic adhesive.

Pressure-sensitive hot melt adhesives are thermoplastic rubber-based adhesives. They are characterized by the fact that they do not fully set, instead remaining permanently sticky. This allows for an excellent adhesive bond even when the glue is cold. In this case, the required contact pressure is the key to creating a sufficient coat between the contact adhesive and the joined part, which is why this group of adhesives is also referred to as “PSA-pressure-sensitive adhesives” (Figure 20).

Styrenic block copolymers based PSAs are the latest type which are introduced into the market. They are generally blends of triblocks of styreneisoprene-styrene (SIS) and styreneisoprene diblocks blended with a low-molecular-weight and high- T_g resin based on C5 rings that is miscible with the isoprene phase and not miscible with the styrene phase. It is compulsory to state that a tackifying resin is a necessary component of approximately any class of PSA [26].

Silicone pressure-sensitive adhesives are high-performance adhesives that can be utilized over a wide range of temperatures, from -40 to 300°C (Figure 21).

They bond to both low energy and high-energy surfaces. Silicone polymers based on gum contain dimethylsiloxy and diphenylsiloxy groups (Figure 22) [37].

The molecular weights of solvent-borne silicones are preferably in the range from 500,000 to 1,500,000 Daltons [38]. The crosslinking of silicone PSAs containing methyl or/and phenyl groups can be achieved thermally between 120 and 150°C using organic peroxide.

With respect to performance, the characteristics of PSA are generally determined by their ingredients. The insert to the right gives a brief summary based on ingredient type [1, 4, 13, 14].

The main applications are as follows:
Temporary bonding (re-bonding not required; easy removal preferred).
Bonding “hard to bond adhered (e.g., PP, PE, PTFE, and EPDM).
Temporary bonds (e.g., adhesive processing of nameplates, adhesive coatings on labels, films).
Primary processing of adhesive components (e.g., double-sided adhesive tape).
Repeated peeling and adhesion (requiring enhanced re-adhesion and peeling properties).
It’s important to select the appropriate type of PSA for your needs.



Figure 20.
PSA hot melt.

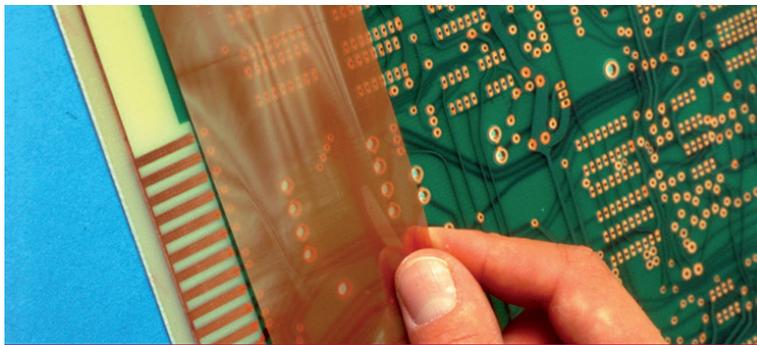


Figure 21.
Silicone PSA application in electronic circuits.

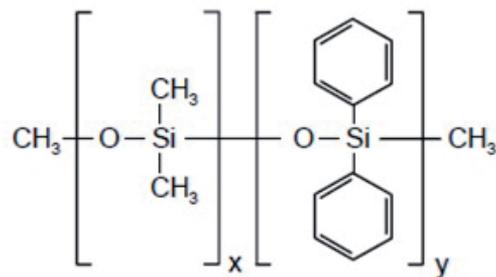


Figure 22.
Silicone PSA structure.

