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Investigations of UV-crosslinkable water-soluble acrylic pressure-sensitive adhesives

RAPID COMMUNICATION

Summary — Titled adhesives based on acrylic acid (AA) or β-acryloyloxy propionic acid (APA) and butyl acrylate (BA) were synthesized. Unsaturated photoinitiators were introduced into their chains, namely: 4-acryloyloxy benzophenone (ABP), 2-hydroxy-1-[4-(2-acryloyloxy-ethoxy) phenyl]-2-methyl-1-propanone (ZLI 3331) or phenyl-1(1-acryloyloxy)-cyclohexyl ketone (PAC). These products were plastified with polyoxyethylene glycols (PEG) differing in molecular weight (400 — 1010 Da) or polyoxypropylene glycols (PPG). The effects of chemical compositions of comonomers, plasticizer types and contents as well as effect of pH on the following basing properties of obtained aqueous adhesive systems (PSA) were investigated: water solubility, cohesion and adhesion. Dependence of water solubility of selected plasticized PSAs on UV curing time was also determined. PSA based on 70 wt. % of AA and 30 wt. % of BA with addition of 0.5 wt. % of ABP as photoinitiator/comonomer, plastified with 60 — 120 phr of PPG has been found as optimal.

Key words: polyacrylic pressure-sensitive adhesives, photoinitiators introduced, plasticizers, UV-curing, water solubility, adhesion, cohesion.

Typical water-soluble adhesives were known in the art of natural products such as dextrin, gelatines, casein or starch or in the art of synthetic products such as poly(vinyl alcohol). Under dry conditions, however, this type of products lacks elasticity and viscosity, showing no pressure-sensitive adhesive properties. This kind of conventional water-soluble adhesives has disadvantages such as low strength at elevated temperature and poor ageing resistance. The possible range of suitable initial synthetic polymers is also very limited. On the one hand a large number of natural or synthetic polymers, by their nature, show no adhesive properties. On the other hand, the adhesives/adhesive tapes industry resort to raw materials which are produced in large quantities and therefore at low cost. It is not necessary to develop new base polymers, but rather it is sufficient to modify selectively the polymers selected according to the commercial criteria.

An unusual and interesting challenge is that of providing a pressure-sensitive adhesive (PSA) with a certain water-solubility, which depends greatly on the hydrophilic properties of the groups incorporated into the polymer chain [1].

Several years ago 3M [2], Beiersdorf [3], Nitto [4], Lohmann [5] and Orafol [6] invested in development of solvent-based acrylic PSAs. These are distinguished by many features including excellent ageing resistance, thermal resistance and consistency of the properties of tack, bonding strength and shear strength. The water-soluble acrylic-based adhesives which Orafol already developed or is currently developing are characterized by excellent strength at elevated temperatures, high adhesion to different paper surfaces and complete water-solubility over a wide pH-spectrum. Although the possibilities of the acrylic components, acrylate monomers, have been more or less exhausted as far as the chemical structure is concerned, nevertheless there is wide scope for formulations by varying the copolymer composition and modifying the synthesized polymers.

The research and development of UV-crosslinkable water-soluble acrylic PSAs with self-adhesive properties are interesting scientific areas with full innovation and expect exciting for further industrial application. Photoreactive water-soluble PSAs based on acrylic polymers are still something of a speciality. They are applied as one- and two-sided tapes or as carrier-free films for web splicing in the paper industry. A challenging area of

