

UV-crosslinkable solvent-free acrylic pressure sensitive adhesive low viscosity systems and their application

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The technology of solvent-free acrylic pressure-sensitive adhesives (PSA) with low viscosity at room temperature has been developed. The novel acrylic PSAs contain photoreactive acrylic polymer and photoreactive diluents can be used after UV-crosslinking for manufacturing of mounting tapes, protective films, sign and marking films and structural adhesive tapes.

Key words: acrylic PSA, solvent-free, low viscosity, mounting tapes, structural tapes

Sieciowane UV bezrozpuszczalnikowe poliakrylanowe kleje samoprzylepne o niskiej lepkości i ich zastosowanie

Opracowano technologię syntezy sieciowanych promieniowaniem UV bezrozpuszczalnikowych poliakrylanowych klejów samoprzylepnych o niskiej lepkości w temperaturze pokojowej. Nowe kleje poliakrylanowe zawierające fotoreaktywny polimer oraz fotoreaktywne rozcieńczalniki mogą być stosowane po usieciowaniu UV do produkcji taśm montażowych, folii ochronnych, folii dekoracyjnych oraz adhezyjnych taśm strukturalnych.

Słowa kluczowe: bezrozpuszczalnikowe samoprzylepne kleje poliakrylanowe o niskiej lepkości, taśmy montażowe, taśmy strukturalne

1. Introduction

Since their introduction half a century ago, pressure-sensitive adhesives (PSA) have been successfully applied in many areas. They are used to produce self-adhesive tapes, labels, sign and marking films and protective films as well as in biomedical electrodes, dermal dosage systems for pharmaceutical and medical applications. The self-adhesive articles market is dominated by acrylic solvent-borne, water-borne or solvent-free PSA systems (Fig. 1). Here the solvent-free acrylic PSA in form of typical hotmelts, warmmelts and new low viscosity systems (LVS) are still most common [1].

Three properties which are useful in characterizing the nature of pressure-sensitive adhesives are tack (initial adhesion), peel adhesion (adhesion) and shear strength (cohesion). The first measures the adhesive's ability to adhere quickly, the second its ability to resist removal by peeling, and the third its ability to hold in position when shearing forces are exerted. The performance of acrylic pressure-sensitive adhesives, such

as tack, peel adhesion and shear strength, synthesized by polymerization of acrylate monomers are to a large degree determined by the molecular weight of PSA copolymer, polymerization method and especially by the

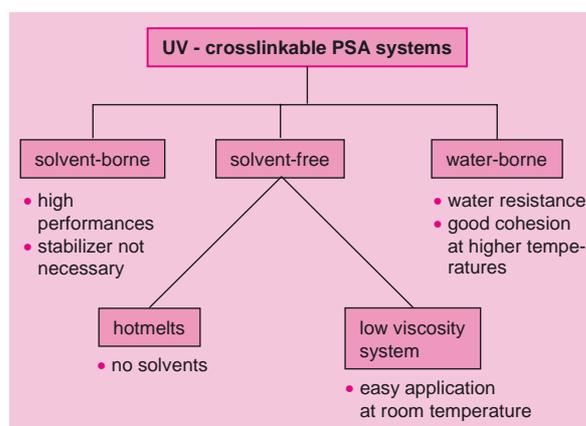


Fig. 1. Types of acrylic pressure-sensitive adhesives
Rys. 1. Rodzaje poliakrylanowych klejów samoprzylepnych

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type and quantity of the crosslinking agents added to the PSA or crosslinking methods [2].

2. Solvent free acrylic pressure sensitive adhesives

The application of solvent-free pressure-sensitive adhesives offers incontestable advantages such as reduction of solvent emission, saving space, energy and processing time so it permits for savings in capital investment and production costs as well [3]. For an easy and homogenous coating without any volatile compound while maintaining properties of the final product, viscosity of solvent-free pressure-sensitive adhesives must be lowered. Therefore, the classical hot-melts are coated in a molten stage at high temperatures between about 100°C and 140°C, and low-viscosity systems have reduced viscosity by using of reactive diluents of so they can be perfect coated at the room temperature (Fig. 2).

The production of this new developed class of solvent-free acrylic PSA is conducted in first step by solvent polymerisation. For some new special acrylic hot melts the polymerisation process is started at higher monomer concentrations. In view of the future degassing process, mixture of different solvents is being avoided [4]. At the end of the polymerisation step, the

polymer solution shows a polymer content of more than 50 wt.% (Tab. 1).

