

Photoreactive solvent free acrylic PSA for manufacturing of carrier free tapes

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The manufacturing of carrier-free self-adhesive tapes using UV-crosslinkable photoreactive solvent-free acrylic pressure-sensitive adhesives (PSA) has been described. The main role in this kind of technology play the UV-initiated polymerization and UV-initiated crosslinking processes.

Key words: photoreactive acrylic PSA, solvent-free, carrier-free, UV-crosslinking and UV-polymerization

Fotoreaktywne bezrospuszczalnikowe poliakrylanowe kleje samoprzylepne do produkcji bežnośnikowych taśm klejących

Opisano proces wytwarzania bežnośnikowych taśm samoprzylepnych z zastosowaniem bezrospuszczalnikowych poliakrylanowych klejów samoprzylepnych. Główną rolę w tego typu procesie technologicznym odgrywają: inicjowana promieniowaniem UV polimeryzacja oraz inicjowany UV proces sieciowania fotoreaktywnych klejów samoprzylepnych.

Słowa kluczowe: fotoreaktywne poliakrylanowe kleje samoprzylepne, bezrospuszczalnikowe, bežnośnikowe, sieciowanie UV, polimeryzacja UV

1. Introduction

Typical foam tapes are foam-like pressure-sensitive adhesives, with a foamed polymer carrier that is coated with a PSA. The foam carrier provides excellent conformability and stress distribution. In some applications, the PSA is coated first on a flexible PUR, PE or other foam and then laminated onto the carrier surface. The opposite surface of the foam may also be provided with a PSA layer. Double sidedcoated tapes with PUR or PE foam carrier have to satisfy requirements for stress relaxation, stress distribution, mechanical resistance, sealing and anticorrosion, and reinforcing and vibration/noise damping. The typical double-sided adhesive tapes contain between 30 and 150 g/m² of pressure-sensitive adhesive layer per side.

Double-sided tapes used in buildings must have the same expectancy as the building elements. Such mounting tapes can replace other classic (mechanical) methods of fixing. For instance, a glass-mounting tape is specially designed to bond two sheets of glass around the edges for a composite glass with a strengthening layer. The old method used black butyl tape to create a layer of air between two sheets. Such tapes give a long-lasting waterproof seal [1].

One embodiment of a pressure-sensitive adhesive tape without carrier is commonly called a "transfer tape" or "carrier-free tape".

Transfer tapes are tapes without carrier. They have a solid-state component only temporarily. The sheet backing is a release liner, and is use, the exposed adhesive surface of this tape is placed in contact with a desired substrate, the release liner stripped away, and the newly exposed adhesive surface bonded to the second surface. Their construction includes a release liner and the adhesive core. The adhesive core may be a continuous homogenous adhesive layer or a semicontinuous heterogeneous adhesive layer. The typical transfer carrier-free adhesive tapes have a thickness between 30 and 2000 g/m² (Fig.1).

Modern transfer carrier-free adhesive tapes have the following properties:

- High temperature resistance
- Good environmental resistance
- Conformability to the substrate shape
- High or medium transparency
- Variable adhesive thickness
- Excellent cohesion and very good peel performance on various range of substrates

Tack, peel and shear properties determine the performances of pressure-sensitive adhesive. Temperature, aging film thickness, crosslinking rate and post crosslinking parameters influence PSA applications directly for a wide end use market.

