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Development in the area of UV-crosslinkable solvent-based pressure-sensitive adhesives with excellent shrinkage resistance

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Abstract

Solvent-based UV-crosslinkable pressure-sensitive adhesives (PSA) present a new class of products that offers the potential to produce a novel generation of ultraviolet cured self-adhesive products with excellent shrinkage resistance. A variety of solvent-based pressure-sensitive adhesives were prepared by synthesis in ethyl acetate with solid content on 50 wt.% with 2-ethylhexyl acrylate, methyl acrylate, acrylic acid, N-vinyl caprolactam and unsaturated photoinitiators: 4-acryloyloxy benzophenone, allyl benzoine and phenyl-(1-acryloyloxy)-cyclohexyl ketone. The main emphasis is given to the influence of viscosity and molecular mass of synthesized adhesive on their shrinkage. Further trials show the effect of the UV-crosslinking process with UV-lamp and comparison with acrylics PSA crosslinked with metal chelates aluminium acetylacetonate and titanium acetylacetonate on shrinkage. Further examinations describe the influence of various factors such as UV exposure time and UV dose on very relevant PSA performance such as shrinkage on coated PVC carrier.

Keywords: Shrinkage; UV-crosslinking; Pressure-sensitive adhesive (PSA); Acrylics; Unsaturated photoinitiators; Viscosity; Molecular mass; Metal chelates

1. Introduction

Pressure-sensitive adhesives (PSAs) represent a system that actually dates back to the invention of the self-adhesive articles in 1935 when R. Stanton Avery produced the first coating unit using a wooden cigar box with two holes cut in the bottom [1].

Pressure-sensitive adhesives can be defined as a special category of adhesive which in dry form are permanently tacky at room temperature. They are used to produce self-adhesive labels, foils and tapes [2].

UV-crosslinkable solvent-based acrylics consist of acrylic copolymers with chemically built-in photoreactive groups. After the carrier for the label, foil or tape production has been coated with the solvent-based UV-crosslinkable acrylate, dried at 110 °C, the adhesive film is crosslinked with UV radiation. By this crosslinking procedure, the molecular mass of the adhesive is built up in order to obtain the level of cohesion demanded by the application in question. UV-induced crosslinking is a rapidly expanding technology on pressure-sensitive adhesives area resulting from its main advantages such as solvent-free process, efficient and economical energy used and new properties and quality of chemical crosslinking bonding.

Ultraviolet (UV), the most popular of the new cure techniques today, starts from 100 nm wavelengths and goes up to 400 nm. The commonly found industrial lamps range from 200 to 400 nm. Conventional medium pressure mercury-vapour lamps are used as the light

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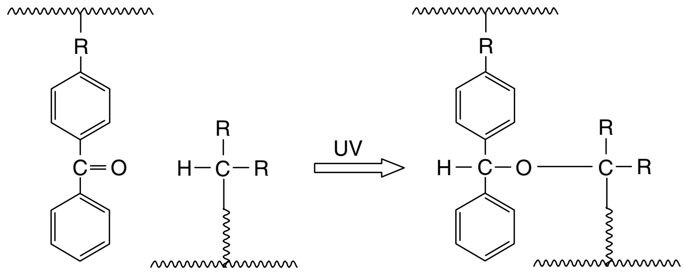

Fig. 1. UV initiated crosslinking reaction with PSA based on polyacrylate (R = alkyl or alkylene group).

source. Mercury lamps (low, medium, high pressure) are used with power between 80 and 120 W/cm, which includes UV stations with six and more UV lamps as state of art with power of 120–250 W/cm. A particularly important feature of the commercially crosslinking behaviour of UV-acrylics is that they only crosslink at certain wavelengths, principally in the band between 315 and 400 nm (UV-A area). A shorter wavelength can show the same deterioration to pressure-sensitive adhesives as would occur from exposure to sunlight and so should be screened out. Other wavelength bands do not contribute significantly to the crosslinking of solvent-based UV-acrylics [3].

Normally acrylics PSA absorb the entire light radiation below 300 nm. In order to accomplish acceptable crosslinking with transparent pressure-sensitive adhesives only, UV absorption in wavelengths above 300 nm are of importance. Since in general energy of 350–410 kJ/mol is required for stimulation of for example benzophenone derivatives, an UV wavelength range about 300–410 nm is required [4,5].

