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Pressure-sensitive adhesives based on acrylics

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Contents

Abbreviations

ABBP – 4-acryloyloxybutoxy benzophenone

ABO – 4-acryloyloxy benzophenone

AEBP – 4-acryloyloxyethoxy benzophenone

AFERA – Association des Fabricants Europeens de Rubans Auto-Adhesifs

AHBP – 4-acryloyloxyhexoxy benzophenone

Al – aluminum

AlACA – aluminum acetylacetonate

ASTM – the American Society for Testing and Materials

Co – cobalt

Cr – chrome

EB – electron beam

EBC – electron beam crosslinking

EVA – ethylene-vinyl acetate

Fe – iron

HMA – hot-melt adhesive

HMDI – cycloaliphatic dicyclohexylmethane

HMPSA – hot melt pressure sensitive adhesive

IPDI – isophorone diisocyanate

ISO – international organization from standardization

LVS – low viscosity systems

MEK – methyl ethyl ketone

MI – melt indices

Mn – manganese

MQ – functional siloxane resin

Ni – nickel

NR – natural rubber

PIB – polyisobutylene

PPDI – diphenylene diisocyanate

PSA – pressure-sensitive adhesives

PSTC – pressure-sensitive tape council

PU – polyurethane

PVC – polyvinyl chloride

SBS – styrene-butadiene

SIS – styrene-isoprene

TDI – toluene diisocyanate

T_g – transition temperature

Ti – titanium

TMDI – 2,2,4-trimethyl-hexamethylene diisocyanate

UV – ultraviolet

VOC – volatile organic compound

Zn – zinc

Zr – zirconium

Introduction

A pressure-sensitive adhesive (PSA) is a class of adhesive material that adheres to a substrate under light pressure and can be removed cleanly, on demand, without leaving residues on the substrate. They can be defined as a viscoelastic material, which in a solvent-free state remains permanently tacky at room temperature. To exhibit this property, a PSA should have cohesive strength that is much higher than its adhesion strength to the substrate. Mechanically, a PSA is a soft, sticky substance; consequently, a supporting backing is often required to convert it into commercially useful forms, such as tapes and labels [1, 2]. The purpose of this review is to describe the various aspects of pressure-sensitive adhesives based on acrylics.

1. The history of pressure-sensitive adhesives and self-adhesive materials

In the long history of this technology, pressure-sensitive adhesives and tapes as we know them are a fairly recent concept. However, to trace their origins, one needs to study the history of adhesives as a whole, including the many failures and near misses along the way, as well as the fusion of various technologies, which eventually led to their development. Since the dawn of history, people have learned of the healing powers of certain leaves and plants. There is archaeological evidence indicating that adhesives have indeed been found on primitive tools. More than 6000 years ago, on the arrival of the Egyptian Civilization, the art of healing was already a profession. A primitive tape concept used by Egyptians was the use of a paste of starch in water applied to cloth strips. It indicates that surgical bandages, made of a mixture of fat and honey, were in use. There is very little known of the other raw materials used in Egyptian/Greek times for surgical dressings. It is known, though, that resins, pitches and so on, were in common use in other trades and professions, for instance in the shipbuilding industry, and such resins would no doubt work well as tackifying resins in pressure-sensitive adhesive systems [3].

Pressure-sensitive adhesives were in wide use since the late 19th century, starting with medical tapes and dressings. The earliest was awarded in 1845. This was for a surgical pressure-sensitive adhesive that used natural rubber as the base, and pine gum as the tackifier, with balsam of Peru, turpentine, and spirits of turpentine also being added. Ninety years later Stanton Avery developed and introduced the self-adhesive label. Two major industries resulted from these innovations: pressure-sensitive tapes and labels [3–5].

In the late 1800s and early 1900s, the development first of the bicycle and then the automobile and their need for tires, allowed the rubber industry to flourish. Greater demands were placed on the industry to develop improved rubber-based products, and this improved technology naturally filtered into the existing adhesive tape industry. Industrial tapes were introduced in the 1920s and 1930s followed by self-adhesive labels in 1935. While various materials in roll form were available early in the 20th century that could have been used as adhesive tape

backings, cotton cloth remained the backing of choice, with manufacturing geared to producing surgical tape. The history of PSAs was described by Villa [2, 4, 6].

Minnesota Mining and Manufacturing Company, popularly known as 3M, was the supplier of sandpaper to the automobile industry in the 1920s, their brand is known as "Wetordry™". Richard Drew, then a laboratory technician for 3M would occasionally call at the automobile plants and body repair shops to take developmental samples of sandpaper for testing. There followed a whole series of patents by 3M on pressure-sensitive adhesive tapes, which laid the cornerstone of the industrial adhesive tape industry. The patents were awarded in 1933 for the transfer of his masking tape know-how to cellophane film, making the first pressure-sensitive film tape, giving the world the generic name of "Scotch" tape [3, 7–9].

The major raw materials for pressure-sensitive adhesives in the mid-thirties were natural rubber, either as pale crepe, smoked sheet rubber, or wild rubber, with reclaimed rubber for primer formulations, coumarone gum resin, burgundy pitch, pine oil, wood resin and gum olibanum as tackifiers, liquid paraffin, or mineral oil, lanolin, and beeswax as softeners, zinc oxide as filler, with whiting as filler for prime coats, and benzol or low-boiling-point aliphatic petroleum hydrocarbons as a solvent. There was little else available [6, 8].

In the 1940s hot-melt adhesives were introduced. The post-war times brought with them exploration, and initial investigations began with balloons being sent into the stratosphere. It was soon learned that adhesives would be needed that were capable of functioning at extremely low temperatures. A research contract was to develop such an adhesive, and from it came Dow Corning's silicone pressure-sensitive adhesive, which could perform in the range from −62 to 260°C, the forerunner of other low/high temperature silicone pressure-sensitive adhesive systems [2, 6–10].

On the arrival of the 1970s, a very large proportion of the raw materials used by the adhesive tape industry were petroleum-derived. The 1980s continued to bring raw material upgrades and new products, particularly in the area of alternate hot-melt elastomers, but little in the way of changes in pressure-sensitive adhesive technology. Product and process development in the industry continues in its upward spiral as can be seen by the number of related patents, which are granted every week throughout the world. Continuing environmental concerns now force the industry to look to other coating techniques than solvent-

based systems, with calendaring the original technique still holding its own as a 100% solids system capable of laying down a heavy coat of adhesive at reasonably high speeds. Work continues to develop effective crosslinked hot-melt adhesive systems to replace those based on natural rubber, and water-based adhesive systems now becoming more viable, with a greater selection of raw materials to choose from, and with an improvement in economics. But the number and uses of pressure-sensitive adhesive and tape products continue to grow as the capability of the pressure-sensitive adhesive system improves, and as the user continues to be educated as to their potential [3, 6, 8, 9].

At the end of the 1980s and during the early 1990s 3M, Beiersdorf, BASF and Lohmann presented the first solvent-free pressure-sensitive adhesive acrylics crosslinked with UV radiation. Six years later 3M Company presented a new adhesive tape with pressure-sensitive thermosetting adhesives, the semi-structural adhesive tape [7–10].

2. Kind of pressure-sensitive adhesives according to used polymer

There are many criteria for the division of pressure-sensitive adhesives. The pressure-sensitive adhesive market includes many polymeric raw materials. There are used natural rubber, various types of synthetic rubber, such as styrene-butadiene and ethylene copolymers, polyvinyl ether, polyurethane, acrylic, silicones, and ethylene-vinyl acetate-copolymers. However, basic pressure-sensitive adhesive formulations are acrylics, rubbers and silicones. Kind of PSA according to use polymer can be divided into acrylic, rubber, silicone, polyurethane, polyester, EVA and polyether pressure-sensitive adhesives (Fig. 2.1) [3, 10].
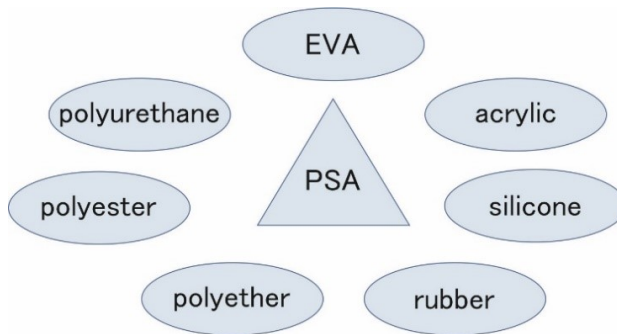
Fig. 2.1. Kind of PSA according to used polymer

2.1. Acrylic pressure-sensitive adhesives

Acrylic polymers are the most commonly used self-adhesives, having replaced compounded natural or synthetic resin. Acrylic offers oxidative stability and resistance to UV radiation are inherently tacky and can be adapted to a variety of uses by copolymerizing two or more monomers, including nonacrylates such as vinyl acetate, N-vinyl pyrrolidone, or N-vinyl caprolactam. The composition of acrylic polymers that are inherently pressure-sensitive is a combination in the polymer chain of soft (low glass transition temperature T_g), hard (high glass transition temperature T_g) and functional monomers. Normally acrylic PSAs contain typical hard and soft monomers, as well as the types of functionalities

that can be incorporated into the polymer chain. Although the pressure-sensitive acrylic adhesives may be dwarfs in terms of quantity, they are giants when considered from the quality point of view. Only through these acrylic specialties was it possible to succeed in drafting the present surprisingly efficient generation of medical pressure-sensitive adhesive tapes and other self-adhesive materials medical grade for prominent assembly projects at justifiable cost for medical applications [10–12].

The most important requirements for a pressure-sensitive adhesive, such as high tackiness (adhesion by the touch), high cohesion (inner stability), high stickiness (adhesion), UV, solvent, and temperature stability are outstandingly fulfilled by acrylics. Solvent-borne, water-borne or solvent-free acrylic PSAs offer several advantages such as excellent aging characteristics and resistance to elevated temperatures and plasticizers, exceptional optical clarity due to the polymer compatibility, non-yellowing and free of residual monomers (Fig. 2.2).
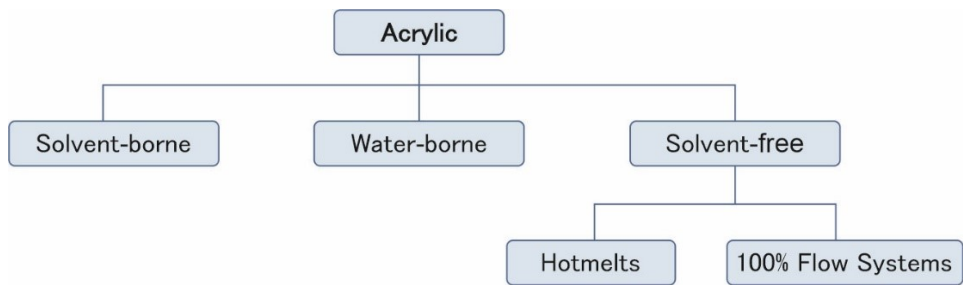
Fig. 2.2. Acrylic type of pressure-sensitive adhesives

They also have the highest balance of adhesion and cohesion and excellent water resistance. Acrylics are harder than rubbers. This can be seen in a less aggressive tack and slower build-up of peel strength. Lower adhesion to non-polar polyolefins is caused by the polar chemistry of acrylics [11–15].

2.2. Rubber pressure-sensitive adhesives

Natural rubber (NR) is known to exhibit various outstanding properties due to its ability to crystallize under stretching; reinforcing fillers are necessarily added into NR in most cases to gain the appropriate properties for specific applications. In general, NR alone has a very low level of adhesion to many types of surfaces. It is well known that PSA performances, especially adhesion (peel strength), tack

(probe tack, ball tack and loop tack) and holding power (shear strength), depend strongly on the viscoelastic properties of the adhesives. In formulating a rubber-based pressure-sensitive adhesive, an elastomer provides the elastic component, whereas a low-molecular-weight tackifying resin imparts the viscous component. Because NR alone is not sufficient to provide the required adhesion and tack, it is necessary to blend tackifier resins (for example, aliphatic or aromatic hydrocarbons, polyterpenes, rosin derivatives) with NR to improve its wettability to the adherend and to achieve rapid and effective bonding. At specific blend ratios, these rubber–resin blends become pressure-sensitive adhesives, while at other concentrations, they do not provide adequate performances as PSAs. It is necessary to select the proper types and concentration of tackifier in order to obtain good performance of PSA [2, 10, 16, 17].

