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## Photoreactive UV-crosslinkable warm-melt acrylic pressure-sensitive adhesives

*Since their introduction half a century ago, pressure-sensitive adhesives (PSA) have been successfully applied in many areas. The self-adhesive articles market is dominated by acrylic solvent-borne, water-borne or solvent-free PSA systems. Here the solvent-free acrylic PSA in form of typical hot-melts, warm-melts and new low viscosity systems (LVS) are still most common. The goal of this article is to review the industrial application of new generation of radiation curable warm-melt acrylic pressure-sensitive adhesives (PSAs) in comparison with typical conventional hot-melts adhesives. New generation of radiation-curable acrylic warm-melt PSAs containing unsaturated photoinitiator, incorporated during polymerization process into polymer chain, and photoreactive diluents added to PSA systems after polymerization allows producing of wide range of self-adhesive materials, such as labels, mounting tapes, masking and splicing tapes, and sign and marking films.*

*Key words: acrylics, hot-melts, UV-crosslinking, reactive diluents, pressure-sensitive adhesives, warm-melts.*

## Fotoreaktywne, sieciowalne UV, termotopliwe samoprzylepne kleje poliakrylanowe

*Kleje samoprzylepne (PSA) od czasu wprowadzenia ich na rynek pół wieku temu są z powodzeniem stosowane w wielu dziedzinach. Rynek artykułów samoprzylepnych jest zdominowany przez produkty rozpuszczalnikowe, wodorozcieńczalne lub bezrozpuszczalnikowe – na bazie poliakrylanów. W zastosowaniach komercyjnych największą popularnością cieszą się bezrozpuszczalnikowe akrylanowe materiały samoprzylepne w postaci typowych klejów termotopliwych, użytych do powlekania na ciepło i gorąco, bądź nowych systemów o niskiej lepkości (LVS). Celem tego artykułu jest przegląd zastosowań przemysłowych akrylanowych klejów samoprzylepnych nanoszonych na podłoże na ciepło oraz sieciowanych promieniowaniem UV w porównaniu z typowymi tradycyjnymi klejami stosowanymi na gorąco. Nowa generacja sieciowalnych promieniowaniem UV, akrylanowych termotopliwych klejów samoprzylepnych zawierających nienasycony fotoinicjator, wbudowany w trakcie polimeryzacji w łańcuch polimeru, oraz fotoreaktywny rozcieńczalnik dodany do układu PSA po procesie polimeryzacji, daje możliwość produkcji szerokiej gamy materiałów samoprzylepnych, takich jak etykiety, taśmy montażowe, maskujące, łączące oraz wszelkiego rodzaju folie dekoracyjne.*

*Słowa kluczowe: akrylany, kleje termotopliwe, sieciowanie UV, rozcieńczalniki reaktywne, kleje samoprzylepne, powlekanie na ciepło.*

### I. Solvent-free pressure-sensitive adhesives

Pressure-sensitive adhesives (PSAs) are nonmetallic materials used to bond other materials, mainly on their surfaces through adhesion and cohesion [1]. The difference between PSAs and other adhesives, such as contact adhesives, is in the permanent surface stickiness of the PSAs before, or after, the application. Adhesion and cohesion are phenomena, which may be described thermodynamically and chemically, but actually they cannot

be measured precisely. It was shown that the most important bonding processes are bonding by adhesion and bonding with PSAs [2]. Since their introduction half a century ago, PSAs have been successfully applied in many fields. They are used in self-adhesive tapes, labels, sign and marking films and protective films as well as in dermal dosage systems for pharmaceutical applications, in biomedical electrodes, the assembly of automotive parts, toys, and electronic circuits and keyboards. In the last fifty years or so, PSAs have made tremendous strides from what was virtually a black art to what is now a sophisticated science. So much so that both the few larger manufacturers of self-adhesive articles and their even larger suppliers now use very expensive equipment to study pressure-sensitive adhesive behavior: tack (initial adhesion), adhesion (peel adhesion) and cohesion (shear strength).

