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Synthesis of new solvent-borne acrylic pressure-sensitive adhesives with low shrinkage[*)]

Summary — Polyacrylic pressure-sensitive adhesives based on 2-ethylhexyl acrylate, ethyl acrylate, methyl acrylate or acrylic acid were synthesized in ethyl acetate. The effects of kind and amount of crosslinking agent on peel adhesion and shear strength of the adhesives crosslinked with the compounds selected from the groups of metal chelates, multifunctional propylene imines or amine resins were investigated. Dependences of peel adhesion as well as shear strength of UV-crosslinked adhesives on the kind and amount of photoinitiator, crosslinking time and UV radiation dose were determined. On the basis of the results obtained the crosslinking agents were selected and their minimal amounts were found, ensuring acceptable value of film shrinkage (<0.5 %). The amount of selected crosslinking agents, needed to keep the shrinkage below this level, was determined.

Key words: acrylic pressure-sensitive adhesives, crosslinking agents, UV crosslinking, photoinitiators, shrinkage, shear strength.

SYNTEZA NOWYCH, ROZPUSZCZALNIKOWYCH, AKRYLOWYCH KLEJÓW SAMOPRZYLEPNYCH CHARAKTERYZUJĄCYCH SIĘ MAŁYM SKURCZEM

Streszczenie — Badane poliakrylanowe kleje samoprzylepne na podstawie akrylanu 2-etyloheksylu, akrylanu etylu, akrylanu metylu oraz kwasu akrylowego (tabela 1) syntetyzowano w octanie etylu. Badano wpływ rodzaju i ilości środków sieciujących na adhezję oraz wytrzymałość na ścinanie klejów sieciowanych wybranymi związkami z grupy chelatów metali (rys. 2 i 3), wielofunkcyjnych propylenoimin (rys. 4 i 5) oraz żywic aminowych (rys. 6 i 7). Określono także zależność adhezji i wytrzymałości na ścinanie usieciowanych ultrafioletem klejów od ilości i rodzaju fotoinicjatora (rys. 8 i 9), czasu sieciowania (rys. 10 i 11) oraz dawki promieniowania *UV* (rys. 12 i 13). Na podstawie przeprowadzonych badań wybrano rodzaje związków sieciujących i wskazano ich minimalne ilości (rys. 14 i 15) potrzebne do zapewnienia akceptowalnej wartości skurczu folii (<0,5 %). Określono ponadto jakiej ilości wybranych środków sieciujących należy użyć, by skurcz klejów nie przekraczał wspomnianego poziomu (rys. 16).

Słowa kluczowe: akrylanowe kleje samoprzylepne, związki sieciujące, sieciowanie, fotoinicjatory, skurcz, wytrzymałość na ścinanie.

Although several acrylic polymers have been used successfully as pressure-sensitive adhesives (PSA) in a variety of industries, a property inherent to all acrylic PSA which negatively impacts tack and adhesion performance is shrinkage on PVC surfaces upon crosslinking. This phenomenon is attributed to the formation of a three-dimensional, covalently crosslinked network during crosslinking, which reduces intermolecular distances between the monomers used to form the crosslinked network.

For example, before crosslinking, the molecules which comprise the acrylate PSA are separated by their characteristic van der Waals's radii. Upon crosslinking, these intermolecular distances are reduced due to the formation of covalent bonds between monomers which produces the desired highly crosslinked PSA material. This reduction of intermolecular distances creates internal stress throughout the crosslinked network, which is manifested by reduced adhesion of PSA adhesive to both the substrate and the object attached to [1].

UV-induced crosslinking is a rapidly expanding technology in pressure-sensitive adhesives area resulting from its main advantages such as solvent-free process, efficient, showing economical energy consumption and giving new properties and quality of chemical crosslinking bonding [2]. This crosslinking process found interesting application for producing photoreactive PSA sys-

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tems of high performance used in the coating industry for PVC signed and marked films.

The idea of replacing of the conventional PSA systems crosslinked at room temperature or two-component PSA systems crosslinked at elevated temperature, with single-component UV-activated PSA became very attractive to manufacturing industries [3].

The most important features of the crosslinked polyacrylate PSA, such as adhesion, cohesion and of course shrinkage can be controlled through the crosslinking agent type and amount, and in the case of UV-crosslinkable adhesives by UV dosage [4—7]. Crosslinking of PSA with ultraviolet light can be done directly after the application. There are used mercury lamps (low, medium, high pressure) of power between 80 and 160 W/cm which include UV stations with six and more UV lamps of power 160 to 250 W/cm.

Normally polyacrylates absorb the entire light radiation below 300 nm. In order to accomplish acceptable crosslinking of transparent PSA only UV wavelengths above 300 nm are of importance — UV wavelength range about 300 to 400 nm is required.

Increasing attention is paid to a new class of unsaturated copolymerizable photoinitiators and polymerization with others acrylic monomers as well as the properties of synthesized PSA containing these photoinitiators after UV crosslinking, such as shrinkage [4].