When PSAs were made of NR and resins, their use was restricted to low technology such as adhesive plasters and packaging or covering tapes. High damping rubber vulcanizates with good physical properties and classically high damping were achieved by either using a rubber with inherent high damping or by adding high levels of fillers and plasticizers to one which has low damping. Both approaches failed to provide the necessary combination of properties and this problem was sought by using a second elastomer which is more polar than NR with an appropriate polar plasticizer [2, 16–20].

2.3. Silicone pressure-sensitive adhesives

Silicone pressure-sensitive adhesives (Fig. 2.3) are widely used in pressure-sensitive tapes and labels when application conditions or the nature of substrate surfaces surpass the performance boundaries of organic-based PSAs. A combination of the unique properties of silicones, such as high Si–O–Si backbone flexibility, low intermolecular interactions, low surface tension, excellent thermal stability and high UV transparency, often explains why silicone PSAs have superior performance at high- and low-temperature extremes, excellent electrical properties, chemical resistance and outstanding weathering resistance compared to organic PSAs. They are inert and very hydrophobic but still have reasonable moisture permeability [1, 10, 21–23].

Silicone PSAs are usually comprised of high-molecular-weight silanol-functional silicone polymers (although vinyl-functional polymers are used in addition-curable PSAs) and silanol-functional MQ siloxane resins (Fig. 2.4).
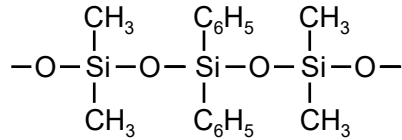
Fig. 2.3. The general structure of a silicone polymer

M unit   Q unit
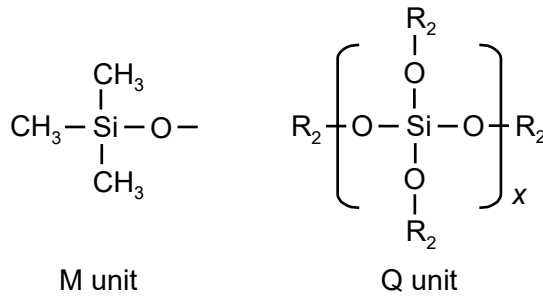
Fig. 2.4. The structural unit found in MQ silicone risen

The dimethyl groups around the Si–O–Si polysiloxane backbone are responsible for low surface tension properties and the ability of silicone PSAs to wet out and bond to substrates with low-energy surfaces, such as Teflon® and Kapton® films. The MQ siloxane resin provides adhesion performance and superior high-temperature stability [1, 24].

Since their commercial introduction in the 1960s, silicone PSAs have found use in a variety of applications. Some of the long-established applications for silicone PSAs are found in industrial operations (masking, splicing, roller wrapping) as well as in electrical and electronics, medical care and healthcare, and automotive sectors. Since the year 2000, there has been much interest in new uses for silicone PSAs, especially in applications such as medical and industrial tapes. The following examples describe the growing range of potential commercial uses where silicone PSAs are being used and exploited [1, 21–24].

2.4. Polyurethane pressure-sensitive adhesives

Polyurethanes (PUs) are a distinctive class of polymers because they have a wide range of applications due to their properties which can be voluntarily adapted by the variation of their components. Ever since the discovery of polyurethanes by Otto Bayer and co-workers in 1937, these have been developed as a unique class of synthetic polymers with a wide variety of applications [25, 26]. The PU

has very flexible chemistry with soft and hard blocks in its structure, which are responsible for its hydrox-mechanical properties. In PU-PSAs, the hard isocyanate (–NCO) segment is responsible for the hydrox-mechanical properties while the soft hydroxyl (–OH) segment provides the wetting properties. The PU has many characteristics when used as an adhesive e.g. widely applicable for most of the surfaces, involves with the surface by hydrogen bonding, low molecular weight i.e. small molecular size provides higher moisture or air transmission rate, form covalent bond with substrates that have active hydrogen atoms, and can be engineered for high-performance applications. The most important performance characteristics of PU-based PSAs are the adhesive properties (e.g. tack, peel adhesion, and shear resistance), the moisture – or air – transmission rate and shrinkage. Polyurethane pressure-sensitive adhesive exhibits many of the industry's most severe requirements in terms of performance, environment and ease of practical application. They have been widely used in self-adhesives, sealants and electrical products owing to their low glass transition temperature (T_g) between –40 and –60°C, hydrophobicity, acid-base resistance and excellent dielectric properties. In many industries, the research, development and application on the coating technology area having a lower chemical impact on occupational health and environment are warmly welcomed especially when it is accompanied by robust application conditions and high standards of performance. Polyurethane adhesives reportedly have high adhesion and extended wear time. For certain specific applications, they are increasingly being utilized [10, 26–29].

2.5. Polyester pressure-sensitive adhesives

Polyester adhesives may be divided into two distinct groups: saturated (thermoplastic) and unsaturated (thermosetting). The saturated polyesters are reaction products of difunctional acids and difunctional alcohols or glycols. Their adhesive applications are minor, except in hot melts (high performance). The unsaturated (thermosetting) polyesters, which require a catalytic cure, have a few uses as adhesives. These usually involve the bonding of polyester substrates. Polyester adhesives are also used in patching kits for the repair of fiberglass boats, automobile bodies, and concrete flooring. Other minor uses include bonding polyester laminates to polyester or metal, and as adhesives for optical equipment [7–9, 30]. Polyester PSAs are newly engendering plastic adhesives the synthesis of which is based on the ester linkage.

2.6. Pressure-sensitive adhesives based on EVA

Ethylene-vinyl acetate (EVA) has a wide range of melt indices (MIs) and good adhesion properties to various adherents, and it is not expensive. Therefore, EVA copolymer is the most popular thermoplastic polymer used in the hot-melt adhesive HMA industry. General EVA copolymers used in HMAs have 18–40 wt.% of vinyl acetate content and their MIs are 2–400 dg/min. The properties of EVA copolymers are mainly determined by their vinyl acetate contents and their MI. In general, MI means the melt flow property of polymer materials at fixed pressure and temperature. Thus, high MI means superior injection molding property. These are the least costly resin materials used in hot melts. Their applications include bonding paper, cardboard, wood, fabric, etc., for use at –34 to 49°C. Compounded versions can be used for non-load-bearing applications up to about 71°C. EVAs represent the highest volume of hot-melt adhesives used, primarily in packaging and wood assembly applications. The domain structure of EVA copolymers consists of stiff and partially crystalline polyethylene blocks and flexible, soft, and polar amorphous vinyl acetate blocks. Tackifiers are commonly added to impart tack to HMA and pressure-sensitive adhesive based on EVA and styrenic block copolymers. The tackifier must be reasonably compatible with the base polymer, have a very low molecular weight relative to the base elastomer, and have a glass transition temperature (T_g) that is higher than that of the base elastomer. Therefore, the addition of tackifiers modifies viscosity, rheology and adhesion properties. PSAs based on EVA are used in production patches with transdermal drug delivery in the pharmaceutical industry [30–32].

2.7. Polyether pressure-sensitive adhesives

Polyether PSA has ether bonds as polyurethanes. The polyurethanes synthesized from polyether polyol are termed polyether urethanes. Although most polyurethanes presently used are of the polyether type because of their high resistance to hydrolysis. These polyether urethanes are rubbery and relatively permeable [32, 33]. Polyether PSAs are newly engendering plastic adhesives the synthesis of which is based on the ether linkage.

3. Kind of acrylic pressure-sensitive adhesives according to polymerization method

Pressure-sensitive adhesives based on acrylic according to the polymerization method can be divided into solvent-based, water-borne and solvent-free acrylic pressure-sensitive adhesives. Solvent-borne, water-borne and solvent-free acrylic PSAs are nowadays predominantly manufactured by polymerization from a wide selection of acrylic, methacrylic and other monomers, often with low levels of monomers having pendant functional groups in a refluxing organic solvent in the presence of an initiator, such as organic peroxides or azo compounds: Solvent-borne PSA acrylics offer several advantages such as excellent aging characteristics and resistance to elevated temperatures and plasticizers, exceptional optical clarity due to the polymer compatibility and non-yellowing [3].

3.1. Solvent-borne acrylic pressure-sensitive adhesives

Solvent-based acrylic pressure-sensitive adhesives are a very interesting group of polymers with self-adhesive properties. The research and development of these polymers is quite an interesting scientific terrain with full innovation and exciting further development in this area is expected [34]. Unconventional properties of solvent-based acrylic pressure-sensitive adhesives meant that they are now widely used for the production of both technical and medical self-adhesive materials. The performance of pressure-sensitive adhesives characterized by a viscosity, adhesion, cohesion and contraction depends on the molecular weight of adhesives used for the manufacture of polymers, methods of polymerization, the nature of the solvent and initiator used in the polymerization process and especially on the type of crosslinker and crosslinking technology used. From the information in the literature, it is known that the most effective way of modifying the properties of pressure-sensitive adhesives, in order to obtain a material with a specific profile is the cross-linking process [35].

High performance of solvent-based acrylic-PSA characterized by high shear strength and high shrinkage [36]. Solvent-based UV-crosslinkable acrylic pressure-sensitive adhesives present a new class of products that offers the potential

to produce a novel generation of ultraviolet cured self-adhesive products with excellent shrinkage resistance. After the carrier for the label, foil or tape production has been coated with the solvent-based UV-crosslinkable acrylate, dried at 110°C, the adhesive film is crosslinked with UV radiation. By this crosslinking procedure, the molecular mass of the adhesive is built up in order to obtain the level of cohesion demanded by the application in question. UV-induced crosslinking is a rapidly expanding technology on pressure-sensitive adhesives area resulting from its main advantages such as solvent-free process, efficient and economical energy used and new properties and quality of chemical crosslinking bonding [37].

3.2. Water-borne acrylic pressure-sensitive adhesives

Water-borne adhesives – polymer particles (acrylates, rubbers, polyurethanes, polychloroprene) are dispersed in water. The mechanism of hardening involves evaporation water or ingress it into connected elements. The water evaporation can be accelerated by used heating and airflow air. These ecological adhesives receiving without containing organic solvents are used to bonging leather, paper and wood [38, 39].

Water-borne self-adhesives are known in the art of natural products such as dextrin, gelatin, casein, or starch, or in the art of synthetic products such as polyvinyl alcohol. Under dry conditions, however, this type of product lacks elasticity and viscosity, showing no pressure-sensitive adhesives properties. These typical natural water-borne adhesives have disadvantages such as little thermal strength and little resistance to aging. On the one hand, a large number of natural or synthesized polymers, by their resorts to raw materials which are produced in large quantities and therefore at a low cost. An unusual and interesting challenge is that of giving a pressure-sensitive adhesive a certain water-borne, which depends greatly on the hydrophilic properties of the group incorporated into the polymer chain [34].

Biodegradable water-based pressure-sensitive adhesives are a very interesting novel group of polymers with self-adhesives properties. The research and development of these polymers is quite an interesting scientific terrain with full innovation and exciting further development in this area is expected [40]. A challenging area of biodegradable water-soluble PSA application constitutes their use for water-dispersible labels and medical devices like surgical tapes and biomedical

electrodes. They are characterized by high mechanical and thermal performances that are not commercially available on the market. Their composition, synthesis method and technical details are described in the great number of patents and are hidden from producers. Biodegradable water-soluble self-adhesives are known in the art of natural products such as dextrin, gelatin, casein or starch, or in the art of synthetic products such as polyvinyl alcohol. Under dry conditions, however, this type of product lacks elasticity and viscosity, showing no pressure-sensitive adhesive properties [3, 34].

Water-borne acrylic PSAs are nowadays predominantly manufactured by polymerization from a wide selection of acrylic, methacrylic and other monomers, often with low levels of monomers having pendant functional groups in a refluxing organic solvent in the presence of an initiator, such as organic peroxides or azo compounds: solvent-borne PSA acrylics offer several advantages such as excellent aging characteristics and resistance to elevated temperatures and plasticizers, exceptional optical clarity due to the polymer compatibility and non-yellowing [41]. They also have the highest balance of adhesion and cohesion and excellent water resistance. Lower adhesion to nonpolar polyolefins is caused by the polar chemistry of acrylics. Acrylics polymer chemistry is expanding through the introduction and utilization of new raw materials, new polymerization process, new modification methods, new crosslinking agents and new crosslinking kind and technology. Water-borne acrylic PSAs offer several advantages such as excellent aging characteristics and resistance to elevated temperatures and plasticizers, exceptional optical clarity due to the polymer compatibility, non-yellowing and free of residual monomers. They also have the highest balance of adhesion and cohesion and excellent water resistance. Acrylics are harder than rubbers. This can be seen in a less aggressive tack and slower build-up of peel strength. Lower adhesion to non-polar polyolefins is caused by the polar chemistry of acrylics [3, 42].