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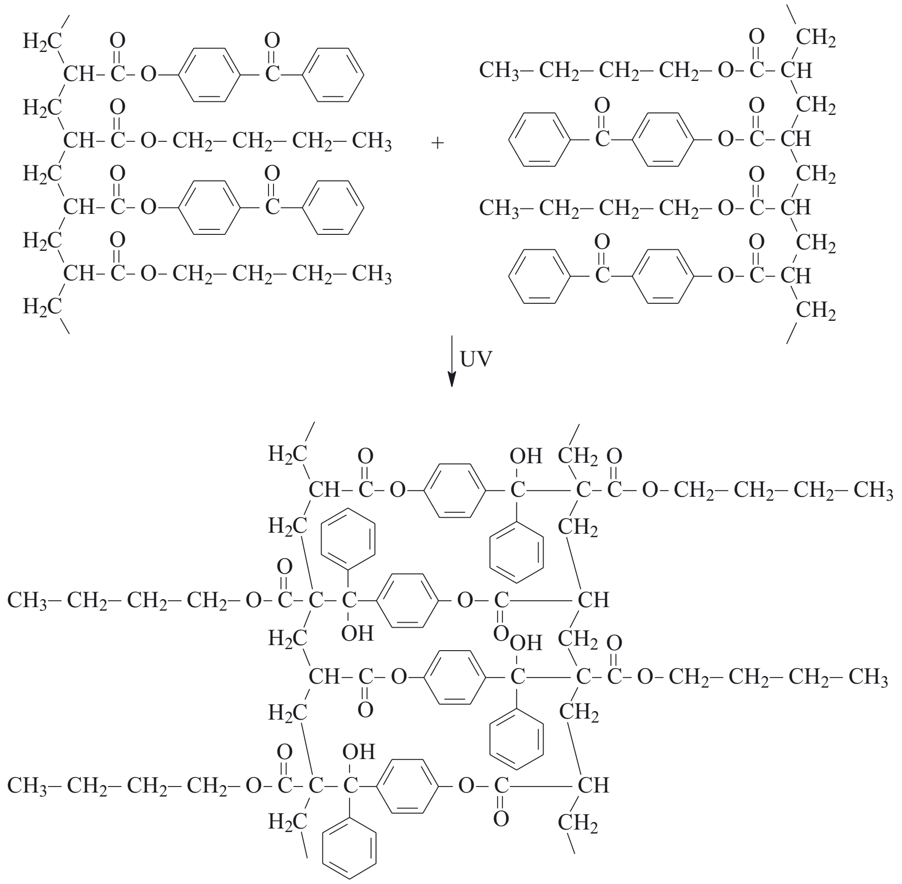


Scheme A. UV initiated crosslinking reaction of acrylic PSAs based on butyl acrylate and 4-acryloyloxy benzophenone

photoreactive water-soluble PSAs application is their use for water-removable labels, medical devices like surgical tapes and bio-electrodes [7].

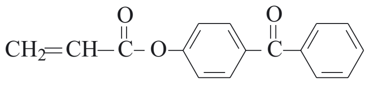
The crosslinking mechanism of UV-crosslinkable acrylic PSAs based on butyl acrylate and containing photoreactive benzophenone derivatives incorporated into polymer backbone is presented in Scheme A [8]. During UV exposure the intermolecular benzophenone derivative H-abstractor structures are excited and react by hydrogen abstraction with the neighboring tertiary carbon atoms of the polymer side chains.

This work is a continuation of earlier study of UV-crosslinkable PSAs [9—11]. Its aim is to find the best compositions of such adhesives, the types and concentrations of unsaturated fotoinitiators, comonomers and plasticizers as well as to select UV-curing time.

EXPERIMENTAL

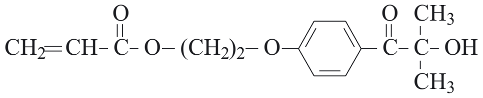
Materials

The following monomers were used: butyl acrylate (BA), acrylic acid (AA) (both delivered by BASF, Germany) and β-acryloyloxy propionic acid (APA) (from TCI, Japan). 2,2′-Azo-diisobutyronitrile (AIBN) were also purchased from TCI (Japan). Solvents, ethyl acetate and acetone, were purchased from Shell (Netherlands).



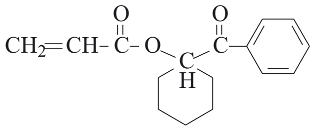
(I)

4-acryloyloxy benzophenone (ABP)



(II)

2-hydroxy-1-[4-(2-acryloyloxy-ethoxy)phenyl]-2-methyl-1-propanone [ZLI 3331]



(III)

phenyl-(1-acryloyloxy)-cyclohexyl ketone (PAC)

Plasticizers — polyoxyethylene glycols (PEG 400 and PEG 1000) and polyoxypropylene glycols (PPG 400 and PPG 1010) were supplied by Dow Chemicals (USA). Numbers in the plasticizers′ symbols denote their molecular weights. Unsaturated photoinitiators (used as comonomers), namely 4-acryloyloxy benzophenone (ABP, I), 2-hydroxy-1-[4-(2-acryloyloxy-ethoxy) phenyl]-2-methyl-1-propanone (ZLI 3331, II) and phenyl-(1-acryloyloxy)-cyclohexyl ketone (PAC, III), were synthesized by Chemitec (Germany).