Crosslinking mechanism of UV photoreactive acrylic PSA containing photoreactive benzophenone derivatives has been thoroughly investigated. Formula I presents schematically for example UV-crosslinked acrylic PSA by using 4-acryloyloxy benzophenone (ABP).

During UV exposition the intermolecular benzophenone derivatives (H-abstractors) structures are excited and react with the neighbouring C-H positions of polymer side chains. UV crosslinkable acrylic PSA shows excellent oxidation resistance what means inert gas atmosphere is not necessary [8].

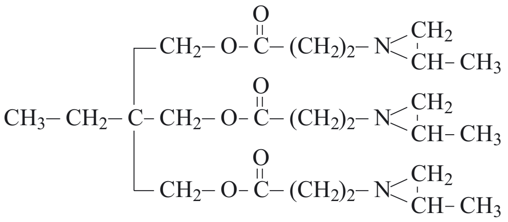
The target of this work was the development of solvent-based acrylic PSA of high performance in regard to PVC surfaces and with low or very low shrinkage (*S*). Acceptable level of shrinkage is $S \leq 0.5$ mm.

EXPERIMENTAL

Materials

Technical grade commercial crosslinking agents were purchased from the following suppliers:

— metal chelates, *i.e.* titanium(IV) acetyloacetonate (TiACA) and aluminum(III) acetyloacetonate (AlACA) from DuPont, propylene imines trismethylolpropan-tris-(*N*-methylaziridinyl) propionate (Neocryl CX-100, Formula II) from ICI and tris 1-(2-methyl)aziridinyl phosphineoxide (MAPO, Formula III) from Arsynco;



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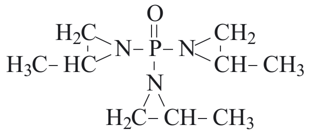


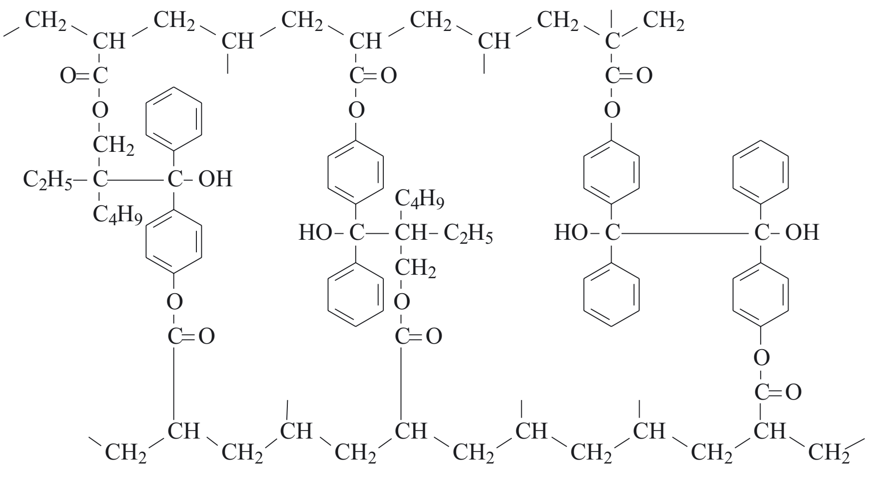
(III)

— amino resins, *i.e.* hexamethoxymethyl melamine (Cymel 303) and methoxymethyl ethoxymethyl benzoquanamine (Cymel 1123) from Cytec.

The basic acrylic PSA were synthesized in ethyl acetate (50 wt. % of solid content) at solvent boiling temperature [7] from the monomers specified in Table 1, using 1.0—2.0 wt. % of different kinds of unsaturated photoinitiators. All the monomers are supplied by BASF.

Table 1. Kinds and amounts of monomers used to syntheses of acrylic PSA

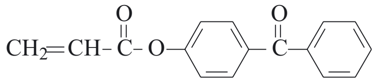
Monomer	Amount, wt. %
2-Ethylhexyl acrylate	49.0 to 50.9
Ethyl acrylate	25.0
Methyl acrylate	20.0
Acrylic acid	4.0



(I)

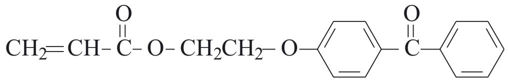
As unsaturated photoinitiators the following substances were used:

— acryloxybenzophenone (ABP, Formula IV), synthesized by dr Milker from Klebstoff GmbH, Horhausen,



(IV)

— 4-(2-acryloxyethoxy)benzophenone (AEBP, Formula V), benzoine acrylate (BAC, Formula VI) and phenyl-(1-acryloxy)-cyclohexyl ketone (PAC, Formula VII) synthesized in Szczecin University of Technology,



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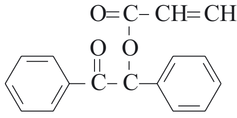

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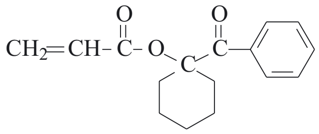
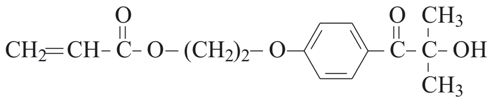


(VII)

— 2-hydroxy-1-[4-(2-acryloyloxyethoxy)phenyl]-2-methyl-1-propanone (ZLI 331, Formula VIII) supplied by Merck Darmstadt.