An unusual and interesting challenge is that of giving PSA a certain water solubility, which depends greatly on the hydrophilic properties of the groups incorporated into the polymer chain. The glass transition temperature T_g of the water-soluble raw monomers (Fig. 3.1) is the main criterion for the adhesive properties and water solubility of the synthesized copolymers. The preferred tackifying but water-insoluble alkyl acrylates (Fig. 2.4) reduce T_g and improve the tack and adhesion properties [43].
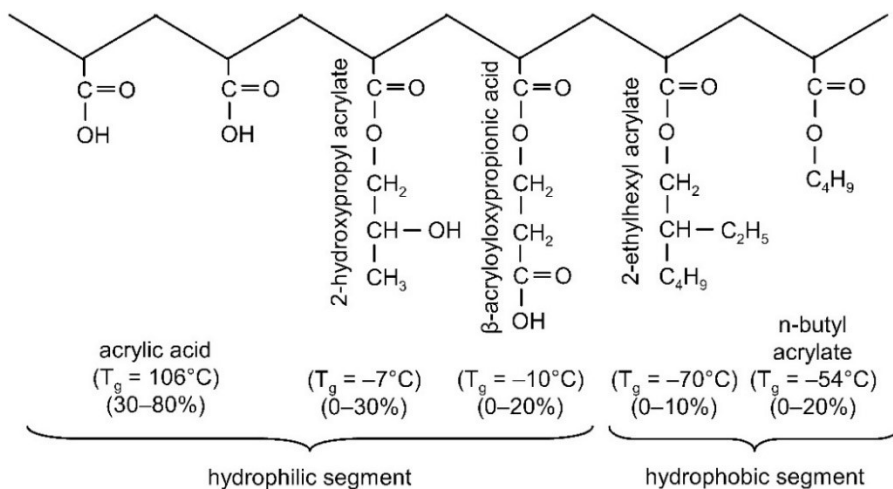
Fig. 3.1. Polymer chain scheme of water-soluble acrylic PSA [43]

3.3. Solvent-free acrylic pressure-sensitive adhesives

Environmental regulatory legislation restricting and/or eliminating the use of solvents in adhesives had spurred the growth and development of solvent-free adhesives. This growth of solvent-free adhesives has come at a time of constantly changing end-use environments, such as increasingly difficult surfaces to ad-herer to and use under extreme conditions, despite the technological challenges of going from solvent-based technologies to solvent-free technologies. Adhesive technologies can generally by classified by their mode of application (such as ex-trusion, roll coating, etc.), the type of chemistry or the end use of the adhesive [44].

Solvent-free pressure-sensitive adhesives are used among other things for the production of self-adhesive mounting tapes (single or double) and carrier-free adhesive tapes for the production of labels, decorative and protective. They are also used in medical products such as patches, adhesive electrodes, patches of active substances and adhesive hydrogels [45]. Solvent-free PSA achieved real practical significance in the 70s with the appearance of thermoplastic rubber, the styrene-butadiene (SBS) and styrene-isoprene (SIS) block copolymers. These thermally reversible or physically crosslinking products allow the formulation of solvent-free PSA with good processing performance. For this reason, they repre-sent a promising advantage to the substitution of rubber solutions. The dimen-sion of this substitution is surprising because these adhesives satisfy the require-

ments only in a very limited way. There is no need here to describe in detail the typical disadvantages such as unacceptable temperature resistance, unacceptable oxidation resistance or poor resistance to plasticizers [46, 47].

To the solvent-free pressure-sensitive adhesives belong the so-called thermo-melt. Hot-melt, it can be coated at a temperature of 100 to 140°C and low viscosity systems (LVS), which can be coated at room temperature. Generally, it can be said that solvent-free pressure-sensitive adhesive can be the most beneficial obtained from solvent pressure-sensitive adhesives where, as a medium, acetone or MEK are used. During stripping of such pressure-sensitive adhesives, adhesive gelation was observed, and the content of the organic solvent is a trace [12].

The adhesives must frequently be subjected to the exigencies of the process in order to achieve the melt characteristics required. It is primarily for this reason that solvent-free PSA based on SBS/SIS block copolymers have not achieved the performance expected of them and are only able to substitute rubber solutions in a limited field of application. According to BASF solvent-free self-adhesives achieve a relatively small, but stable, market share. The ideal would be to link the proven good PSA properties of acrylic PSA produced or formulated in solvents or water with solvent-free acrylic self-adhesive systems. Acrylic pressure-sensitive adhesives which are UV-crosslinked, or which are polymerizable on the carrier are promising solutions to reach this ideal. The desire to use PSA without having to deal with organic solvents has been existing since self-adhesive products have been in mass production. The hot-melt types, dispersion types, and other technologies of solvent-free PSA have been hydroxyl for a number of the PSA applications. However, technologies to substitute solvent-free types of PSA in sectors requiring high performance in terms of weather resistance or heat resistance have not been completed, and therefore acrylic PSAs of the solvent type continue to be widely used [46, 47].

Solvent-free adhesives in particular based on acrylics, obtained by separating the organic solvent from the previously synthesized pressure-sensitive adhesive of the solvent by distilling off the volatile components under reduced pressure [45, 48]. The solvent stripping process can be carried out directly after the polymerization process or at any time after receipt of the solvent from the adhesive. In the case of solvent-free adhesives, the adhesive layer of the adhesive after the crosslinking reaction formed is liquid at room temperature or elevated temperature, solvent-free polymer. The first term melt adhesive acrylic adhesive

UV cross-linkable was introduced by BASF in 1996. Works on the new solvent-free pressure-sensitive adhesives are dictated by the tightening of regulations for the protection of the right environment and the rising prices of organic solvents [12].

4. The concept of acrylic pressure-sensitive adhesives design

Every concept of pressure-sensitive adhesives design can be separated for flew important gropes such as monomer selection, solvent selection, polymerization initiators selection, molecular weight and crosslinking PSA selection and polymerization methods selection. All parts of designing PSA have an impact for further properties of created acrylic pressures-sensitive adhesives.

4.1. Monomer selection

The preferred choice for the manufacture of acrylic pressure-sensitive adhesives is commercially available tackifying acrylic acid alkyl esters with C_4 to C_{12} carbon atoms in the alkyl group together with other commoners such as vinyl carboxylic acid or water-soluble hydroxyalkyl acrylates. The most important members of this class of substances are listed in the overview below (Tab. 4.1) [49–51]:

Tab. 4.1. Monomers choice to design acrylic PSA

Name	Monomer type	T_g [°C]
n-octyl acrylate	tackifying alkyl acrylates	−80
2-methylheptyl acrylate	tackifying alkyl acrylates	−72
2-ethylhexyl acrylate	tackifying alkyl acrylates	−70
Isooctyl acrylate	tackifying alkyl acrylates	−70
Butyl acrylate	tackifying alkyl acrylates	−54
Ethyl acrylate	hardening alkyl acrylates	−24
Methyl acrylate	hardening alkyl acrylates	6
β-acryloyloxypropionic acid	vinyl carboxylic acids	−10
Acrylic acid	vinyl carboxylic acids	106
Vinylphosphonic acid	vinyl carboxylic acids	137
2-hydroxyethyl acrylate	hydroxyalkyl acrylates	−15
2-hydroxypropyl acrylate	hydroxyalkyl acrylates	−7

1. Tackifying alkyl acrylates – alkyl acrylates supply the initial adhesion owing to the low glass transaction temperature (T_g). They reduce the glass transition temperature of the polymer and give it tack and adhesion.
2. Hardening alkyl acrylates – are included to provide internal strength and improve plasticizer resistance.
3. Vinyl carboxylic acids – give the PSA water-solubility and improve the adhesion to polar substrates with high surface energy. They raise the glass transition temperature and create active crosslinking centers to ameliorate the shear strength.
4. Hydroxyalkyl acrylates – give the PSA hydrophobicity and water-solubility. They de-crease the T_g of the synthesized water-soluble copolymers

4.2. Selection of solvents, water-borne systems

During the design acrylic pressure-sensitive adhesives selection of system (water--borne or solvent-borne) is largely dependent on the properties of the monomers used (mainly their solubility) and desired qualities properties of the final product. In this case, the design of the acrylic PSA at the stage of selection of the monomers shall be determined whether it is to be soluble in water or organic solvents.

4.3. Polymerization initiators

Acrylate pressure-sensitive adhesives are prepared by radical polymerization. As polymerization initiators are used compounds easily disintegrate into free radicals. These include alkyl hydroperoxides, dialkyl peroxides, acetyl peroxide, and inorganic type persulphate or hydrogen peroxide. Also, the compounds may be used, which break-up of free radicals is initiated via heat, UV radiation or gamma radiation. Free radicals are usually unstable distinguishing high activity particles having an unpaired electron. Typical initiators of radical polymerization, applicable on an industrial scale for the production of self-adhesive acrylate adhesives are benzoyl peroxide, 2,2'-azobis(isobutyronitrile) [12, 34, 43–48].

4.4. Molecular weight of synthesized PSAs

Molecular weight and molecular weight distribution affect the adhesive properties of acrylic PSAs. Low molecular weight polymers generally have good tack but poor

mechanical strength, and they are unacceptable for normal PSA applications. An increase in molecular weight generally enhances the cohesive strength of the polymers (Fig. 4.1). In general, higher molecular weight acrylic PSAs are more tolerant to skin-penetration enhancers and, compared to the corresponding low molecular weight acrylic PSAs, can accept a higher loading level. Acrylic PSAs that have the optimal distribution of low and high molecular weight components show balanced properties of tack, adhesion and cohesive strength. The molecular weight of acrylic polymers can be controlled by the mode of polymerization and the polymerization conditions (such as reaction temperature and reaction duration). Various modes of polymerization may be employed. For example, polymerization may be performed in a batch process in which all components are charged at the start of polymerization, or a semi-batch process with the partial charge at the start of the reaction, and then the delayed, progressive addition of monomers, solvents or initiators during the course of polymerization. Acrylate pressure-sensitive adhesives characterized by good properties generally have an optimal average molecular weight [3, 51–53].
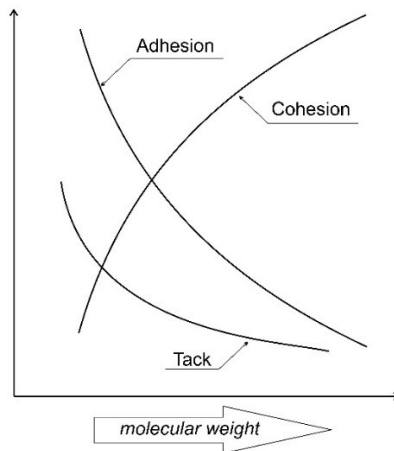

Fig. 4.1. The influence of the molecular weight of the acrylic pressure-sensitive adhesive on the basic properties

4.5. Polymerization methods

Acrylic pressure-sensitive adhesives are produced by copolymerization of acrylic esters, acrylic acid and other functional monomers. The free-radical initiated polymerization process can be performed either in organic solvent systems or

aqueous emulsion. Various monomers can be copolymerized to obtain different pendant ester groups on the backbone. These side-chain pendant groups are used to effect the desired adhesive properties, solubility and permeability. Unlike the PIBs and silicones, the organic solvent-based and emulsion acrylic PSA prepared directly from polymerization are the final, ready-to-use adhesives. Dispersions obtaining in emulsion polymerization using a semi-continuous reaction scheme. A pre-emulsion with monomers, with part of the water and the emulsifying agents and the initiator, is fed to the balance of the water phase in the reactor at a constant rate. No monomer accumulation was observed at any time. Therefore, it was assumed that the reaction was starved-fed. When monomer addition was complete, the reaction was continued. Finally, the adhesives were filtered through a 100 mesh screen to remove the low amount of grit formed during the polymerization. New types of polymerizations have been developed, such as living radical polymerization using functional monomers and including (meth) acrylates. With conventional radical polymerization, as the polymer growth terminal is always in the active radical state, it is easy for the side reactions to occur, such as bimolecular coupling or disproportionation, generally making it difficult to achieve precise control of polymerization. However, with living radical polymerization, polymer growth terminals are temporarily protected by carbon halide bonding and through reversibly and radically severing this bond, it is possible to control and facilitate polymerization. On account of this, the monomer is completely consumed and growth is temporarily suspended. However, by adding another monomer it is possible to restart polymerization. Therefore, the position of the functional group can be controlled and block polymerizations are also possible. Since polymerization is comparatively mild, it is possible to carry out polymerization without solvents [3, 54–56].