Table 1. *Solvent-borne polymerisation processes*
Tabela 1. *Procesy polimeryzacyjne z udziałem rozpuszczalnika*

Polymerisation process	old	new
Polymer concentration [wt.%]	50 to 60	60 to 80
Solvent system	acetone, ethyl acetate, hexane	ethyl acetate

This means that in this first production step a reduction of the organic solvent is possible. The fact that this beforehand eliminated solvent does not have to be removed during the following degassing process leads to decreased production costs and reduced ecological damage. At the moment, the degassing in the reactor after the polymerisation process seems to be a practicable way to produce acrylic hotmelts from solvent-borne systems (Fig. 3). With the evaporation process the production of the acrylic hotmelt PSA is finished. Solvent recovery permits an almost completely closed solvent circulation [5].

Presently, this method seems to be a useful practice way of solvent-free acrylic PSA hot-melts manufacturing from solvent based systems. The organic solvents

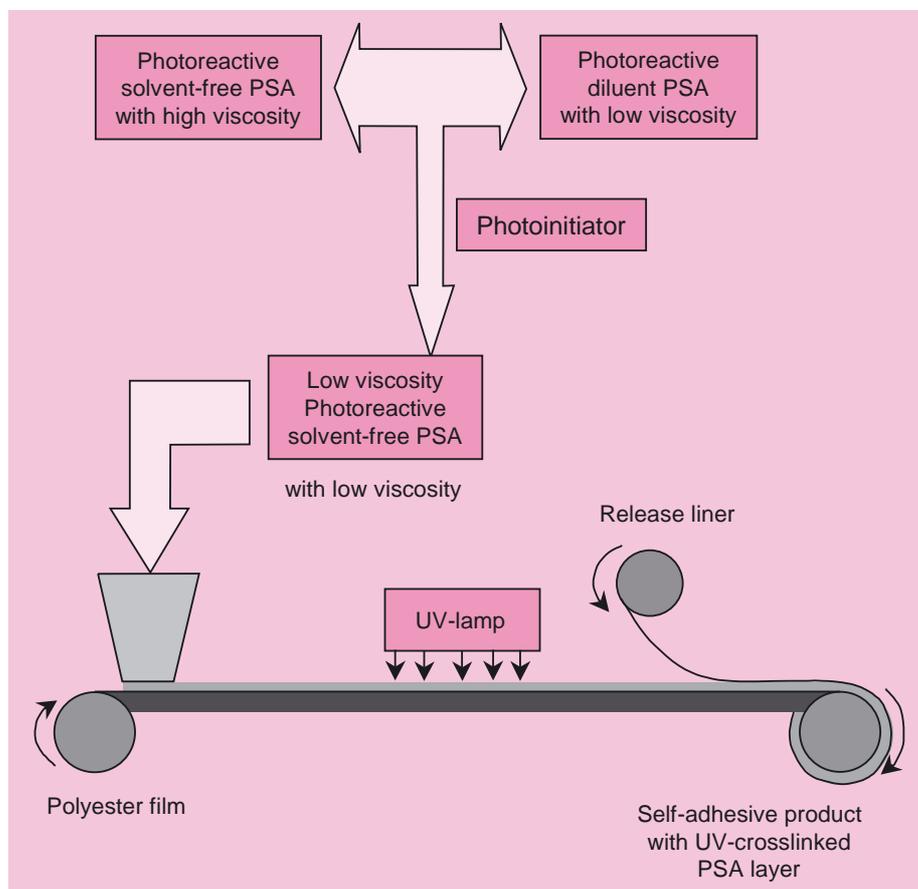


Fig. 2. *Solvent-free low viscosity acrylic PSA systems*

Rys. 2. *Bezrozpuszczalnikowe poliakrylanowe kleje samoprzylepne o niskiej lepkości*