The crosslinking mechanism of photoreactive acrylics PSA containing photoreactive benzophenone derivatives has been thoroughly investigated and it is presented schematically (Fig. 1) [6].

During UV exposition the intermolecular benzophenone derivatives H-abstractors structures are excited and react with the neighboring C–H positions of polymer sidechains [7].

2. Experimental

The following experiments were conducted to study the influence of diverse parameters such as kind and amount of unsaturated photoinitiators and ultraviolet curing time and UV dose on shrinkage of solvent-based acrylic pressure-sensitive adhesive. The investigated PSA was synthesized with between 56 and 56.95 wt.% of 2-ethylhexyl acrylate (2-EHA), 34 wt.% of methyl acrylate (MA), 5 wt.% of acrylic acid (AA), 4 wt.% N-vinyl caprolactam (VC) and between 0.05 and 1.0 wt.% of benzophenone photoinitiators by polymerization in organic solvent like ethyl acetate [8,9]. The solvent-based PSA were synthesized with solid content on 50 wt.% and very efficient radical initiator AIBN-concentration of 0.1 wt.%. The dosage time was 3 h.

2-Ethylhexyl acrylate (2-EHA), methyl acrylate (MA) and acrylic acid (AA) are purchased from BASF (Germany). Ethyl acetate, 2,2′-azo-diisobutyronitrile and N-vinyl caprolactam were available from Merck (Germany). Aluminium acetylacetonate and titanium acetylacetonate are purchased from Degussa (Germany). The unsaturated photoinitiators such as 4-acryloyloxy benzophenone (ABP) (Fig. 2), allyl benzoine (AB) (Fig. 3), phenyl-(1-acryloyloxy)-cyclohexyl ketone (PAC) (Fig. 4) are purchased from by Chemitec GmbH (Germany).

The investigated photoreactive UV-crosslinked pressure-sensitive adhesive were cured with ultraviolet light lamp UVAPRINT 40 CE from IST Company with UV-A wavelength between 315 and 380 nm.

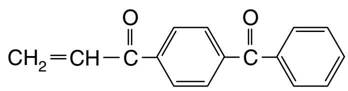

Fig. 2. 4-acryloyloxy benzophenone (ABP).

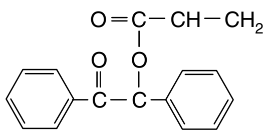

Fig. 3. Allyl benzoine (AB).

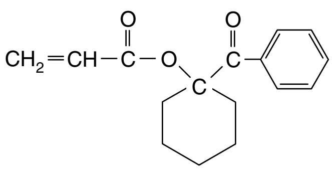

Fig. 4. Phenyl-(1-acryloyloxy)-cyclohexyl ketone (PAC).

Because of the volume of the publication I purposely restrained myself to investigating only the shrinkage of crosslinked self-adhesives. In a subsequent article I will present the influence of UV crosslinking on tack, adhesion strength and cohesion.

2.1. Shrinkage (S or l_r)

Shrinkage presents the percentage (*S*) or milimeter (l_r) change of dimensions of the foil covered with UV-crosslinkable pressure-sensitive adhesives and attached to the glass after keeping it 1 week at temperature of 70 °C. The shrinkage value lower than 0.5% is the cleared optimum for PSA with high performance for PVC surfaces [8].

The viscosity of synthesized solvent-based PSA was measured with viscosimeter RM 180 Rheomat from Rheometric Scientific Company and their molecular mass $\overline{M}_w$ was certained with HPLC-System with Isoctratic Pump & DRI-Detector from HP Company.

3. Results and discussion

3.1. Influence of the unsaturated photoinitiators on viscosity and molecular mass of synthesized solvent-based PSA

The synthesized pressure-sensitive adhesives containing unsaturated photoinitiators are shown in Tables 1–3. The influence of the copolymerizable photoinitiators and their concentration on viscosity and molecular mass are depicted in the graphs shown in Figs. 5 and 6.