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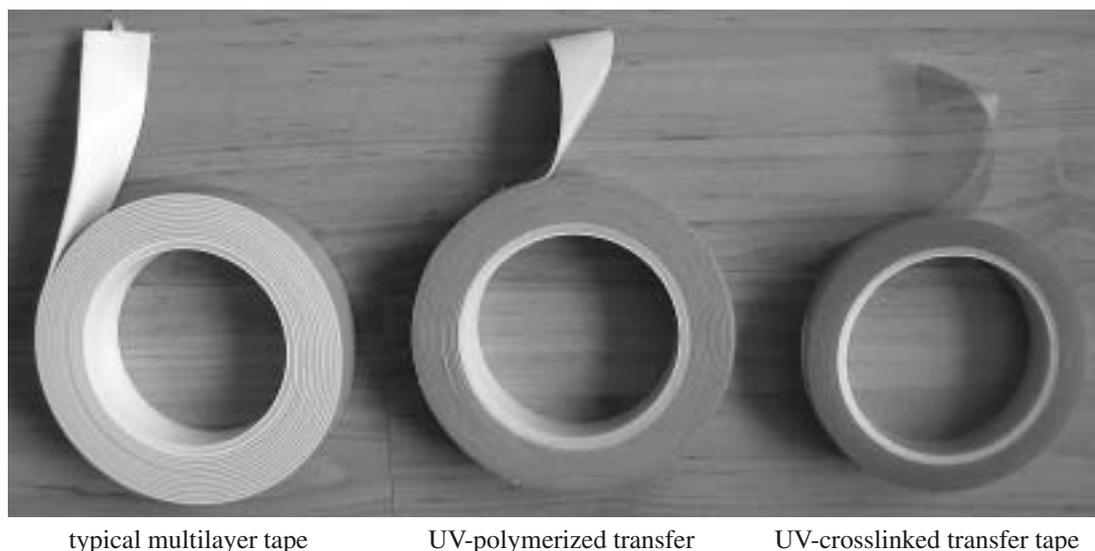


Fig. 1. Typical double-sided and carrier-free adhesive tapes

Rys. 1. Typowe dwustronne oraz beżnośnikowe taśmy samoprzylepne

2. Typical multi-layer tapes

The typical double-coated pressure-sensitive adhesive tape comprises a flexible support having on opposite faces chemically different pressure-sensitive adhesive layers which are physically incompatible, thus enabling the tape to be wound directly upon itself into a roll for storage and shipment. The tape is made by successively coating and drying solutions of two different pressure-sensitive adhesives onto opposite faces of a flexible web. To test for the incompatibility of the two pressure-sensitive adhesives, a solution of one of the pressure-sensitive adhesives is coated onto an undried coating of the other, and the coatings are simultaneously dried at room temperature for 24 hours to evaporate the solvents. Physical incompatibility is demonstrated by peeling the dried layers apart.

All the samples were made by lamination. The solvent-borne acrylic PSA is coated on the adhesive carrier

or release paper and dried in the back oven. On this adhesive layer is coated the next solvent-borne acrylic PSA and the complete laminate is dried in the back oven again (Fig. 2) [2].

Many applications of multi-layer transfer tapes require durability of the adhesive bond. Such durability is desired whenever the objects being bonded will be subjected to stress during the period in which the continued bonding is desired. For instance, a wall-mounted plaque is under the constant stress of the force of gravity and further may be accidentally jolted or impacted, or a furniture item with segments bonded together may have substantial stress operative at that bond during normal use. One area in which pressure-sensitive adhesive bonding is considered highly desirable, despite the critical need to optimize the durability of the bond provided thereby, is the attachment of automotive trim items, such as automobile side-moldings, insignia, and the like. There is a trend in the automotive industry against mechanical attachments of such items involving, particularly for vehicles which under normal use can otherwise be expected to be used for many years. In

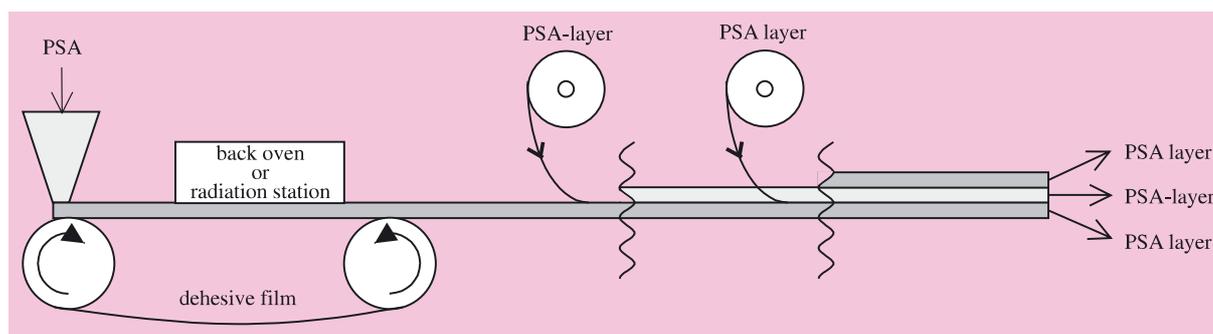


Fig. 2. Manufacturing of conventional multi-layer tape

Rys. 2. Produkcja konwencjonalnych taśm wielowarstwowych

addition, the use of pressure-sensitive adhesive bonding, if such can be applied with reasonable ease, permits the trim items to be selected and applied after the vehicle leaves the place of manufacture. Given the normally-encountered stresses on such type of attachment, including besides gravity various impact or tearing stresses, and given the environmental conditions that a typical vehicle is subjected to, the adhesion, and continued adhesion, and durability of such form of attachment is extremely important.