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There are seven main polymer groups of PSAs, namely acrylics, rubbers, silicones, polyurethanes, polyesters, polyether and ethylene-vinyl acetate copolymers (EVA). Acrylic PSAs, in comparison with other groups of PSAs, can be modified in a greater variety, allowing optimization for diverse market applications [3]. It is significant to note that as early as 1941 a polypropyl acrylic ester, known as Acronal 4, from I.G. Farben, was being used as a one component pressure-sensitive adhesive, the first indication of an acrylic PSA system [4].

Although the acrylic PSAs may be dwarfs in terms of quantity, they are giants when considered from the quality point of view. Only by means of these acrylic specialties was it possible to succeed in drafting the present surprisingly efficient generation of high quality of self-adhesive products. Pressure-sensitive adhesive acrylics can be applied in forms as a solvent-borne, as a water-borne (dispersions) and as a solvent-free system, especially acrylic hot-melts characterized by very high coating temperatures between 130 and 150°C. The market of pressure-sensitive adhesives is dominated by traditional formulations of solvent-borne or water-borne adhesives based on acrylics. Despite the developments of energy-efficient solvent-recovery methods, environmental legislation drives research towards alternative production methods to coating from solution. Water-borne acrylic PSAs wide spread for many different applications, however, the presence of surfactants [5], and the lesser control over the molecular structure did not allow to apply them to the most demanding uses. Commercial photoreactive acrylic pressure-sensitive adhesives are known in the form of hot-melts coated at higher temperature, usually from 130 to 150°C. Research equipment for hot-melts is very expensive, so warm-melt systems demand cheaper and less complicated research methods.

Today's strict environmental regulation and all above-mentioned arguments bring about introducing solvent-free photoreactive PSAs, especially hot-melt acrylic PSAs. The application of UV curing PSAs hot-melts offers incontestable advantages like reduction of solvent emission, saving space, energy and processing time so permit savings in capital investment and production costs as well [6]. 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, hot-melts are coated in a molten stage at high temperature, and systems with low viscosity have reduced viscosity by diluents so they can be coated at temperatures between 70 and 100°C, known in technology as warm-melts.

Thermal or UV radiation curing can provide the curing of solvent-free PSAs. Thermal curing is possible only in case low-viscosity systems, because hot-melts coating demand high temperature, which would lead to premature curing. Consequently, UV-curing can be applied to hot-melts and warm-melt PSAs as well.

UV technology is well established in the market and allows the production of a wide range of photocurable acrylic PSAs with interesting features.

## 2. Goal of research and development work

Our work present development on warm-melt photoreactive PSAs area based on acrylics, which were manufactured by using of solvent-free acrylic PSAs containing photoreactive diluents and additional photoinitiators. Properties of created warm-melt photoreactive solvent-free acrylic PSAs with lower viscosity can be examined paying special attention to application as one-side, double-side or transfer pressure-sensitive tapes with different layer's thickness.

## 3. Manufacturing technology of acrylic warm-melt PSAs

Technology of warm-melt acrylic photoreactive PSAs manufacturing is presented in Fig. 1. After obtaining photoreactive hot-melt acrylics, composition is diluted with photoreactive diluents, which viscosity is much lower than for hot-melts. The amount of added photoreactive diluents depends on expected viscosity of final warm-melt self-adhesive compositions. The viscosity is inversely proportional to photoreactive diluents content. In order to get lower viscosity of photoreactive acrylic PSAs one should add adequate amount of photoreactive diluents. After addition of photoreactive diluents the

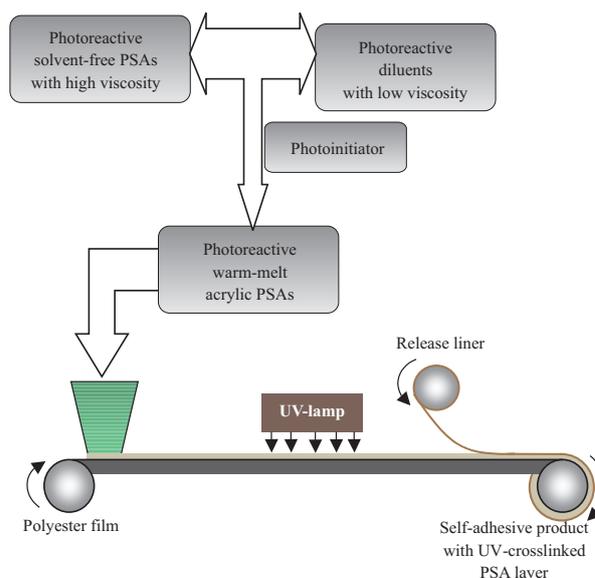


Figure 1. Manufacturing of one-sided self-adhesive products using acrylic PSA warm-melts