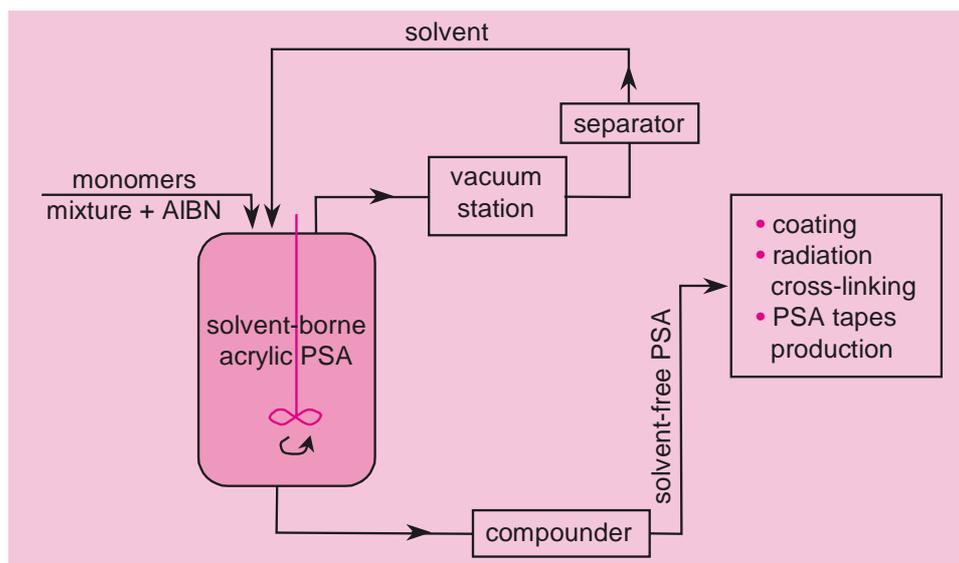


Fig. 3. Batch synthesis concept of solvent-free acrylic PSA

Rys. 3. Koncepcja syntezy bezrozpuszczalnikowego kleju poliakrylanowego w reaktorze

and free monomers are removed and solvent-free highly viscous material can be processed on a hot-melt coating machine at temperatures between 100 and 150°C. Higher temperature (approx. 150°C) applied over an extended period (24 hours) had no adverse effect on the adhesive properties [6].

3. Photoreactivity adjustment of acrylic PSA

The idea of replacing the conventional solvent-borne, water-borne or solvent free conventional cross-linkable systems with photoreactive UV cross-linkable systems became very attractive to manufacturing industries. However, it is only in the past 20 years that the use in particular of the very reactive mono or multifunctional acrylic pressure-sensitive adhesives (PSA) has resulted in a growing market for UV radiation cross-linkable products, finding uses in the fields of automobile, building, labels, protective films, electronics, medical applications, printing and the optics industry [7]. First of all very interesting for industrial applications are acrylic PSA characteristic through by excellent adhesive (tack and peel adhesion) and cohesive (shear strength) properties, excellent thermal and ageing performances.

The basic chemistry of photoreactive UV cross-linkable adhesives is the conversion of light energy into chemical energy. This energy conversion takes place through the use of chemical species photoinitiators which, upon absorption of a particular wavelength of light, photochemically produce reactive radicals or ions capable of initiating a rapid chain reaction. With the use of novel unsaturated photoinitiators (Fig. 4), new developed photoreactive adhesives and commonly available UV sources (UV lamps, UV lasers) it is possible to

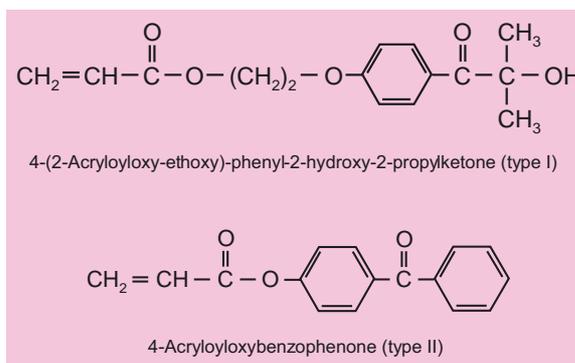


Fig. 4. Unsaturated copolymerizable radical photoinitiators

Rys. 4. Nienasycone zdolne do kopolimeryzacji fotoinicjatory rodnikowe

manufacturing of high performance UV cross-linkable PSA and high quality self-adhesive articles.

A suitable photoinitiator system must first present high initiation efficiency. This means that it must have a high absorption in the emission range of the UV source and the excited states thus formed must have both a short life time to avoid quenching by oxygen or monomer molecules and split into active radicals with the highest possible quantum yield. Also the photoinitiator must be soluble in the self-adhesive acrylic polymers used and not affect the colour, toxicity and degradation of the UV-cross-linked acrylic PSA [8].

All kinds of acrylic PSA 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. They also have the highest balance of adhesion and cohesion and an excellent water resistance. Acrylics are harder than rubbers. This can be seen in a less aggressive tack and slower build-up of peel