Table 1
Viscosity and molecular mass of synthesized PSA containing 4-acryloyloxy benzophenone (ABP)

PSA No	Monomers (wt.%)					η (Pa s)	M_W (Dalton)
	2-EHA	MA	AA	VC	ABP		
1	57.00	34.00	5.00	4.00	0	3.5	830,000
2	56.95	34.00	5.00	4.00	0.05	3.5	835,000
3	56.90	34.00	5.00	4.00	0.10	3.6	842,000
4	56.70	34.00	5.00	4.00	0.30	3.8	863,000
5	56.50	34.00	5.00	4.00	0.50	4.0	887,000
6	56.25	34.00	5.00	4.00	0.75	4.4	915,000
7	56.00	34.00	5.00	4.00	1.00	5.2	973,000

Table 2
Viscosity and molecular mass of synthesized PSA containing benzoine acrylate (BAC)

PSA No	Monomers (wt.%)					η (Pa s)	M_W (Dalton)
	2-EHA	MA	AA	VC	BAC		
8	57.00	34.00	5.00	4.00	0	3.5	830,000
9	56.95	34.00	5.00	4.00	0.05	3.5	834,000
10	56.90	34.00	5.00	4.00	0.10	3.5	824,000
11	56.70	34.00	5.00	4.00	0.30	3.3	813,000
12	56.50	34.00	5.00	4.00	0.50	2.9	776,000
13	56.25	34.00	5.00	4.00	0.75	2.6	745,000
14	56.00	34.00	5.00	4.00	1.00	1.7	683,000

Table 3
Viscosity and molecular mass of synthesized PSA containing phenyl-(1-acryloyloxy)-cyclohexyl ketone (PAC)

PSA No	Monomers (wt.%)					η (Pa s)	M_W (Dalton)
	2-EHA	MA	AA	VC	PAC		
15	57.00	34.00	5.00	4.00	0	3.5	830,000
16	56.95	34.00	5.00	4.00	0.05	3.5	828,000
17	56.90	34.00	5.00	4.00	0.10	3.5	832,000
18	56.70	34.00	5.00	4.00	0.30	3.6	842,000
19	56.50	34.00	5.00	4.00	0.50	3.7	864,000
20	56.25	34.00	5.00	4.00	0.75	4.1	902,000
21	56.00	34.00	5.00	4.00	1.00	5.0	954,000

The following conclusions can be inferred from experimental results:

- the increase in the unsaturated photoinitiators content of 4-acryloyloxy benzophenone (ABP) and phenyl-(1-acryloyloxy)-cyclohexyl ketone (PAC) corresponds with the increase of viscosity of synthesized pressure-sensitive adhesive;
- in general the increase of unsaturated photoinitiators ABP and PAC amount increases the molecular mass of synthesized PSA;
- the use of allyl benzoine (AB) influences negatively the viscosity and the molecular mass of acrylics PSA;
- from the investigated unsaturated benzophenones, the best results for viscosity and molecular mass were given by photoinitiators ABP and PAC.

3.2. Influence of the investigated unsaturated photoinitiators and their amount on shrinkage

It was the aim to examine the influence of investigated unsaturated photoinitiators on shrinkage of synthesized pressure-sensitive adhesive after UV-curing with UV-lamp.

In order to compare the influence of unsaturated photoinitiators on the shrinkage during the UV crosslinking an H-abstractor (ABP) was selected together with α-cleavage photoinitiators PAC and AB of different reactivity.

The solvent-based pressure-sensitive adhesives were cast with a knife coater with 60 g/m^2 on, using a silicon paper, and after drying laminated directly on PVC foil. The adhesive was then crosslinked by ultraviolet light

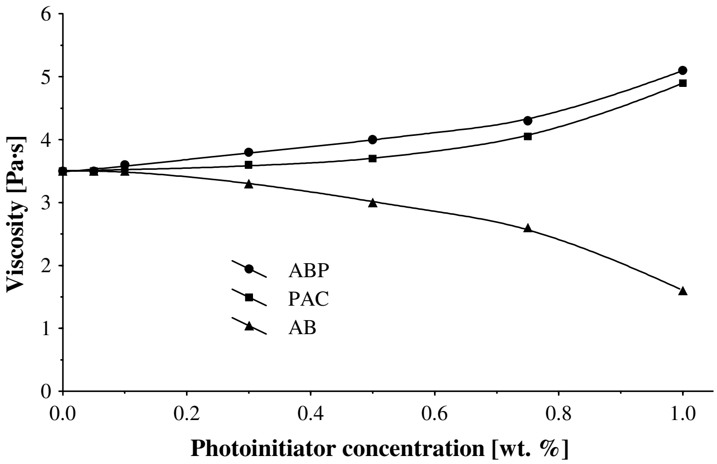

Fig. 5. Effect of photoinitiator amount on viscosity.

