Materials Science-Poland, Vol. 23, No. 4, 2005

Development trends in pressure-sensitive adhesive systems

Z. CZECH[1*], R. MILKER[2]

[1]Szczecin University of Technology, Polymer Institute, al. Piastów 17, 70-310 Szczecin, Poland

[2]Klebstoff GmbH, Industriepark 23, D 56593 Horhausen, Germany

Pressure-sensitive adhesives (PSA) present an interesting class of products that offers a potential to produce a novel generation of self-adhesives with a great number at excellent properties. The term *pressure-sensitive* describes adhesives that are aggressively and permanently tacky in the dry form 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. Acrylic self-adhesive polymers are nowadays synthesized from a wide selection of acrylic ester monomers, often with low levels of monomers having pendant functional groups. The three basic types of acrylic common today are solvent-borne, water-borne, and solvent-free acrylic PSAs. They can be used in the production of single- and double-sided self-adhesive tapes, foil labels, carrier-free tapes, self-adhesive bioelectrodes, and decorative PVC signs and marking films. A pressure-sensitive adhesive requires a balance of cohesive strength and viscoelastic properties. These characteristics are based on three parameters: tack, adhesion, and cohesion.

Key words: *pressure-sensitive adhesive; acrylic polymer*

1. Introduction

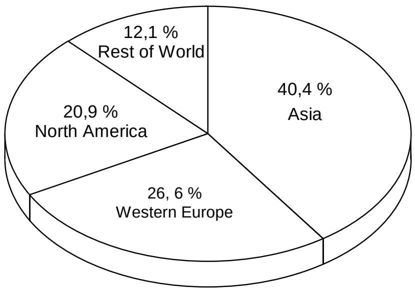


Fig. 1. Market share in production of pressure-sensitive adhesive tapes

The market and technology of high-performance PSAs are expanding rapidly. A growing market is the result of expansion in both current and new application areas.

* Corresponding author: e-mail: Zbigniew.Czech@ps.pl

Self-adhesive polymers possess inherent properties due to their structure that make them unique. The world market for pressure-sensitive adhesive tapes will expand at 5.5% p.a., reaching 25.4 billion m^2 worth $ 20.8bn in 2006 (Fig. 1) [1].

2. Pressure-sensitive adhesives

For commercially used PSA systems with excellent performance levels, synthetic polymers based on acrylics, silicones, polyurethanes, and polyesters are preferred (Fig. 2). These technologies exist in the market of PSA today [2].

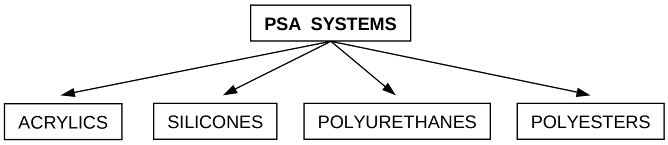


Fig. 2. PSA types used for the production o self-adhesive articles

2.1. Acrylics

Acrylates and other suitable monomers are copolymerised to yield an acrylic copolymer of a specific composition. Crosslinking agents are usually added for improved cohesion. Acrylics can be synthesized in organic solvents. In this case, no further formulation is generally needed, although it is done from time to time in order to fine-tune their properties. Acrylics can also be synthesized in water but surfactants need to be added to make the polymer dispersible. The third group of acrylics is solvent-free acrylic PSA (Fig. 3) [2].

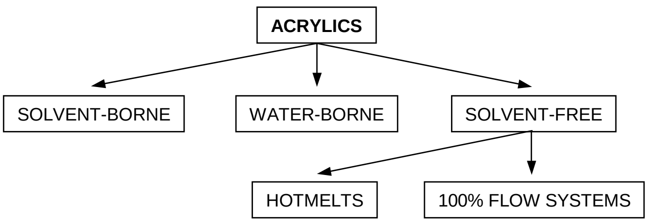


Fig. 3. Acrylic types of PSAs

2.1.1. Solvent-borne acrylic PSAs

The market and technology of high performance solvent-borne acrylic pressure -sensitive adhesives are still expanding. A growing market is the result of expansion in both current and new application areas [3].

The composition of acrylate polymers that are inherently pressure-sensitive is a combination of soft (low T_g), hard (high T_g), and functional monomers in the polymer chain (Fig. 4) [4].