Moreover, a pressure-sensitive adhesive system suitable for attachment of automotive vehicle trim, and other applications where like durability is desired, should not merely be initially adhesive and cohesive, but also maintain, and preferably improve in, such properties with the passage of time. Adhesive systems that initially deform to conform to the substrates but then tend to revert from such deformation place additional stress upon the bond and decrease in durability with time, and thus are not desirable for long-term durable attachments. It has been found that the adhesive and cohesive and time and environmental durability properties vary with the nature of the support material used, and hence such support material is contributing to the system beyond its function as a carrier [3].

3. UV-polymerisation

Modern adhesive tape technologies are growing in so many different directions-new applications, new materials, new techniques, new specialties-that a technologist seeking to design a new product or to improve a process may sometimes overlook one of the new technologies in reactive systems that yield improved bonding and aging properties-UV polymerization and UV crosslinking.

The modern technology concerns photopolymerizable pressure-sensitive adhesive tapes comprising a plurality of contiguous layers which can not be delaminated. Each of the layers comprises a photopolymerized matrix of polymer chains, and at least one of the outer layers is photopolymerized to a pressure-sensitive adhesive state.

A new "thick" transfer pressure-sensitive tapes comprising a plurality of superimposed simultaneously photopolymerized layers, at least one outer layer being an acrylic pressure-sensitive adhesive layer, said layer comprising at least one alkyl acrylate ester monomer, contiguous layers defining an interface there between, each of said layers comprising a photopolymerized