4.6. Crosslinking of PSAs

The mechanical and physic-chemical properties of pressure-sensitive adhesives are determined to a great extent by the type and quantity of crosslinking agent added by a modification to the polymerizate. There are two ways to effect crosslinking of acrylic PSAs. The first approach is crosslinking during the PSA manufacturing process. A small number of acrylates or methacrylates with multiple unsaturation can be copolymerized with the acrylic esters to obtain a lightly crosslinked network during polymerization. Examples of such monomers include diethylene

glycol diacrylate, trimethylolpropane trimethacrylate, and hexamethylene glycol dimethacrylate. This in situ crosslinking during polymerization usually leads to a viscous polymer solution and makes processing more difficult. The second approach can be performed by the patch manufacturer. In this approach, crosslinking of the acrylic polymer occurs through the pendant functional groups of the polymer when they are coated and dried in the oven. Monomers with functional groups are introduced into the polymer chain during polymerization. Functional groups commonly used for crosslinking are carboxylic, hydroxyl, epoxy, amide, and organo-silane. Examples of monomers with such functionality are acrylic and methacrylic acid, hydroxylethyl acrylate, hydroxylpropyl acrylate, glycidyl acrylate and methacrylate, acrylamide, and 3-methacryloxylpropyl trimethoxylsilane. Crosslinking agents are often used to activate the crosslinking reaction. Various organic metal crosslinking agents, such as aluminum or titanium acetyl acetonates, metal alkoxides, and polybutyl titanate, have been found to be effective in crosslinking polymers that contain carboxylic and hydroxyl groups. Polybutyl titanate has been reported to produce a 'yellowish' dried adhesive on an estradiol patch, whereas the aluminum acetyl acetonate-crosslinked adhesive was clear. The epoxy groups of glycidyl monomers, such as glycidyl acrylate or methacrylate, react with carboxyl groups without any crosslinking agent [3, 34, 36].

5. Performance of acrylic pressure-sensitive adhesives

It is generally accepted that acrylic pressure-sensitive adhesives' performances, such as peel adhesion, tack, and shear strength, depend strongly on the viscoelastic properties of the PSAs. A balance of tack, peel, and cohesion is very important in designing the acrylic PSAs exhibiting good utility properties [2, 3].

5.1. Adhesion-cohesion balance

The term pressure-sensitive describes adhesives, which in the dry form are aggressively and permanently tacky at room temperature and firmly adhere to a variety of dissimilar surfaces upon mere contact, without the need of more than finger or hand pressure. PSAs possess adhesion, required for bonding and debonding, and cohesion necessary against debonding. Adhesion is characterized by tack and peel, whereas cohesion is described by shear resistance, and partially by peel. The special balance of these properties, the adhesion/cohesion balance, embodies the pressure-sensitive character of the adhesive. The efficiency of the bonding process is related to the adhesive's ability to exhibit viscous flow. In order to achieve peel adhesion, the bonding stage involves some dwell time. During this time, the adhesive must flow in the absence of any externally applied forces. The more liquid-like the behavior of the polymer under these conditions, the more pronounced the degree of bond formation. The debonding process involves a more rapid deformation of the adhesive mass. The polymer's resistance to deformation at higher strain rates becomes very important; the higher this resistance, the higher the force which must be applied to separate the adhesive from the adherent (i.e. the peel resistance). Therefore, high tack, high peel strength adhesives should exhibit good flow at low strain rates, but good resistance to flow at higher strain rates. A proper balance between high tack, peel adhesion, and high cohesion is necessary in most cases. The behavior of any pressure-sensitive adhesive can be reduced to three fundamental and interconnected physical properties: tack, adhesion (peel adhesion), and shear resistance (cohesion). A clear understanding of each property and term is essential [3, 55–57].

5.2. Tack (initial adhesion)

Tack is defined as the debonding force per area of contact and expressed as N/m^2. Tack may also be defined as the property of a material that enables it to form a bond of measurable strength immediately upon contact with another surface, usually with low applied pressure. Tack is the adhesive property related to bond formation. It is the property that enables the adhesives to form a bond with the surface of another material upon contact under light pressure. Tack can be described as the adhesion property whereby adhesives will adhere tenaciously to any surface when it comes in contact with only a pressure which is not more than finger pressure. The American Society for Testing and Materials (ASTM) definition of pressure-sensitive tack requires the bond established to be of measurable strength. Loop tack test is essentially a peel test involving low contact pressure and short application time. Tack is the ability of two materials to resist separation after bringing their surfaces into contact for a short time under light pressure. Measured indirectly, it depends not only on the interfacial and bulk properties of the PSA and the properties of the carrier but also on the employed measurement method and conditions. Therefore, even though all methods are used to evaluate tack at low contact pressures and short contact times, the values obtained by different test methods should not be compared. This is due to the fundamental differences found among the tests or the subtle differences due to differing standard testing procedures [2, 15, 56, 58]. Acrylic pressure-sensitive adhesives exhibiting tack over 8 N/25 mm possessed good utility properties.

5.3. Peel adhesion (adhesion)

Adhesion is one of the most ubiquitous phenomena in nature and technology; it is complex, multifaceted, and governs processes from cell adhesion to bio-fouling. The thermodynamic concept of quantifying the adhesion on a fundamental molecular level is the work of adhesion. It combines all the fundamental interfacial forces responsible for the adhesion of two different surfaces. Many theoretical models explain forces occurring at the interface. Those models are described by adhesion theories which are known as mechanical interlocking, adsorption or thermodynamic, electrostatic, chemical bonding, diffusion, the adhesive effect of thin liquid films and weak boundary layers. Theories though are based on fracture mechanics, surface properties (wetting and adsorption), diffusion and electrostatic or chemical

interaction. The term adhesion can be understood in two different approaches. The first outlined above has strictly theoretical expansion and the second called practical adhesion means in fact the force necessary to break the adhesive bond, to separate two surfaces being in contact. As the first consists of many interfacial interactions, the latter is the sum of these interactions and dissipative energy losses related to the mechanical response of interface, its rheology especially. This value is determined in technology and the most common is peel test. Through the years many experimental tests have been standardized (ASTM, PSTC, ISO, AFERA). Peel adhesion is the average load per unit width of the bond line required to separate bonded materials and its unit is N/mm [2, 41, 48, 59]. Acrylic pressure-sensitive adhesives exhibiting peel adhesion over 10 N/25 mm possessed good utility properties.

5.4. Shear strength (cohesion)

Cohesion refers to the property of "shear strength" or resistance of applied PSA to failure when subjected to shearing forces. According to ASTM definitions of cohesion include "The propensity of a single substance to adhere to itself, the internal attraction of molecules towards each other; the ability to resist partition from the mass; internal adhesion; the force holding a single substance together". The most important means to influence the cohesion of PSAs are tackification and crosslinking. PSAs possess typical viscoelastic properties, which allow them to respond to both a bonding and a debonding step. For permanent adhesives the most important step is the debonding one; the adhesive should not break under debonding (mainly shear and peel) forces (i.e., permanent adhesives must provide a higher level of cohesive or shear strength than removable adhesives). In addition to the size of the interactions between the molecules, cohesion depends also on other factors, including physical state, or the microstructure of the material. The higher degree of organization molecules in the body greater the forces of cohesion – the largest in solids (max value in crystals), and the almost complete lack of them in the exhaust. Also have significant impact structural defects such as micro-cracks, cavitation or transmission of mechanical stress. In the case of adhesives especially important factor is the temperature which, when reached critical value specific to a particular material will induce decohesion, that is breaking the cohesion forces of the body and the separation of the parts. The most common cause of decohesion in bonding occurs in the so-called weak boundary layer of material with lower mechanical strength. At one end of the spectrum, with high stress or a rapidly increasing stress,

the behavior will be largely elastic and the adhesive will separate at the interface leaving a trace of adhesive residue, or the tape backing will break. At the other end of the spectrum, the liquid component of the adhesion can respond fully, allowing molecular disentanglement within the adhesive resulting in cohesive failure. Typical shear resistance testing is performed with a controlled area of adhesive tape (pressure-sensitive adhesive layer) applied to a standard test surface. Because shear failure is the inability of the pressure-sensitive adhesive to resist continuous stress, any task that is a measure of stress relaxation within the adhesive gives meaningful data. A high shear-resistant adhesive will maintain the stress, while a poor shear-resistant adhesive will relieve the stress quite rapidly. Shear strength is defined as the shear force per unit area of testing and its unit is N/m^2 [2, 3, 55, 60–62]. Acrylic pressure-sensitive adhesives exhibiting shrinkage over 72h possessed good utility properties.

5.5. Shrinkage

The concept of the shrinkage phenomenon is not widely described in the available literature (including pressure-sensitive adhesives). In the case of articles on PSA's are coming to generally understand the definition of shrinkage like "becomes smaller than its original size" (not described in the article) and effect of the tested agent on adhesive. Shrinkage is next to adhesive properties (tack, adhesion) and mechanical properties (cohesion) one of the important useful properties in characterizing the nature of pressure-sensitive adhesives. Shrinkage is the most important property, especially when using adhesive to production films used in the manufacture of decorative banners and adhesive film. Shrinkage depends inter alia on the type of monomers used in the polymerization process, the polymer molecular weight and methods or compounds of cross-linking used in the technology of the self-adhesive materials. For PSA acceptable shrinkage is less than 0.5%. Shrinkage is a very important criterion in the evaluation of the long-term performance of PSAs. Generally, shrinkage is a time-dependent phenomenon, a parameter of dimensional stability, which affects all pressure-sensitive coatings. It depends on the liquid as well as on the solid components of the laminate and their interaction (s. migration, penetration plasticizer resistance, curl, etc.). Shrinkage presents the percentage (S) or millimeter (Ir) change of dimensions of the film covered with PSA and attached to the glass after keeping it for 1 week at temp. of 70°C [29, 36, 42, 63–67].

5.6. Other important properties

Wettability is a property of substances (objects) on their interaction with liquids. Involves are covering a macroscopic layer of liquid gas-filled vessel walls. When the liquid phase is an unstable as a bulk phase. The effect of full wetting occurs when the surface tension of the liquid is lower than the surface tension of a solid. Analyzing the thermodynamic description of the wetting resulting from Young's equation would be expected to completely wet the metal surface by the liquid (e.g. water, cement), since the liquid's surface tension is much smaller than the surface tension of metals. In fact, it should be taken into account kinetic factors and the conditions of measurement. The observed results may therefore differ materially from those thermodynamic equilibrium equations of described in Young and accept only qualitative. Young's equation is based on the theoretical considerations, so every experience, to confirm it contains a certain area of uncertainty, hampering the interpretation of the results. Good wettability of the bonding occurs if the contact angle defined between the tangent to the contour of the bead of adhesive and the substrate glued is less than 30°. In many publications, the concept of σ surface tension σ [mN/m] and the surface free energy γ [mJ/m^2] are used interchangeably, although they are not the same values. Surface tension is the force tangent to the surface, acting on the unit length, and the surface free energy is the work needed to create a new surface unit, the separation of the two phases is in equilibrium. Surface energy is also defined as the difference between the total energy of all the atoms (molecules) and the surface energy, which would be found within the body. Based on experimental studies, it was found that the effect of the surface energy includes a layer of thickness equal to the average particle forming several solid. In the combinations of adhesive is indicated to provide high energy surface area, but it must take into account their increased susceptibility to absorption of steam, gases and impurities. The small surface tension is determined that the material has a low energy surface and is, therefore, less wettable. Large values of the surface tension of solids due to their high melting point and cohesive energy. Important from the point of view of functional connections are impact at the micro-level. High viscosity adhesives, e.g. in the form of a paste, no activity in both the wetting and the melt on the surface bonded, which reduces the resistance has an inaccurate penetration of the resulting adhesive in the inequality [38, 68, 69].