Synthesis of water-soluble PSA

The water-soluble PSAs were synthesized based on soluble "hard" monomers — AA or APA [12] (10—90 wt. %) and insoluble "soft" monomer — BA (90—10 wt. %) at a boiling point of the solvent mixture acetone/ethyl acetate (70:30 v/v) at presence of 0.1 wt. % AIBN. Copolymerization process was carried out for 4 hours to reach 45 wt. % solid content of acrylic pressure-sensitive adhesive. Selected acrylic PSAs based on 70 wt. % AA or 70 wt. % APA and 30 wt. % BA were synthesized with the addition, as supplementary comonomer, of unsaturated photoinitiator chosen from ABP, ZLI 3331 or PAC, in concentration between 0.1 to 1.0 wt. % refered to acrylic monomers content.

Modification, UV-crosslinking and coating

The synthesized water-soluble PSAs containing unsaturated photoinitiator built into polymer structure and modified by adding suitable polyoxyalkylene glycol were cast with knife coater with 60 g/m^2 on 25 μm polyester film Hostaphan RN from Hoechst (Germany), dried for 10 min at 105 °C and cured for 3 min (with exception of curing time influence investigations) with ultraviolet light lamp U 350-M-I-DL from IST Company at UV-A wavelength between 315 to 380 nm at constant UV dose 300 mJ/cm^2. UV-exposure has been measured using an integrating radiometer Dynachem^{TM} Model 500, available from Dynachem Corporation, 2631 Michelle Drive, Tustin, CA 92680.

Methods of testing

Water-solubility test

The sample of synthesized acrylic PSA (5 g) was placed in a 1 L beaker containing 500 g of distilled water with different pH values (pH = 4.7 or 11). The tested adhesive was stirred at room temperature in distilled water at 3000 rpm and observed for determination full-solubility time.

Adhesion and cohesion

The adhesion and cohesion were measured according to the manner described in [11], according AFERA 4001 and AFERA 4012, respectively (AFERA — Association des Fabricants Europeans de Rubans Auto-Adhesifs). The cohesion was determined in this case at 70 °C only.

RESULTS AND DISCUSSION

Influence of the kind and amount of carboxylic acid and pH value on water-solubility of acrylic PSAs

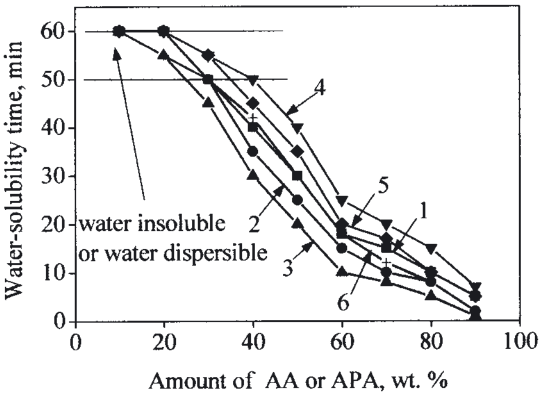


Fig. 1. Dependence of kind and amount of acid monomer and pH value on water-solubility time of PSA: 1 — AA/BA, pH = 4; 2 — AA/BA, pH = 7; 3 — AA/BA, pH = 11; 4 — APA/BA, pH = 4; 5 — APA/BA, pH = 7; 6 — APA/BA, pH = 11

Water-solubility of the synthesized acrylic copolymers at different pH values (4.7 and 11) is illustrated in Fig. 1. It is evident that increase in water-soluble monomer — AA or APA concentration — and increase in pH value improve water-solubility of acrylic PSAs containing hydrophilic carboxylic groups in the polymer structure. For polymers containing carboxylic groups originated from acrylic acid a shorter dissolving time was observed. For further trials the water-soluble PSAs containing 70 wt. % AA or 70 wt. % APA with acceptable solubility time between 10 and 20 min were selected.