Rys. 1. Produkcja jednostronnie samoprzylepnych produktów przy użyciu termotopliwych akrylanowych klejów samoprzylepnych

external photoinitiator must be applied, as additional source of free radicals [7].

The obtained photoreactive acrylic warm-melts are characterized by viscosity from about 2 to 10 Pa·s at temperatures between 70-100°C, that allows their coating at this moderate temperatures area without using of 140°C and higher temperatures.

## 4. Experimental

Manufacturing of photoreactive warm-melt acrylic PSAs was conducted in following stages:

- Synthesis of photoreactive solvent-borne acrylic PSAs
- Evaporation of polymerization medium to obtain solvent-free PSAs
- Addition of photoreactive diluents to decrease PSAs viscosity
- Addition of external photoinitiators as a source of free radicals during exposure of UV-radiation

Basic PSAs were synthesized by free-radical polymerization in solvent mixture ethyl acetate/acetone at boiling point of about 72°C. Free-radical polymerization proceed with participation of radical initiator AIBN (2,2'-azo-bis(isobutyronitrile) and addition of unsaturated photoinitiator 4-acryloyloxyethoxy benzophenone (AEBP) (Fig. 2).

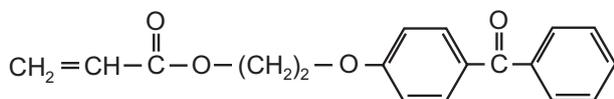


Figure 2. Unsaturated photoinitiator 4-acryloyloxyethoxy benzophenone (AEBP)

Rys. 2. Nienasycony fotoinicjator 4-akryloilooksyetoksybenzofenon (AEBP)

Table 1. Glass transition temperature of acrylic monomers used for synthesis of PSAs

Tabela 1. Temperatura zeszklenia monomerów akrylanowych używanych do syntezy klejów samoprzylepnych

Monomer	T <sub>g</sub> of homopolymer [°C]
2-ethylhexyl acrylate (2-EHA)	-70
ethyl acrylate (EA)	-26
isobornyl acrylate (IBA)	+94
acrylic acid (AA)	+106
4-acryloyloxyethoxy benzophenone (AEBP)	+138

The main criterion to assess the usefulness of monomers to manufacture acrylic PSAs is glass transition temperature (T<sub>g</sub>). In Table 1 the monomers used for polymerization process with glass transition temperature of their homopolymers are presented.

The synthesis of solvent-borne acrylic PSAs was performed under the following conditions:

- Concentration of monomers mixture in solvent-borne PSA: 60 wt.%
- Chosen organic solvent: mixture: ethyl acetate/acetone (4:1)
- Concentration of radical initiator-AIBN according to amount of monomers: 0.3 wt.%
- Composition of synthesized acrylic PSAs: 2-EHA: (50-70 wt.%), EA: (15-30 wt.%), IBA: (5-15 wt.%), AA: (2-10 wt.%) and AEBP (0.1-2 wt.%)

From literature survey and previous research [8] it was found that complete distilling organic solvent off from solvent-borne PSAs with 60 wt.% polymer content is only possible if PSAs viscosity, measured at room temperature, is between 1.5 and 3.0 Pa·s. Changing synthesis conditions as dosage time of monomer mixture allows to regulate the viscosity of solvent-borne acrylic PSAs. Syntheses of chosen acrylic PSAs were leading the same as formerly only with changing dosage times of monomer mixture, which were: 30 min, 45 min, 1 h, 2 h and 3 h.

Viscosities of synthesized PSAs were measured with Rotational Viscometers RM from Rheometric Scientific (Tab. 2).