6. Crosslinking methods of solvent-borne acrylic pressure-sensitive adhesives

The crosslinking of PSAs is a useful process in the repertoire of general design procedures and is recognized throughout many of the applications of PSAs. In nomenclature used, 'crosslinking' is a correlation of a network that relates to a net of interconnected chains. Polymeric networks or crosslinked systems consist of interconnected macromolecules, which extend into all three dimensions. Individual molecule chains in the crosslinking are interconnected into, effectively infinitely large molecules. Because of the huge length of the starting polymeric chains, only small amounts of a crosslinking additive are needed to accomplish complete crosslinking, which is a crosslinking covering the total volume of the PSA. The larger the starting molecules are the larger the probability that they will participate in the network concentration at a given amount of crosslinking additive. Therefore, polymers with the lowest molecular weight tend to remain without ties to the network when a low crosslinking degree applies because the polydisperse characteristics of polymers are usually normal [45, 70].

6.1. Goal of crosslinking

Physicochemical and mechanical properties of pressure-sensitive adhesives such as adhesion, cohesion and tack depend largely on the type and amount of crosslinking agent used, as well as on the method of crosslinking. The process of crosslinking pressure-sensitive adhesives is designed to enhance the cohesion of the adhesive, which next adhesion and tack decide on the allocation of the adhesive and the finished product is considered the essential criterion for applying pressure-sensitive adhesives. Shear strength of pressure-sensitive adhesive after curing increases, and the adhesion and tack are reduced. Crosslinking can be considered a critical factor of the PSA in the application stage. It is known that non-crosslinked or crosslinked only at the cost of hydrogen bonding polymer used as a pressure-sensitive adhesive does not have sufficient strength of the thermal-mechanical, and therefore can not be used as a pressure-sensitive adhesive. With the aid of chemical bonds, an increase in cohesion may be accomplished du-

ring the drying of the PSA coating in the drying step. Logically, the tackifying properties of the PSA coat, such as tack and adhesion decrease (Fig. 6.1). The time which can be utilized after the crosslinking agent containing PSAs is set up, is called the pot life. After a second period, the so-called gel point is reached, and the PSA can no longer be modified (Fig. 6.2).
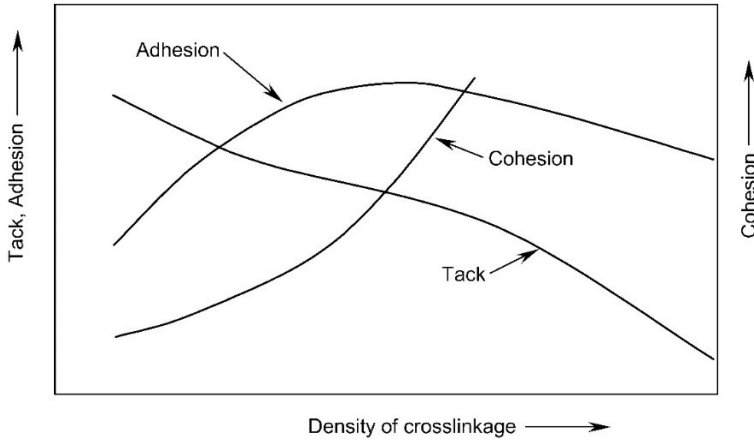
Fig. 6.1. General effects of the crosslinking to the acrylic PSA properties [45]
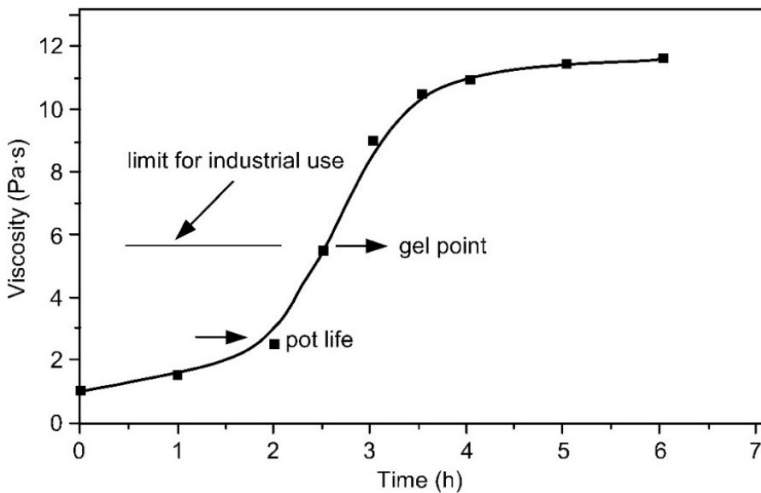
Fig. 6.2. Ability to modify a crosslinker containing PSAs versus time [45]

The curve applies in general to each crosslinking agent containing a PSA system. That means that a fast crosslinking system has a short pot life, and a slow crosslinking system has a long pot life. Fast crosslinking PSA systems for industrial use with a short pot life are often used with two-component application equipment,

which mixes and adds the reactive components just before coating. The technology of pressure-sensitive adhesives commonly used is the following compounds and cross-linking methods:

- – metal salts of organic acids, for example: titanates, zirconates;
- – metal chelates, e.g. iron acetylacetonate, aluminum acetylacetonate;
- – metal acid esters;
- – amino resins;
- – peroxides;
- – epoxy resins;
- – organic functional silanes;
- – multifunctional monomers, e.g. 1,4-butanediol acrylate, allyl vinyl ether;
- – multifunctional isocyanates, e.g. toluene diisocyanate, hexamethylene diisocyanate;
- – multifunctional propyleneimine, derivatives of 2-methylaziridine;
- – UV radiation;
- – flow of electrons [12, 34, 45, 71].

6.2. Physical crosslinking

Pressure-sensitive adhesives in physical crosslinking are also linked by hydrogen bonds when the polymerization carrier is removed. Also, van der Waals forces should be mentioned, which are noticeable in all PSAs free of crosslinking agents and more or less connect the molecule chains by secondary valence forces in a narrow-spaced network. The hydrogen bonds also belong to secondary valence crosslinking and are based on a dipole–dipole attraction of polar groups such as $-COOH$, $-CONH_2$ or $-OH$. If, therefore, such polar groups are present at appropriate distances in an overall nonpolar PSA, the chains are more strongly connected at places where such groups are present in comparison with other places. This causes the characteristic features of crosslinking. The hydrogen bonding existing between polymer chains in PSA systems is fully reversible. A distinction has to be made not only between the hydrogen bridges forming intramolecular and intermolecular crosslinking but also the intramolecular crosslinking between two groups in one individual polymer chain, which is more or less undesired. Only intermolecular crosslinking between the neighbored polymer chain contributes actively to the increase in shear strength. Hydrogen bonds

are three to four times as strong as van der Waals forces. Consequent PSAs with hydrogen bonds are significantly stronger than those which are interconnected only by van der Waals forces. Secondary valence crosslinkings are in general distinguished from primary valence crosslinkings by their thermo-reversible nature. When warmed-up the crosslinking is lost and during cooling it is formed again [45, 72].

6.3. Chemical crosslinking

Chemical crosslinking of a PSA is usually performed during dressing manufacture, using electron beam or radiation curing. Such a cross-linked adhesive may well have reduced peel strength, but frequently also has less tack and initial adherence it is a less strong adhesive. The recognition that higher initial adherence can be desirable, led to the development of an acrylic PSA which behaves as a conventional adhesive on the dressing, but which may be chemically cross-linked at the time of removal, thus making it an adhesive in which bonding can be 'switched off' when desired. The means of effecting the switch is the exposure to visible light, which makes the process safe and easy to apply almost anywhere. Naturally, though, the adhesive must be shielded from bright lights until the time of removal [73–75].

6.3.1. Crosslinking of acrylic PSA by use of multifunctional unsaturated monomers

The use of multifunctional monomers in radiation crosslinking is very common. A multifunctional vinyl monomer promotes rapid free-radical propagation reaction leading to network (crosslinking) polymer structures through grafting via their double bonds. The multifunctional unsaturated acrylic monomer is used in the treatment of the polymer film to reduce the UV-radiation intensities to obtain optimum properties or to achieve an increased cure state at the same UV-radiation intensities [76].

6.3.2. Metal acidesters

Metal acidesters with iron, hafnium, zirconium and aluminum atoms (Fig. 6.3) are particularly efficient as crosslinking agents. The addition of alcohol as a stabilizer after the vaporization of which, in the drying chamber together with other solvents, the crosslinking reaction starts spontaneously is characteristic for

these crosslinking systems. The crosslinking reaction takes place via the carboxyl groups of the copolymer from vinyl carboxylic acid [4, 34, 77, 78].
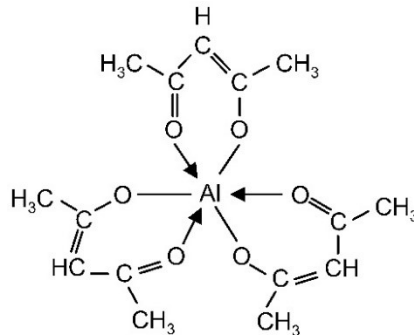
Fig. 6.3. Chemical structure of aluminum acetylacetonate (AlACA)

6.3.3. Metal chelates

The transition metals having a coordination number greater than 2, typically 4, 6 or 8 (exemplified by Zn, Ni, Mn, Fe, Co, Cr, Al, Ti or Zr), form with 2,4-pentanedione (acetylacetone) chelate complexes known as acetylacetonates (Fig. 6.4).

M – central metal atom
a + b + c = n-metal valence
b = 0 or 1
R = alkyl group
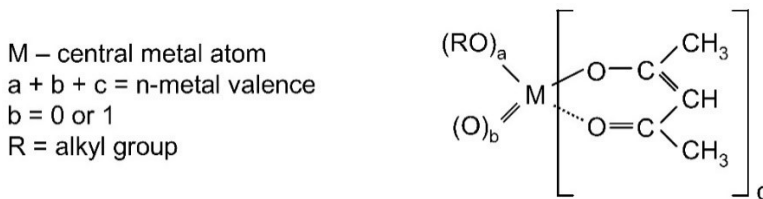
Fig. 6.4. General formula of metal acetylacetonates

The hydrogen atoms of the methylene group $-CH_2-$ accordingly the induction effect of the neighboring ketone group are very mobile. Therefore, the acetylacetonates show the keto-enol antimerism. The central hydrogen atom of the chelate rings is accessible to electrophilic substitution. The following chelating agents can also be used as chelating β-diketones: 2-acetylhexanone, 1,3-diphenyl-1,3-propanedione, 1-phenyl-1,3-butandione, 1,3-diphenyl-1,3-pentandione, 2,4-hexandione, 3,5-heptanedione, 3-phenyl-2,4-pentandione, 2,2,6,6-tetramethyl-3,5-heptandione or 1,1,1-trifluro-2,4-pentandione. The equilibrium between the ketone and enol form of the β-diketone stabilizes slowly at room temperature. Metal chelates that react with the acrylic polymer chains containing carboxylic groups are particularly efficient as crosslinking agents. Chelate-forming

reactions are usually exothermic and therefore, the liberated alcohol does not need to be distilled to make the reaction complete. Indeed, such is the physical nature of the chelates that it is often more desirable to leave the liberated isopropanol in the product as a solvent to facilitate handling. Only capable of forming coordinate bonds with two donor atoms is a metal atom with maximum valence six. The chelates are therefore manufactured by adding up to two moles of a chelating agent to one of metal acid ester. A typical example is metal chelate titanium acetylacetonate, which is formed by reacting isopropyl titanate with two moles of acetylacetone, respectively (Fig. 6.5). Acetylacetone reacts in its enol form with organic derivatives of Zn, Ni, Mn, Fe, Co, Cr, Al, Ti and Zr to form metal acetylacetonate. Characteristic for crosslinking systems containing metal chelates is the addition of alcohol as a stabilizer, after the vaporization of which (in the drying channel together with other solvents) the crosslinking starts spontaneously. Pressure-sensitive adhesive acrylics containing the above-mentioned crosslinking agents are, therefore, called room temperature crosslinking pressure-sensitive adhesives. Most of the pressure-sensitive adhesives will benefit from a short crosslinking time at a temperature higher than the volatilization temperature of the polymerization solvent and the solvent stabilizer. The crosslinking time and temperature will depend upon the particular required acrylate ester monomers used, the chelating agent, the optional copolymerizable comonomer used, if any, the metal chelate used, the volatilization temperature of the reaction by-product after crosslinking, and the required end use for the acrylic PSA [36, 37, 79–81].

