

Influence of Selected Photoinitiators on Important Properties of Photoreactive Acrylic Pressure-Sensitive Adhesives

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Received 27 August 2010; accepted 2 March 2011

DOI 10.1002/app.34445

Published online 26 July 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Photoreactive solvent-borne pressure-sensitive adhesives are not commercially available in the market. The reason for it is that the UV-initiated crosslinking has sense only in the case of solvent-free self-adhesive systems. Investigations conducted in Institute of Chemical Organic Technology have shown that the photoreactive solvent-borne acrylic PSA are conventional crosslinked solvent-borne acrylic PSA used as crosslinking agents typical metal chelates as titanium acetylacetonate (TiACA), aluminum acetylacetonate (AlACA) or thermal reactive crosslinker melamine-formaldehyde resin Cymel 303 clear considered. The main purpose of the investigation was to study the influence of diverse photoinitiators on main properties, such as shrinkage, tack, peel adhesion, and shear strength of solvent-based acrylic pressure-sensitive adhesives. The interesting alternative to conventional photoinitiators is unsaturated photoinitiators described in this

article. Following unsaturated photoinitiators were used: 4-acryloyloxy benzophenone, 4-acryloyloxyethoxy benzophenone, and 4-acryloyloxybutoxy benzophenone. The influence of the crosslinking agents or crosslinking methods was determined in relation to the reaction time and to the concentration versus adhesion properties. The increase of photoinitiator concentration causes in the decrease of the shrinkage. Increasing the UV dose during the crosslinking of acrylic PSA film leads clearly to better shrinkage resistance. The best results of the lowest shrinkage value of 0.35% were given by using 4-acryloyloxy benzophenone. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 118–123, 2012

Key words: pressure-sensitive adhesive; acrylic PSA; photoreactive PSA; photoinitiator; crosslinking; photocrosslinking

INTRODUCTION

Pressure-sensitive adhesives (PSA) have been defined as a special category of adhesives, which in the dry state are aggressively and permanently tacky at room temperature and firmly adhere to a variety of different surfaces upon contact without the need of more than finger or hand pressure.¹ Pressure-sensitive adhesives form a permanent tacky film after the evaporation of the solvent or water phase or after cooling of a hot melt.

Typical polymers applied as compounds to produce pressure-sensitive adhesives are acrylic, natural or synthetic rubbers, silicones, polyesters, polyurethanes, or polyethers. Among the aforementioned polymers, acrylic pressure-sensitive adhesives demonstrate excellent adhesive and cohesive properties simultaneously with superiors thermal and ageing

performances. The most important properties, which characterize the nature of pressure-sensitive adhesives are adhesive properties (tack and peel adhesion) and shear strength (cohesive property).²

Acrylic pressure-sensitive adhesives

Acrylic pressure-sensitive adhesives are developed as solvent-borne, water dispersion, or solvent-free systems (hot melts). Solvent-free pressure-sensitive adhesives are relatively new group of self-adhesive technical and medical products and demonstrate many advantages in opposite to solvent basis pressure-sensitive adhesives. The main aspect is reduction of environmental impact to a minimum during production and exploitation.³

Crosslinking

In production of acrylic pressure-sensitive adhesives we use acrylic copolymers, whose chains are crosslinked only by hydrogen bonds or inter penetrating systems that cause insufficient cohesion of product.

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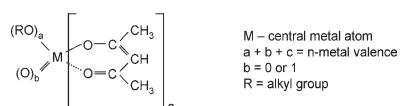


Figure 1 General formula of metal acetylacetonates.