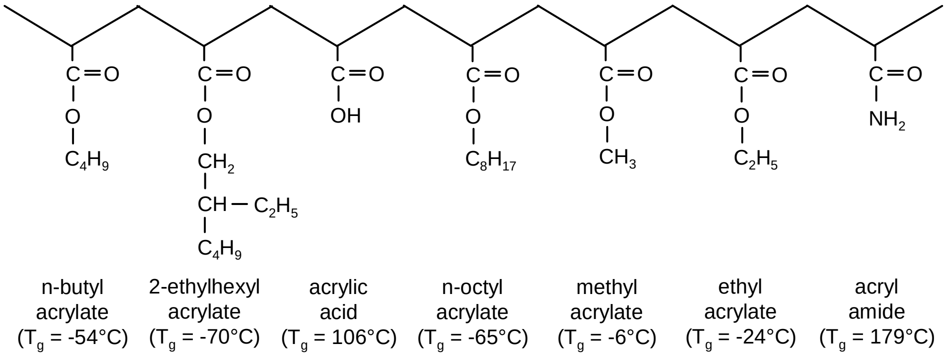


Fig. 4. Scheme of the chain composition of acrylic pressure-sensitive adhesives

Tack and peel adhesion are imparted by soft or low glass transition temperature monomers such as *n*-butyl, 2-ethylhyxyl, and *n*-octyl acrylate. Harder monomers, such as methyl and ethyl acrylate, are included to provide internal strength. Functional monomers, such as acrylic acid and acrylic amide, are incorporated for specific adhesion to desired substrates and in order to provide reactive sites for crosslinking reactions.

Solvents containing acrylic PSAs can also become an efficient technology in the future for water-soluble PSAs, UV-crosslinkable PSAs, and structural acrylic adhesives (Fig. 5).

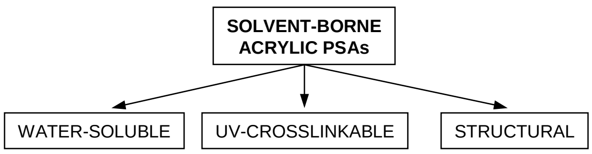


Fig. 5. The kinds of solvent-borne acrylic PSAs

Water-soluble acrylic PSAs. Water-soluble polyacrylate pressure-sensitive adhesives are used primarily in the production of industrial single-sided, double-sided, and transfer adhesive tapes, which are being increasingly used in the paper industry to splice paper webs during manual and flying reel changing. A special area of use resides in the manufacture of water-soluble labels. The latest application is in the field of medical products, where neutral electrodes and adhesive tapes for securing operating theatre sheets are of special importance [5].

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. 6) is the main criterion for the adhesive properties and water solubility of the synthesized copolymers. The preferred tackifying but water-insoluble alkyl acrylates (Fig. 6) reduce T_g and improve the tack and adhesion properties.

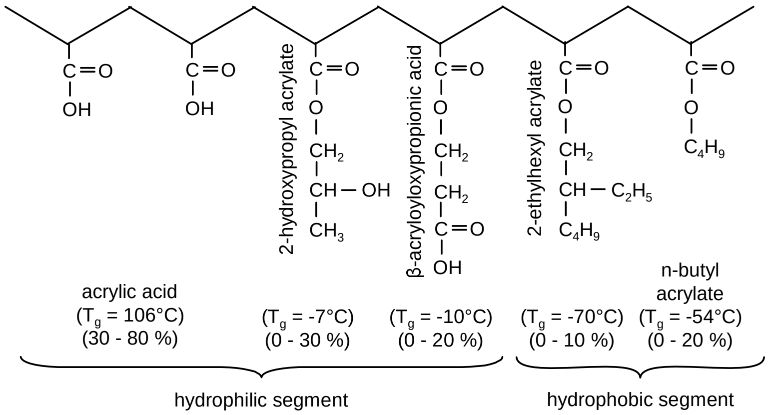


Fig. 6. Polymer chain scheme of water-soluble acrylic PSAs

UV-crosslinkable acrylic PSAs. In the case of saturated acrylic pressure-sensitive adhesives, the photogeneration of initiator radicals by α-cleavage photoinitiators or

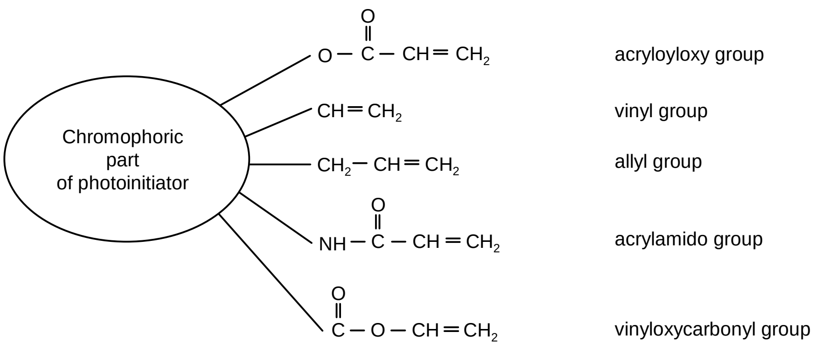
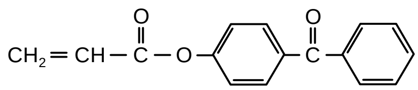


Figure 7. General examples of the chemical structure of unsaturated photoinitiators

H-abstraction photoinitiators is followed by a reaction with the acrylic chain that produces a new radical reacting with a neighbouring acrylic chain.

