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Solvent-based acrylic pressure-sensitive adhesives of low shrinkage

The technology of solvent-based acrylic pressure-sensitive adhesives (PSA) characterized by low shrinkage has been developed. The new acrylic PSA are synthesized using typical acrylate monomers and crosslinked using conventional crosslinking agents and UV-technology. Self-adhesive acrylics of very low shrinkage are used for the production of mounting and splicing tapes, sign and marking films or labels with PVC carrier.

Key words: pressure-sensitive adhesives, shrinkage, crosslinkers, photoinitiators, UV-technology, PVC carrier

Rozpuszczalnikowe poliakrylanowe kleje samoprzylepne o małym skurczu

Opracowano technologię syntezy rozpuszczalnikowych poliakrylanowych klejów samoprzylepnych charakteryzujących się małym skurczem. Tego rodzaju kleje otrzymywane są przez polimeryzację typowych monomerów akrylanowych i sieciowane za pomocą typowych związków sieciujących oraz z wykorzystaniem technologii UV. Rozpuszczalnikowe kleje poliakrylanowe o małym skurczu stosowane są do produkcji materiałów samoprzylepnych na nośniku PVC, takich jak: taśmy montażowe, taśmy łączące, banery oraz folie dekoracyjne i etykiety.

Słowa kluczowe: kleje samoprzylepne, skurcz, związki sieciujące, fotoinicjatory, technologia UV, nośnik PVC

1. Introduction

Since their industrial introduction half a century ago, acrylic pressure-sensitive adhesives (PSA) have been successfully applied in many industrially areas. They are used in mounting tapes, splicing tapes, masking tapes, self-adhesive labels, sign and marking films, protective films and as well as in medical applications, such adhesive as plasters, OP-tapes, dermal dosage systems and biomedical electrodes [1].

Pressure-sensitive adhesives are high molecular nonmetallic materials characterizing themselves by amorphous structure and low glass transition temperature T_g about -25°C , used to connect other materials, mainly on their surfaces through tack, adhesion, cohesion and shrinkage. Tack (initial adhesion), adhesion (peel adhesion), cohesion (shear strength) and shrinkage (mechanical properties) are phenomena, which may be described thermodynamically and chemically, but actually they cannot be measured precisely [2]. The function of PSA is to ensure instantaneous adhesion upon application of a light pressure. Shrinkage takes place either through differential thermal expansion between the mold material and the polymer or through micro-structural changes in the polymer after molding and is ability to hold in position when shear forces are applied [3].

In the giant field of adhesives the PSA make a low percentage but the acrylic solvent-borne pressure-sensitive adhesives with about 165,000 tons per annum in Europe (2011) are very important position within this group. The properties of acrylic pressure-sensitive adhesives, such as tack, peel adhesion, shear strength and shrinkage are to a large extent determined by the kind of monomers, molecular weight of acrylic copolymer, polymerization method and especially by the type and quantity of the crosslinking agents added to the PSA after polymerization [4].

2. Shrinkage of acrylic PSA

Shrinkage is the phenomenon changing the original dimensions of polymer with or without changing its original shape. This is the result of built-in and “process-in” tensions. The carrier material is tensioned during manufacturing and conversion. Such material suffers undergoes relaxation as a function of time and temperature. For instance, the shrinkage of extruded PVC is partially the result of such tensions arising during the extrusion of the film. Cast and calandered PVC films are more dimensionally stable. In the case of pressure-sensitive adhesives their shrinkage is among other things dependent on molecular weight, and kind and concentration of crosslinking agents added after polymerization to improve the shear strength [5].

Before crosslinking, the molecules, which comprise the acrylics PSA, are separated by their characteristic

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van der Waals 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 the PSA adhesive to both the substrate and the object attached thereto.

Shrinkage presents the percentage change of dimensions of the PVC film covered with PSA after PSA crosslinking and attached to the glass after keeping it 4 weeks at temperature of 70°C. With unacceptable shrinkage greater than 0.5 % other properties of PSA as tack, peel adhesion and shear strength were neglected [6-8].

3. Influence of selected conventional crosslinking agents on the shrinkage of solvent-based acrylic PSA

The target of this investigation was the development of solvent-based acrylic PSA for coating of poly(vinyl chloride) (PVC) for manufacturing of sign and marking films with high performance (good tack, peel adhesion and high shear strength) and low shrinkage. The shrinkage of acrylic PSA was evaluated according to FINAT FTM 14. Acrylic PSA characterized by shrinkage performance higher than 0.5 % or 0.5 mm are not acceptable in area of self-adhesive sign and marking films.