For this reason the main properties of pressure-sensitive adhesives synthesized by copolymerization of acrylic monomers in organic solvent mixture depend only on a few percent of crosslinking agents added to formulation. This small quantity of improvement achieves interchain crosslinking and causes in increase of properties like shear, shrinkage, chemical, and heat resistance. Unfortunately, it has negative influence on adhesive properties like tack and peel adhesion.⁴

The main conventional crosslinking agents for solvent-borne acrylic pressure-sensitive adhesives are:

- metal acidesters
- metal chelates
- polyfunctional isocyanates
- polycarbodiimides
- multifunctional propylene imines
- amino resins

Metal chelates (Fig. 1) that react with the acrylic polymer are particularly efficient as crosslinking agent. For chelate complexes synthesis we use organic compound containing the transition metals, whose coordination number is greater than 2, typically 4, 6, or 8 (e.g., Zn, Ni, Mn, Fe, Co, Cr, Al, Ti, Zr), and acetylacetonate. The most suitable metal chelates as crosslinking agent for industrial crosslinking of solvent-base acrylic PSA appears to be aluminum(III) acetylacetonate (AlACA), and titanium(IV) acetylacetonate (TiACA).⁵

In the crosslinking reaction metal acetylacetonates (e.g., AlACA) react with acrylic acid built in acrylic polymer chain and give the product as in Figure 2. Groups which are essential in this process are carboxylic groups from acrylic acid and hydroxyl group from alcohol. Conventional crosslinking with the presence of metal chelate has to proceed with the addition of stabilizer, which in this case is alcohol. Crosslinking starts at the drying channel, while alco-

hol and solvents are evaporating from pressure-sensitive adhesive layer. That's why acrylic PSA with those crosslinking agents are named room-temperature crosslinking PSA.⁶

Very interesting group of crosslinking agents are amino resins. This group can be divided into melamine-formaldehyde resins, benzoguanamine resins, glycoluril resins, and urea resins. Amino resins are characterized by their lack of reaction in room-temperature and rising crosslinking speed with increase of temperature above 100°C. Crosslinking reaction of solvent-based acrylic PSA with used melamine-formaldehyde resins is presented in Figure 3.⁷

UV-crosslinkable solvent-borne acrylic PSA

The synthesized photoreactive solvent-borne acrylic PSA are very interesting alternative to the conventional crosslinked acrylic PSA. The UV light can be aimed directly where acrylic PSA systems should be crosslinked. It also requires a photoinitiator to absorb the impinging light and induce photocrosslinking. A suitable conventional photoinitiator: α -cleavage photoinitiators (Type I) or H-abstraction photoinitiators (Type II) is used in UV-crosslinking technology.

A very interesting alternative to conventional photoinitiators are the unsaturated photoinitiators. The most typical directions, however, are in the development of initiators Type I and II, e.g., acrylated, vinylated, allylated, acrylamidated, or vinyloxyated.

Copolymerizing the unsaturated photoinitiator into the backbone of the acrylic pressure-sensitive adhesive copolymer allows crosslinking of the acrylic PSA with ultraviolet radiation, after formation of the copolymer. Further, incorporation of the unsaturated copolymerizable photoinitiators into the acrylic polymer backbone, before the crosslinking therefore, greatly increases the efficiency of the crosslinking obtainable by inclusion of the photoinitiator monomer in the adhesive, as compared with addition of an aromatic ketone compound which is not initially copolymerized into the copolymer. It should be noted that only small amount of unsaturated copolymerizable photoinitiator monomer is needed to achieve useful degrees of crosslinking.⁸

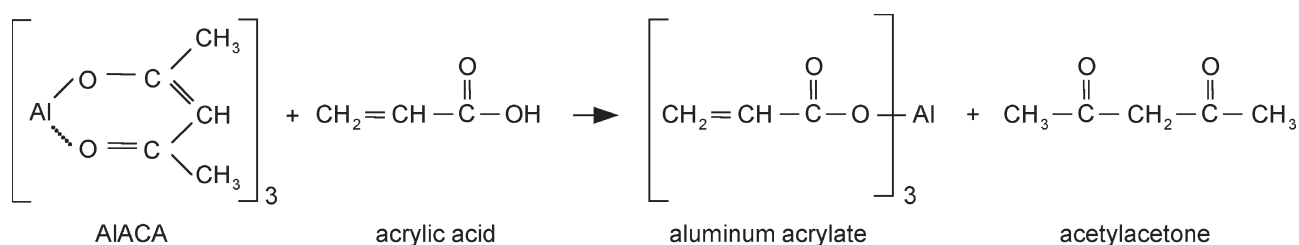


Figure 2 Reaction between aluminum acetylacetonate and acrylic acid.