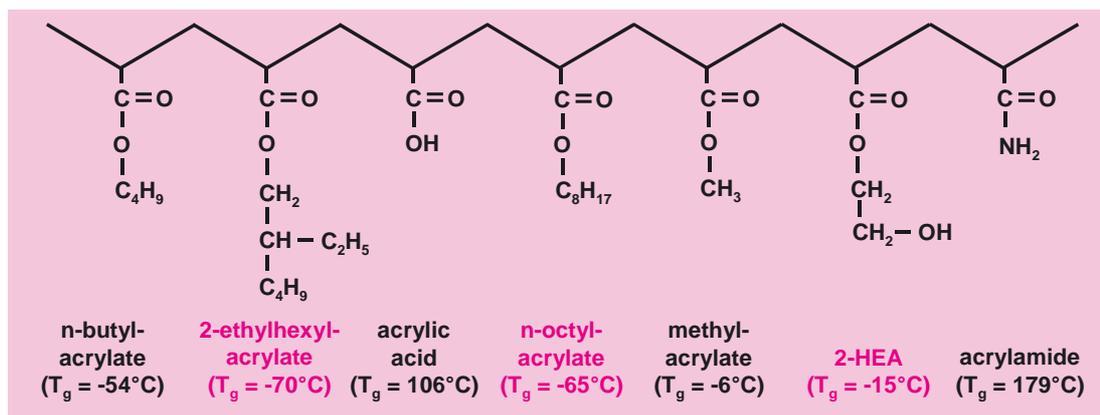


Fig. 5. Architecture of acrylic PSA polymer chain using typical acrylate monomers

Rys. 5. Architektura łańcucha polimeru akrylanowego zawierającego typowe monomery akrylanowe

strength. Lower adhesion to non-polar polyolefins is caused by the polar chemistry of acrylics. The versatility of acrylate chemistry is inherently useful in the design of high performance pressure-sensitive adhesives. A broad raw material base and a versatility of polymerization processes lend themselves to design of base polymers with unique properties (Fig. 5). Typical acrylic PSA contain no photoreactive groups and are with it radiation resistant [9].

The glass transition temperature (T_g) and the amorphous properties are the main issue for self-adhesive properties of various polymers, allowing the selection of raw materials for PSA applications. For permanent adherent pressure-sensitive adhesives T_g ranges from about -70°C to -25°C [5].

Photoreactive chemically UV-cross-linkable acrylic PSA consists of polymer backbone molecules that are modified with photoreactive groups. The physicochemical and mechanical properties of photoreactive pressure-sensitive adhesives are determined to a high degree by type and concentration of the photoreactivity.

Modification of the main polymer chain with copolymerizable photoinitiators

It is well known that components of pressure-sensitive adhesive systems, which are not chemically linked, can migrate into the PSA surface of the finished coating. These effects usually degrade gloss, adhesion and mechanical properties and can interfere with many applications. Extractability of photoinitiator by-products by food in contact with these adhesive coatings excludes their use for food packaging materials. Copolymerizing the unsaturated photoinitiator, especially based on benzophenones, into the backbone of the acrylic PSA copolymer allows the cross-linking with ultraviolet radiation. Performed polymer structures that crosslink directly under the influence of ultraviolet energy require special photosensitive groups to effect network formation (Fig. 6) [10].

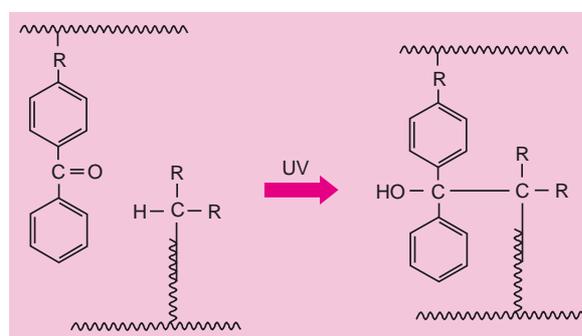


Fig. 6. Crosslinking by use of unsaturated photoinitiators incorporated into polymer chain

Rys. 6. Sieciowanie z udziałem nienasyconych fotoinicjatorów wbudowanych w łańcuch polimerowy

4. Performance adjustment of pressure sensitive adhesives

The most important properties of the UV-cross-linkable acrylics pressure-sensitive adhesives, such as tack, peel adhesion and shear strength, can be controlled by the UV dosage (cross-linking density). The UV-dose can be controlled by adjusting the power of the lamps and/or the speed at which the substrate is passed under the lamps in the production plant. With UV-cross-linkable acrylic PSA, the ratio of tack and peel adhesion to shear strength (cohesion) can be varied within wide limits, by controlling the amounts of UV energy applied to the adhesive film after it has been coated. Films formed by UV-cross linked acrylic adhesive become more cohesive as more radiant energy is applied, while their tack and peel adhesion decrease. This effect is the result of the cross-linking that takes place when the film is exposed to UV radiation. The effect of the UV radiation dose [mJ/cm^2], described as density of cross-linking, on the adhesive properties and cohesion is shown schematically in Fig. 7.