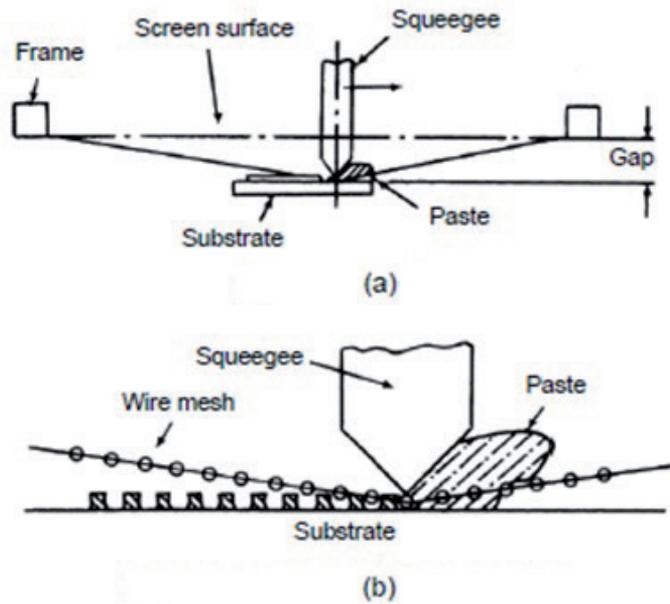


Figure 23. Screen printing: (a) Pattern making (b) Printing.

Screen printing which is one application of PSAs initiates with stretching a piece of screen (mesh) over a frame and securing it into place. After that, a photoreactive emulsion that cures when light is irradiated onto it is applied to the mesh. Then, the desired pattern is placed onto the emulsion-coated mesh (**Figure 23**). In the next stage, the sealant emulsion was used to form a resist when being exposed to light. To remove the unhardened emulsion, the screen is washed, and the pattern emerges as an opening not covered by the resin which can be used as the plate for screen printing. For printing, ink is then placed inside the frame, and the plate is placed over the substrate to be printed. The pattern is transcribed onto the substrate when the ink is pushed out of the opening with the linear pressure from the squeegee. This process can be repeated many times to mass produce substrates with the same pattern [39].

Before the film assembly on LCD, other processes including punching, transporting and inspecting are necessary. Thus, the application of a protective film is compulsory to protect the surface of the optical films from contaminants or scratching. A sketch of a polarizing plate with a protective film is demonstrated in **Figure 24**. The substrates of the protective film are typically fabricated using polyethylene (PE) or polyethylene terephthalate (PET) with pressure-sensitive adhesives (PSAs) coated on one side. PSAs are viscoelastic materials that can adhere to various substrates upon application of light contact pressure in short contact time [40].

There are two different major classes of medical adhesives available [41]:

- Permanent or tissue adhesives (glue).
- Removable adhesives (pressure-sensitive adhesives).
- Other than acrylics, there are other types of PSAs for medical applications:
- Silicone-based adhesives, which are used in transdermal drug delivery systems (drug delivery). These devices are in need of an inert adhesive and biocompatible system.

- Polyvinyl ether-based adhesive, which are used in permeable skin patches.
- Polyvinyl pyrrolidone-based adhesives, which are used for high moisture absorption applications, such as ostomy bags and mounts, without the loss of adhesion.
- Urethane-based adhesives, which are used for sustained released wound dressings and urethane implants.

The biggest amount of the pressure-sensitive adhesives on the market is for wound protection. The applications for PSAs are:

- Transdermal drug delivery.
- Adhesive bandage or plasters.
- Adhesive drapes.
- Ostomy bag mounts: construction of an opening in the human skin. For example, a tracheostomy.
- Intravenous needle attachments, like morphine perfusion.
- Electro medical procedures.
- Microporous tapes.

Drug-loaded adhesive patches delivering the therapeutic agent, when applied to the skin, at a controlled rate, through the skin to the systemic circulation and to the target organs are transdermal drug delivery (TDD) systems. For maintaining intimate contact between the patch and the skin surface, adhesives are used in TDD applications. Many types of adhesives might be considered to be used for application of TDD patches although PSAs are preferred. There are other factors to be considered in the selection and use of PSAs for TDD systems in addition to the usual properties of PSAs such as tack, adhesive and cohesive strength including compatibility, biocompatibility, delivery system compatibility, formulation, and acceptable regulatory status being equivalent supporting documentation or the availability of drug master files [42].

The adhesive matrix or drug-in-adhesive (DIA) design in its simplest form is directly applied into the PSA matrix. DIA's design configuration is shown in **Figure 25a**.

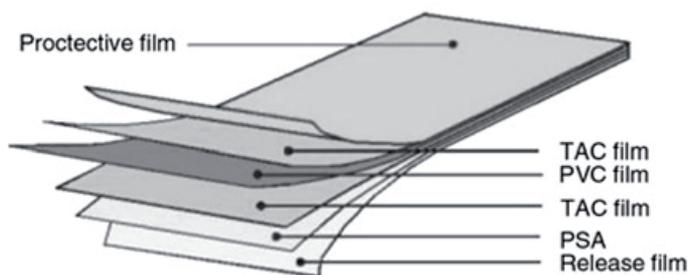


Figure 24.
A polarizing plate with a protective film.

