

Synthesis of photoreactive solvent-free acrylic pressure-sensitive adhesives in the recovered system

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The present paper discloses a novel photoreactive solvent-free acrylic pressure-sensitive adhesive (PSA) systems, especially suitable for the so much adhesive film applications as the double-sided, single-sided or carrier-free technical tapes, self-adhesive labels, protective films, marking and sign films and wide range of medical products. The novel photoreactive solvent-free pressure-sensitive adhesives contain no volatile organic compounds (residue monomers or organic solvent) and comply with the environment and legislation. The synthesis of this new type of acrylic PSA is conducted in common practice by solvent polymerisation. After the organic solvent are removed, there remains a non-volatile, solvent-free highly viscous material, which can be processed on a hot-melt coating machine at the temperatures of about 100 to 140°C.

Keywords: polymerization, unsaturated photoinitiator, organic solvent, acrylic PSA, devolatilizing of solvent.

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INTRODUCTION

Solvent-free pressure-sensitive adhesives potentially offer significant economic and environmental advantages over crosslinkable solvent systems. They are the compositions that combine the properties of solvent-free hot melt adhesives with the properties of pressure-sensitive adhesives¹. The hot melts are solids at room temperature, melt upon the application of heat, and regain their solid form on cooling. The PSA are aggressive and permanently tacky at room temperature, and adhere to surfaces by the application of light finger pressure². The combination of these properties provide compositions that are melts at elevated temperatures and cool to form a permanently tacky solid coating that adheres to contact. These PSA are most commonly used applied to various substrates, such as paper, cloth, metal, and plastic films, which are then converted into tapes and labels for use in the packaging industry, particularly in marking, sealing and bonding applications, or for use in the health and pharmaceutical industry, particularly in bandages or transdermal drug delivery systems³.

A good workable hot melt PSA must exhibit high cohesive strength at room temperature and later after crosslinking at higher temperatures, low shrinkage on substrates, retention of pressure-sensitive properties during storage and use, and a relatively fluid viscosity at commonly employed application temperatures of 100 to 140°C. Although very low molecular weight will yield a hot melt with sufficient fluidity, the resulting adhesives lack cohesive strength. High molecular weight polymers give better cohesive strength, but are too viscous at the common application temperatures to be easily coatable on substrates⁴.

To circumvent these problems, low molecular weight polymers have been made with unsaturated copolymerizable photoinitiators on the side chains. The photoreactive polymers, especially acrylic PSA, is than crosslinked by UV irradiation to provide sufficient cohesion and tack⁵⁻⁷.

An outsider on this range of hot melts are 100%-systems based on acrylics. Strictly speaking, the term „acrylic hot melt” is misleading for this type of adhesives. Since this name does not stand for the well-known hot melt adhesives but for solvent-free PSA which can be melt coated. So, acrylic hot melts are the ecologically beneficial alternative to the common solvent-borne acrylic adhesives⁸.

The production of this new type of acrylic PSA is conducted in common industrial practice 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 are being avoided. 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

Polymerisation process	old	new
Starting concentration [wt.%]	50 to 60	60 to 80
Solvent system	acetone, ethyl acetate	ethyl acetate
Final polymer content [wt.%]	30 to 50	50 to 60

This means that in this first production step a reduction of about 50 wt.% of the 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.

The various methods of degassing solvent-borne acrylic polymers solutions describe the following three processes: in a tunnel dryer, in a batch kneader and degassing in the reactor (Tab. 2).

Table 2. Volatile organic compound (VOC) concentration after degassing⁹

Devolatilizing	Tunnel Dryer	Batch Kneader	Polymerisation Reactor
VOC [wt.%]	2 to 3	1.5 to 2	under 0.3

At the moment, the degassing in the reactor after the polymerisation process seems to be a practicable way to produce acrylic hot melts from solvent-borne systems. During the degassing process viscosity will increase so that special reactor designs and sufficient heat input is necessary. However, the thermal stability of the acrylic PSA is an essential point of concern in this case. In the future further possibilities have to be tested because all present processes are not optimised with respect to the fact that acrylic polymers require special conditions during the devolatilizing step.