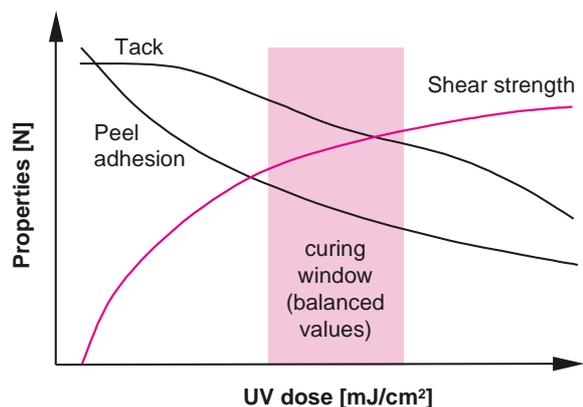


Fig. 7. Tack, peel adhesion and shear strength as a function of UV dose

Rys. 7. Tack, adhezja oraz kohezja jako funkcja dawki UV

5. Solvent free photoreactive pressure sensitive adhesive low viscosity systems (PSA-LVS)

Photoreactive solvent-free pressure-sensitive adhesive low viscosity systems (PSA-LVS) contain generally photoreactive self-adhesive polymers, photoreactive diluents, radical photoinitiators and multifunctional monomers. The presence of photoreactive diluents is very important for the manufacturing of PSA-

LVS and their application to produce a wide range of self-adhesive materials. Typical compositions of PSA-LVS are presented in Fig. 8.

Diverse photoreactive diluents are added to the solvent-free photoreactive acrylic hotmelts PSA in order to reduce the high hotmelts viscosity. Commercial available or developed hotmelt PSA are characterized at room temperature by viscosity above 1000 Pa·s, which enables its coating at the temperature lower than 100°C. Mostly the available on the market photoreactive diluents possess viscosity between 0.3 and 10 Pa·s. Therefore, the addition of photoreactive diluents allows the formulation of solvent-free low viscosity systems for coating the manufactured PSA-LVS even at room temperature. Prerequisite for viscosity reducing is compatibility of photoreactive diluents (Fig. 9) with photoreactive hotmelt PSA.

After the selected compatible photoreactive diluents (Genomer/Rahn, Ebecryl/Cytec) and Laromer/BASF) are added to hotmelt acrylic PSA, the viscosity at room temperature are measured and in Fig.10 presented.

A small difference between viscosities of solvent-free PSA-LVS using chosen photoreactive diluents was observed. In addition, the viscosity of PSA-LVS with the weight ratio of PSA to photoreactive diluent of 1:1 is very high and reaches viscosity values between 77 and 100 Pa·s. All three investigated reactive diluents allow on production of typical at room temperature coatable solvent-free pressure-sensitive adhesive low viscosity systems (PSA-LVS) with viscosities between 3 and 35 Pa·s containing photoreactive diluents with the weight ratio to photoreactive hotmelt PSA of between 2:1 and 3:1 (Fig. 11).

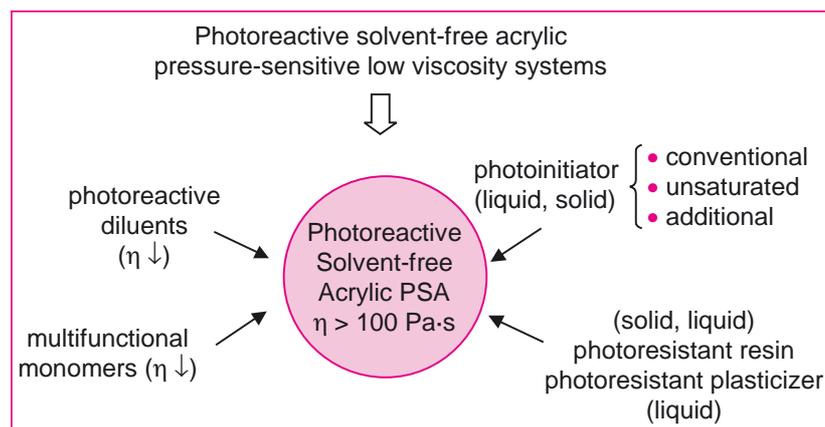


Fig. 8. Composition of photoreactive solvent-free PSA-LVS

Rys. 8. Kompozycja fotoreaktywnych bezrozpuszczalnikowych klejów samoprzylepnych o niskiej lepkości