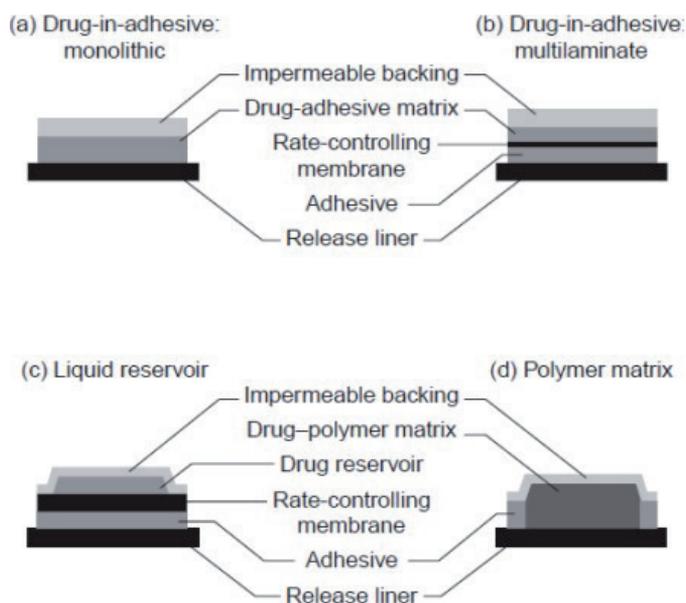


Figure 25.
Typical designs of TDD systems.

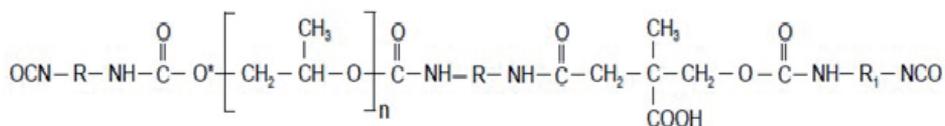


Figure 26.
Structure of polyurethane based PSA.

The adhesive matrix transfers several properties, including peel adhesion, control over drug delivery rate and storage of the drug, and it also governs their partitioning into the stratum corneum. An impermeable backing film supports DIA matrix on the topside and on the side facing the skin there is a lamination with a removable release liner [1, 42].

There is also a contribution of the extraordinarily diverse chemistry of polyurethanes to the development of efficient adhesives applying only to a limited degree to PSAs for which the number of patent publications is surprisingly small. Solvent free 2-K PSAs on the basis of polyether polyols and isocyanates are available on the market (**Figure 26**) [27].

Previous studies have shown [43] that aliphatic polyesters with molecular weights ranging from 10,000 to 50,000 Dalton and T_g between -25 and -47°C can give us excellent adhesion. An example of this method is the acrylation of polyester PSAs containing end groups of hydroxyl. Introduction of an unsaturated architecture can also be practically achieved via the reaction of the OH-groups of a polyester chain with the corresponding acrylic or unsaturated isocyanate compounds [44].

4. Manufacturing of PSAs

The manufacture of pressure-sensitive raw materials and adhesives can be carried out off -line or in-line. As illustrated in **Figure 27**, both technological

modalities include various chemical technologies. Generally, off-line synthesis yields pressure-sensitive raw materials or PSAs; in-line technology leads to simultaneous PSA and PSP (pressure-sensitive products) manufacture [24].

As illustrated in **Figure 28**, off-line synthesis (1) allows polymer-based PSA formulation to be coated (2) and (if necessary) transforms (mainly by cross-linking) in PSP.