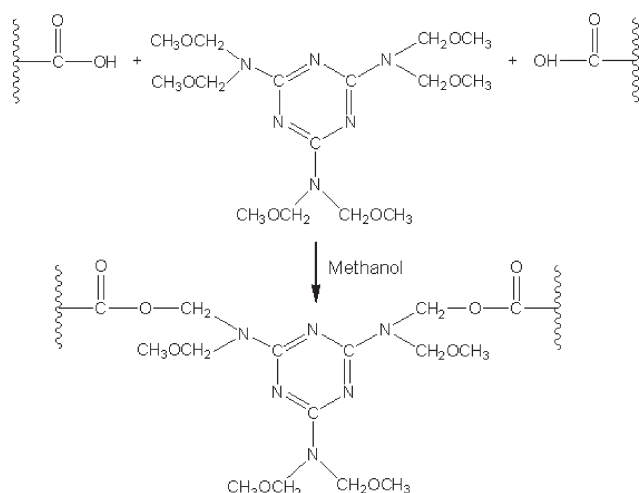


Figure 3 Crosslinking reaction of PSA acrylics containing carboxylic groups with a melamine-formaldehyde resin.

The novel unsaturated photoinitiators tested showed the best PSA properties were for Type II photoinitiator containing acryloyloxy group, such as: 4-acryloyloxy benzophenone (ABP). ABP (Fig. 4) was the most efficient Type II photoinitiator for the common solvent-based acrylic self-adhesives.

The crosslinking mechanism of photoreactive acrylic PSA, containing photoreactive benzophenone incorporated into polymer backbone, has been thoroughly investigated. During UV exposure the intermolecular benzophenone H-abstractor structures are excited and react by hydrogen abstraction with the neighboring tertiary carbon atom positions of the polymer side chains (Fig. 5).⁹

The target of the investigation was to study the influence of diverse photoinitiators on main properties, such as shrinkage, tack, peel adhesion, shear strength of solvent-based acrylic pressure-sensitive adhesives.

EXPERIMENTAL

Synthesis of solvent-borne acrylic pressure-sensitive adhesive was performed with 50 wt % of solid content in organic solvent; ethyl acetate. The model solvent-borne PSA was synthesized using 50 wt % of 2-ethylhexyl acrylate, 25 wt % of butyl acrylate, 20 wt % of methyl acrylate, between 3.9 and 4.8 wt % of acrylic acid, between 0.05 and 1.0 wt % of photoinitiator ABP (Fig. 4), AEBP (4-acryloyloxyethoxy benzophenone), or ABBP (4-acryloyloxybutoxy benzophenone) (Fig. 6) and 0.1 wt % of radical starter AIBN. The concentration of aluminum acetylaceto-

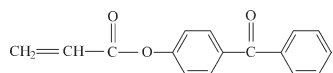


Figure 4 The 4-acryloyloxy benzophenone (ABP).