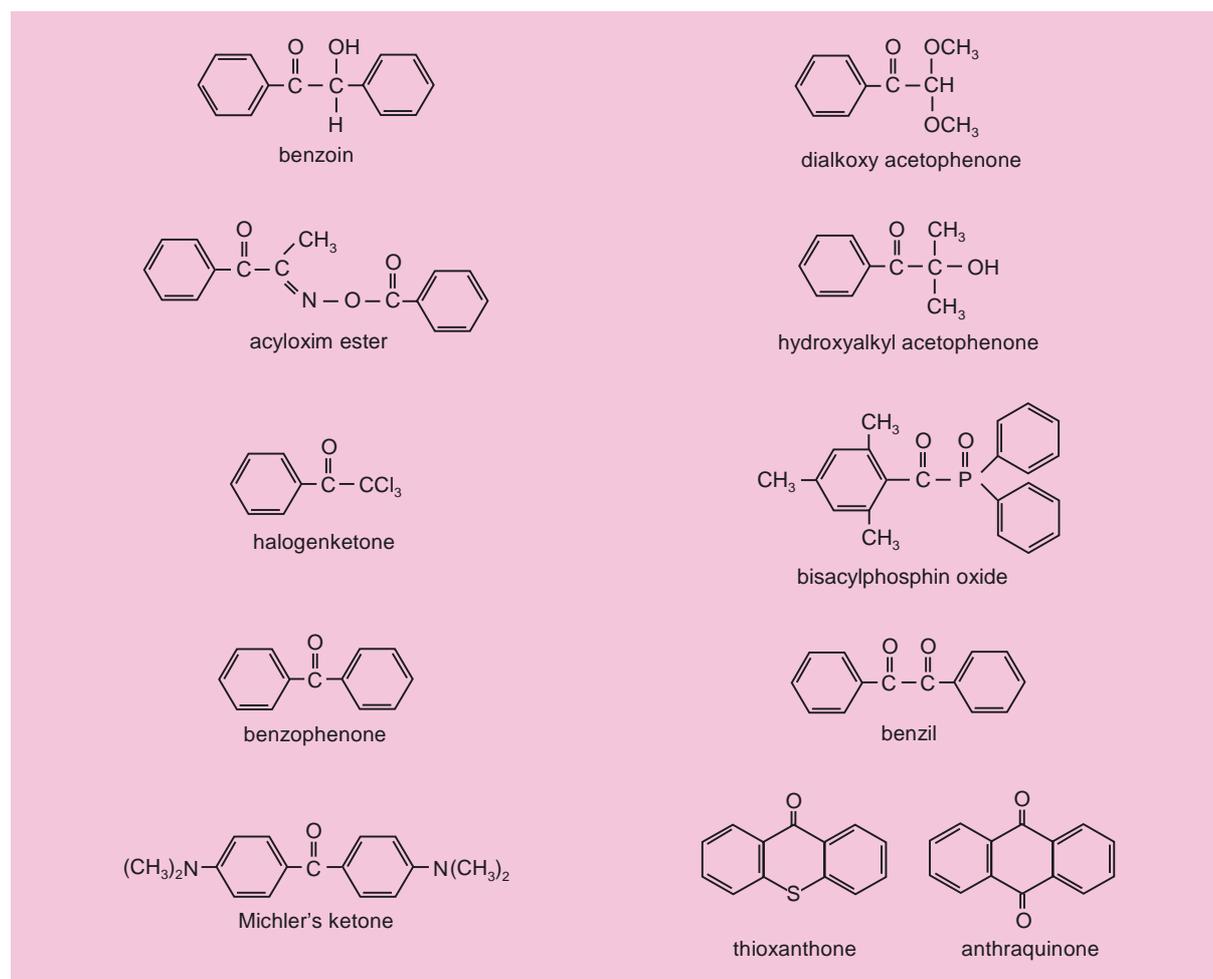


Fig. 3. Photoinitiators used for UV initiated polymerization

Rys. 3. Fotoinicjatory stosowane w polimeryzacji inicjonowanej UV

matrix of acrylic polymer chains, and a photoinitiator (Fig. 3) [4], said polymeric chains extending from the matrix of one of said layers through said interface into the matrix of a contiguous layer, prior to polymerization, whereby said layers cannot be delaminated.

The manufacturing also relates to a process for making a pressure-sensitive carrier-free adhesive tape comprising the following steps:

- Preparing a plurality of coatable compositions, each of said coatable compositions comprising at least one photopolymerizable monomer; at least one of said coatable compositions being curable to a pressure-sensitive adhesive state, monomers of each of said coatable compositions being copolymerizable when blended and subjected to photopolymerization conditions;
- Sequentially coating said coatable compositions to provide a plurality of superimposed layers with contiguous layers defining an interface therebetween, with one composition which is curable to a pressure-sensitive adhesive state being coated as a first or last layer;
- Permitting migration of photopolymerizable monomers through said interface between contiguous layers, and;
- Subjecting said superimposed layers to irradiation to simultaneously photopolymerize said monomers in each layer, and to provide polymeric chains comprised of copolymers of copolymers of photopolymerizable monomers originating from contiguous layers extending through said interface therebetween; thereby to produce a tape having layers which cannot be delaminated [5].

Each of the layers of tapes comprises a photopolymerizable matrix comprising acrylic polymeric chains. These matrices may comprise a multitude of polymers; however, all polymers used in such matrices must be photopolymerizable, preferably by the UV radiation of the spectrum between 200 and 400 nm. At least one layer must be photopolymerizable to a pressure-sensitive adhesive state. Such pressure-sensitive-adhesive layer of the novel tape has a photopolymerizable matrix comprising an acrylic pressure-sensitive adhesive.

The acrylic pressure-sensitive adhesives useful in the present tape construction are alkyl acrylates, preferably monofunctional unsaturated acrylate esters of non-tertiary alkyl alcohols, the molecules of which have from 1 to about 14 carbon atoms. Included within this class of monomers are, for example, isooctyl acrylate, isononyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, hexyl acrylate or *n*-butyl acrylate with low glass transition temperature T_g (Tab. 1).

The alkyl acrylate must be copolymerized with polar copolymerizable monomers. The polar copolymerizable monomers are incorporated into the balanced monomers for specific adhesion to desired substrates and to provide sites in form of active centres for cross-linking. They can be selected from strongly polar copolymerizable monomers such as acrylic acid, hydroxyalkyl acrylates, acrylamides or substituted acryl-

amides, or from moderately polar copolymerizable monomers such as *N*-vinyl pyrrolidone or acrylonitrile. These polar monomers are characterized through high T_g (Tab. 2).