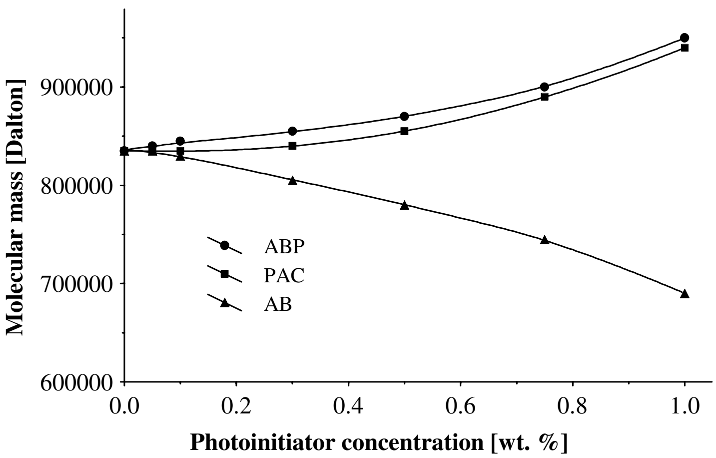

Fig. 6. Effect of photoinitiator amount on molecular mass.

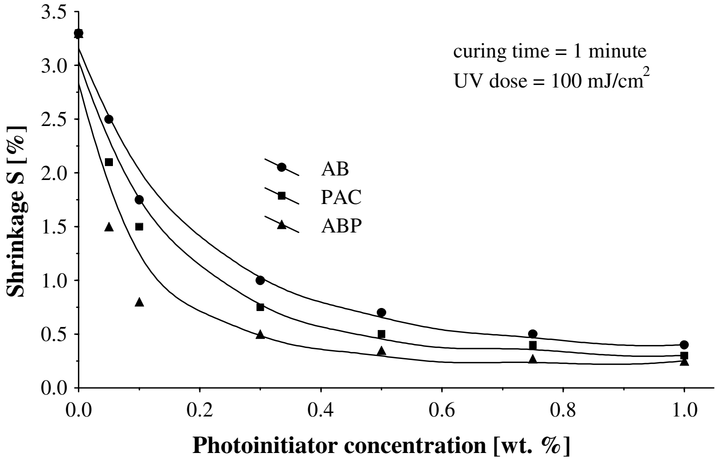

Fig. 7. Effect of photoinitiator amount on shrinkage.

using a 100 mJ/cm^2 UV dose. The influence of unsaturated photoinitiators and their concentration on shrinkage by the same crosslinking time 1 min are shown in Fig. 7.

Fig. 7 shows the positive effect of kind and amount of unsaturated photoinitiator on the shrinkage of the acrylics PSA by a 1 min exposure to UV light by 100 mJ/cm^2 UV dose. The data suggest that a low shrinkage value is attained at a concentration of approximately 0.3 wt.% photoinitiator.

3.3. Influence of the crosslinking time and UV dose on shrinkage

The phenomenon of shrinkage of PSA is a result of the crosslinking time that takes place when the PSA film is exposed to UV radiation. In Fig. 8 the influence of crosslinking time on shrinkage of PSA by the same concentration of unsaturated benzophenones is shown.

In general, it can be said that the use of unsaturated photoinitiators 4-acryloyloxy benzophenone (ABP) and phenyl-(1-acryloyloxy)-cyclohexyl ketone (PAC) gave the best results of shrinkage. For about 30 s of curing time the optimum of shrinkage value with the use of ABP was observed. By using of PAC the achieve of low shrinkage about 0.5% is possible after 120 s exposing to UV light. When allyl benzoine (AB) was used instead of ABP or PAC, crosslinked PSA film with low shrinkage was achieved only after the long curing time about 180 s. In the evaluated solvent-based acrylic PSAs the photoreactivity of ABP and PAC containing acryloyloxy-group was inferior to AB containing allyl group.