(VIII)

The unsaturated photoinitiators were incorporated into the polymer chain directly during the polymerization process [11].

Sample preparation

The solvent-based PSA formulations were cast with a knife coater with about 60 g/m^2 coat weight, dried 10 min at temp. 105 °C and after drying in the case of incorporating of unsaturated photoinitiator cured 3 min by ultraviolet light using a 100 mJ/cm^2 mercury vapour UV lamp (from IST company, Germany) of UV-A wavelength between 315 to 380 nm and transferred on the PVC film. The UV-exposure can be measured using an integrating radiometer Dynachem$^{\mathrm{TM}}$ Model 500, available from Dynachem Corporation, 2631 Michelle Drive, Tustin, CA 92680.

Method of testing

Shrinkage presents the percentage (S) or millimeter (I_r) change of dimensions of the film covered with UV-crosslinkable PSA and attached to the glass after keeping it for 1 week at temp. of 70 °C [9, 10].

Shear strength and peel adhesion are determined by standard AFERA (Association des Fabricants Europeens de Rubans Auto-Adhesifs). Exact details are found in AFERA 4001 (peel adhesion) and AFERA 4012 (shear strength).

The molecular weight studies were performed using a liquid chromatograph LaChrom system: RI Detector L-7490 and LaChrom UV Detector L-7400 from Merck Hitachi equipped with a PLgel 10^6 Å column from Hewlett Packard.

RESULTS AND DISCUSSION

Effect of PSA molecular weight on shrinkage

The result showing the influence of the molecular weight of PSA layers crosslinked using 0.1 wt. % AlACA on their shrinkage is presented in Fig. 1.

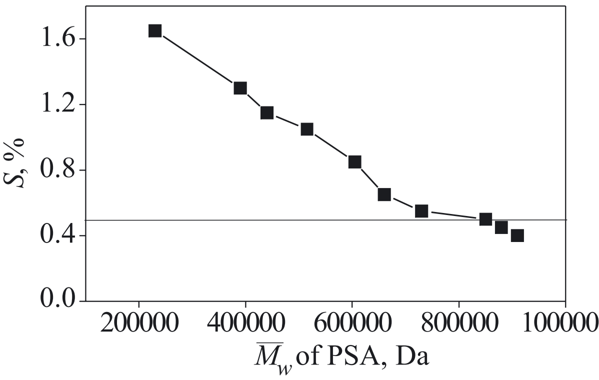


Fig. 1. Effect of weight-average molecular weight ($\overline{M}_w$) of acrylic PSA on shrinkage (S)

An increase in the molecular weight leads to reduction in shrinkage. For molecular weight values greater than about 850 000 Da, the shrinkage level under 0.5 % was observed.

The investigated synthesized solvent-based basic acrylic PSA were characterized after addition of isopropyl alcohol as stabilizer by the following important physical performance:

— amount of solid content: 40 wt. %,

— viscosity: 2.1—3.6 Pa · s,

— weight average molecular weight $\overline{M}_w$: 501 000—630 000,

— number average molecular weight $\overline{M}_n$: 213 000—230 000,

— polydispersity $D = \overline{M}_w / \overline{M}_n$: 2.35—2.74.

Influence crosslinking agent on PSA main properties

Metal acetylacetonates

Preferred metal chelate crosslinking agents AlACA and TiACA have been selected accordingly to their solubility in common organic solvents, taking into account the preliminary values of cohesion. Metal chelates have been used in concentrations between 0.1 and 1.0 wt. % as referred to the acrylic polymer solids.

The influence of the tested metal chelates on the peel adhesion and shear strength of the acrylic PSA is illustrated in the Figs. 2 and 3.

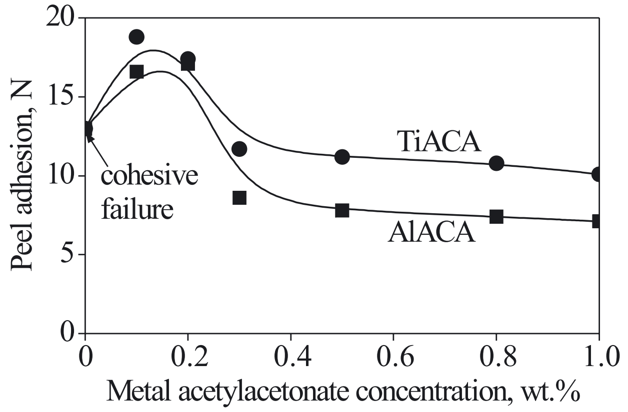


Fig. 2. Effects of kind and concentration of metal acetyloacetonate on PSA peel adhesion