A very interesting alternative to conventional photoinitiators are unsaturated photoinitiators. The most typical directions, however, are in the development of functionalised type I and type II initiators, e.g. acrylated, vinylated, allylated, acrylamidated, or vinyloxylated (Fig. 7) [6].

A typical behaviour of tested novel unsaturated photoinitiators showed that the best PSA properties were achieved for the type II photoinitiator 4-acryloyloxy benzophenone (ABP):



ABP was the most efficient H-abstractor for the common solvent-based acrylic self -adhesives [7].

Structural acrylic PSAs. This new adhesive, known as structural bonding tape, is an acrylic pressure-sensitive tape impregnated with an epoxy that cures under heat. This product can be cured in an oven at about 145 °C for 20 min or hot bar cured.

The composition of PSA polymers (before the curing process begins they are inherently pressure-sensitive) is a combination of soft acrylate monomers with low T_g and hard epoxy monomers with high T_g in the polymer chain (Fig. 8) [8].

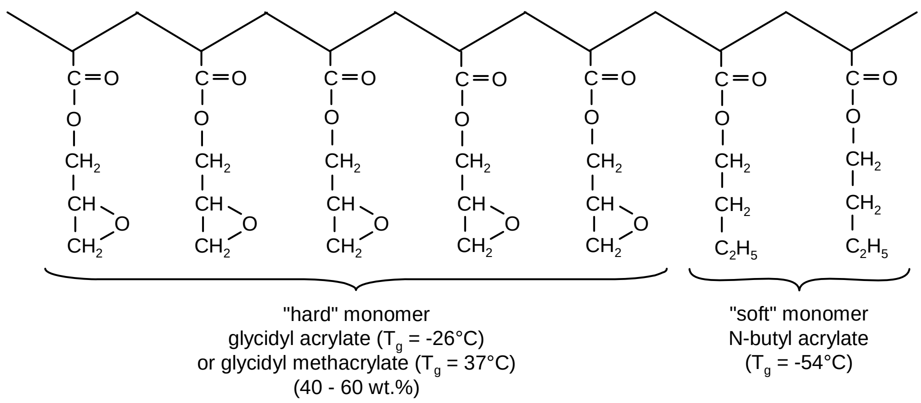


Fig. 8. The polymer chain architecture of a structural acrylic adhesive

The acrylic ester/epoxy resin pressure-sensitive thermosetting adhesive is an initially tacky and conformable thermosetting adhesive, which is obtained from a blend comprising epoxy resin or a mixture of about 20–60 wt. % epoxy resin and 0,5–10 wt. % heat-activatable hardener for the epoxy resins.

2.1.2. Solvent-free acrylic PSAs

Deficiencies of hot melt pressure-sensitive adhesives made of traditional solvent-free acrylic PSA are due to the use of relatively low molecular weight polymers, which results in limited heat and plasticiser resistance. Other groups of solvent-free acrylic PSAs are 100% systems, characterized at room temperature coated flow polymers. Solvent-free acrylic pressure-sensitive adhesives are crosslinked using UV radiation [9].

UV-crosslinkable acrylic HMPSAs. Crosslinkable acrylic hot melt PSAs (HMPSAs) that are designed to be crosslinked by a UV-lamp or UV-laser light are now available. These products offer high processing speeds, relatively low application viscosity at higher temperatures, high resistance to plasticisers and solvents, aggressive tack, and very high heat resistance after crosslinking.

UV-acrylic hot melts consist of acrylic copolymers with chemically built-in photoreactive groups. They are free of solvents and are processed in the form of hot melts. After the acrylic film for self-adhesive material production has been coated with the UV-acrylic hot melt, the adhesive film is crosslinked with UV radiation.

UV-crosslinkable 100% acrylic systems. Since these are 100% solid adhesives, it is easy to coat heavy depositions at a good speed. Viscosity can be modified within certain limits by changing added photoreactive diluents.