Influence of the kind and amount of unsaturated photoinitiators incorporated into polymer backbone on cohesion of PSAs at 70 °C

It was the aim to evaluate the influence of the concentration of various investigated unsaturated acryloyloxy photoinitiators such as ABP, ZLI 3331 and PAC on selected acrylic PSAs cohesion after UV-crosslinking. The

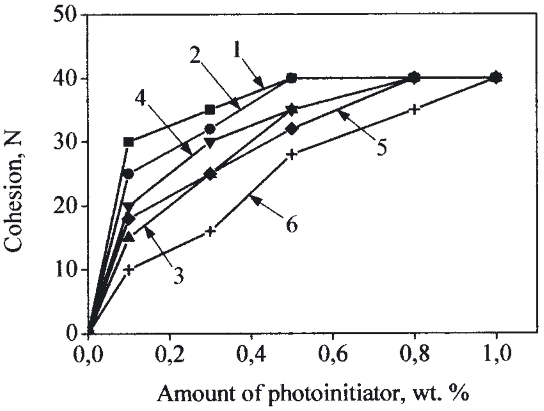


Fig. 2. Effect of kind and concentration of unsaturated photoinitiator and kind of monomer [(AA or APA)/BA = 70:30 wt. %] on PSA cohesion at 70 °C: 1 — AA/ABP, 2 — AA/ZLI 3331, 3 — AA/PAC, 4 — APA/ABP, 5 — APA/ZLI 3331, 6 — APA/PAC; all samples contain 30 wt. % of BA

results are shown in Fig. 2. All tested unsaturated photoinitiators let obtain an adequate improvement in shear strength of crosslinked PSAs at 70 °C. The relatively high cohesion was observed for the use of about 0.5 wt. % of ABP, 0.5 wt. % of ZLI 3331 and for about 0.8 wt. % of PAC (in the system with APA only). UV-crosslinked water-soluble acrylic PSAs based on AA show better thermal performances than the similar adhesives based on APA. For further trials with different plasticizers we selected ABP in concentration of 0.5 wt. % as photoinitiator.

Influence of the kind and amount of plasticizers on PSAs adhesion to the paper

The plasticizer may be at least one water-soluble plasticizer, or a combination of them. Suitable water-soluble plasticizers are, for example, used by us polyethylene glycols PEG 400 and PEG 1000 or polypropylene glycols PPG 400 and PPG 1010. The effect of the type and amount of investigated plasticizer on peel adhesion to paper (fax-paper) of water-soluble acrylic PSAs is presented in Fig. 3. As expected, increase in PEG or PPG concentration affects positively adhesion of water-soluble acrylic PSA to paper. With the same system of monomers the best peel adhesion results were achieved using low molecular PEG 400 and PPG 400.

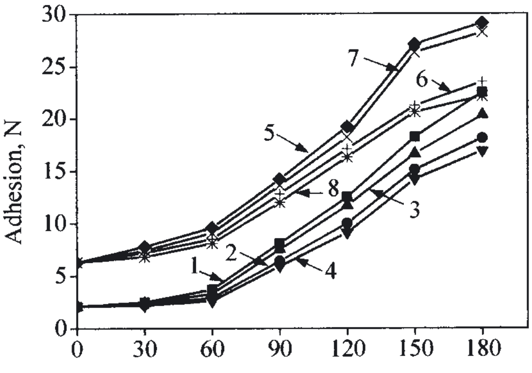


Fig. 3. Effect of kind and concentration of water-soluble plasticizers on PSA adhesion to paper: 1 — AA/PEG 400, 2 — AA/PEG 1000, 3 — AA/PPG 400, 4 — AA/PPG 1010, 5 — APA/PEG 400, 6 — APA/PEG 1000, 7 — APA/PPG 400, 8 — APA/PPG 1010; all samples contain 30 wt. % of BA and 0.5 wt. % of ABP

Influence of the kind and amount of plasticizers on PSAs cohesion

The influence of kind and amount of evaluated plasticizer on cohesion (at temperature 70 °C) of water-soluble acrylic PSAs after UV-crosslinking is presented in Fig. 4. PSAs based on 70 wt. % of AA or 70 wt. % of APA, 30 wt. % of BA and 0.5 wt. % of ABP were tested. A rapid breakdown of cohesion was noticed within the amount of plasticizer range of about 60 to 120 phr, while beyond about 120 phr of plasticizer the cohesion failure *versus* the carrier occurs. In this case, oppositely than in case of adhesion, the use of PPG 1010 and PEG 1000 with higher molecular weights gives the best results. This fact enables the application of PPG 1010 (curve 4 and 8) in the amount 60—120 phr, as the best plasticizer for the production of UV-crosslinkable water-soluble self-adhesive splicing tapes, for use at high temperatures. Additionally as it was shown, using of AA as water-soluble main monomer results in highest quality UV-crosslinked water-soluble acrylic PSAs (curve 4).