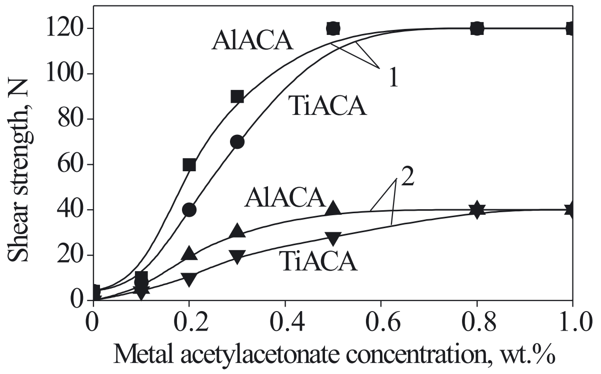


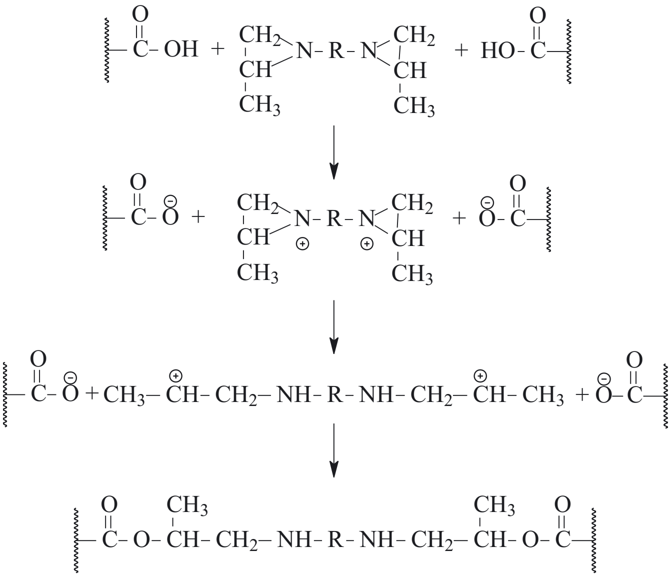
Fig. 3. Effects of kind and concentration of metal acetylacetonate on PSA shear strength at temp. 20 °C (1) and 70 °C (2)

For small concentrations of aluminum acetylacetonate (AlACA) or titanium acetylacetonate (TiACA) an improvement in PSA properties, like peel adhesion and shear strength, has been observed. The maxima of peel adhesion for about 0.15 wt % of TiACA and AlACA are achieved. PSA layers crosslinked with TiACA are unusually tacky. After exceeding a threshold of 0.2 wt. % investigated metal chelates, the peel adhesion levels decrease.

The cohesion results show that TiACA and AlACA differ in ability to improve the strength of the crosslinked acrylic PSA. Aluminum acetylacetonate (AlACA) is a better crosslinking agent than titanium acetylacetonate (TiACA). In order to reach the shear strength of 120 N at room temperature and 40 N at 70 °C it is necessary to use about 0.5 wt. % of tested AlACA and about 0.7 wt. % of TiACA.

Multifunctional propylene imines

Crosslinking of solvent-based acrylic PSA can be carried out by the use of propylene imine crosslinking agent a molecule that has two or more 2-methylaziridine groups capable to react with the functional carboxylic groups in the polymer chain (Scheme A).



Scheme A. Crosslinking of carboxylated PSA initiated by propylene imines

The oxygen of the nucleophilic carboxylic group causes the opening of the tensioned propylene imine rings while the hydrogen atoms accompanying the carboxylic groups protonate the nitrogen atoms. Multifunctional propylene imines can also be used for crosslinking of carboxylic functional acrylic pressure-sensitive adhesives. The crosslinking reaction takes place at room temperature.

The experiments in order to study the influence of selected propylene imines Neocryl CX-100 and MAPO as crosslinking agents on peel adhesion and shear strength were carried out. The results for synthesized solvent-borne PSA crosslinked with multifunctional propylene imines at levels between 0.1 to 0.9 wt. % were presented in Figs. 4 and 5.

In similarly conducted previous experiments for both investigated propylene imines the peel adhesion maximum for 0.1 wt. % of crosslinking agent was observed. An increase in propylene imine crosslinking agent concentration negatively influences peel adhesion. In opposition to the adhesive properties, the shear strength level reaches high values. The highest cohesion values were observed even for the small amounts (0.3 wt. %) of propylene imine Neocryl CX-100. As can be seen from the Figs. 4 and 5, propylene imine Neocryl CX-100 is a more useful crosslinking agent than MAPO with central phorphorus heteroatom. As illustrated, Neocryl CX-100 gives