Table 1. *Tackifying monomers suitable for photopolymerization*

Tabela 1. *Monomery podwyższające lepność kleju stosowane w procesie fotopolimeryzacji*

Monomer	(Homopolymer) T_g [°C]
2-ethylhexyl acrylate	-70
isooctyl acrylate	-70
<i>n</i> -octyl acrylate	-65
isononyl acrylate	-58
hexyl acrylate	-57
decyl acrylate	-56
<i>n</i> -butyl acrylate	-54

Where superior cohesive strengths are desired, the pressure-sensitive adhesives matrix of the novel tape should be crosslinked. Preferred crosslinking agents for an acrylic pressure-sensitive adhesive are internal crosslinkers multifunctional unsaturated monomers such as 1,6-hexanediol diacrylate, divinyl benzene, 1,4-butanediol diacrylate, divinyl adipate, diallyl fumarate or triallyl cyanurate.

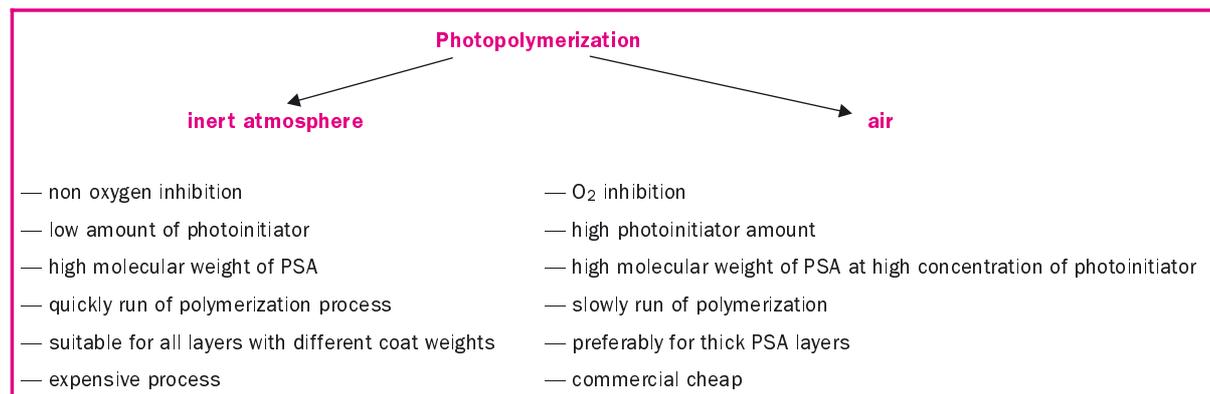
Table 2. *Polar substances used as comonomers by photopolymerization*

Tabela 2. *Monomery polarne stosowane jako komonomery w procesie fotopolimeryzacji*

Monomer	(Homopolymer) T_g [°C]
2-hydroxyethyl acrylate	-15
acrylonitril	+97
acrylic acid	+106
<i>N</i> -isopropyl acryl amide	+134
<i>N</i> -vinyl pyrrolidone	+170
acryl amide	+205

Photopolymerization is preferably carried out in an inert atmosphere, such as nitrogen. An inert atmosphere can be achieved by temporarily covering the photopolymerizable coating with a plastic film which is transparent to UV radiation, and irradiating through the film in air. If the photopolymerizable coating is not covered during photopolymerization, the permissible oxygen content of the inert atmosphere can be increased by mixing the coating with a combustible tin compound (Fig. 4).

Fig. 4. *Difference between photopolymerization in an inert atmosphere and in air*
 Rys. 4. *Różnica pomiędzy fotopolimeryzacją w atmosferze inertyjnej oraz w powietrzu*



4. UV-crosslinking

Industrial applications of UV crosslinkable materials have grown tremendously over the past decade. An entire industry has evolved based on the existence of chemicals, which respond to UV light. The growing success of UV crosslinking technologies in a wide variety of industrial products and processes can be attributed to the productivity and environmental benefits that result from such technologies. UV technology is well established in the market and allows the production of a wide range of UV-crosslinkable PSA with interesting features [6-7].