With the devolatilizing process the production of the acrylic hot melt PSA is finished. Solvent recovery permits an almost completely closed solvent circulation. All further production steps can now be carried out solvent-free.

The synthesised acrylic solvent-free PSA are crosslinked by the use of UV radiation. New developments are dealing with UV crosslinking and no backing problems are to be reported. A very important factor of economic interest are the lower equipment cost. UV crosslinking, however, is mostly limited to thin PSA layers¹⁰.

THE GOAL OF THIS WORK

The following work was study the influence of significant steps in the UV technology of photoreactive solvent-free acrylic PSA such as solvent-borne synthesis in ethyl acetate of photoreactive acrylic PSA, the degassing process under vacuum, using of the recovered solvent ethyl acetate for the new synthesis again, UV crosslinking of coated PSA layers and investigation of the main layers properties as tack, adhesion, cohesion and shrinkage.

EXPERIMENTAL

The investigated acrylic PSA were synthesised by the use of 2-ethylhexyl acrylate (2-EHA) butyl acrylate (BA), methyl acrylate (MA), acrylic acid (AA) and unsaturated photoinitiator 4-acryloyloxy benzophenone (ABP) by polymerisation in ethyl acetate with the solid content of 60 wt.%, AIBN-concentration of 0.1 wt.%, dosage time of 2 h and the post-reaction time of 5 h.

The mentioned acrylic monomers and ethyl acetate were purchased from BASF (Germany), 2,2'-azodiisobutyronitrile (AIBN) was available from Degussa (Germany) and the unsaturated photoinitiator ABP by ChemCycle (Germany).

The synthesised photoreactive solvent-free acrylic PSA were liberated from ethyl acetate and residue monomers, and after coating with four thickness of 30, 60, 90 and 120 g/m² coat weight on polyester film, crosslinked using a ultraviolet light lamp U 350-M-I-DL from IST Company.

The recovered ethyl acetate was used for the synthesis of solvent-borne acrylic PSA with the same starting composition again. After the polymerization after the removal of volatile organic compound, the obtained photoreactive acrylic PSA as self-adhesive layer was crosslinked with UV radiation.

The influence of the UV dose of tack, adhesion, cohesion and shrinkage was tested. The three first properties were determined by standard A.F.E.R.A. (Association des Fabricants Europeens de Rubans Auto-Adhesifs) procedures. Exact details can be found in AFERA 4015 (tack),

AFERA 4001 (peel adhesion) and AFERA 4012 (shear strength).

RESULTS AND DISCUSSION

Influence of AA and ABP content on viscosity of photoreactive solvent-borne acrylic PSA.

The aim of this chapter was to examine the influence of very important monomers such as acrylic acid and unsaturated photoinitiator 4-acryloyloxy benzophenone on viscosity effect of solvent-borne acrylic pressure-sensitive adhesives.

The viscosity η of synthesised solvent-borne acrylic PSA, measured with a Rheomat RM 189 from Rheometric Scientific with spindle No 3 at 23°C, versus AA and ABP concentration is presented in Tab. 3 and Figs. 1 – 2.