Table 2. Viscosity of solvent-borne PSA synthesized with different dosage time of monomers

Tabela 2. Lepkość rozpuszczalnikowego kleju samoprzylepnego podczas syntezy różniących się czasem dozowania monomerów

Dosage time		30 min	45 min	1 h	2 h	3 h
Viscosity of solvent-borne PSAs η [Pa·s]	PSA1	3.7	3.2	3.1	2.5	2.2
	PSA2	3.8	3.6	3.1	2.7	2.4
	PSA3	4.1	4.7	3.5	2.9	2.6
	PSA4	4.4	4.2	3.8	3.1	2.8
	PSA5	4.9	4.4	4.2	3.5	3.1

For removing of polymerization medium ethyl acetate/acetone was designed acrylic PSA 3 (η=2,9 Pa·s and dosage time = 2 h) with following composition: 2-EHA: 54 wt.%, EA: 30 wt.%, IBA: 10 wt.%, AA: 5 wt.% and AEBP:1.0 wt.%.

Organic solvents have to be evaporated in order to get solvent-free PSA from synthesised solvent-borne PSA 3. Removing of polymerization medium was conducted under a vacuum at high temperature after the polymerization is finished. After evaporation, solvent can be turned back to the process circulation and used again for polymerization. Volatile compounds in solvent-borne PSAs are solvent and unreacted free monomers. The free monomers removal of PSAs is more difficult, according to their high boiling-point temperatures. The amount of free-monomers in solvent-borne PSA depends on the reaction condition, post-reaction time and kind of acrylic monomers. Their amount in solvent-free PSAs oscillates between 0.1 and 0.4 wt.% of total polymer mass. After polymerization, the organic solvent was first remo-

ved from the polymerization reactor under atmospheric pressure with rising temperature from room temperature to 130°C. The second step of distillation was the removing of organic solvent at the temperature of 130°C and under vacuum 1 mm Hg with the use of oil vacuum pump DOA-V510-BN from GAST Manufacturing Inc. The second step last until all solvent was evaporated [8].

Diverse photoreactive diluents were added to chosen hot-melt acrylic PSAs in order to reduce the viscosity, which enable coating of solvent-free PSA at temperature between 70 and 100°C. This temperature is the typical coating temperature for warm-melt PSAs. Solvent-free acrylic PSA 3 is characterized at room temperature by viscosity above 1000 Pa·s, which enables its coating above 70-100°C. Most of commercial photoreactive diluents has viscosity below 3.0 Pa·s. Therefore, addition of low viscosity photoreactive diluents allows coating of obtained solvent-free acrylic PSA even at temperature between 70 and 100°C. The effective photoreactive diluents are acrylates or urethane-acrylates based monomers or multifunctional oligomers. Most of evaluated mixtures were no miscible, few of them was partially miscible, which means that occurred separation of two phases. One of all tested commercial available photoreactive diluents appeared to be homogenous with solvent-free PSA 3. This suitable photoreactive diluent (RV) Genomer 1122 was available from Rahn. It was been investigated Genomer 1122 with 1:2, 1:3 and 1:4 weight ratio to PSA 3 after addition of 3 wt.% of external photoinitiator Irgacure 127 from Ciba to synthesized hot-melt PSA 3.

The synthesized warm-melt was coated at 80°C with the use of special coater HM-PSA DWT/EC-C109 from BASF with heating panel with coat weight of 60 g/m<sup>2</sup> on silicon paper and then transfer on the polyester film Hostaphan RN from BASF. After coating the PSA layer was crosslinked under UV-lamp to get products in form of one-sided self-adhesives tapes to measure their adhe-



Figure 3. UV-lamp AKTIPRINT-mini 18-2 from Technigraf with mobile band  
Rys. 3. Lampa UV AKTIPRINT-mini 18-2 z ruchomą taśmą – firmy Technigraf

sive and mechanical properties. The samples were cross-linked with UV dose of 900 mJ/cm<sup>2</sup> using UV-lamp AKTIPRINT-mini 18-2 from Technigraf with mobile band (Fig. 3).