Pressure-sensitive products (PSPs) are multilayer constructions based on solid state materials and coated component. Therefore, the production of the PSPs includes the manufacture and assembly of the individual components. The manufacture of the components includes the manufacture of both the solid-state carrier materials (face stock and release liner) and the coating components (adhesive, adhesive, primer, etc.) Generally, the buildup of the PSP from its components is carried out by coating and laminating and leads to a web-like product that must be confectioned. **Table 1** presents the manufacturing technology of main PSPs and demonstrates that the manufacture of PSPs by coating of a solid-state carrier with a liquid pressure-sensitive adhesive (PSA) is the main procedure to produce various

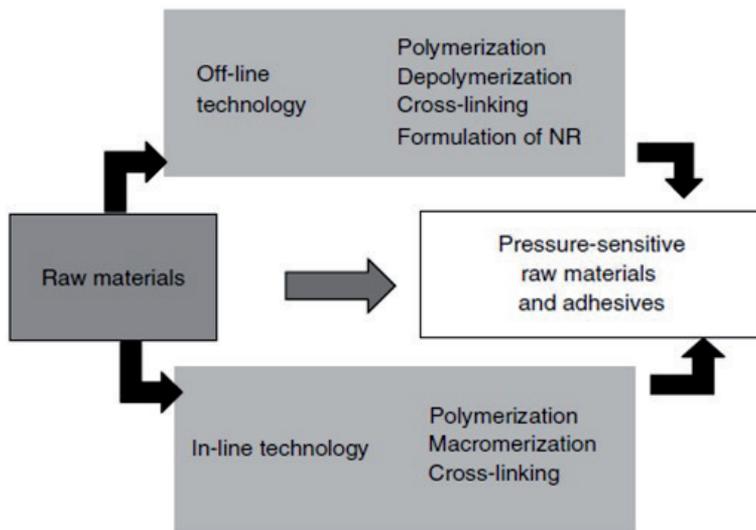


Figure 27. Principles of manufacture technology for pressure-sensitive raw materials and adhesives [24].

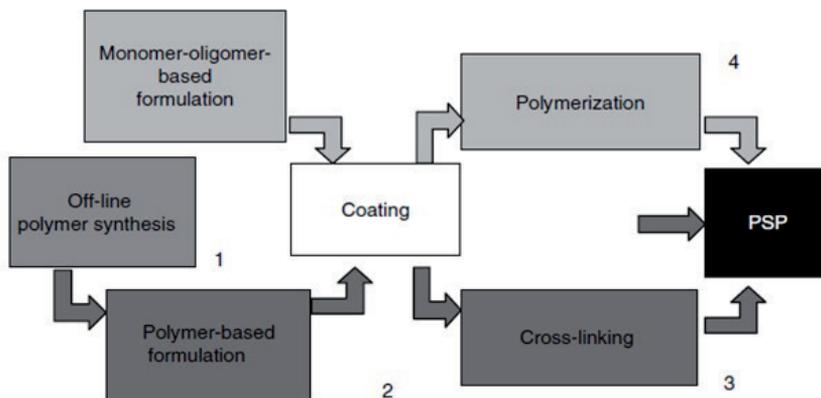


Figure 28. Manufacturing steps for PSPs [24].

Manufacturing procedure	Parameter					PSP	
	Free choice of product components		Running speed				On-line manufacture
	Carrier	Adhesive	Very good	Good	Fair		
Coating	●	●	●			●○	Label, tape, protection film
Extrusion coating	--	--		●		●○	Tape, protection film
Coextrusion	--	--			●	●○	Tape, protection film

Note: ●, preferred; ●○, possible.

Table 1. Manufacturing technology of main PSPs [24].

PSPs. The principal coating component is the PSA. Other coating components are used to allow the anchorage of the adhesive on the carrier (e.g., primer) and its debonding from the laminate (e.g., release agent) and to protect or finish the adhesive or the carrier (e.g., printing inks, lacquers) [1, 6, 17, 24].

PSAs manufacturing includes the manufacture of the raw materials and also their formulation. PSAs can be found in different forms such as solutions, dispersions, or hot-melt adhesives. Water-borne PSAs can be used in certain cases without any additional formulation. Solvent-based acrylic PSAs may also be used without further formulation. PSA manufacture is originally based on the blending and dissolving of different raw materials, none of which exhibits a PSA character lonely.