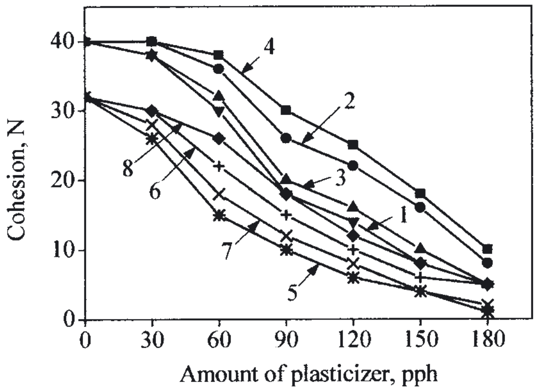


Fig. 4. Effect of kind and concentration of water-soluble plasticizers on PSA cohesion. Denotations of curves see Fig. 3; all samples contain 30 wt. % of BA and 0.5 wt. % of ABP

Influence of UV-crosslinking time of water-soluble PSAs on their water-solubility

The water-solubility test was conducted using water-soluble copolymers: AA/BA (70:30) and APA/BA (70:30) containing unsaturated photoinitiator ABP incor-

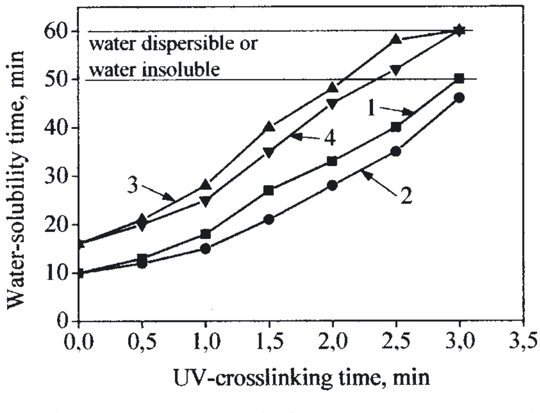


Fig. 5. Influence of UV-crosslinking time on water-solubility time of examined acrylic PSAs containing various PPG plasticizers in amount 100 phr: 1 — AA/PPG 1010, 2 — AA/PPG 400, 3 — APA/PPG 1010, 4 — APA/PPG 400; pH = 7; all samples contain 30 wt. % of BA and 0.5 wt. % of ABP

porated into polymer structure and modified with PPG 400 or PPG 1010. The effect of UV-crosslinking time on water-solubility at pH = 7 is shown in Fig. 5.

The increase in UV-crosslinking time corresponds of course with the decrease in water solubility, but for acrylic PSAs based on acrylic acid the UV-crosslinking time of 3 min is acceptable for water-solubility time under 50 min. Replacement of AA with APA deteriorates water-solubility.

CONCLUSIONS

From the evaluated UV-crosslinkable water-soluble acrylic pressure-sensitive adhesives, the best results, after UV-crosslinking, concerning the balance between water-solubility, adhesion to paper and cohesion were obtained for acrylic copolymers based on acrylic acid (70 wt. %), butyl acrylate (30 wt. %) and 4-acryloyloxy benzophenone (0.5 wt. %) and modified with polyoxypropylene glycols in amounts 60—120 phr.

REFERENCES

1. Czech Z.: *Polimery* 1996, **41**, 22.
2. *US pat*. 4 413 080 (1982).
3. *EU pat*. 058 382 (1982).
4. *US pat*. 4 442 258 (1980).
5. *EU pat*. 699 726 (1995).
6. Milker R., Czech Z.: *Polimery* 1990, **35**, 326.
7. Milker R., Czech Z.: *Polimery* 1987, **32**, 182.
8. Czech Z.: "Crosslinking of Solvent-Borne Pressure--Sensitive Adhesives Based on Polyacrylates", Publishers of Technical University, Szczecin 2004.
9. Czech Z.: *Polimery* 2003, **48**, 375.
10. Czech Z.: "Crosslinking of Acrylic PSAs", Publishers of Technical University, Szczecin 1999.
11. Czech Z., Urbala M.: *Polimery* 2004, **49**, Nr 11—12
12. Czech Z.: *Adhäsion* 1996, **10**, 24.

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