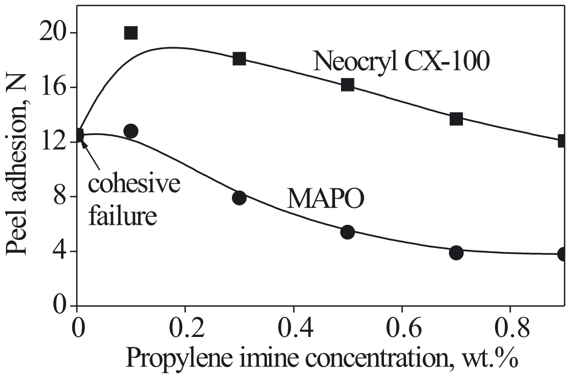


Fig. 4. Effects of kind and concentration of propylene imine crosslinking agents on peel adhesion of PSA

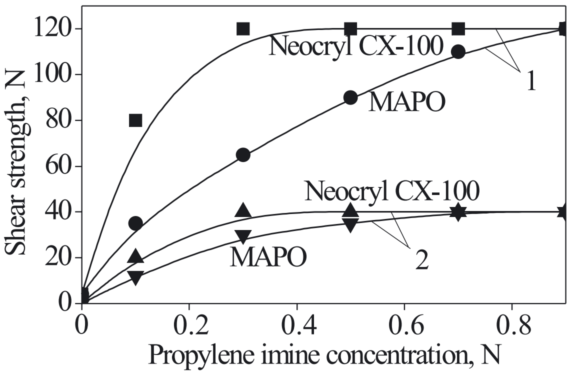


Fig. 5. Effects of kind and concentration of propylene imine crosslinking agents on shear strength of PSA at temp. 20 °C (1) and 70 °C (2)

the best balance between adhesion and cohesion among the selected propylene imine crosslinked acrylic PSA.

Amino resins

Amino resins constitute an interesting class of crosslinking agents, for the diverse polymers for use in thermoset coatings including carboxyl-, hydroxyl- or amide groups. They can be classified into four main groups, as melamine-formaldehyde resins [12], benzoguanamine resins, glycoluril resins and urea resins. They are characterized by their reactive end groups, generally classified as fully alkylated, partially alkylated and containing high imino groups, and enable to undergo controlled crosslinking reaction and precisely adjust the required adhesive properties. It is their special feature that their crosslinking rate is practically zero at room temperature while it increases exponentially above 100 °C. That means that the crosslinking ensues only during the drying of the PSA layer in the drying oven [13]. The amino resins can be used for the crosslinking of solvent-borne PSA acrylics at elevated temperature between 105 and 150 °C.

The goal of these experiments was to find the most suitable amino resin crosslinking system for solvent-based acrylic PSA without losing important properties (peel adhesion and shear strength) in comparison with other tested crosslinking systems. In the first step the most used amino resins: highly methylated melamine resin Cymel 303 and highly alkylated benzoguanamine resin Cymel 1123 are evaluated. The results of the investigations carried out are presented in Figs. 6 and 7. Melamine crosslinking agents are tested after drying of the crosslinkable PSA for 10 min at temp. 140 °C.

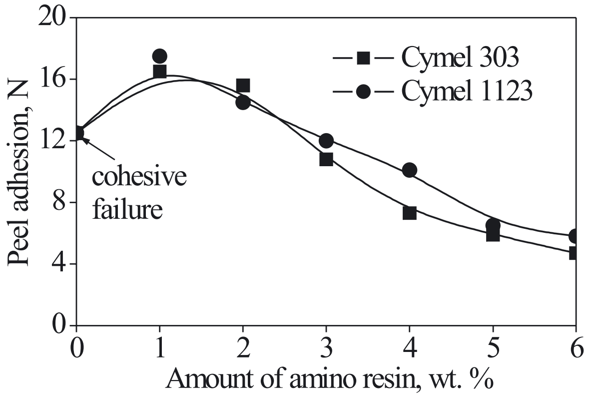


Fig. 6. Effects of kind and concentration of amino resin crosslinking agent on peel adhesion of PSA

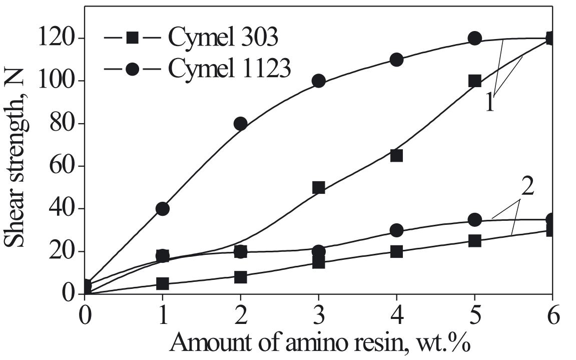


Fig. 7. Effects of kind and concentration of amino resin crosslinking agent on shear strength of PSA at temp. 20 °C (1) and 70 °C (2)

It can be seen that benzoguanamine derivative Cymel 1123 compared with the melamine resin crosslinking agent Cymel 303 decreased similarly the adhesion-related performance such as peel adhesion for amounts greater than 3.0 wt. %. For 1.0 wt. % of amino crosslinking agent the higher values of peel adhesion were observed. The acrylic PSA crosslinked with Cymel 1123 shows better thermal and shear performance than those with Cymel 303 crosslinking agent.