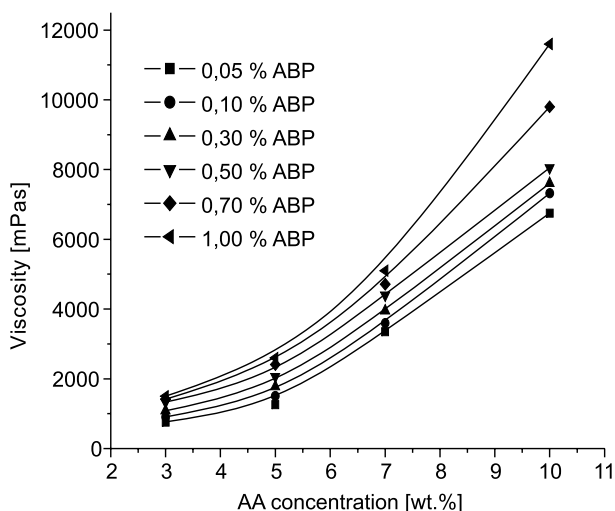


Figure 1. The effect of acrylic acid amount on the PSA viscosity

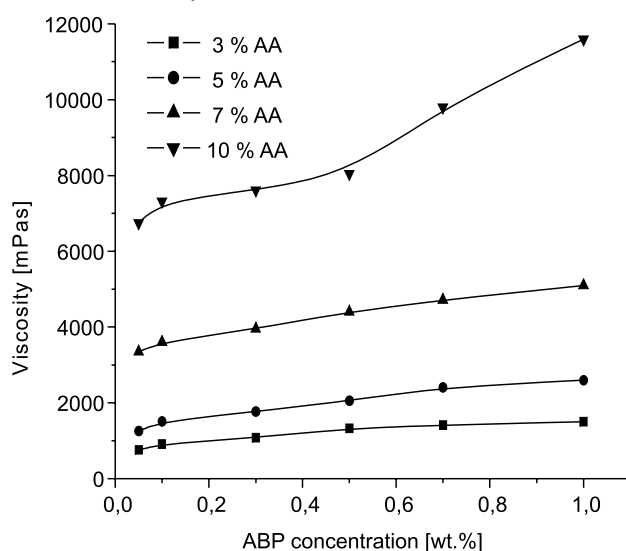


Figure 2. The effect of 4-acryloyloxy benzophenone amount on the PSA visco

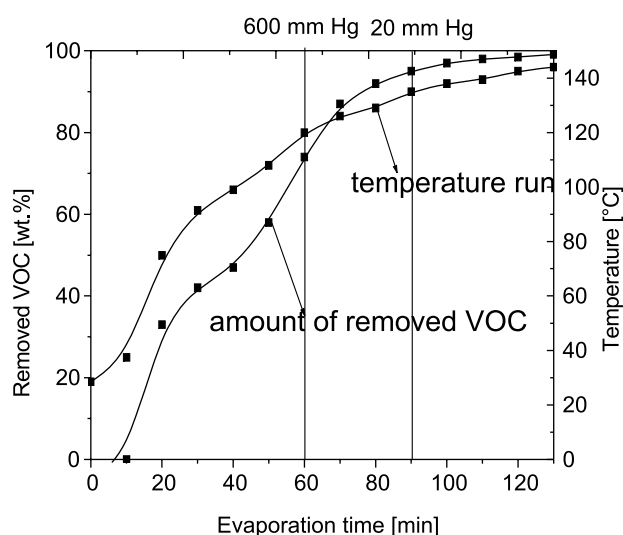
The mentioned in Tab. 3 results demonstrate that the increase of acrylic acid level increases the viscosity of photoreactive solvent-borne acrylic PSA. In summary, the greatest viscosity of synthesised photoreactive acrylic PSA was registered for 10.0 wt.% acrylic acid and 1.0 wt.% of unsaturated photoinitiator ABP (Fig. 1).