3.1. Synthesis of solvent-based acrylic PSA

Experiments were conducted using solvent-based acrylic PSA synthesized from 65 wt.% 2-ethylhexyl acrylate (2-EHA), 30 wt.% methyl acrylate (MA) and 5 wt.% acrylic acid (AA) in ethyl acetate in presence of 0.1 wt.% 2,2'-azo-bis-isobutyronitrile (AIBN) with 50 wt.% polymer content. All components are available from BASF (Germany). After polymerization the synthesized acrylic PSA was stabilized with 30 wt.% propanol-2 and crosslinked with between 0.05 to 0.6 wt.% metal chelates aluminum acetylacetonate (AlACA) or titanium acetylacetonate (TiACA) available from Du Point. The solvent-based acrylic PSA containing mentioned metal chelates were cast with a knife coater with 60 g/m² dry adhesive coat weight on the silicon paper, dried 10 min at 105°C and after drying applied on to the PVC film.

3.2. Influence of metal chelates on the shrinkage of acrylic PSA

The influence of the concentration of metal chelates aluminum acetylacetonate (AlACA) or titanium acetyla-

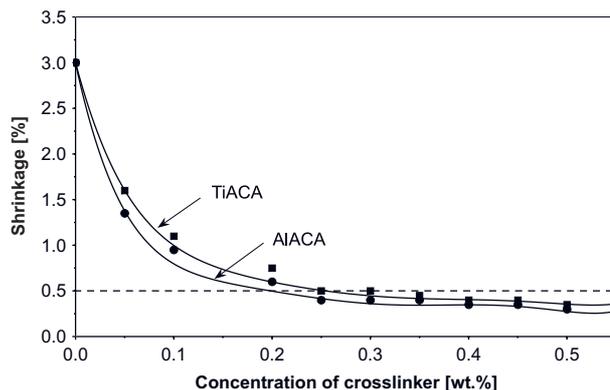


Figure 1. Shrinkage of acrylic PSA crosslinked with AlACA or TiACA

Rys. 1. Skurcz poliakrylanowych PSA sieciowanych za pomocą AlACA lub TiACA

cetonate (TiACA) on shrinkage of synthesized solvent-borne acrylic pressure-sensitive adhesives containing is illustrated in Fig. 1.

As expected, the increase of the metal chelate crosslinking agents AlACA or TiACA concentration corresponds with the decrease of shrinkage of acrylic PSA. By using AlACA in comparison to TiACA the slightly lower shrinkage resistance was observed. For this reason the TiACA in PSA technology is becoming more and more replaced by AlACA as a crosslinker for solvent-borne acrylic PSAs. Up to 0.2 wt.% AlACA or 0.2 wt.% TiACA the shrinkage values of 0.6 % and 0.75% were not satisfactory. Above these concentrations of both metal acetylacetonates the shrinkage level dropped under 0.5%.

3.3. Influence of thermal cross-linking agents on the shrinkage of acrylic PSA

The solvent-based acrylic pressure-sensitive adhesive formulations, containing selected thermal reactive crosslinking agents: N-methylol acrylamide (N-MAA), polycarbodiimide Permutex XR-5580 or amino resins: Cymel 303, Cymel 370 and Cymel 1123 were cast with a knife coater with 60 g/m² dry adhesive coat weight on the siliconized paper, dried 10 min at 140°C and after drying applied on to the PVC film. N-methylol acrylamide, Cymel 303, Cymel 370 and Cymel 1123 were purchased from Dyno Cyanamid (USA) and Permutex XR-5580 from Stahl Chemie (Holland).

The shrinkage profiles of solvent-borne acrylic PSAs crosslinked by use of various crosslinking agents, such as N-methylol acrylamide (N-MAA), polycarbodiimide Permutex XR-5580 or amino resins: Cymel 303, Cymel 370 and Cymel 1123, are shown in Fig. 2.

The best shrinkage results of 0.35 % and 0.45 % were achieved for 5.0 wt.% N-methylol acrylamide or 5.0 wt.% methoxymethyl ethoxymethyl benzoguanami-