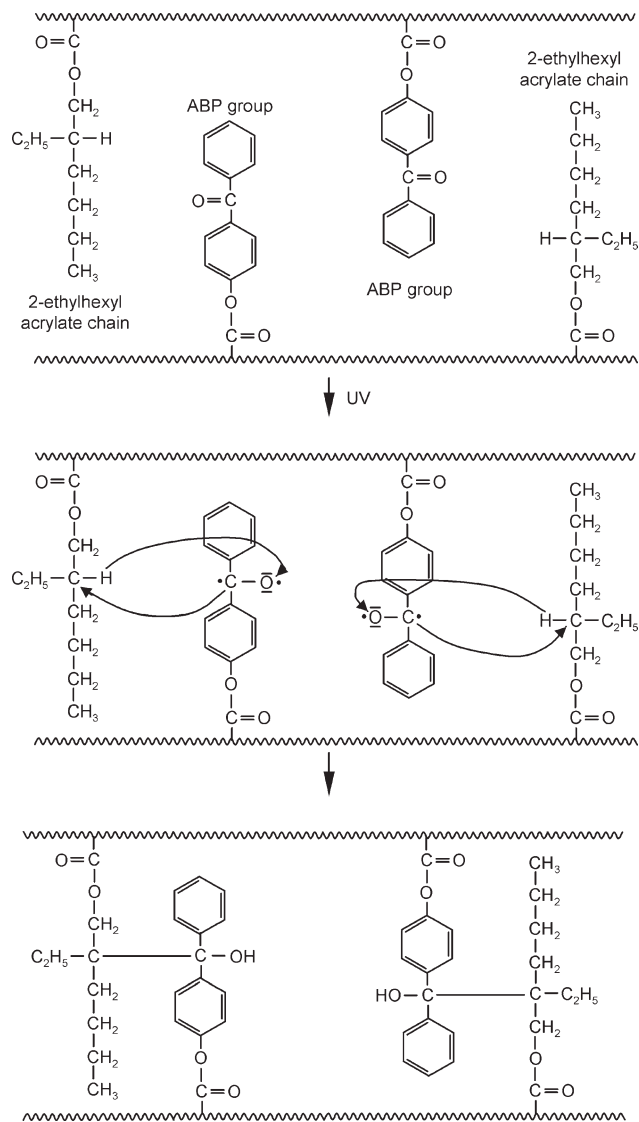


Figure 5 UV crosslinking of acrylic PSA using the unsaturated H-abstractor ABP.

nate (AlACA), titanium acetylacetonate (TiACA), and Cymel 303 ((hexamethoxymethyl) melamine)) (Fig. 9) was in the range from 0.05 to 1.0 wt %. The polymerization process was carried out under the dosage time of 2 h and postreaction time of 4 h.

The monomers: 2-ethylhexyl acrylate, butyl acrylate, methyl acrylate, and acrylic acid were available from BASF (Germany). The radical starter AIBN and the investigated unsaturated acryloyloxy benzophenones were purchased from ChemCycle (Germany), but the crosslinking agents: metal chelates aluminum acetylacetonate (AlACA) and titanium acetylacetonate (TiACA) from Degussa (Germany), and the amino resin Cymel 303 from Cytec (Belgium), respectively.

After polymerization about 60 g m⁻² of obtained photoreactive solvent-borne acrylic pressure-sensitive adhesives were coated on polyester film and

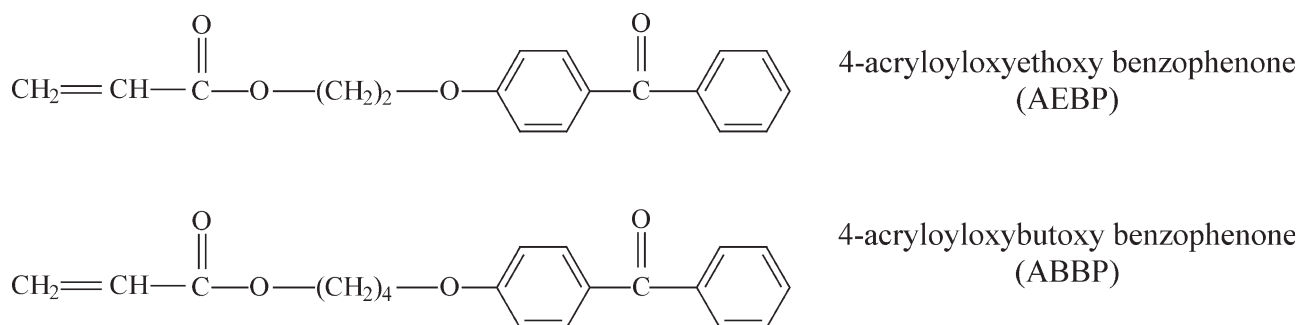


Figure 6 The 4-acryloyloxy benzophenones.

dried for 10 min at 105°C in the drying canal. PSAs layers were crosslinked using ultraviolet light lamp AKTIPRINT-mini 18-2 with transport band with the speed between 3 and 10 m min⁻¹ and variable UV dose between 200 and 1000 mJ cm⁻².

The following properties: tack, peel adhesion, shear strength, and shrinkage 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). Administrative address: 60, rue Auber-94408 Vitry Sur Seine Cedex, France. Those tests were conducted with the use of testing machine Zwick/Roell Z-25.