Table 3. Solvent-borne acrylic PSA containing diverse amounts of AA and ABP

Acrylic PSA No	Concentration of monomers [wt.%]					η_{60} wt.% [mPa·s]
	2-EHA	BA	MA	AA	ABP	
1	43.95	33.0	20.0	3.0	0.05	760
2	43.90	33.0	20.0	3.0	0.10	910
3	43.70	33.0	20.0	3.0	0.30	1080
4	43.50	33.0	20.0	3.0	0.50	1330
5	43.30	33.0	20.0	3.0	0.70	1410
6	43.00	33.0	20.0	3.0	1.00	1500
7	41.95	33.0	20.0	5.0	0.05	1260
8	41.90	33.0	20.0	5.0	0.10	1510
9	41.70	33.0	20.0	5.0	0.30	1770
10	41.50	33.0	20.0	5.0	0.50	2060
11	41.30	33.0	20.0	5.0	0.70	2410
12	41.00	33.0	20.0	5.0	1.00	2600
13	39.95	33.0	20.0	7.0	0.05	3350
14	39.90	33.0	20.0	7.0	0.10	3600
15	39.70	33.0	20.0	7.0	0.30	3950
16	39.50	33.0	20.0	7.0	0.50	4400
17	39.30	33.0	20.0	7.0	0.70	4710
18	39.00	33.0	20.0	7.0	1.00	5100
19	36.95	33.0	20.0	10.0	0.05	6750
20	36.90	33.0	20.0	10.0	0.10	7320
21	36.70	33.0	20.0	10.0	0.30	7610
22	36.50	33.0	20.0	10.0	0.50	8050
23	36.30	33.0	20.0	10.0	0.70	9800
24	36.00	33.0	20.0	10.0	1.00	11600

The received results shown that the increase of unsaturated photoinitiator ABP level increases a little bit the viscosity of investigated solvent-borne acrylic PSA. The greatest influence on the viscosity has been observed for PSA containing 10.0 wt.% acrylic acid.

From the previous trials with the remove of polymerization medium under a vacuum resulted that the viscosity of solvent-borne acrylic PSA with 60 wt.% polymer greater than about 3000 mPa·s at 20°C can lead to problems with the evaporation of volatile organic compound. Further investigations with suitable solvent-borne acrylic PSA ($\eta < 3000$ mPa·s) were conducted using 3.0 and 5.0 wt.% acrylic acid (Tab. 1). Earlier commercial trials have shown that the best performances were observed for acrylic PSA containing 5.0 wt. AA and 0.5 wt.% ABP.

**Figure 3.** Temperature and the amount of the removed VOC during the evaporation time

Evaporation of volatile organic compounds from solvent-borne acrylic PSA

For further investigations the solvent-borne acrylic PSA 10 with viscosity of 2060 mPa·s at 20°C was choose. The evaporation process was performed in two steps, which are illustrated in Fig. 3:

- first step: evaporation under atmospheric pressure at about 100 – 120°C
- second step: evaporation under vacuum 20 – 30 mm Hg

For industrially evaporation of VOC the using of polymerisation reactor seems to be a practicable way to produce of the solvent-free acrylic PSA from solvent-borne systems. The finished solvent-free acrylic PSA contained 0.3 wt.% of VOC. The due to evaporation received VOC were examined by the use of gas chromatograph Varian CP-3800 (Tab. 4).

Table 4. GC analysis of VOC removed from photoreactive solvent-free acrylic PSA

Composition [wt.-%]	VOC from solvent-free acrylic PPSA	Removed solvent
Ethyl acetate	0	98.2
2-EHA	0.27	0.85
BA	0.03	0.60
MA	0	0.35
AA	0	0

Synthesis of solvent-borne photoreactive acrylic PSA using the removed solvent

The removed solvent containing 98.2 wt.% ethyl acetate and 1.8 wt.% residue monomers: 0.85% 2-EHA, 0.6 wt.% BA and 0.35% MA permits an almost completely closed solvent circulation. The new synthesised acrylic PSA 25 contains 5.0 wt.% AA and 0.5 wt.% ABP, analogical to acrylic PSA 10, shows a viscosity of 2110 mPa·s at 60 wt.% polymers.

Influence of the UV dose of the investigated properties of both synthesised acrylic PSA

The synthesised acrylic PSA 10 and PSA 25 were, after evaporation of VOC, coated at 140°C with diverse coat weights of 30, 60, 90 and 120 g/m² on the polyester film and crosslinked with UV radiation between 100 and 1000 mJ/cm² UV dose. The greatest attention was dedicated the tack (Fig. 4), adhesion (Fig. 5), cohesion (Fig. 6) and shrinkage (Fig. 7) according the AFERA.