For preparation recipes for PSAs, formulating must be done via changing the adhesive composition, by addition of different macro- or micromolecular compounds with elastomeric or viscous, surface active or chemically stabilizing properties; antimicrobial agents must also be added to the adhesive. PSAs should have a Tg of about -15° to -5°C . Latexes' sensitivity to bacteria resides in the moderate pH and presence of polyvinyl alcohol. Blending a high Tg, hard resin with a lower Tg elastomer provides a desirable formulation. Considering labels, PSA coating and converting, and end-use require other special performance requirements which can be obtained only through formulating. For the formulation of PSAs, it is needed to produce tailored adhesives for each one of the intended applications. Parameters including the converting technology of the adhesive, the coating technology, the end-use properties, and economical criteria influence the formulation of PSAs. The first reason for formulating is the necessity to improve the adhesive properties. Rubber based PSAs do not possess appropriate intrinsic tack and peel adhesion. Most viscoelastic materials with intrinsic tack being obtained via the synthesis do not show enough peel adhesion to nonpolar surfaces, and soft, tacky PSA raw materials exhibit too low shear adhesion. In cases of water borne or solvent borne acrylic PSAs, the removability of the PSA must be improved. Therefore, a proper balance between high tack, peel adhesion, and high cohesion has to be achieved using formulation. Formulating for high tack and peel (tackification), using viscous formulating agents such as tackifiers and plasticizers decreases the shear adhesion. A high cohesion level may be achieved by the rubber-like component of the adhesive or by partial cross-linking [6, 15, 22, 24].

There are rubber-like (elastic) and liquid like (viscous) PSA components.

Natural raw materials with rubber-like properties and natural resins or plasticizers may be used in order to formulate an adequate recipe. Physical modification allows the use of these materials in a suitable state [22, 27].

Natural rubber is used as a solution, and manufacture of the PSAs implies dissolution of the rubber. In fact a slight mechanochemical destruction of the rubber occurs in parallel with the dissolution process. At least theoretically a preclendering (i.e., a controlled depolymerization of the natural rubber) is possible, but not economically viable. There are only a few special uses (like protective films) where mastication of the rubber must be carried out. Masticated rubber was used for tapes. Pressure-sensitive adhesives exhibiting low tack, for bonding onto themselves, also are formulated on the basis of masticated natural rubber [4–4]. The high molecular weight portion of natural rubber is insoluble in solvents and therefore natural rubbers must be milled to a Mooney viscosity of 53–75 or below, to obtain solubility at 10–30% solids in solvent [6].

Solvent-based PSAs are tackified elastomers, tackified or untackified viscoelastomers, or tackified plastomers. Both (the tackified and the untackified recipe) need adhesive solutions as a blending medium; that is, mixing of the components occurs in solvents. Classic, solvent-based adhesives were formulated with natural rubber (NR) and tackifier resins. Later, synthetic rubber-like products were introduced. Acrylics, vinyl acetate (VAc) copolymers, silicones, polyurethanes (PURs), and other viscoelastomers enlarged the choice of raw materials for solvent-based PSAs and the diversity of the required equipment. Solvent-based acrylics need a special design, but less formulation. It is well known that various materials can be used as adhesives [45–47], among which acrylic polymers are the most popular ones for PSA applications because of the inherent unique properties. Acrylic PSAs, generally borne in an organic solvent, must possess correspondingly suitable 180° peel strength, high shear strength and appropriate tack for optical film applications. The adhesive properties of acrylic PSAs are critically determined by the monomer compositions, the initiators, the crosslinking agents and the tackifiers of acrylic PSAs [48–50].

The main differences between solvent-based and water-based systems are that solvent based systems are homogeneous and water-based ones are heterogeneous; solvent-based systems have low molecular weight (limited by the solubility/viscosity of macromolecular compounds), whereas water-based ones possess higher molecular weight; solvent based systems may be formulated without non adhesive components, but water-based systems must include technological additive. Started with rubber–resin PSA solutions, label coating now uses mostly acrylic, water-based PSAs. Therefore, the formulation of PSAs for labels is mainly a formulation of water-based compounds. In practice, it consists of the blending of liquid-state components, that is, the viscoelastomer dispersion and the tackifier dispersion. It should be taken into account that in a different manner from true solutions, water-based dispersions have a limited (4-year) shelf life, narrow storage-temperature intervallum (–30 to +70°C), and low shear stability. First step of the manufacturing process is the emulsion polymerization process of acrylic monomers in a polymerization reactor plant. After that, this water borne acrylic polymer solution called latex has to be mixed with other additives to be formulated as a PSA applicable for PSP applications. Blending acrylic dispersions requires a test of compatibility, adjustment of pH, and, after the addition of solvent, plasticizers, or fillers, storage time. Peel improvement after longer storage times for a tackified acrylic dispersion is also necessary [1, 6, 7, 15, 51, 52].