However, benzoguanamine resins make even better these properties but they are more expensive than melamine resins. Therefore a mixture of melamine and benzoguanamine resins may be used to achieve a cost-benefit compromise.

Influence UV-initiated crosslinking conditions on PSA main properties

It is well known that components of PSA systems which are not chemically linked (pigments, fillers, plasticizers, conventional photoinitiators and by-product of conventional saturated photoinitiators after UV exposure) can migrate to the PSA surface of the finished coating. Migration usually deteriorates the gloss, adhesion and mechanical properties and can interfere with many applications. Extractability of photoinitiator by-product by food in contact with these adhesive coatings excludes the use for food packaging materials.

Copolymerizing the unsaturated photoinitiator into the backbone of the acrylic PSA copolymer allows crosslinking with ultraviolet radiation, after formation of the copolymer. The most typical directions, however, are in the development of functionalized acrylated, vinylated, allylated, acrylamidated or vinyloxylated chromophores of type I and type II photoinitiator. Such functionalized chromophores will themselves either co-react with the crosslinked acrylic PSA or are capable to copolymerize to produce acrylic self-adhesive copolymers, which are not extractable.

Kind and amount of photoinitiator

Performance indicators such as peel adhesion and shear strength of the synthesized acrylic PSA, containing the selected evaluated unsaturated photoinitiators ranging from 0.1 to 2.0 wt. % but no crosslinking agent, crosslinked using 100 mJ/cm^2 UV radiation dose, after 3 min UV-crosslinking time are illustrated in Figs. 8 and 9.

By applying the unsaturated photoinitiators, one could state that a small increase in UV-crosslinked acrylic PSA peel adhesion could be achieved by the use of unsaturated efficient photoinitiators: ABP or ZLI 3331 incorporated into the acrylic polymeric chain. The maximum of peel adhesion was reached for unsaturated photoinitiator concentration between 0.1 and 0.3 wt. % (Fig. 8). The highest strength values at 20 °C equal 120 N and at 70 °C equal 40 N reached by the use of H-abstractor ABP and α-cleavage photoinitiator ZLI 3331 are obtained using more than 0.3 wt. % of very efficient photoinitiator, although the most efficient photoinitiator was ABP.

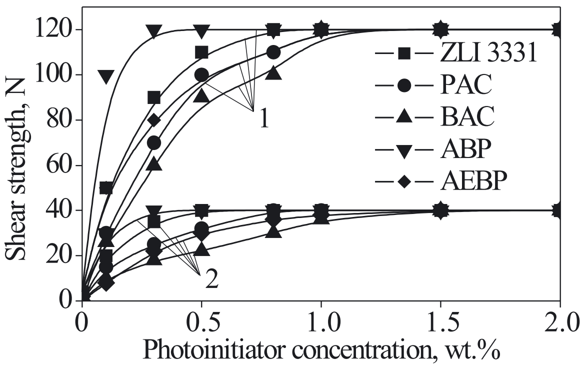


Fig. 9. Effects of kind and concentration of photoinitiator on shear strength of PSA at temp. 20 °C (1) and 70 °C (2)

UV-crosslinking time

The UV-crosslinking time effect on the performance of UV-crosslinked acrylic PSA for selected amount 0.3 wt. % of the photoinitiators ABP and ZLI 3331 for UV radiation dose of 100 mJ/cm^2, is shown in Figs. 10 and 11.

After UV-crosslinking time about 1.5 min, the peel adhesion maximum values were observed for 0.3 wt. % of photoinitiators ABP and ZLI 3331. Longer curing time decreases the peel adhesion level.

Excellent cohesion values equal 120 N at 20 °C and 40 N at 70 °C for 0.3 wt. % of ABP were observed after 1.5 and 2 min UV-crosslinking time respectively. The use of 0.3 wt. % of ZLI 3331 yielded a maximal shear strength equal 90 N at 20 °C and 35 N at 70 °C.

UV dose

The UV-curing effect of the most efficient acryloyloxy-photoinitiators: ABP and ZLI 3331, in selected amount of 0.3 wt. %, on peel adhesion and shear strength at UV dose between 50 and 250 mJ/cm^2, for 3 min. UV-crosslinking time, is shown in Figs. 12 and 13.