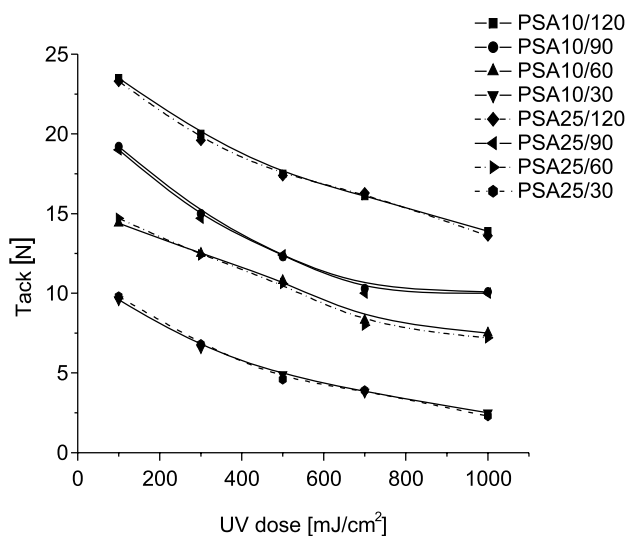


Figure 4. Tack of the UV crosslinked PSA synthesized in ethyl acetate and in the removed solvent

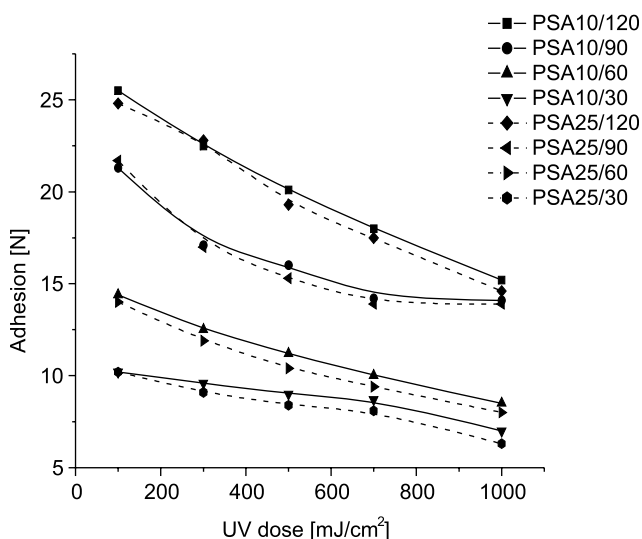


Figure 5. Adhesion of the UV crosslinked PSA synthesized in ethyl acetate and in the removed VOC

The best tack and peel adhesion values by application of photoreactive solvent-free acrylics PSA 10 and PSA 25 were observed from a UV dose of 100 mJ/cm² and for a thick layer of 120 g/m². This is comprehensible because the adhesive properties as tack and adhesion are very high for relatively thick layers and short UV crosslinking times, and a little UV doses. As it seems from the Figs. 4 – 5 the increasing of the UV radiation doses leads clearly to deterioration of tack and adhesion. In the practice no significant differences in tack and adhesion between the acrylic PSA 10 and acrylic PSA 25 were observed.

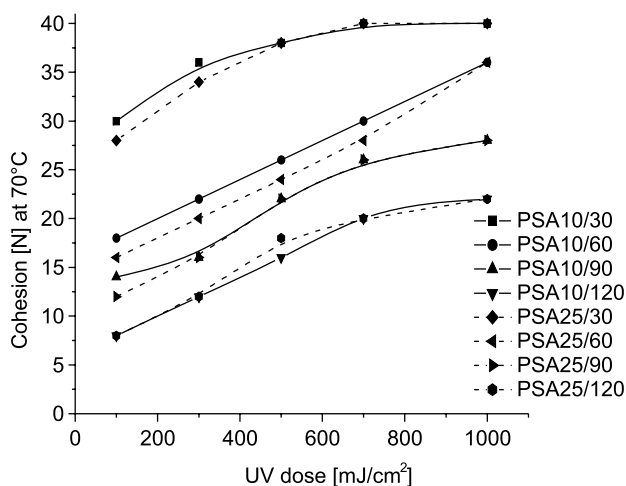


Figure 6. Cohesion of the UV crosslinked PSA synthesized in ethyl acetate and in the removed VOC

As shown in Fig. 6, the increase of UV dose from 100 to 1000 mJ/cm² is sufficient to obtain an adequate improving in cohesion of crosslinked photoreactive acrylic PSA at 70°C.