Radiation crosslinkable acrylic PSAs designed to react with UV light offer a good alternative to other

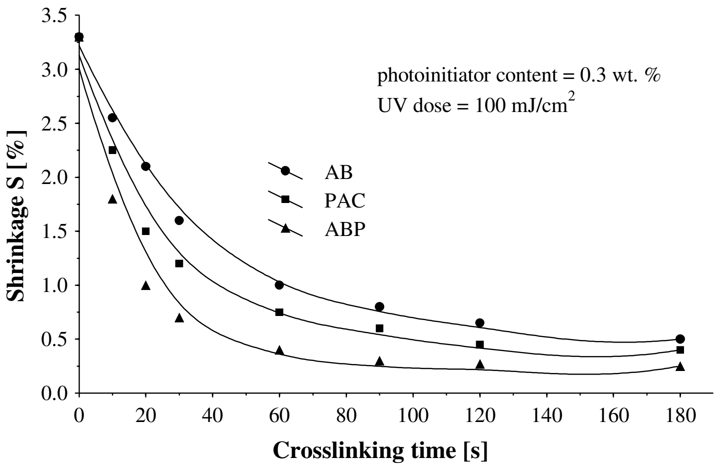

Fig. 8. Influence of crosslinking time on shrinkage.

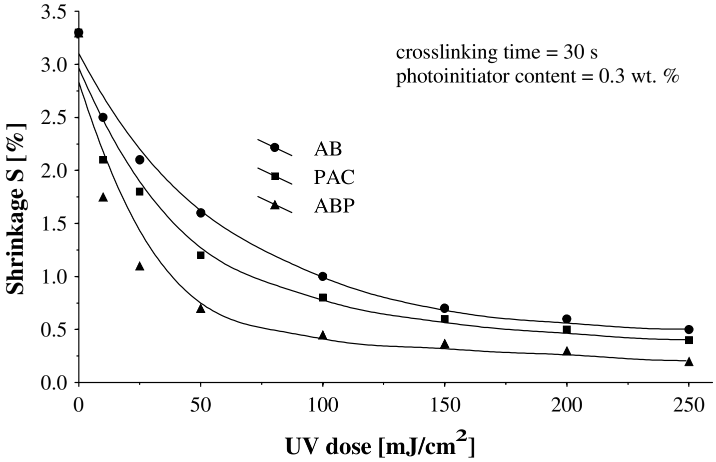

Fig. 9. Influence of UV dose of shrinkage.

crosslinked solvent–based adhesives. To further investigate the performance like shrinkage of these UV-crosslinkable adhesives, pattern curing is a new technology that makes it possible. It allows introduce at a level of curing the same PSA formulations and the same crosslinking time. The quantity of radiation energy to which the pressure-sensitive adhesive film is exposed is expressed by the UV-dose (mJ/cm^2). 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.

The influence of the UV dose in the UV-A wavelength band on shrinkage by the constant values of other parameters (30 s crosslinking time and 0.3 wt.% of photoinitiator) are presented in Fig. 9.

The optimum shrinkage results were obtained when the UV dose was between 50 and 150 mJ/cm^2. Increasing the UV dose during the crosslinking of acrylic PSA film leads clearly to lesser shrinkage performance. The use of about 100 mJ/cm^2 UV dose guaranteed the low level of shrinkage. The best results of the lowest shrinkage values were given by 4-acryloyloxy benzophenone (ABP).

3.4. Comparing tests between conventional and UV-crosslinked PSA

The best product with excellent low shrinkage of the solvent-based UV-crosslinkable pressure-sensitive adhesive containing unsaturated photoinitiator 4-acryloyloxy benzophenone was tested according to the shrinkage performance and was compared with the same basic PSAs crosslinked with metal chelates: aluminium acetylacetonate (AlAcA) and titanium acetylacetonate (Ti-