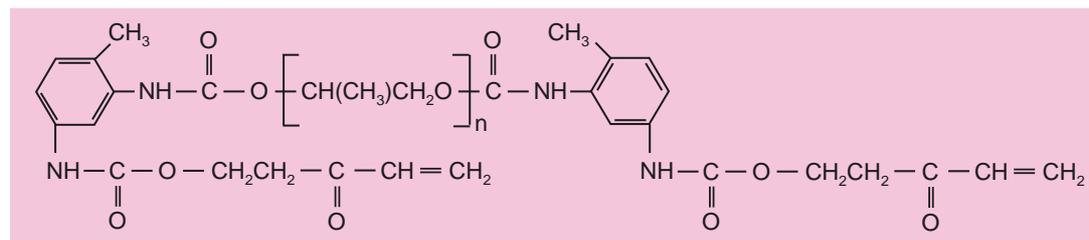


Fig. 9. Photoreactive diluent (RV) based on urethane acrylate

Rys. 9. Rozcieńczalnik fotoreaktywny (RV) na bazie uretanoakrylanu

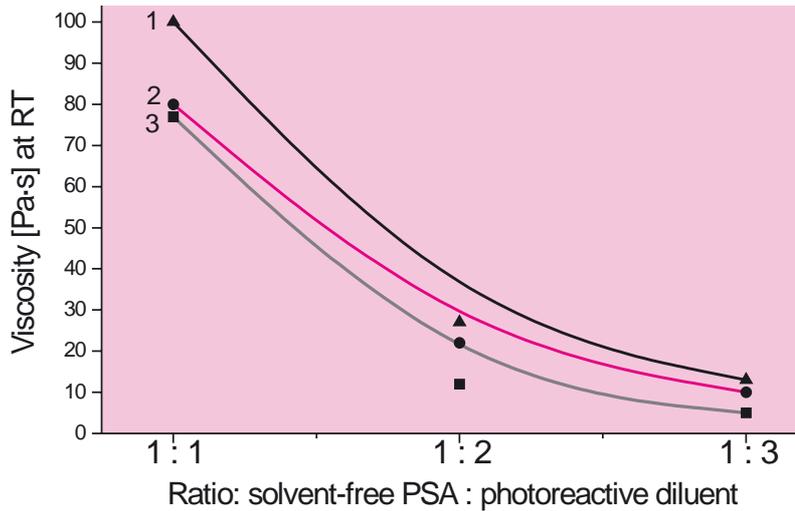


Fig. 10. The viscosity of low viscosity PSA (PSA-LVS) containing photoreactive diluents: 1 – Ebecryl, 2 – Laromer, 3 – Genomer
 Rys. 10. Lepkość fotoreaktywnych bezrozpuszczalnikowych klejów samoprzylepnych o niskiej lepkości zawierających rozcieńczalniki fotoreaktywne: 1 – Ebecryl, 2 – Laromer, 3 – Genomer

Fig. 11. Temperature influence on the viscosity of solvent-free photoreactive PSA-LVS
 Rys. 11. Wpływ temperatury na lepkość bezrozpuszczalnikowych fotoreaktywnych klejów samoprzylepnych o niskiej lepkości

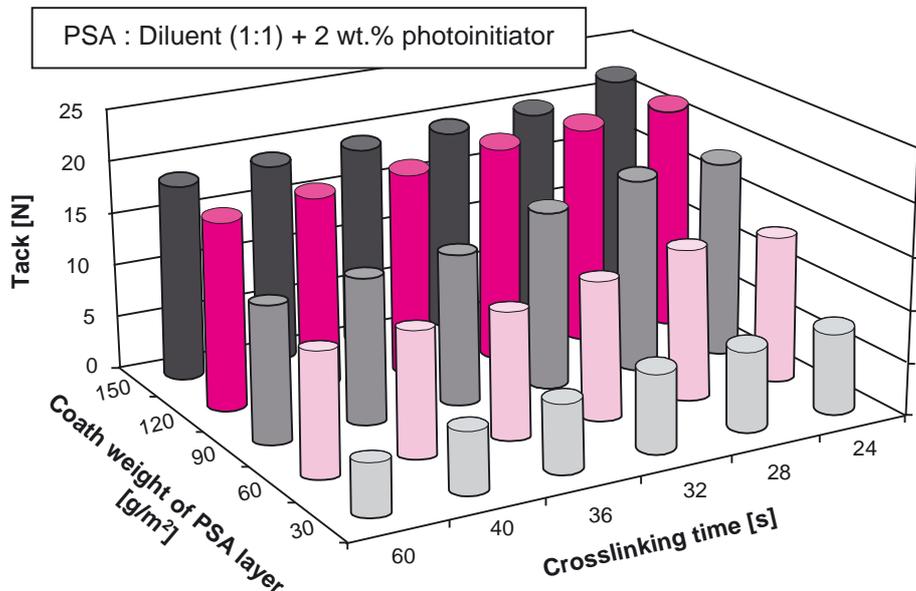
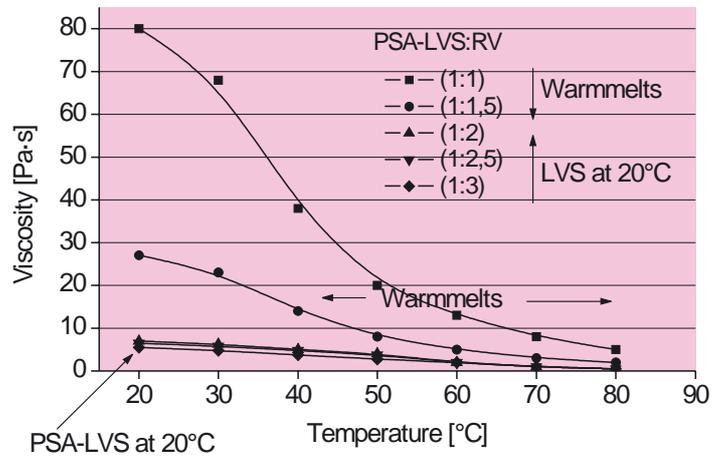