Fig. 6.5. Synthesis of titanium acetylacetonate

6.3.4. Multifunctional isocyanates

Multifunctional isocyanates are particularly efficient as crosslinking agents. The molar ratio of NCO/OH in acrylic pressure-sensitive adhesives with multifunction isocyanates the crosslinking condition (especially for curing time). Usually, an increase in the molar ratio of NCO/OH can enhance crosslinking density, and hence simultaneously, lead to the increase of tensile strength and modulus with an expense of elongation. The multifunction isocyanates are very important for the introduction of urethane groups into the polymer. Depending on their structure, the final properties of the polymer are influenced. Besides isophorone diisocyanate (IPDI), cycloaliphatic dicyclohexylmethane (HMDI) and aliphatic diisocyanate 2,2,4-trimethyl-hexamethylene diisocyanate (TMDI) are used. The aromatic toluene diisocyanate (TDI) and diphenylene diisocyanate (PPDI) are more difficult to handle. It is the result of their high reactivity to water. Some of the newer production processes allow them to be built in [82–84].

6.3.5. Polycarbodiimides

Polycarbodiimides are very efficient crosslinking agents for the carboxylic group containing polymers in water, such as polyurethanes, polyacrylates and latexes. Examples of the mechanism of the reaction between carboxylic groups and poly-carbodiimine during crosslinking of PSA acrylic were showed (Fig. 6.6).
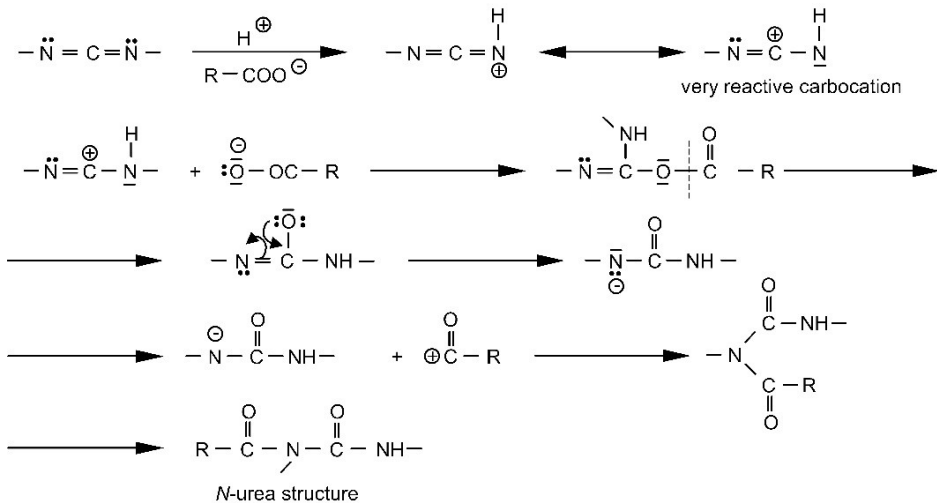

Fig. 6.6. Mechanism of reaction between carboxylic groups and polycarbodiimine during crosslinking of PSA acrylic [45]

They are an environmentally friendly replacement for the former frequently used polyaziridines and in particular they are non-mutagenic. A great step forward in the development of crosslinkers is the polycarbodiimides containing additional functional groups which contribute to the crosslinking. At applying the polymers in the water together with these polycarbodiimides an additional inter-polymer network is formed by the additional functional groups. As a result, the film properties, such as the film strength, water and chemical resistance, abrasion properties, of the obtained film are enhanced. Polycarbodiimides are generally synthesized through a catalytic cycle from isocyanate compounds. In this catalytic cycle, a pholspholene catalyst first reacts with an isocyanate, upon which a rearrangement occurs and carbon dioxide is liberated. This intermediate species can subsequently react with another isocyanate group after which the pholspholene catalyst is regenerated and a carbodiimide moiety is formed. When multifunctional isocyanates are used, the newly formed carbodiimide-containing molecule can again undergo the carbodiimide forming reaction and products can be made with multiple carbodiimide moieties. The first polycarbodiimides that appeared on the scene were solvent-based ones, followed soon by solvent-based ones that were dispersible in water. A great step forward in the development of polycarbodiimides as crosslinkers was multifunctional polycarbodiimides. These solvent-based polycarbodiimides contain additional functional groups, and this combination of carbodiimide and other functional groups in the crosslinker results in an increased crosslinker capacity, since both the carbodiimide and the additional reactive functional group contribute to the crosslinking. The additional reactive functional group can be any functional group with reactivity towards functional groups in an aqueous polymer dispersion, emulsion or solution, or towards corresponding groups, for instance by self-condensation or self-addition. Examples are, amongst others: dialkylacetal, imine, alkoxysilane, aziridine, epoxide, azetidine, oxazoline or imidazoline. These agents are coupled to the polycarbodiimide chains by means of another functionality that is reactive towards either the isocyanate or the carbodiimide group. When a polyisocyanate crosslinker is used in a typical water-based leather finish having no hydroxyl or other isocyanate-reactive groups then the term stoichiometry is not a useful concept. However, the situation is quite different for polycarbodiimide crosslinking since most of the aqueous polymers are used, whether acrylic or polyurethane, do have available functionality (carboxylic acid) that can react with a carbodiimide. Even though one can in principle address carbodiimide crosslinker

dosage in stoichiometric terms, it is not useful to do so. Two main reasons are that few end-users will be in a position to calculate a stoichiometry without intimate knowledge of the makeup and functionality, not only of the main polymeric binders, but also of the carboxy-functional materials that may be present in the form of thickeners and dispersants. One is compelled to run dosage ladders to determine optimum crosslinker levels. The second reason is based on the empirical observation that in soft coating systems, such dosage ladders often produce optimum crosslinker levels that bear no relationship to stoichiometry. In other words, studies with stoichiometry as the independent variable have revealed no special virtue as regards to performance in the use area of leather finishing. For leather finishing, typical use levels are often below stoichiometric [82, 85–87].

6.3.6. Polyfunctional propylene imines

Propyleneimines are three-membered ring compounds containing a single nitrogen atom in the ring. They were first prepared in 1890 by Hirsch from 2-bromopropylamine. Commercial production of methylaziridine began in Germany in 1938 by IG Farbenindustrie. Propyleneimine contains aziridine groups that react with carboxylic groups; hence it essentially acts as an adhesive through crosslinking reactions. Propyleneimine and methylaziridine, although chemically quite similar to ethyleneimine, are less volatile, more commercially available, and considered easier to handle. However, their toxicity and flammability mean that they should be handled with care. Propyleneimine undergoes largely the same reactions as ethyleneimine, and although it polymerizes rapidly in the presence of acids, useful polymers are difficult to prepare and at present are not commercially available. The crosslinking of PSAs with multifunctional propyleneimines is mainly based on the carboxyl groups offered by the vinylcarbonic acids within the polymer chain. The oxygen of the nucleophilic carboxyl group causes the opening of tense propyleneimine rings, while the hydrogen atoms accompanying the carboxyl groups protonate the nitrogen atoms. Multifunctional propyleneimines have proved to be versatile and highly effective crosslinking agents for acrylic PSAs (which contain acrylic acid in the polymer chain) and other adhesive types containing carboxylic groups. Moreover, two-component acrylic formulations tend to have long pot lives, typically up to 8 h with little thickening or precipitation, whilst coatings that rely on drying crosslink under low-energy conditions, i.e., at ambient temperatures. Polyfunctional propylene imines are functional 2-methylaziridine

derivate (Fig. 6.7) which hydroxyl very reactive low energy crosslinking agents in carboxylated polymers. The high reactivity hydroxyl can be ascribed to ring strain inherent in the terminal aziridine groups. Ring-opening is acid-catalyzed, proceeding initially via protonation hydroxyl tertiary nitrogen atom. Hydroxyl crosslinking application the polyfunctional propylene imines are added hydroxyl final compounded coating just prior to use. These pressure-sensitive adhesives acrylics have a pot life of about 8 to 36 h. The level of propylene imines used will depend on the desired properties hydroxyl finished adhesive coating. The crosslinking of pressure-sensitive adhesives with multifunctional propyleneimines is mainly based on the carboxyl groups offered by the vinylcarbonic acids within the polymeric chain. The oxygen of the nucleophilic carboxyl group causes the opening of the tense propyleneimine rings while the hydrogen atoms accompanying the carboxyl groups protonate the nitrogen atoms (Fig. 6.8) [34, 78, 88, 89].
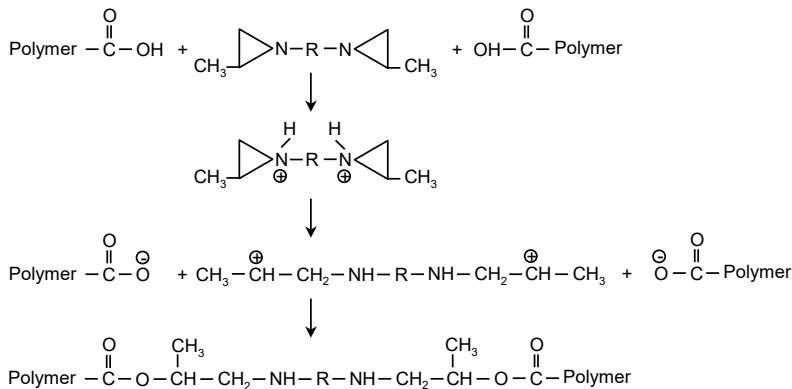

Fig. 6.7. Crosslinking of carboxylated PSA initiated by propyleneimine

A – n-valent organic or inorganic group

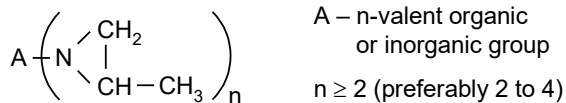$n \geq 2$ (preferably 2 to 4)

Fig. 6.8. The chemical formula of polyfunctional propylene imine crosslinkers

General multifunctional propyleneimine groups containing compounds are known for over 35 years. Along with the progress in the field of organic synthesis the chemical structure of propyleneimine crosslinkers was adapted to the developments in polymer chemistry. The application of such crosslinkers is product-oriented and only mentioned for special formulations. In the early 1980s, 3M was particularly active in this sector presenting new ideas about the structure and

application of polyfunctional propyleneimines. Regarding their chemical structure the multifunctional propyleneimine crosslinkers can be prepared by the following reactions (Fig. 6.9) [78, 87–90]:

a) Reaction products from multifunctional carboxylic acid chlorides and propyleneimine: This range of crosslinking agents is also known as bisamide crosslinking agents (BCA).

b) Reaction products from multifunctional isocyanates and propyleneimine: This reaction is based upon the reactivity of the propyleneimine ring and the N=C=O-groups.

c) Propyleneimines based on s-triazine: As a result of the reaction between propyleneimine and cyanuric acid chloride or tris-(2-carboxyethyl)iso-cyanurate we find the following crosslinker.

d) Reaction products from multifunctional acrylates and propyleneimine: Propyleneimine reacts with the double bond of the acryloyl group.

e) Propyleneimines with central heteroatoms: Mainly phosphorus and sulfur serve as heteroatoms.