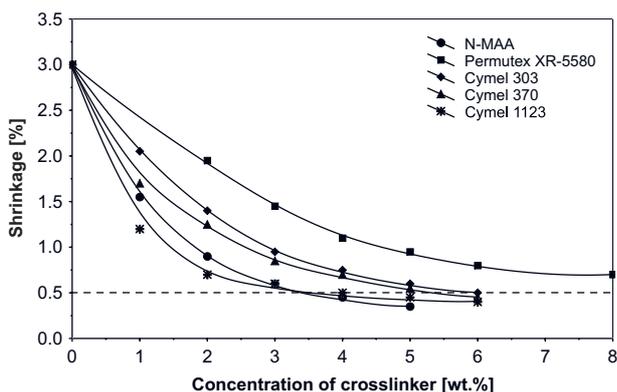


Figure 2. Shrinkage of acrylic PSA crosslinked with N-MAA, Permutex XR-5580 or selected Cymel resins
Rys. 2. Skurcz akrylanowych PSA sieciowanych za pomocą N-MAA, Permutexu XR-5580 oraz wybranych żywic Cymel

ne Cymel 1123. Completely unacceptable were shrinkage runs for acrylic PSA crosslinked with polycarbodiimide Permutex XR-5580. Thermal reactive crosslinkers are not especially suitable for application in technology of acrylic PSA with low shrinkage.

3.4. Influence of diisocyanate IPDI and propylene imine crosslinkers on the shrinkage of acrylic PSA

Polyfunctional propylene imines (aziridines) are functional methylaziridine derivatives (Fig. 3), which perform as very reactive low energy crosslinking agents in carboxylated polymers [9].

The high reactivity of propylene imine crosslinkers can be ascribed to ring strain inherent in the terminal aziridine groups. Ring opening is acid catalyzed, proceeding initially via protonation of the tertiary nitrogen atom. Effective utilization of aziridine chemistry is dependent very much upon the availability of an active H^+ to protonate the aziridine ring. Unlike many other products used to crosslink polymer acrylics, temperature is not a major factor in the use of aziridine chemistry [10].

In Fig. 4 the influence on shrinkage of acrylic PSA, prepared similar as for shrinkage evaluation using metal chelates, is shown for isophorone diisocyanate (IPDI) and propylene imine crosslinkers N,N'-bis-propylene



Figure 3. Chemical formula of polyfunctional propylene imine crosslinkers

Rys. 3. Formuła chemiczna polifunkcyjnych środków sieciujących typu iminopropylenu

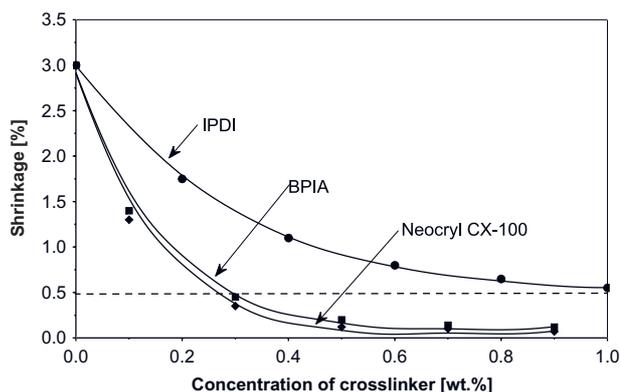


Figure 4. Shrinkage of acrylic PSA crosslinked with selected propylene imines

Rys. 4. Skurcz poliakrylanowych PSA sieciowanych wybranymi propylenoiminami

isophthalic acid amide (BPIA) and trimethylolpropane-tris-(N-methylaziridynyl) propionate (Neocryl CX-100) at concentrations between 0.1 wt.% and 0.9 wt.%, typical for these kinds of crosslinkers.

It can be seen that the lowest shrinkage values are obtained using the tested propylene imines as crosslinkers in amounts above 0.2 wt.%. By using 0.3 wt.% of Neocryl CX-100 an excellent shrinkage resistance of 0.2% was observed. In comparison to the selected propylene imine, the shrinkage, measured for acrylic PSAs, crosslinked with IPDI is entirely unsatisfactory. At first this seems surprising, but can be explained by an influence of higher reactivity of propylene imine derivatives compared to multifunctional isocyanates in reaction with carboxylic groups of acrylic acid being in the acrylic polymer chain.

3.5. Influence of unsaturated and additionable photoinitiators on the shrinkage of acrylic PSA

Alternatively, the photoinitiator can be incorporated into the backbone during polymerization. Photoinitiators suitable for polymerization should have good solubility, should react completely in the polymerization process, should be high temperature resistant and should not form photolytic fragments which tend to migrate with a strong specific odor after the UV radiation. Substances of this type include ethene unsaturated UV reactive benzophenones, benzoines, acetophenones with the following structure (Fig. 5) [11].