The UV-exposure can be measured using an integrating radiometer Dynachem™ Model 500, available from Dynachem Corporation, 2631 Michelle Drive, Tustin, CA 92680.

The coated warm-melt acrylic PSA layers were cross-linked under UV lamp with crosslinking times between 4 and 32 second. There was evaluated tack (according to AFERA 4015 – Fig. 4), peel adhesion (according to AFERA 4001 – Fig. 5) and shear strength on the stainless steel (according to AFERA 4012 at 20°C and 70°C – Fig. 6).

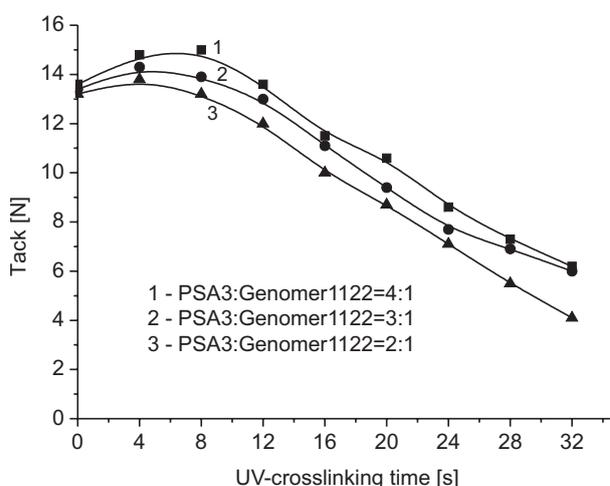


Figure 4. Tack of UV-crosslinked warm-melt acrylic PSAs versus UV-curing time

Rys. 4. Tack sieciowanych promieniowaniem UV termotopliwych akrylanowych klejów samoprzylepnych w zależności od czasu sieciowania

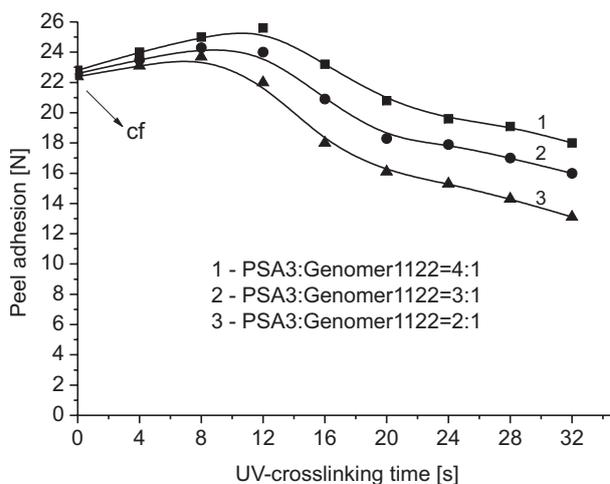


Figure 5. Peel adhesion of UV-crosslinked warm-melt acrylic PSAs versus UV-curing time

Rys. 5. Adhezja sieciowanych promieniowaniem UV termotopliwych akrylanowych klejów samoprzylepnych w zależności od czasu sieciowania

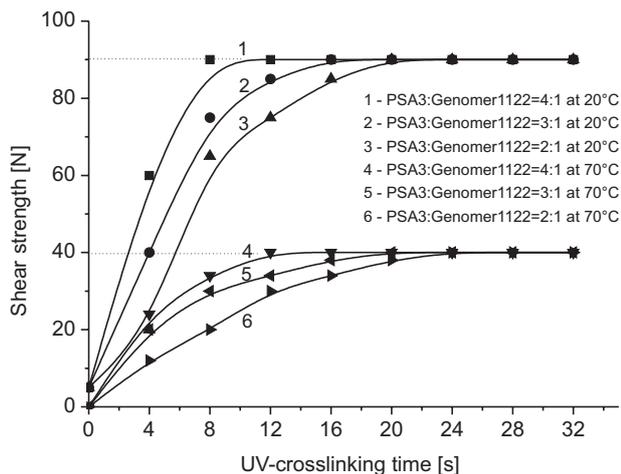


Figure 6. Shear strength at 20°C and 70°C of UV-crosslinked warm-melt acrylic PSAs versus UV-curing time  
Rys. 6. Kohezja w temp. 20°C oraz 70°C sieciowanych UV termotopliwych akrylanowych klejów samoprzylepnych w zależności od czasu sieciowania