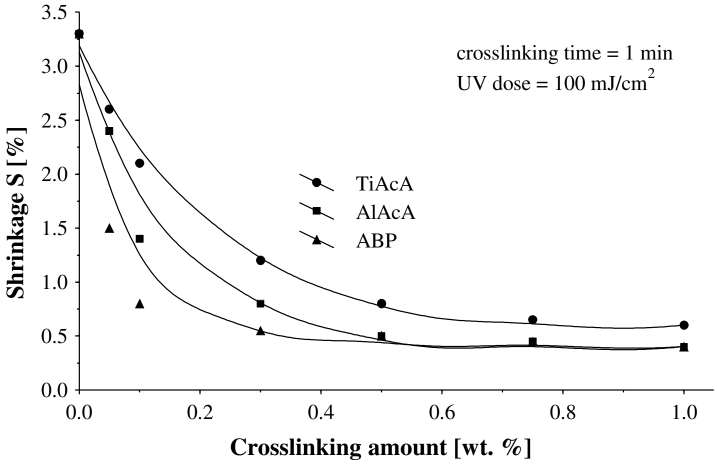

Fig. 10. Dependence of unsaturated photoinitiator or metal chelates content on shrinkage.

AcA). The results obtained after UV-crosslinking are presented in Fig. 10 [2].

It is relatively difficult to differentiate among the final properties of the products tested. However, it is distinctively clear that the shrinkage performance of basic PSA product containing unsaturated photoinitiator ABP is after UV-crosslinking superior to the commercial products [9] crosslinked with metal chelates which is clearly shown in Fig. 10. The excellent shrinkage in the case of use 4-acryloyloxy benzophenone was achieved by 0.1 wt.% of ABP. The same level of shrinkage was achieved with about 0.75 wt.% of AlAcA. The use of crosslinker TiAcA is not suitable for pressure-sensitive adhesive with low shrinkage.

4. Conclusions

From the evaluation of the experiments discussed in this publication, it can be concluded that:

- From the investigated unsaturated photoinitiators, the best shrinkage performance was achieved with 4-acryloyloxy benzophenone (ABP) and phenyl-(1-acryloyloxy)-cyclohexyl ketone (PAC). The most efficient photoinitiator was undoubtedly 4-acryloyloxy benzophenone.
- The high effectiveness of ABP is explained by its structure, stabilizing by mesomery the free radical being formed after UV irradiation. Such free radical is in the case of PAS less stable.
- 4-acryloyloxy benzophenone (ABP) is a little more reactive than phenyl-(1-acryloyloxy)-cyclohexyl ketone (PAC). Allyl benzoine (AB) is, because of the presence of allyl group, the least photoreactive among investigated photoinitiators.
- Increasing the amount of unsaturated, most efficient for shrinkage photoinitiator increases viscosity and molecular mass of solvent-based synthesized pressure-sensitive adhesive acrylics.
- There is a clear dependence of shrinkage of UV-crosslinkable solvent-based PSA acrylics on their viscosity and molecular mass.
- The increase of the unsaturated photoinitiator concentration ABP up to 0.3 wt.% improves the shrinkage performance tremendously. The shrinkage value goes down on the low level beneath 0.5%.
- After crosslinking time about between 20 and 30 s the shrinkage of PSA obtained ABP achieves a low level beneath 0.5%. The prolongation of the crosslinking time greater than 60 s brought no change of shrinkage.
- UV-crosslinking process with UV dose varying from 10 to 250 mJ/cm^2 gives a optimum shrinkage level and shrinkage $\leqslant 0.5\%$ when the UV dose was between 50 and 150 mJ/cm^2.
- Comparative studies between the best solvent-based pressure-sensitive adhesive acrylics containing 4-acryloyloxy benzophenone and other PSA crosslinked with commercial crosslinking agents such as aluminium acetylacetonate or titanium acetylacetonate showed the clear superiority of the basic PSA acrylic with investigated unsaturated photoinitiator, concerning each property tested. During the UV crosslinking of PSAs containing ABP no products of photoinitiator photolysis are found. The reaction of UV crosslinking—when using ABP—occurs much quicker than when using TiAcA and AlAcA.

5. Prospects for solvent-based PSA acrylics with low shrinkage

Solvent-based pressure-sensitive adhesive acrylics with excellent shrinkage properties will play a major role in the production of self-adhesive products such as decorative PVC foils, synthetic material labels and similar products still in the developmental stage.

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