Shrinkage presents the percentage or millimeter change of dimensions of the PVC foil covered with PSA after PSA crosslinking and attached to the glass plate after keeping it 6 weeks at temperature of 70°C. With shrinkage greater than 0.5% or greater than 0.5 mm other properties were neglected.

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

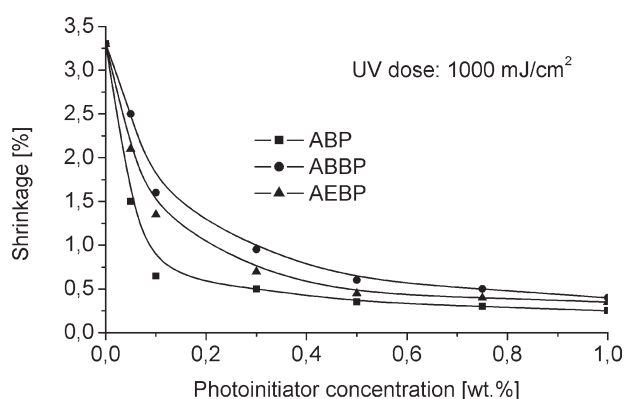


Figure 7 Effect of photoinitiator kind and amount on shrinkage.

RESULTS AND DISCUSSION

Influence of the photoinitiator concentration on shrinkage

Figure 7 shows the positive effect of kind and amount of unsaturated photoinitiator on the shrinkage of the acrylic PSA by the UV dose of 1000 mJ cm⁻². With the increase of photoinitiator concentration the shrinkage is getting lower. Because of the higher concentration of photoinitiator it causes denser acrylic PSA crosslinking. The lowest shrinkage was obtained with the use of 4-acryloyloxy benzophenone, which has the shortest alkyl carbon chain between double bond and chromophoric group. Even the unsaturated photoinitiator containing shortest alkyl chain gave the UV-crosslinked acrylic PSA layers the compacted crosslinking structure and with it the best shrinkage resistance. The data suggest that an acceptable level of shrinkage is attained at a concentration of ~ 0.3 wt % of photoinitiator.

Influence of the UV dose on shrinkage

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

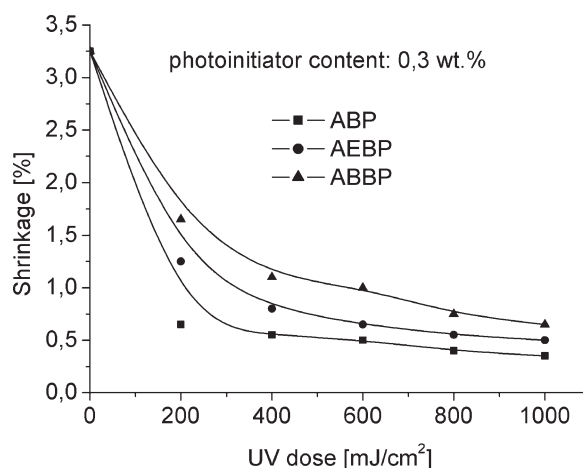
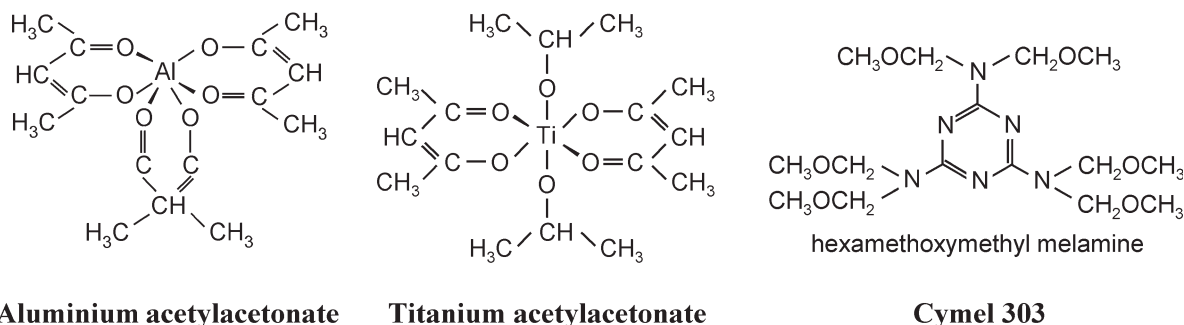


Figure 8 Influence of UV dose of shrinkage.