It was unequivocally shown (Fig. 4) that the low UV-crosslinking of investigated warm-melts acrylic PSAs increases their tack. The maxima of tack were observed for UV-crosslinking time of 4s for warm-melt acrylic PSAs containing Genomer 1122 in the ratio PSA: Genomer 1122 = 3:1 and 2:1. For acrylic warm-melt PSA3:Genomer 1122 = 4:1 the maximum of tack for UV-crosslinking time of 8 s was noticed. Longer UV-crosslinking time influences the tack values negatively.

An increase of UV-radiation curing time of the investigated warm-melt acrylic PSAs containing reactive diluent Genomer 1122 can lead to a bigger effect on peel adhesion (Fig. 5) than in the case of tack (Fig. 4). This is a consequence of the effect of „light” curing using UV-radiation interior 4 to 12 s. For longer UV-curing times the peel adhesion decreases. In the case of uncured warm-melt acrylic PSAs a cohesive failure of (the measured cohesion was unacceptable) was observed.

The incorporation of selected unsaturated photoinitiator 4-acryloyloxyethoxy benzophenone (AEBP) into

acrylic polymer chain brought about a more rapid increase of shear strength after UV-curing at the measured temperatures 20°C and 70°C (Fig. 6). Excellent cohesion values, of 90 N at 20°C and 40 N at 70°C for 8 and 12 s UV-curing time for warm-melt acrylic PSAs containing 20 wt.% Genomer 1122 (PSA 3:Genomer 1122 = 4:1) were observed.

## 5. Conclusion

The presented test results have been proven that this group of developed photoreactive warm-melt acrylic PSAs characterized by extraordinarily high shear strength at 20°C and 70°C, very high peel adhesion and good tack by using of photoinitiator 4-acryloyloxyethoxy benzophenone (AEBP) predestinate these products for a wide range of applications. UV-curable warm-melts acrylic PSAs containing reactive diluent Genomer 1122 and unsaturated photoinitiator AEBP are characterized by excellent performance which enabled their applications in medicine leading to an interesting application for the production of medical self-adhesive products and high-performance technical mounting tapes, masking and splicing tapes, protective films, sign and marking films and high quality labels.

## References

1. Benedek I., „Developments in Pressure-Sensitive Products”, Taylor & Francis a CRC Press Book, New York, USA, 2006, 630.
2. Benedek I., „Pressure-Sensitive Design and Formulation, Application”, Brill, 2, Leiden, Boston, 2006, 500.
3. Czech Z., Petech R., Zych K., Pol. J. Chem. 2009, 11, 4, 7-12.
4. Houwink R., Salomon G., Int. J. Adhes. Adhes. 1982, 2, 17.
5. Mallégo J., Gorce J.-P., Dupont O., Jeynes C., McDonald P. J., Keddie J. L., Langmuir 2002, 18, 11, 4478-4487.
6. Tauber A., Scherzer T., Weiss I., Mehnert R., J. Coat. Technol. 2002, 74, 41-47.
7. Milker R., Czech Z., Wesolowska M., Pol. J. Chem. 2007, 9, 2, 5-9.
8. Czech Z., Butwin A., Elastomery 2008, 12, 5-6, 3-10.

## Drodzy Czytelnicy,

czasopismo „Elastomery” od kilkunastu lat pełni rolę łącznika pomiędzy jednostkami naukowo-badawczymi a przedsiębiorstwami wykorzystującymi w praktyce osiągnięcia nauki; wierzymy, że tak będzie nadal.

Mając nadzieję w dalszym ciągu spełniać Państwa oczekiwania, chcielibyśmy zaprosić do publikowania na łamach naszego czasopisma artykułów z dziedziny chemii, fizykochemii i technologii elastomerów, informacji o osiągnięciach swoich firm, wynalazkach, doktoratach oraz wydanych książkach.

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