Fig. 12. Tack of developed PSA-LVS as function of the coat weight and cross-linking time
 Rys. 12. Tack bezrozpuszczalnikowych klejów samoprzylepnych jako funkcja gramatury kleju oraz czasu sieciowania

The most efficient solvent-free photoreactive PSA-LVS, chosen owing to the first conducted investigations, consist of photoreactive acrylic hotmelt and pho-

totoreactive diluent in the weight ratio of 1:1 containing 2 wt.% of conventional radical photoinitiator was coated at 40°C as warmmelt on polyester film with the

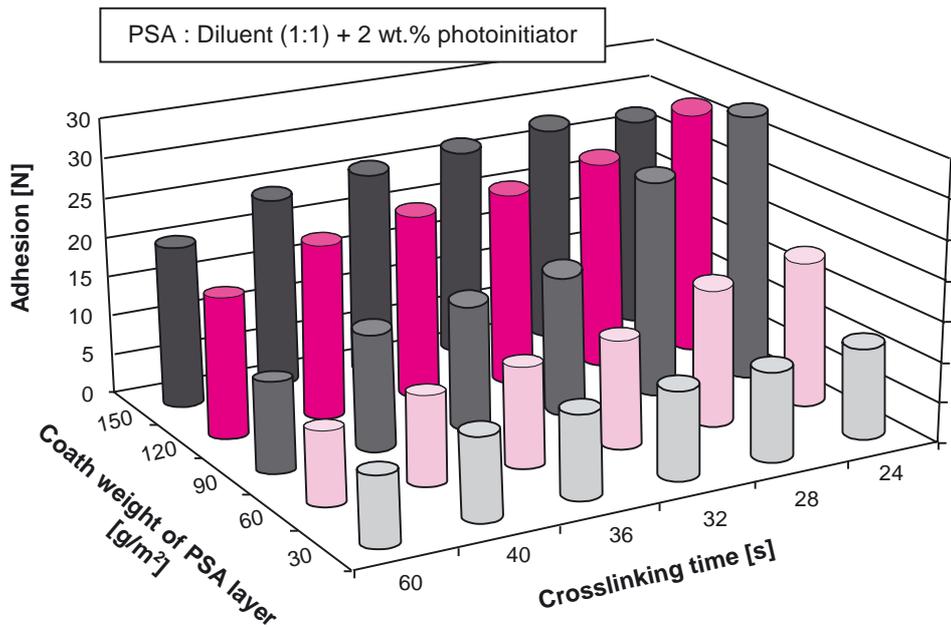


Fig. 13. Adhesion of developed PSA-LVS as function of the coat weight and cross-linking time

Rys. 13. Adhezja bezrozpuszczalnikowych klejów samoprzylepnych jako funkcja gramatury kleju oraz czasu sieciowania