The UV dose can be controlled by adjusting the power of the lamps and the speed at which the substrate is passed under the lamps in the production plant (Fig. 9) [10]:

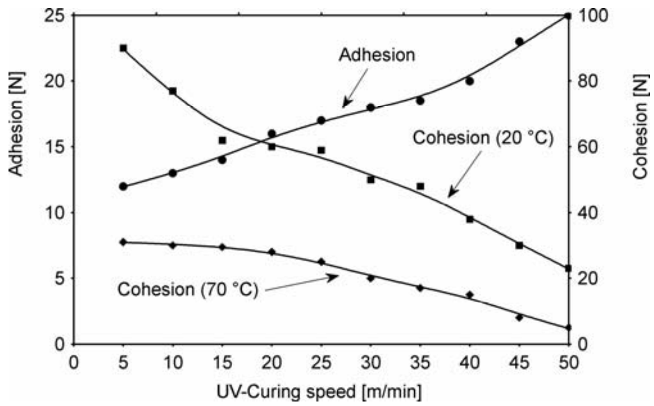
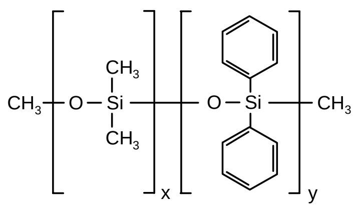


Figure 10. Adhesion and cohesion forces of coated 100% acrylic PSA systems vs. UV-curing speed

2.2. PSA silicones

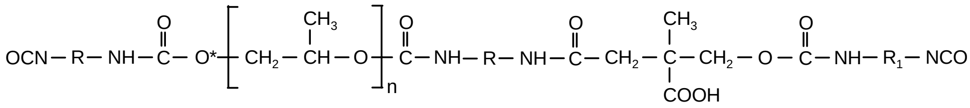
Silicone pressure-sensitive adhesives are high-performance adhesives that can be utilized over a wide range of temperatures, from –40 to 300 ºC. They bond to both low energy and high-energy surfaces. Silicone polymers based on gum contain dimethylsiloxy and diphenylsiloxy groups



The molecular weights of solvent-borne silicones are preferably in the range from 500 000 to 1 500 000 Daltons [12]. The crosslinking of silicone PSAs containing methyl or/and phenyl groups can be achieved thermally between 120 and 150 °C using organic peroxide.

2.3. PSA polyurethanes

The extraordinarily diverse chemistry of polyurethanes has also contributed to the development of efficient adhesives. This applies only to a limited degree to pressure-sensitive adhesives, however, for which the number of patent publications is astonishingly small. Ready for coating, solvent free 2-K PSAs on the basis of polyether polyols and isocyanates are not available on the market



2.4. PSA polyesters

Previous studies have shown [13] that excellent adhesion can be obtained with aliphatic polyesters with molecular weights ranging from 10 000 to 50 000 Da [14] and glass transition temperatures T_g between –25 and –47 ºC.

A typical example of this approach is the acrylation of polyester PSAs containing end hydroxyl groups. In practice, the introduction of an unsaturated architecture can also be achieved through the reaction of the OH-groups of a polyester polymer chain with the corresponding acrylic or unsaturated isocyanate compounds [15].

3. Conclusion

The ever-changing high performance pressure-sensitive adhesive market continues to expand and to present new challenges. To date, the industry has seen a strong growth in traditional applications and the emergence of new applications. The chemistry of polymers with self-adhesive properties has taken on an additional dimension with the introduction of various raw materials, polymerisation techniques, and crosslinking methods. This expansion of the technology ensures that future performance and environmental requirements will be met.

References

[1] *Pressure-Sensitive Industry*, Yearbook (2004), 28.

[2] CZECH Z., *Crosslinking of PSA based on acrylics*, Press House Politechnika Szczecińska, Szczecin, 1999, ISBN: 83-87423-18-1.

[3] MILKER R., CZECH Z., Adhäsion, 33 (1989), 20.
[4] CZECH Z., Ekoplast, 23–24 (2003), 31.
[5] CZECH Z., Polimery, 41 (1996), 22.
[6] MILKER R., CZECH Z., J. Appl. Polymer Sci., 87 (2003), 1354.
[7] BROCKMANN W., MEYER-ROSCHER B., *Relation of Pressure-Sensitive properties and UV crosslinking technology*, TAPPI Hot Melt Symposium, Atlanta, USA, 1998, 174.
[8] CZECH Z., URBALA M., MARTYSZ D., Polymer Adv. Techn., 15 (2004), 387.
[9] CZECH Z., Kautschuk Gummi Kunststoffe, 55 (2002), 492.
[10] CZECH Z, MILKER R., J. Appl. Polymer Sci., 87 (2003), 182.
[11] GADDAM N., US Pat. 5,346,980 (1993).
[12] MAZUREK M., US Pat. 5,314,748 (1993).
[13] ACEVADO M., HUBER H., Proceedings RadTech Europe, Lyon (1997), p. 181.
[14] ACEVADO M., HUBER H., 23. Münchener Klebstoff- und Veredelungsseminar (1998), p. 128.
[15] RAMHARACK R., US Pat. 5,391,406 (1995).

Received 23 September 2004
Revised 1 March 2005