Now the photoreactive solvent-free acrylic PSA is made by a one-pot, two-step reaction that eliminates the gelation problem. Monomers are polymerized by solution techniques to form a high solids (50 to 80 wt.% solid content) acrylic copolymer. The functional monomers can be acrylic acid or hydroxy alkyl acrylate. After polymerization the chain is further functionalized with pendant double bonds by reacting the pendant hydroxyls with allyl isocyanate, maleic anhydride, 3-amino propyl vinyl ether or 1-(1-isocyanato-1-me-

thyl ethyl)-3-(1-methyl ethenyl)pentene (m-TMI) or by incorporation in the polymer backbone of unsaturated photoinitiator (Fig. 5). The amount and type of hydroxyls as well as the amount of copolymerizable photoinitiator can be easily regulated. AIBN is used as the initiator and a chain transfer agent is used to control the molecular weight.

The limitations of UV crosslinking include the high cost of photoinitiators, the non-FDA status of many of these photoinitiators, the subsequent UV instability of the crosslinked PSA, the penetration limitations, the non-linearity with line speeds, etc.

5. Performance adjustment of pressure – sensitive adhesives

The most important properties of the UV-crosslinked acrylics pressure-sensitive adhesives, such as tack, peel adhesion and shear strength, can be controlled by the UV dosage. The UV-dose can be controlled by adjusting the power of the lamps or UV-laser (excimer laser) or the speed at which the substrate is passed under the lamps in the production plant. The solvent-borne UV-crosslinkable acrylic PSA is coated directly and the adhesive film is crosslinked by UV-irradiation and in a transfer process, depending on the carrier material, to produce the adhesive properties as required. With the pressure-sensitive adhesive layers starting at about 1000 g/m², which are primarily used for the manufacture of transfer carrier-free pressure-sensitive adhesive tapes the high UV-doses are obtained at production speeds of about 2-20 m/min, if 6 to 10 or more UV-lamps are used.

UV-laser is a high energy, monochromatic light source, whose use within curing is known from stereolithography. Regarding the pressure-sensitive adhesive technology, the excimer laser has the highest chance to be used [8]. The excimer laser was invented in 1975 and

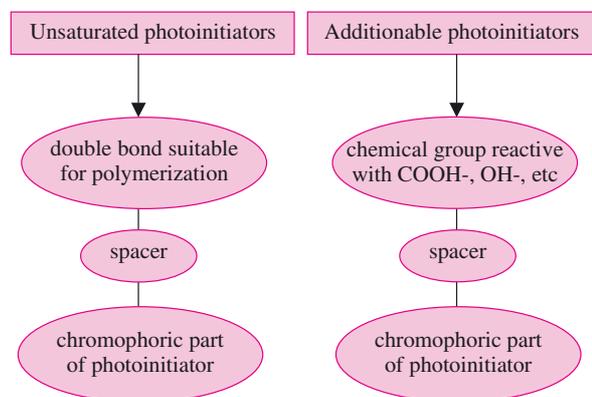


Fig. 5. *Photoreactivity adjustment of acrylic PSA*
 Rys. 5. *Fotoreaktywność poliakrylanowego kleju samo-przylepnego*

is considered in comparison to Nd: YAG-Laser the youngest laser with high radiation power. The most important field is the electronic industry and the photo- and polymer chemistry.

Excimer lasers are very intense pulsed light sources, which radiate UV wavelengths between 170 and 351 nm (Table 3) depending on the noble gas-halogen mixture, and provide a high energy, MW-power which is in the ns-range of radiation times.

Table 3. Wavelengths of excimer laser
Tabela 3. Długości fal lasera ekscymerowego

Active medium	Wavelength [nm]
ArCl	170
ArF	193
KrCl	222
KrF	248
XeCl	308
XeF	351

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 [9] and/or laser-initiated crosslinking [10].

6. Performance of acrylic pressure sensitive adhesives

The influence of the manufacturing methods on the acrylic PSA performances is usually measured versus the following main properties:

- adhesion-cohesion balance
- tack
- 180° peel adhesion
- 90° peel adhesion
- holding power
- static shear test
- delamination Test—a specimen of the tape is immersed in a bath of ethyl acetate at ordinary room temperature, then visually examined periodically. Any visual evidence of delamination is reported as a failure. The test is discontinued if there has been no failure after 24 hours.

7. Summary

Novel developed photoreactive solvent-free acrylic PSA formulations for produce of carrier-free tapes can overcome the challenge of fulfilling the demands of typical photoreactive adhesives. Either by formulation, by application, by UV-initiated polymerisation or UV-initiated crosslinking or by combination of these all parameters, the customer can achieve tailor-made solutions to be innovative and competitive for the future.

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