Fig. 6.9. Multifunctional propyleneimine crosslinkers prepared reactions

6.3.7. Amino resins

Amino resins constitute an interesting class of crosslinking agents, for the diverse polymers for use in thermoset coatings including carboxyl-, hydroxyl- or amide groups. They can be classified into four groups: melamine formaldehyde resins, benzoguanamine, glycoluril or urea resins have been on offer in the last year (Fig. 6.10). In order to obtain a crosslinking effect, these resins need only weak canalization or none at all. Amino resins are characterized by their reactive end groups, generally classified as fully alkylated, partially alkylated and containing high imino groups, and enable to undergo controlled crosslinking reaction and precisely adjust the required adhesive properties. It is their special feature that their crosslinking rate is practically zero at room temperature while it increases exponentially above 100°C. That means that the crosslinking ensues only during the drying of the PSA layer in the drying oven. The amino resins can be used for the crosslinking of solvent-borne PSA acrylics at an elevated temperature between 105 and 150°C (Fig. 6.11) [34, 36, 45, 91].
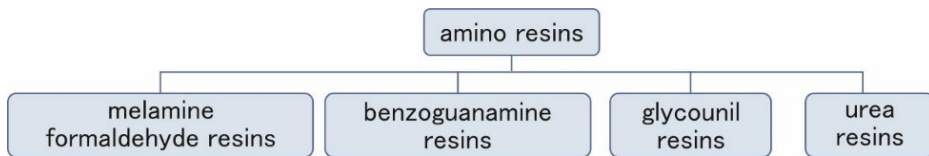

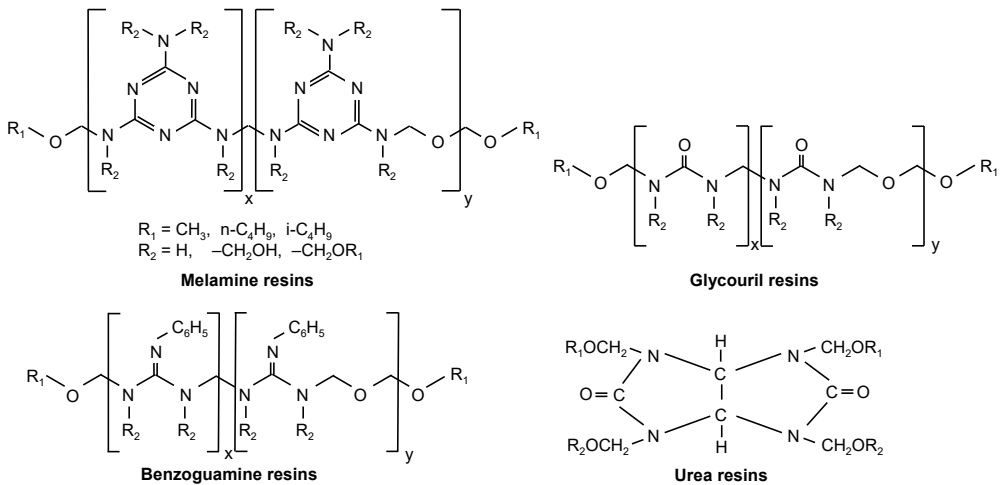**Fig. 6.10.** Kinds of various amino resins

Fig. 6.11. Chemical structure of amino resins

6.3.8. Radiation-Crosslinking

Scientific interest in UV-curable systems developed in the 1940s, when the first patent was granted for unsaturated polyester styrene inks that polymerize readily under UV exposure [2]. Ultraviolet (UV) cross-linking technology is well established in the market and allows the manufacturing of a wide range of various photoreactive UV-crosslinkable pressure-sensitive adhesives (PSA). Industrial applications of UV cross-linkable acrylic PSA have grown tremendously over the last 10 years. The balance between adhesive and cohesive strengths within the cross-linked layers is very important for the performance of UV-cross-linkable PSA. UV radiation is used to induce cross-linking of the photoreactive acrylic PSA formulations containing suitable prepolymers, oligomers, unsaturated multifunctional monomers and conventional or unsaturated photoinitiators [12, 92, 93].

EB-Crosslinking

There are >1400 high-current electron beam (EB) accelerators being used throughout the world in industrial manufacturing operations. The high productivity and controlled energy transfer from this electrically sourced equipment continue to provide added product value to crosslinked wire and cable jacketing, to heat shrinkable tubing and films and in the manufacture of automobile tires. The fastest growing market segment has been the use of EB curing for inks, coatings and adhesives. Excluded in this count are low-current accelerators, such as Van de Graaff generators and pulsed microwave LINACs that are used in many research facilities. The accelerator energies typically needed for given end-use applications are presented in (Tab. 6.1) for unit density materials.

Tab. 6.1. EB penetration – market end-uses

Market segment	Electron energy	Typical penetration
Surface curing	80–300 keV	0.4 mm
Shrink film	300–800 keV	2 mm
Wire & cable	0.4–3 MeV	5 mm
Sterilization	3–10 MeV	38 mm

Most EB accelerators have some common features: 1) electrons are emitted from heated tungsten filaments; 2) electrons are focused into a beam with an extraction electrode; 3) electrons are accelerated within an evacuated space with a strong electric field; 4) electrons pass through a thin titanium-foil window into

air. Industrial electron accelerators operate between 70 keV and 10 MeV, accelerating electrons, which have mass and charge, well beyond the ionization potential for organic or polymeric materials, 10 eV. Initial reports on the use of ultraviolet (UV) and electron beam (EB) technology for pressure-sensitive adhesives (PSAs) began to appear in the late 1960s. It has since been an active area of interest, which indicates a continued belief in technology. Because the tendency, in general, goes towards saturated radiation crosslinkable systems, UV technology has to be preferred. EBC-technology is more and more favored in the area of radiation crosslinkable systems. During UV exposure, the intermolecular H-abstractor structures are excited and react with the neighboring C–H positions of polymer sidechains. The crosslinking mechanism of UV-reactive HMPSA has been thoroughly investigated and is presented schematically. UV crosslinkable HMPSA possesses excellent oxidation resistance, which allows one to work without an inert gas atmosphere. Normally, polyacrylates absorb the entire radiation at <300 nm. To accomplish acceptable crosslinking with transparent PSA layers, only UV wavelengths >∼300 nm are of importance. Because, in general, the energy of 350–410 kJ/mol is required for stimulation of H-abstractors (benzophenone derivatives), a UV wavelength range of ∼300 to 410 nm is required. Such UV radiation is emitted with common UV lamps. Electron-beam-induced polymerization and crosslinking EB curing is the latest technology having many advantages over thermal- and UV-curing techniques. It has more throughput, does not use photoinitiators, and is environmentally clean and safe technology [29, 94–96].

UV-Radiation

UV curing is one of the latest techniques due to its economical (fast curing) and environmental (low VOCs) advantages, but this technique involves the use of photoinitiators and also has the limitation of penetration and it works only with transparent carrier materials [29]. This crosslinking process found an interesting application for producing photoreactive PSA systems of high performance used in the coating industry for PVC signed and marked films. The idea of replacing the conventional PSA systems crosslinked at room temperature or two-component PSA systems crosslinked at elevated temperature, with single-component UV-activated PSA became very attractive to manufacturing industries. This phenomenon is the result of the crosslinking reaction that takes place when the polymer layer is exposed to UV radiation. A photoinitiator is used to absorb the UV radiation and generate upon cleavage or upon intermolecular reaction the

reactive species, free radicals that can initiate the UV-crosslinking. A unique advantage of the UV-crosslinking technology is to provide a precise temporal and spatial control of the setting process which will occur on order, selectively in the illuminated areas. Such performance, together with cost and environmental consideration, are the main reasons why UV-crosslinkable adhesives are being increasingly used and continue to attract attention in various sectors, as shown by the numerous patents taken recently on novel applications of this technology. A crucial factor in developing high-performance UV-crosslinkable acrylic PSA is obviously to ensure an excellent adhesion into the various types of supports. In this respect, the absence of a solvent in the resin formulation is certainly a disadvantage, compared to solvent-borne acrylic PSA. The limitation of the UV-technology in PSA applications results from the fact that crosslinking of the photoreactive occurs only in the illuminated areas so that at least one part of the assembly needs to be transparent to UV radiation. The quantity of radiation energy to which the adhesive layer is expressed by the UV-dose, measured in mJ/cm^2 (Fig. 6.12).
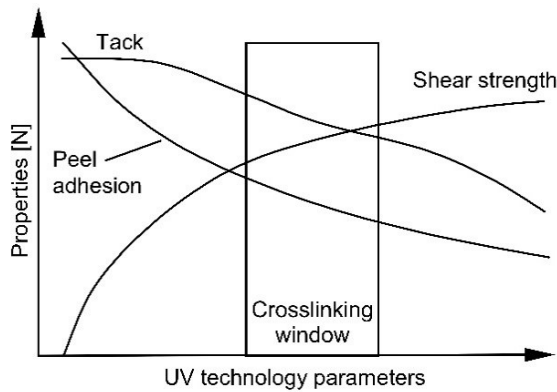

Fig. 6.12. Properties of radiation crosslinked acrylic PSA versus UV-dose

The UV-dose can be controlled by adjusting the power of the lamps and the speed at which substrate is passed under the lamps in the production plant. Crosslinking of PSA with ultraviolet light can be done directly after the application. There are used mercury lamps (low, medium, high pressure) of power between 80 and 160 W/cm which include UV stations with six and more UV lamps of power 160 to 250 W/cm. Normally polyacrylates absorb the entire light radiation below 300 nm. In order to accomplish acceptable crosslinking of transparent PSA only UV wavelengths above 300 nm are of importance – UV wavelength range of about 300 to 400 nm is required [36, 42, 64].

Photoinitiators

Photoinitiators are molecules that create reactive species (free radicals, cations or anions) when exposed to radiation (UV or visible). Synthetic photoinitiators are key components in photopolymers (i.e. photo-curable coatings, adhesives and dental restoratives).

Conventional photoinitiators

Conventional free radical photoinitiators are generally aromatic ketones containing specific substituents on the carbon atoms adjacent to the carbonyl group. There are two conventional photoinitiators following groups [4, 97–99]:

1. In photoinitiators of type I the radicals formed from the decay of excited molecules can reach triplet state. Depending on the mechanism of the degradation reactions, such photoinitiators are divided into α- and β-photodissociating. In the case of initiators α-photodissociating, in contrast to β-photodissociating, basically there is no further breakdown of primary radicals. Typical photoinitiators I type include benzoin and halogenated ketones.
2. In photoinitiators of type II formation of free radicals proceeds by intermolecular hydrogen transfer from the co-initiator to the initiator molecule. UV-irradiation leads to an excited triplet state. Radical initiator is a radical derived from the co-initiator. The best-known photo-initiators of the second kind are benzophenone and its derivatives.

Multifunctional conventional photoinitiators

This group of substances consists of saturated photoinitiators, which contain at least two photoreactive structures in the molecule and form cross-linkage with the polymer by UV radiation. It is possible to obtain so-called migration-free photoinitiators by specific construction, for example, from multifunctional benzophenones. There is the possibility of matching the multifunctional photoinitiators regarding the chemical structure to the commonly used UV sources because of the different UV characteristics. The anchoring in the polymer takes place at protruding alkyl side chains as in typical H-abstractors [96, 100–102].

Photosensitive crosslinking agents

This group consists of UV-activating crosslinkers that have absorption maxima at wavelengths between 330 and 380 nm. The best-known example of this group is

the group of chromophoric substituted bischloromethyl-s-triazine, which function simultaneously as photoinitiator and photocrosslinker. Photosensitive compounds are very effective for the photocrosslinking of acrylic PSAs and ameliorate the adhesive properties (tack and peel adhesion) and cohesion. The shorter alkylene chain yielded the best result for all measured performances Electronically excited fragments (a) suffer homolytic transformation to the radical (b) and a chlorine radical, which abstracts hydrogen from a donor (c) resulting in the formation of hydrogen chloride and the radical (d). Although hydrochloric acid serves as the catalyst in chemical amplification systems, the chain radical (d) may be used to start a chain crosslinking reaction (Fig. 6.13) [96, 103–105].
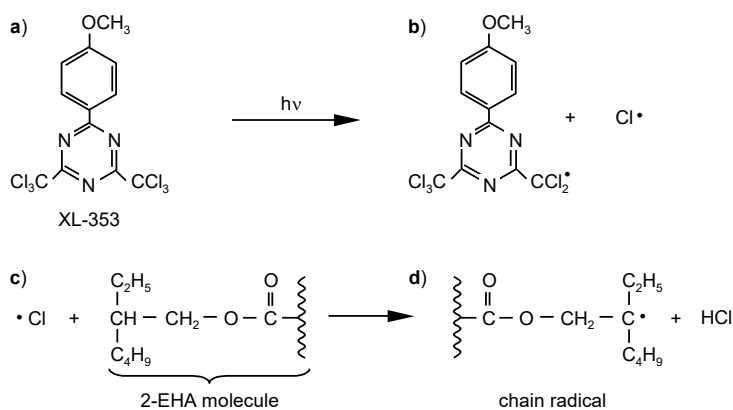
Fig. 6.13. Mechanism of s-triazine photoreactive crosslinker photolysis