Chemical structure of conventional crosslinking agents



Aluminium acetylacetonate

Titanium acetylacetonate

Cymel 303

Figure 9 Chemical structure of conventional crosslinking agents.

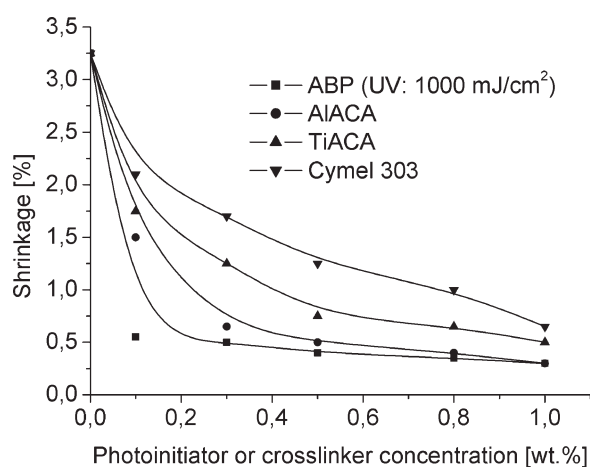


Figure 10 Dependence of unsaturated photoinitiator or metal chelates content on shrinkage.

solvent-borne adhesive systems. To further investigate the performance like shrinkage of these UV-crosslinkable adhesives, pattern curing is a new technology that makes it possible. The quantity of radiation energy for crosslinking of the pressure-sensitive adhesive film is exposed 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 on shrinkage by the constant amount of 0.3 wt % of investigated photoinitiator are presented in Figure 8. The minimal shrinkage values were obtained for the UV dose of 1000 mJ cm⁻². Increasing the UV dose during the crosslinking of acrylic PSA film leads clearly to better shrinkage resistance. More UV radiation during the UV-initiated crosslinking process improves the crosslinking density of PSA layers and thereby ameliorates the shrinkage performances. The use of about 1000 mJ cm⁻² UV dose guaranteed the lowest level of shrinkage. The best results of the lowest shrinkage value of 0.35% were given by using of 4-acryloyloxy benzophenone (ABP).

Comparison tests between the conventional and UV-crosslinked PSA

The best product with excellent low shrinkage of the solvent-based UV-crosslinkable pressure-sensitive

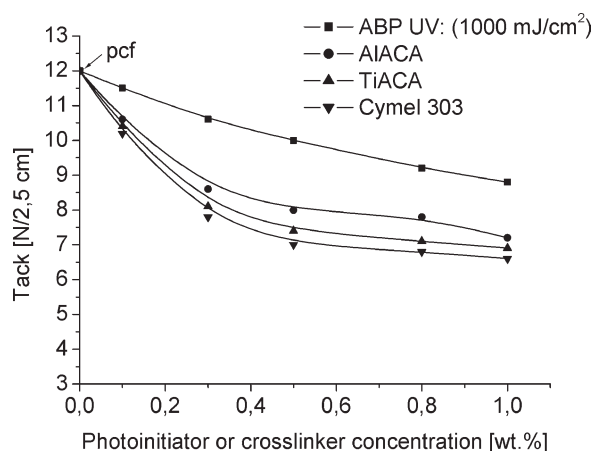


Figure 11 Influence of photoinitiator or crosslinkers amount on the tack of acrylic PSA.