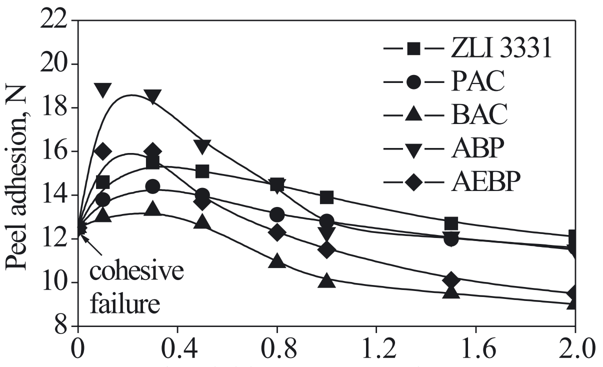


Fig. 8. Effects of kind and concentration of photoinitiator on peel adhesion of PSA

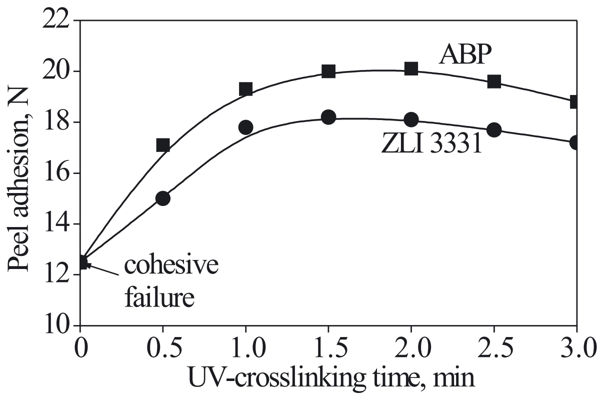


Fig. 10. Effects of kind and photoinitiator and UV-crosslinking time on peel adhesion of PSA

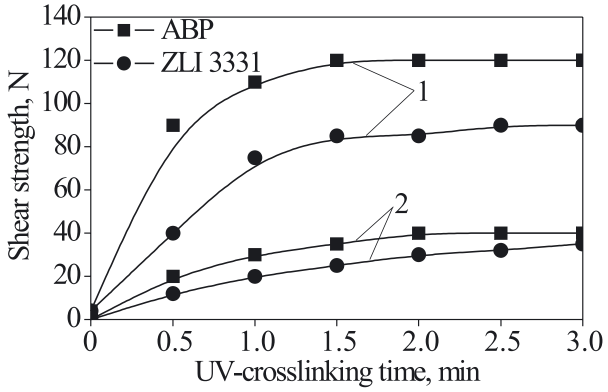


Fig. 11. Effects of kind of photoinitiator and UV-crosslinking time on shear strength of PSA at temp. 20 °C (1) and 70 °C (2)

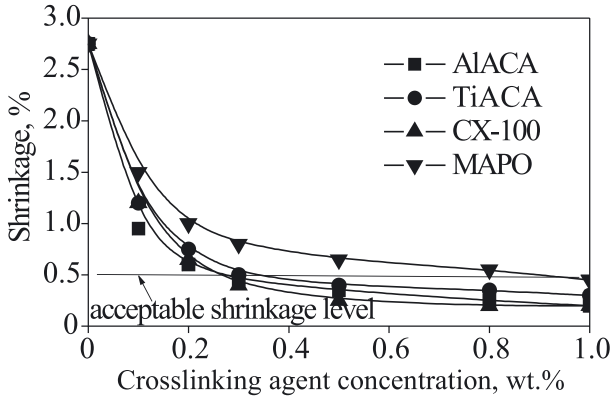


Fig. 14. Effects of kind and concentration of metal chelates and multifunctional propylene imines as crosslinking agents on shrinkage of PSA

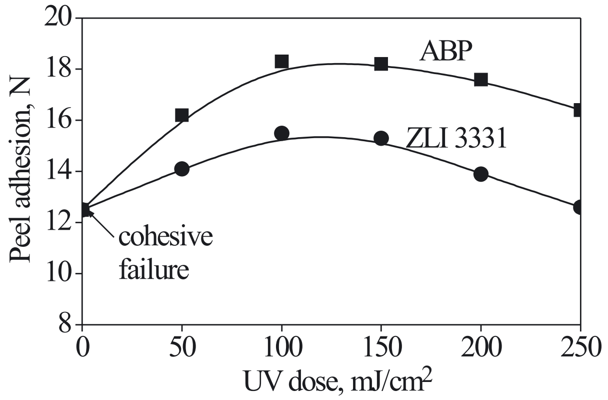


Fig. 12. Effects of the UV dose and kind of photoinitiator on peel adhesion of PSA

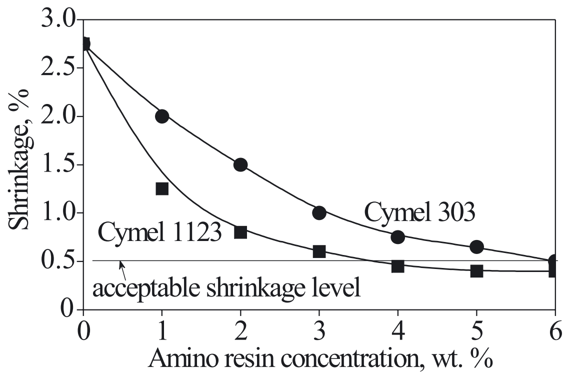


Fig. 15. Effects of kind and concentration of the amino resins as crosslinking agents on shrinkage of PSA