Unsaturated copolymerizable photoinitiators

It is well known that components of PSA systems which are not chemically linked (pigments, fillers, plasticizers, conventional photoinitiators and by-product of conventional saturated photoinitiators after UV exposure) can migrate to the PSA surface of the finished coating. Migration usually deteriorates the gloss, adhesion and mechanical properties and can interfere with many applications. The extractability of photoinitiator by-product by food in contact with these adhesive coatings excludes the use for food packaging materials. Copolymerizing the unsaturated photoinitiator into the backbone of the acrylic PSA copolymer allows crosslinking with ultraviolet radiation, after the formation of the copolymer. The most typical directions, however, are in the development of functionalized acrylated, vinylated, allylated, acrylamidated or vinyloxylated chromophores of type I (Fig. 6.14) and type II photoinitiator (Tab. 6.2).
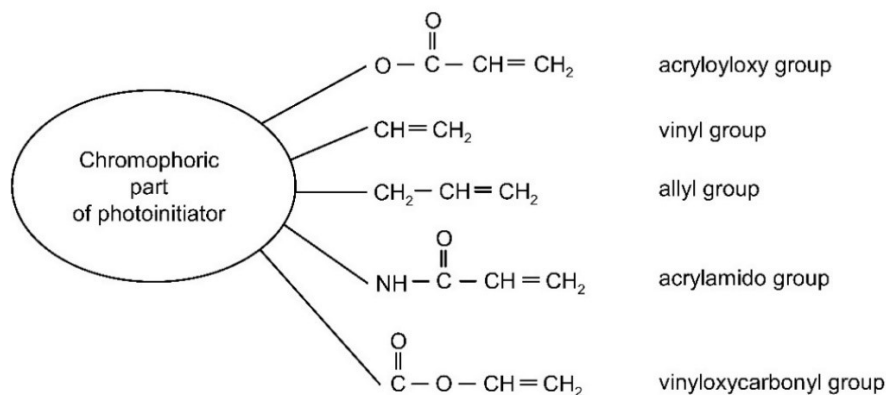
Fig. 6.14. Examples for copolymerizable photoinitiators structure

Tab. 6.2. Polymerizable photoinitiators using by synthesis of acrylic PSA

Photoinitiators	Type	Chemical formula	Chemical name
ABO	II	$CH_2 = CH — C(O) — O —$ (benzophenone structure)	4-acryloyloxy benzophenone
AEBP	II	$CH_2 = CH — C(O) — O — (CH_2)_2 — O —$ (benzophenone structure)	4-acryloyloxyethoxy benzophenone
ABBP	II	$CH_2 = CH — C(O) — O — (CH_2)_4 — O —$ (benzophenone structure)	4-acryloyloxybutoxy benzophenone
AHBP	II	$CH_2 = CH — C(O) — O — (CH_2)_6 — O —$ (benzophenone structure)	4-acryloyloxyhexoxy benzophenone

Such functionalized chromophores will themselves either co-react with the crosslinked acrylic PSA or are capable to copolymerize to produce acrylic self-adhesive copolymers, which are not extractable. Such functionalized chromophores will themselves either co-react with the crosslinked acrylic PSA or are capable of copolymerization to produce acrylic self-adhesive copolymers, which are not extractable. The above-mentioned functionalized unsaturated photoinitiators have also been prepared. Copolymerizing the unsaturated photoinitiator into the backbone of the acrylic pressure-sensitive adhesive copolymer allows crosslinking of the acrylic PSA with ultraviolet radiation, after the formation of the copolymer. Furthermore, incorporation of the unsaturated copolymerizable

photoinitiators into the acrylic polymer backbone, before the crosslinking thereof, greatly increases the efficiency of the crosslinking obtainable by the inclusion of the photoinitiator monomer in the adhesive, as compared with the addition of an aromatic ketone compound which is not initially copolymerized into the copolymer. Because of increased efficiency, only small amounts of unsaturated copolymerizable photoinitiator monomer are needed to achieve useful degrees of crosslinking. Performed polymer structures that crosslink directly under the influence of ultraviolet energy require special photosensitive groups to affect network formation. The unsaturated photoinitiator type II (no presence of by-product after UV crosslinking) is now part of the polymer chain and is, therefore, nonmigratory. The attached photoinitiator gives no harmful by-products on curing and, therefore, presents no problem with toxicity. After UV-initiated crosslinking by using of photoinitiators type II, known as hydrogen abstractors, are formed no photolytically by-products [36, 42, 67, 89].

Photoinitiators suitable for addition

Photoinitiators suitable for addition are from a new group of compounds. On one side is a conventional photoreactive group (e.g. benzophenone rest) and on the other side are groups that tend to addition reaction, such as compounds from the aziridine group. The transformation of the carboxyl group of the copolymer takes place after the polymerization by an addition reaction in the polymerization media without side products and leads to UV crosslinkable highly efficient PSAs Such photoinitiators containing groups propyleneimine obtained by reaction with the appropriate propyleneimine photoreactive carboxylic acid chlorides. These compounds are incorporated into the polymer chain by reaction active groups of photo-initiator of group carboxylic adhesives [96, 106, 107].

Side-chain modification with derivatives containing double bonds

One possibility to introduce photoreactive unsaturated groups is synthesizing the bulk PSA first without photosensitive groups and then introducing them after the polymerization into the polymer structure by distinct chemical methods. A typical example of the latter is the acrylation of the hydroxyl group-containing PSAs on a polyester or polyacrylate base. In practice, the incorporation of an unsaturated architecture is achieved by the reaction of OH–, COOH–, or NH_2– groups of a polymer with corresponding isocyanate compounds allylisocyanate,

isocyanoethylmethacrylate, or *m*-TMI. The pressure-sensitive adhesives obtained in this way are actually suitable for EBC. For UV crosslinking purposes, commercial photoinitiators are added [96, 108, 109].

Performance adjustment of pressure-sensitive adhesives

Acrylate pressure-sensitive adhesives solvent-borne, solvent-free or water-dispersed seem a very interesting and rapidly developing field of science and exhibiting the full innovation potential for further development. Among these solvent adhesives are leading the industry because of the relatively low cost of preparation, high production rates while maintaining similar performance to the other adhesives [110]. The main drivers of performance adjustment of pressure-sensitive adhesives are:
  – the solvent content in the solvent pressure-sensitive adhesives based on acrylate;
  – the weight of glue with which they are coated adhesive tapes based on acrylate adhesives.

From one ton of 50% wt. acrylic pressure-sensitive adhesive can be obtained about 8300 m² of adhesive tapes having a basis weight of 60 g/m² based on the following calculation:

$$\frac{500 \text{ kg} \cdot 10^3}{60 \frac{\text{g}}{\text{m}^2}} \approx 8333 \text{ m}^2$$

UV lamps (spectral)

The most important properties of the crosslinked polyacrylate PSA layer, such as tack, peel strength, and shear resistance, can be controlled by the UV dosage. The solvent-free UV-curable polyacrylates are coated directly or in a transfer process depending on the carrier material. With the PSA layers starting at 60 g/m², which are primarily used for the manufacture of double-sided PSA tapes, a tendency of hardening can be observed. The curing with UV light can be done directly after the application or after passing a cooling zone. Mercury lamps (low, medium, high pressure) are used with power between 80 and 120 W/cm, which includes UV stations with six and more UV lamps as the state of the art with a power of 120– 250 W/cm. The A wavelengths, responsible for UV curing, are in the range 320–400 nm. Spectral emissions of common UV A radiators for this application also contain other wavelengths, for example, that IR shares [96, 110–113].

The word LASER (Light Amplification by Stimulated Emission of Radiation) reveals a technology existing since about 40 years ago. In 1990, Japan had a 43% share the world market of LASER systems, USA had 31%, and Western Europe had 26%. Figure 6.15 is a pie chart of how the world market for LASER in 1989 was distributed over the various LASER types. The reason for the distribution is found in part in the historical introduction of systems, but primarily in the various application fields that the LASER types have conquered. Regarding the PSA technology, the excimer LASERs have the highest chance to be used. The excimer LASER was invented in 1975 and is considered in comparison to Nd:YAG-LASER the youngest LASER with high radiation power. Still, only a few practice-related application areas for excimer LASERs are found because of the relatively short development time. The most important field is the electronic industry, and interesting new technology includes photo- and polymer chemistry. Excimer LASERs are very intense pulsed light sources that radiate UV wavelengths between 170 and 351 nm, depending on the noble gas–halogen mixture, and provide high energy, MW-power that is in the ns-range of radiation times (Tab. 6.3). The advantage of UV radiation from excimer LASERs lies primarily in the tailored UV light spectrum. The excimer LASER with monochromatic UV light offers in comparison to commercial UV lamps with spectral UV light significant advantages in the application possibility of chemical synthesis of macromolecules, in particular in LASER-induced polymerization and/or LASER-initiated crosslinking. The introduction of LASER technology requires new demands to the development of photoinitiators, which are incorporated in the main or side chain. The LASER optic producers also are confronted with a number of tasks. The investment costs of the LASER equipment still constitute the largest application hurdle. The application of LASER equipment in comparison to conventional UV lamps provides the following advantages [96, 112–116]:

- a monochromatic wavelength instead of a spectral one guarantees high reaction speeds;
- the distance between the reflected laser beam and the PSA surface that is radiated is not relevant in comparison to the distance of UV lamp/PSA layer when conventional UV equipment is used;
- the LASER beam is monochromatic and contains no IR parts (no additional heating of the PSA layer or the coated substrate);
- UV curing of "thick" PSA layers (up to 3 mm);

– no problems with the UV curing of PSA containing suitable tackifiers, plasticizers, fillers, and other additives.

Tab. 6.3. Wavelengths of Excimer LASER

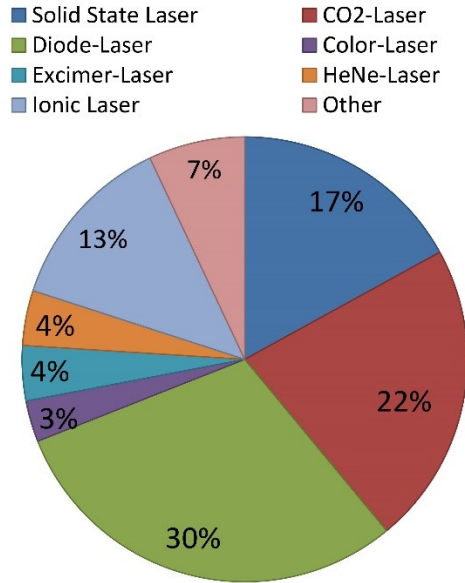| Active Medium	Wavelength (nm)
ArCl	170
ArF	193
KrCl	222
KrF	248
XeCl	308
XeF	351

Fig. 6.15. Distribution of various LASER types

7. Conclusion

Market and technology of high-quality pressure-sensitive adhesives are growing very fast. This development is the result of expansion in both existing and new fields of application of pressure-sensitive adhesives. Self-sealing polymers used for the production of pressure-sensitive adhesives are directly related to their structure, which makes them unique in the world. The global market for self-adhesive tapes was expanding by 5.5% per year. In 2012 it produced worldwide about 1700.5 kilotons of pressure-sensitive adhesives with a value of $ 22.7 trillion. In 2018 the projected increase in world production to about 2208.2 kilotons of pressure-sensitive adhesives with a value of $ 31.64 trillion. Acrylate pressure-sensitive adhesives solvent-borne, solvent-free or water-dispersed seem a very interesting and rapidly developing field of science and exhibiting the full innovation potential for further development. Among these solvent adhesives are leading the industry because of the relatively low cost of preparation, high production rates while maintaining similar performance to the other adhesives, for example solvent-free. Increasing emphasis on environmental protection due to the growing awareness of environmental causes that attempts were made to put pressure-sensitive adhesives soluble and dispersible in water, especially in the fields of the industry's most exposing the environment to contamination from adhesives based on organic solvents such as packaging industrial [3, 40, 43, 110, 117].

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Abstract

The purpose of this review is to describe the various aspects of pressure-sensitive adhesives based on acrylics. Acrylic polymers are the most commonly used self-adhesives, having replaced compounded natural or synthetic resin. The most important requirements for a PSA, such as high tackiness (adhesion by the touch); high cohesion (inner stability); high stickiness (adhesion); UV, solvent, and temperature stability are outstandingly fulfilled by acrylics. Solvent-borne, water-borne, or solvent-free acrylic PSAs offer several advantages such as excellent aging characteristics and resistance to elevated temperatures and plasticizers. Moreover, they exhibit exceptional optical clarity due to the polymer compatibility and non-yellowing and free of residual monomers. They also have the highest balance of adhesion and cohesion and excellent water resistance. Acrylics are harder than rubbers. Acrylic PSAs are used to manufacture a variety of products, such as mounting tapes, labels, protective films, masking tapes, banners. They found application in the production of a wide range of self-adhesive medical products (patches, bandages, tape operations, and biomedical electrodes). Acrylic pressure-sensitive tapes are used to connect a variety of materials such as metal, paper, plastic, glass, wood, and leather. This paper reviews knowledge and advances on the issue of pressure-sensitive adhesives based on acrylic.

Keywords: pressure-sensitive adhesives, adhesion, tack, peel strength, acrylic PSA