Hot melts are based on special designed polymers that need complex formulation. Generally, hot-melt PSAs (HMPSAs) are formulated from thermoplastic

elastomers (TPEs) and viscous (liquid) components. The manufacture of HMPSAs requires mechanical size reduction, micronization of certain elastomers (TPEs are generally pelletized), and molten state mixing of them with other components of the recipe (tackifiers, oils, antioxidants, etc.). Such mixing is carried out discontinuously or continuously [6] with a special apparatus that produces a heat history of the material. For continuous mixers the heat history is very low. Principally, melt mixing can be carried out using a variety of heated mixing equipment. In order of increasing effectiveness, these include vessels stirred with propellers, vessels with high shear (Cowles type) dispersers, planetary mixers, internal mixers (Sigma blade or Banbury type), and modifications of these. In low shear mixers, resins, plasticizers, and stabilizers should be melted first and thermoplastic rubber crumb added incrementally. Where production rates are high enough, continuous mixers are desirable because they reduce degradation of the rubbery mid-block. For hot-melt manufacture, compounding is mixing of the adhesive components at 120 and 200°C, where the shear forces cause a drop in the viscosity. The construction and hydrodynamic characteristics of the mixing equipment may influence the processing performances of HMPSAs; the raw materials used affect it also. For instance, when polyacrylate rubber-based HMPSAs are prepared, high shear mixing is required. As a rule of thumb, increasing mixer shear and temperature lead to better mixing of the adhesive components, a breakdown in molecular weight, and a subsequent increase in tack and reduction in shear performance. In some cases, these effects may be significant enough to overwhelm any effects caused by changing the adhesive formulation; for that reason, some researchers choose to solvent blend and solvent coat samples rather than use a mechanical mixer or extruder. Furthermore, adhesive melt viscosity and shear strength are extremely sensitive to melt processing and subsequent breakdown in molecular weight, whereas tack and peel resistance are relatively robust and will remain relatively unchanged [22, 24].

Generally, the manufacture of PSPs includes the manufacture of solid-state components (e.g., carrier materials for face stock and for release liner), the manufacture of liquid adhesive and nonadhesive components (e.g., PSA, release and primer), and their assembly in a continuous web-like material. The PSA can be coated on or built into the bulk carrier material. The classic way to manufacture a PSP is by coating a carrier material with a PSA. Manufacture of the finished product by carrier coating employs a coating technology completed by other converting steps that are common for web-like products. Web finishing is the coating of liquid product components on solid-state web components or their build into solid-state web components. From the technological point of view, PSPs can be manufactured using coating, extrusion coating, or coextrusion. Generally, coated adhesives are components that are deposited on the surface of a carrier material. The manufacture of PSPs by coating is a common procedure for classic products. Coating technology uses various coating methods; their choice depends on the physical state of the adhesive (e.g., solvent-based, water-based, or HMPSA) and PSP grade. For labels, roll-coating and screen printing offer the best results, but blade, cast, and slot-die coating are used also. For tapes, roll-coating, slot-die coating, extrusion, and calendaring are mostly used, but blade, cast, and spray coating were suggested as well. Protection films are manufactured by roll and blade coating. Different protective are illustrated in **Figure 29** [22, 24, 28].

Coating methods can be classified as impact (i.e., contact) coating (e.g., roll-coating, screen printing) and nonimpact coating (e.g., spray coating, curtain coating) and according to the dosage of the coated material, that is, whether it is in excess or metered (**Table 2**).

There is also manufacturing of PSPs via extrusion process. Actually, pressure-sensitivity of PSPs resides in their coated or built-in pressure-sensitive layer. Buildup