The relatively high cohesion of 40 N was measured for 30 g/m² thick layers.

The target of this investigation was the development of photoreactive solvent-free acrylic PSA for PVC sign and marking films with high performance and low shrinkage. In this case, the greatest attention was attached to the shrinkage parameter. With PSA shrinkage greater than acceptable level 0.3% other evaluated PSAs properties were neglected.

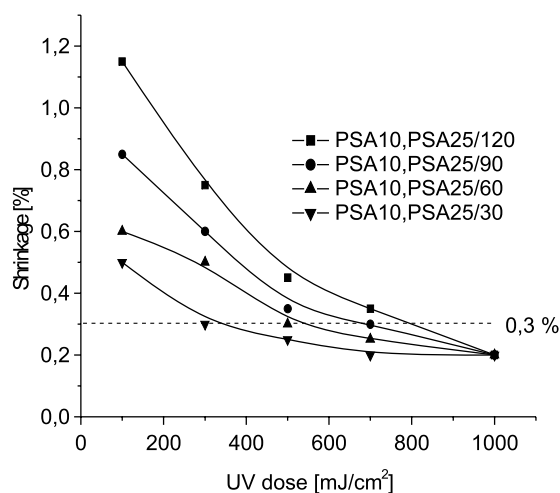


Figure 7. Shrinkage of the UV crosslinked PSA synthesized in ethyl acetate and in the removed solvent

As expected, the increase of the UV dose corresponds with the decrease of shrinkage of acrylic PSA. By using of photoreactive solvent-free acrylic PSA 10 in comparison to acrylic PSA 25 the exactly same shrinkage resistance run and shrinkage values were observed. For this reason a little UV dose between 100 and 500 mJ/cm² in UV crosslinking technology is becoming more and more replaced by greater UV dose of 1000 mJ/cm². Above this level of UV dose the shrinkage values of 0.2% were very low and identical for both investigated acrylic PSA.

Prospects for synthesis of photoreactive acrylic PSA in recovered system

Photoreactive solvent-free acrylic pressure-sensitive adhesives will play a major role in the development and production of new generation of self-adhesive notes, paper and foil labels, double-sided tapes, carrier-free tapes, protective foils, self-adhesive bioelectrodes and medical tapes. The syntheses of those acrylic PSA can be conducted in the recovered organic solvent, in this case ethyl acetate. The incorporation of recovered organic solvent system into PSA technology is very important, among the other things with regard to the economic aspect, for environment protection, and manufacturing of ecological products.

LITERATURE CITED

- (1) Czech Z.: Crosslinking of acrylic PSA, Published by Szczecin University of Technology, Szczecin, **1999** (ISBN 83-87423-18-1).
- (2) Chandran M.: EP 0 608 891, National Starch and Chemical, **1994**.
- (3) Kurzawa R., Czech Z.: Ginekologia po dyplomie, wydanie specjalne, styczeń, **2007**, 1 – 5.
- (4) Benedek I.: Developments in Pressure-Sensitive Products, Edited by Taylor & Francis a CRC Press Book, **2006**.
- (5) Czech Z., Drzycimska A., Klementowska P.: European Coating Journal, **2007**, 2, 26 – 30.
- (6) Czech Z.: DE 195 01 24, Lohmann, **1995**.
- (7) Czech Z.: DE 195 01 25, Lohmann, **1995**.
- (8) Auchter G.: Adhäsion, **1993**, 1 – 2, 14 – 20.
- (9) Czech Z.: Adhäsion, **1996**, 9, 24 – 29.
- (10) Shiaoanung S.: US Patent 5,252,662, Avery Dennison Corporation, **1993**.