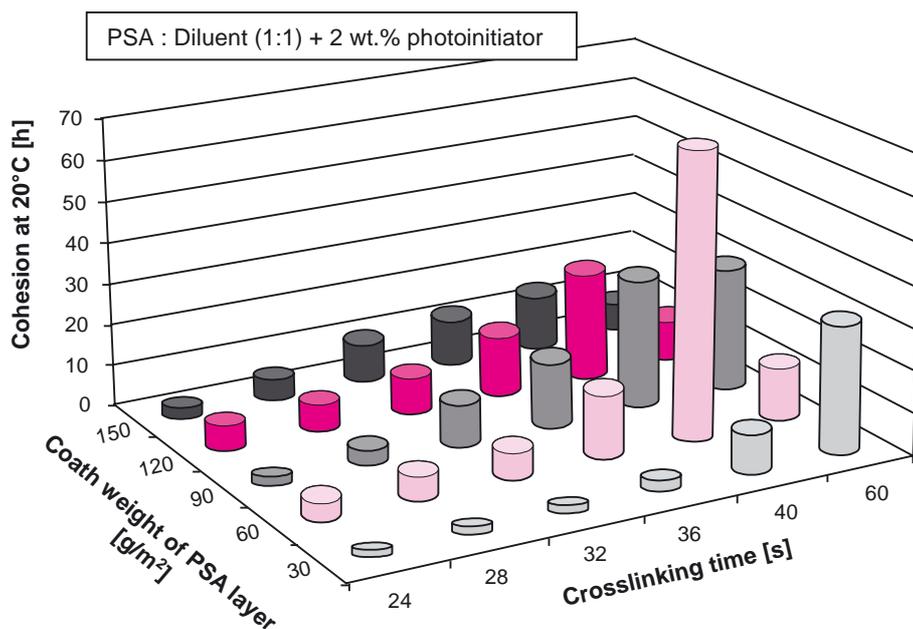


Fig. 14. Cohesion of developed PSA-LVS as function of the coat weight and cross-linking time

Rys. 14. Kohezja bezrozpuszczalnikowych klejów samoprzylepnych jako funkcja gramatury kleju oraz czasu sieciowania

coat weights between 30 g/m² and 150 g/m² and UV-crosslink between 24 s and 60 s under UV-lamp with UV dose of 900 mJ/cm². The developed solvent-free photoreactive PSA-LVS in form of one-sided self-adhesive samples was tested with relation to the main typical PSA properties as tack, adhesion (peel adhesion) and cohesion (shear strength) at 20°C (Figs. 12-14).

The examined results of tack (Fig. 12) indicate that tack increases together with the coat weight of PSA

layer and decreases with the increasing of cross-linking time under UV-lamp. The adhesion diminishes with the increasing of cross-linking time (Fig. 18). Despite the fact that adhesion achieves the best results for PSA-LVS with adhesive layers of 90 and 120 g/m² coat weight, too short cross-linking time causes cohesive failure or partially cohesive failure, which eliminates solvent-free PSA-LVS for potential applications. Better cohesion at 20°C was observed with the cross-linking time increase (Fig. 14). Generally, better cohesion of

tested PSA-LVS was registered for the coat weights of 60 g/m² and 90 g/m². The over-curing of PSA-LVS for 60 g/m² thick and thicker adhesive layers for the cross-linking time from 40 to 60 s causes the decrease of cohesion.

6. General conclusion and outlook

The need to replace solvent containing systems, which still have maintained a large market share in various areas, results in a further push of innovations in the development of solvent-free photoreactive acrylic pressure-sensitive adhesive low viscosity systems (PSA-LVS). As oppose to the classical solvent containing or to the aqueous systems, the developed acrylic solvent-free photoreactive pressure-sensitive adhesive low viscosity systems (PSA-LVS) provides the following advantages:

- Reduction of environmental impacts to a minimum
- Saving of energy costs
- Savings in coasts for space (low investment costs: no drying channel)
- High production speed at pressure-sensitive adhesive coatings
- Production of "thick" self-adhesive carrier-free tapes with PSA layer about 1000 g/m²
- Manufacturing of one-sided or double-sided tapes with PSA layer between 30 and 150 g/m²

The drawbacks of the developed solvent-free photoreactive PSA-LVS are the difficulties with UV-cross-linking process of self-adhesive layers with coat weight below 30 g/m². This phenomenon is lead back on the inhibition of the oxygen.

The development of novel photoreactive solvent-free low viscosity acrylic pressure-sensitive adhesives (PSA-LVS) has recently attracted considerable attention, due to their practical and potential applications in various industrial branches within the comprehensive range of self-adhesive technical products. Solvent free LV-PASs with high performance: high tack, very good adhesion and high cohesion can be formed by using suitable commercial available photoreactive diluents, high reactive photoinitiators and UV-cross-linking as a very efficient cross-linking method. The viscosity of the novel LV-PSAs compositions based on acrylic is sufficiently low to manufacture the developed adhesive at room temperature or at temperatures from 40°C to 80°C as warmmelt, in compare with standard hotmelt adhesives coatable with typical hotmelt equipment at

process temperatures of 120°C-140°C. Contrary to conventional solvent-borne or water-borne PSA systems, which can be used for production of maximal 140 g/m² thick self-adhesive layers, newly developed solvent-free LV-PSAs compositions can be perfectly used and cross-linked within application areas as transfer carrier-free tapes.

The favorable prognosis for design and development of tailor-made PSA-LVS composition, which can cope with both the technical and ecological demands, is therefore a continuing challenge for industrial research and development. Progress in the PSA coating technology will open up for new applications and an extended market penetration of solvent-free UV-cross-linkable acrylic adhesive raw materials. New research and development experiments in the field of novel photoreactive solvent-free LV-PSAs include dual-cross-linkable stable low viscosity systems containing thermal cross-linking-agents, compositions for removable and repositionable self-adhesive products and precursors for the production of the new generation structural PSA tapes.

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