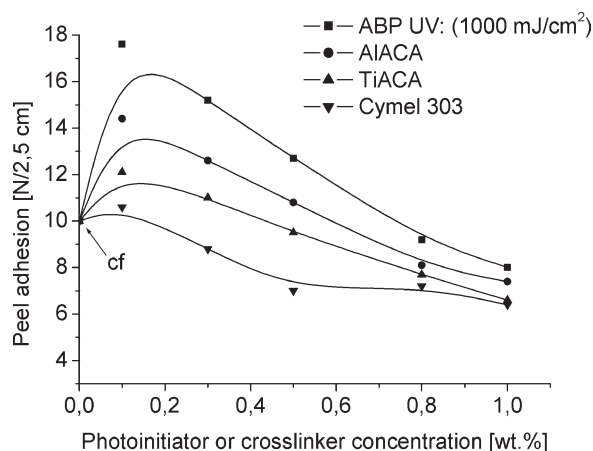


Figure 12 Influence of photoinitiator or crosslinkers amount on the peel adhesion of acrylic PSA.

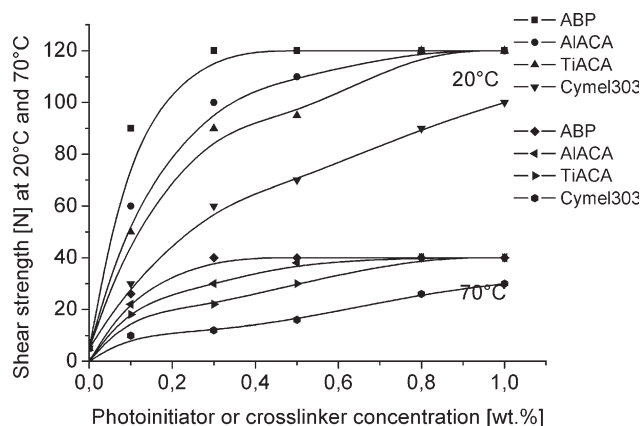


Figure 13 Influence of photoinitiator or crosslinkers amount on the shear strength of acrylic PSA.

adhesive containing unsaturated photoinitiator 4-acryloyloxy benzophenone was tested according to the shrinkage, tack, peel adhesion, and shear resistance. Afterward it was compared with the same model solvent-borne PSA crosslinked with metal chelates: aluminum acetylacetonate (AIACA), titanium acetylacetonate (TiACA), as well as methoxylated melamine Cymel 3003 (Fig. 9).

The shrinkage values, obtained after UV-crosslinking, are presented below. As it can be seen in Figure 10, shrinkage of PSA-containing photoinitiator ABP achieve the very low value for the 0.1 wt % of photoinitiator. Similar value of shrinkage have been observed in case of PSA crosslinked using AIACA with concentration of 0.5 wt %. Other crosslinked PSA attain worse results.

Another performance, which was examined, as tack and peel adhesion are presented in Figures 11 and 12. With the increase of photoinitiator or crosslinker concentration those properties deteriorates. Generally, PSA without any crosslinking agent demonstrate cohesive failure (cf) in peel adhesion and partially cohesive failure (pcf) in tack. The highest value of tack and peel adhesion, without failure, attain PSA that contains ABP photoinitiator concentration at 0.1%.

The best shear strength (cohesion) at 20 and 70°C correlates with the concentration increasing of applied crosslinking agent, and with 0.3 wt % photoinitiator ABP. Even for 0.3 wt % ABP were observed

the shear strength highest values of crosslinked acrylic PSA (Figure 13).

CONCLUSIONS/FUTURE TREND

To summarize, photoreactive solvent-borne acrylic pressure sensitive adhesives containing unsaturated photoinitiator ABP achieve the best self-adhesive performances from other PSA, crosslinked by the use of conventional crosslinking agents. Therefore, one can conclude that the chemical structure of photoinitiator has significant effect on the shrinkage, tack, peel adhesion and shear strength of solvent-based acrylic pressure-sensitive adhesives. The introduction of the polymethylene group into photoinitiator structure leads to the decrease of adhesive and cohesive properties.

All evaluated properties of UV-crosslinkable acrylic PSA are excellent, better than properties of similar acrylic PSA crosslinked using typical metal chelates or amino resins.

The UV-crosslinkable solvent-borne acrylic PSA with excellent properties can play a major role in the production of self-adhesive products such as decorative PVC films, synthetic material labels, and similar products still in the developmental stage. UV crosslinkable acrylic PSAs offer an interesting alternative to other crosslinked adhesive systems.

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