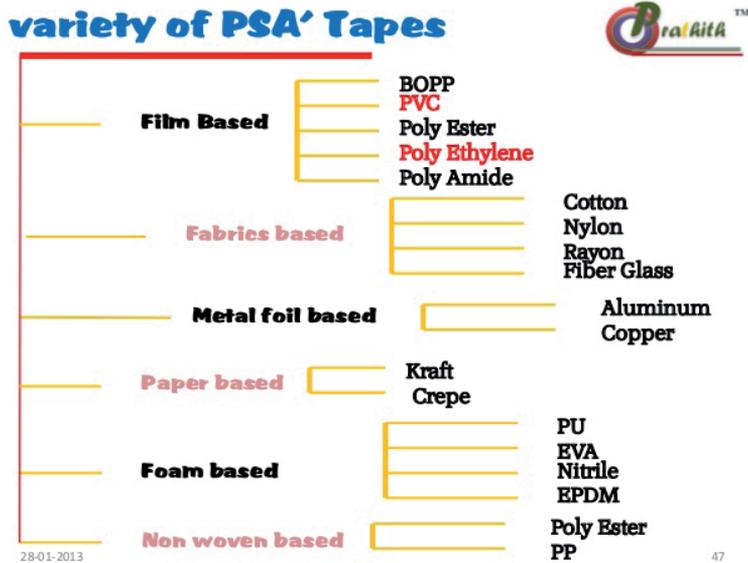


Figure 29.
 Different PSA tapes based on protective films.

Impact coating		Nonimpact coating	
With adhesive excess	With adhesive dosage	With adhesive excess	With adhesive dosage
Knife coating	Slot-die ^c	Air brush ^f	Spray coating ^{d,f}
Roll coating ^a	–	–	Curtain coating ^e
Screen coating ^a	–	–	–
Calendaring ^{b,c}	–	–	–
Main use in other technologies ^c			

^aPrinting (gravure, flexo).
^bRubber processing.
^cPlastic film manufacture (cast, chill-roll film).
^dPrinting (ink jet).
^ePlastic film manufacture (plasticized cast film).
^fLacquering.

Table 2.
 Working principle of different coating devices [24].

of a PSP from its components means the classic manufacture of the finished product which are the carrier material and the PSA, respectively. Practically, other product components such as the release liner and cover film can be built in through one or more layers resulting in a laminate with a complex structure. The PSP can also be manufactured in one step, offering primarily economic advantages if a carrier material with built-in pressure sensitivity is used. As a result, economic considerations forced the development of extrusion-made products. **Table 3** concludes the main properties of the manufacture of adhesiveless and adhesive coated PSPs [22].

When manufacturing PSPs, the final properties of the product and trends in production technology must also be considered. The selection of the PSP components in the manufacturing process of it depends on the product type. There are some limitation in each product class regarding the choice of manufacture equipment and

Raw materials	Manufacturing procedure	PSP
Polyethylene	Extrusion	Protective film
Ethylene-vinyl acetate copolymers	Extrusion, coextrusion	Protective film, business forms
Ethylene-olefin copolymers	Extrusion	Protective film, decoration film
Ethylene-acrylate copolymers	Coextrusion	Protective film, tape
Butene-isobutene copolymers	Coextrusion	Protective film, tape
Vinyl acetate copolymers	Extrusion	Business forms
Vinyl acetate copolymers	Extrusion, casting	Tape

Table 3.
Major raw materials and manufacturing processes for PSPs [22].

laminate components namely printing technology consideration in label manufacture which determines the choice of the label components and manufacturing method. The manufacture of labels should begin with the design process and also include digital artwork and reproduction, origination and pre-press electronic design and artwork plate types, and plate making,. Changes in technology go back to the material components or new technologies used in production. The printing industry has undergone changes to meet these standards. Water-based, solvent-free, and 100% solids adhesives are being used more and more to meet the law of the toxic products emission standards. Food laws get tougher in controlling the effect of migration of various components of the package and also their interaction with the packed products. These changes motivate the use of solvent-free and adhesive-free products.

5. Conclusions

As wholly discussed in this chapter, PSAs as viscoelastic, non-Newtonian flow behavior which is based on the macromolecular nature of the adhesive are increasingly replacing more traditional adhesives because of their ease of use and safe manipulation. Environmental limiting laws drive research toward other production methods to coating from solution in spite of the developments of energy-efficient solvent-recovery methods. Acrylic latexes are so popular for general-use PSAs. However, there is a limitation for their access to the most demanding applications due to the presence of surfactants in their microstructure, which are not easy to eliminate and the lesser control over the molecular structure. The manufacture of pressure-sensitive raw materials and adhesives can be carried out off -line or in-line. An increasingly popular production method is hot-melt, or solventless, technologies. In this process, the viscosity should be lowered enough for an easy coating without the use of any volatile compound. Regarding end-use properties, the future trend for PSAs will be in the direction of heterogeneous polymer structures and also on the incorporation of additional functionalities such as thermal or electrical conductivity or controlled drug release.

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