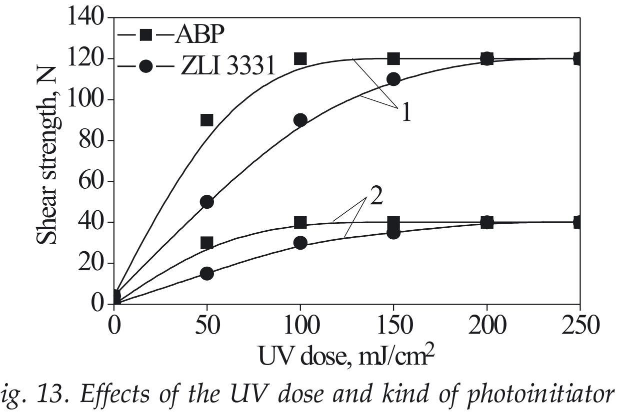


Fig. 13. Effects of the UV dose and kind of photoinitiator on shear strength of PSA at temp. 20 °C (1) and 70 °C (2)

As shown in Fig. 12, the cohesion of UV-crosslinked acrylic PSA containing 0.3 wt. % of ABP or ZLI 3331, indicated by the measured shear strength, increases with elevating emitted UV dose. An increase in UV dose above 100 mJ/cm^2 is sufficient for succeeding in excellent cohesion for H-abstractor ABP and photoinitiator ZLI 3331.

Crosslinking agents and photoinitiators

The influence of the concentration of the evaluated metal chelates: AlACA and TiACA, multifunctional propylene imines: Neocryl CX-100 and MAPO on shrinkage of the synthesized solvent-based acrylic PSA (without photoinitiator) is presented in Fig. 14, and for amino resins: Cymel 303 and Cymel 1123 is shown in Fig. 15.

It can be seen that the acceptable shrinkage values lower than 0.5 wt. % are obtained using the evaluated propylene imine Neocryl CX-100 and metal chelates AlACA and TiACA as crosslinking agents in amounts above 0.3 wt. %. By using 0.3 wt. % of Neocryl CX-100 an excellent lowest shrinkage level of 0.3 wt. % was observed.

The best shrinkage results of 0.4 % and 0.5 % were achieved for 6.0 wt. % of Cymel 1123 and Cymel 303. Completely unacceptable were shrinkage values for acrylic solvent-based PSA crosslinked with amino resins in concentrations lower than 3.0 wt. %.

Figure 16 shows the shrinkage of acrylic PSA containing varying amounts of five examinated photoinitiators: ZLI 3331, ABP and AEBP, BAC and PAC, but no crosslinking agent.

Generally speaking, it has been concluded that all investigated unsaturated photoinitiators tend to generate the best shrinkage resistance. It is interesting to note that the shrinkage of solvent-borne acrylic PSA after UV exposure tremendously decreases, suggesting continued

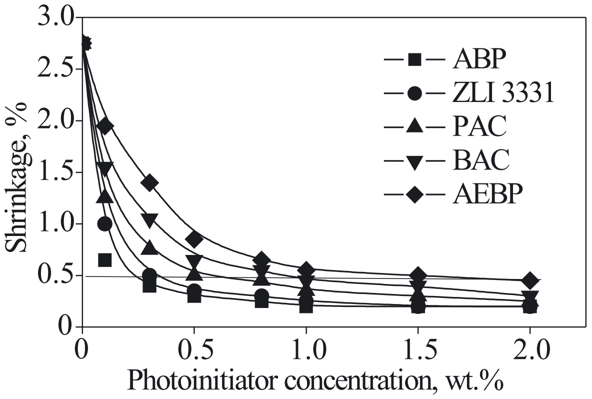


Fig. 16. Effects of kind and concentration of unsaturated photoinitiator on shrinkage of PSA

crosslinkig activity under UV exposure. Acceptable shrinkage values lower than 0.5 wt. % were noticed in the case of ABP or ZLI 3331 at concentration equal 0.3 wt. % of each photoinitiator. Above 0.3 wt. % of ZLI 3331 or ABP, the shrinkage values correspond to less than 0.45 % and 0.3 %, respectively. This has shown that ZLI 3331 and ABP are good alternatives to other saturated and unsaturated photoinitiators, which are weak, when exposed to UV crosslinking, while ZLI 3331 and ABP offer higher shrinkage resistance. The best copolymerizable photoinitiator, referring to very low shrinkage of UV-crosslinked solvent-based acrylic PSA was ABP.

CONCLUSIONS

Solvent-borne acrylic PSA of high performance: high shear strength and high shrinkage resistance, can be formed by crosslinking with selected metal chelates: titanium acetyloacetonate or aluminum acetyloacetonate, with propylene imine Neocryl CX-100 or unsaturated acryloyloxy-photoinitiators ABP and ZLI 3331. Propylene imine Neocryl CX-100 and copolymerizable photoinitiator 4-acryloyloxybenzophenone (ABP) are predominantly used as crosslinking agents and most efficient photoinitiators for solvent-borne acrylic PSA showing excellent shear performance and low shrinkage for PVC signed and marked films.

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