Investigated solvent-based acrylic PSA are synthesized with the same composition as in the case of using of metal chelates TiACA and AlACA. In the main polymer chain were incorporated during polymerization process between 0.05 wt.% and 2.0 wt.% unsaturated photoinitiators, such as: 2-hydroxy-1-[4-(2-acryloyloxyphenyl)-2-methyl-1-propanone (ZLI 3331), copolymeriz-

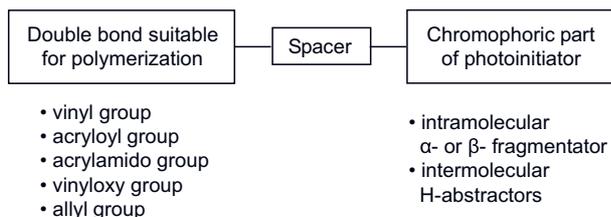


Figure 5. Schematic of photoinitiators suitable for polymerization

Rys. 5. Schematyczny wykaz fotoinicjatorów odpowiednich do polimeryzacji

able H-abstractor 4-acryloyloxybenzophenone (ABP), unsaturated 4-acrylamido-carbonyldioxybenzophenone (ACDB), 4-benzophenylvinyl carbonate (BVCN) and incorporated into side chain additional 4-propyleneimine – carbonyl benzophenone (PCB) according to monomers content. After polymerization the synthesized photoreactive acrylic PSA containing mentioned copolymerizable photoinitiators were cast with a knife coater with 60 g/m² dry adhesive coat weight on the siliconized paper, dried 10 min at 105°C, crosslinked 8 s with UV lamp by 600 mJ/cm² and after UV-crosslinking applied on to the PVC film.

Figure 6 is a graph showing the effect on shrinkage of acrylic pressure-sensitive adhesives containing different amounts of five investigated photoinitiators: ZLI 3331, ABP, ACDB, BVCN and benzophenone PCB.

Generally speaking, it has been concluded that all selected unsaturated photoinitiators and one additional photoinitiator tend to generate the overall best shrinkage resistance. It is interesting to note that the shrinkage of solvent-based acrylic PSA after UV exposure tremendously decreases, suggesting continued crosslinking activity under UV exposure. Excellent shrinkage values of 0.2 % were noticed in the case of ABP and ZLI 3331 for 2.0 wt.% of both photoinitiators.

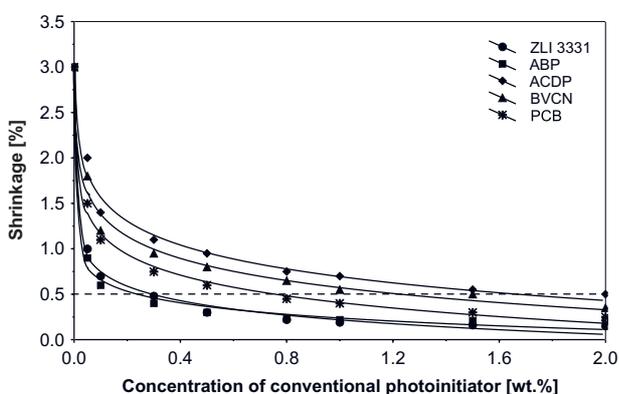


Figure 6. Shrinkage of acrylic PSA containing copolymerizable and additional photoinitiators after UV crosslinking by using of UV lamp

Rys. 6. Skurcz poliakrylanowych PSA – zawierających fotoinicjatory zdolne do kopolimeryzacji i addycji – po sieciowaniu z użyciem lampy UV

Above 0.3 wt.% ZLI 3331 and 0.3 wt.% 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 the other unsaturated photoinitiators. Their only real weakness is still again, when exposed to UV crosslinking, while ZLI 3331 and ABP will offer higher shrinkage resistance. The best copolymerizable photoinitiator, referring to very low shrinkage of UV-crosslinked solvent-based acrylic PSA, was 4-acryloyloxy benzophenone. At already 0.3 wt.% ABP content an acceptable shrinkage of 0.45 % was achieved.

4. Conclusions

Summing up, from the performed evaluation of the experiments referring to shrinkage investigation of crosslinked solvent-based acrylic pressure-sensitive adhesives, by using different crosslinking agents or ultraviolet crosslinking methods, it can be concluded that the best results regarding shrinkage of acrylic PSA on PVC film were obtained by using metal chelates and propylene imines. The best results with respect to shrinkage are observed for aluminum acetylacetonate (AlACA) and amongst multifunctional propylene imines for trimethylolpropane-tris-(N-methylaziridinyl) propionate (Neocryl CX-100).

From the experimental results by application of the UV crosslinking method, can be conclude that the use of 4-acryloyloxybenzophenone (ABP) influences positively the shrinkage resistance of UV-crosslinked acrylic PSA. The combination of acrylic PSA containing ABP as a firm incorporated part of polymer backbone and using UV lamp as UV crosslinking source allows excellent shrinkage performance to be reached.

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