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Influence of the unsaturated benzophenone photoinitiators on shrinkage of acrylic pressure-sensitive adhesives

RAPID COMMUNICATION

Summary — This communicate presents a new class of the unsaturated photoinitiators containing benzophenone groups and their influence on shrinkage of acrylic pressure-sensitive adhesives (PSA) coated on polyvinyl chloride (PVC) film. The main emphasis is given to the influence of this new class of copolymerizable photoinitiators on shrinkage process of acrylic PSA after cross-linking with UV-lamp. Moreover, the influences of various factors such as cross-linking time and concentration of copolymerizable photoinitiators on very relevant PSA properties such as viscosity, molecular weight and shrinkage on PVC film were discussed.
Key words: unsaturated photoinitiators, UV-cross-linking, pressure-sensitive adhesives, acrylates, shrinkage.

UV-induced cross-linking is a rapidly widening technology in pressure-sensitive adhesives (PSA) area due to its main advantages such as solvent free process, efficient and economical energy used and new properties and quality of chemically cross-linking bonding [1]. This cross-linking process found interesting application for producing photoreactive PSA systems with high performance used in the coating of PVC surfaces.

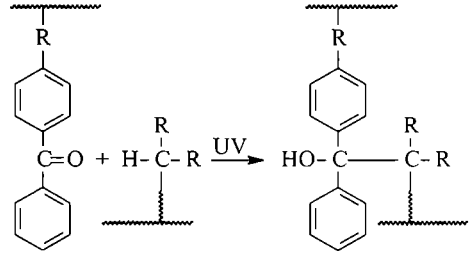
The idea of replacing the conventional two-part thermally cross-linked systems with single-component room temperature UV-activated PSA become very attractive for the industry [2].

The most important features of the cross-linked polyacrylate PSA, such as tack, adhesion, cohesion and of course shrinkage can be controlled by the UV dosage. Cross-linking of PSA with ultraviolet light can be done directly after the application. Mercury lamps (low, medium, high pressure) of power between 80 and 120 W/cm^2 are used. UV stations include six and more UV lamps with a power 120 to 250 W/cm^2.

Normally polyacrylates absorb the entire light below 300 nm. In order to accomplish acceptable cross-linking with transparent PSA, only UV wavelengths above 300 nm are important. In general, energy 350—410 kJ/mol is required for stimulation of benzophenone derivatives, which correspond to UV wavelength range about 300 to 410 nm.

Increasing attention is given to a new class of unsaturated compolymerizable photoinitiators, their copolymerization with others acrylic monomers, and investigation of the properties (*e.g.*, shrinkage) of synthesized PSA containing these photoinitiators after UV cross-linking [3].

The cross-linking mechanism of UV photoreactive acrylic PSA containing photoreactive benzophenone derivatives has been thoroughly investigated [see reaction (1)] [4].



(1)

During UV exposition the intermolecular benzophenone derivatives, showing H-acceptor structures, are excited and react with the neighbouring C-H positions of polymer side chains. UV cross-linkable acrylic PSA show excellent oxidation resistance, which let working without inert gas atmosphere [5].

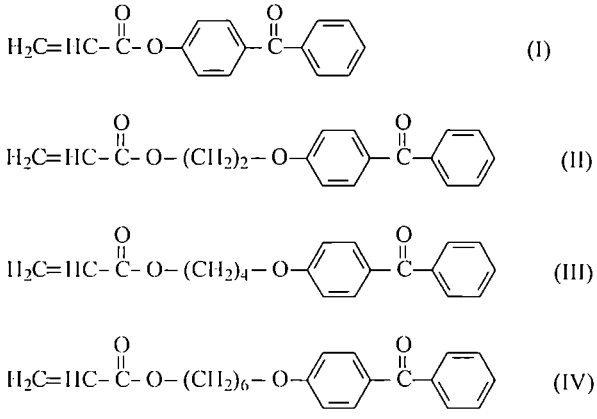
The aim of present study was to investigate the influence of the kind and amount of unsaturated photoinitiators based on benzophenone and UV cured time on shrinkage of acrylic PSA, as well as their viscosities (molecular weights).

EXPERIMENTAL

Materials

2-Ethylhexyl acrylate (2-EHA), methyl acrylate (MA), acrylic acid (AA), ethyl acetate (EA) and 2,2'-azo-diisobutyronitrile (AIBN) were purchased from Tokyo Chemical Industry Co. (Japan).

Unsaturated benzophenones such as 4-acryloyloxy benzophenone (ABP) (I), 4-(2-acryloyloxy-oxyethylene) benzophenone (AEBP) (II), 4-(2-acryloyloxy-oxybutylene) benzophenone (ABBP) (III) and 4-(2-acryloyloxy--oxyhexylene) benzophenone (AHBP) (IV) are synthesized by Chemitec GmbH (Germany).



Synthesis of PSA

The basic PSA was synthesized as a result of AIBN (0.1 wt. %) initiated copolymerization of 62—64.9% 2-EHA, 30% MA, 5% AA in the presence of 0.1—3% copolymerizable benzophenone photoinitiators [(I), (II), (III) or (IV)] in EA. Copolymerization process carried out 2 hours at boiling temperature of the solvent [6]. This way solvent based PSA were synthesized with solid content 50 wt. %.

Curing

The investigated photoreactive UV-cross-linked PSAs were cured with ultraviolet light lamp (U 350-M-I--DL from IST Company) with UV-A wavelength 315—380 nm and at constant UV dose 100 mJ/cm^2. Cross-linking carried out at room temperature. Curing time did not exceed 180 s.

Assessment methods

Shrinkage presents the percentage change of dimensions of the film covered with UV-cross-linkable PSA and attached to the glass after keeping it 1 week at temperature of 70°C.

The viscosity of synthesized solvent-based PSA was measured with viscometer RM 180 Rheomat from Rheometric Scientific Company. Molecular weight (M_w) was determined using HPLC-system with Isocratic Pump & DRI-Detector from HP Company.

RESULTS AND DISCUSSION

Viscosity and molecular weight

The influences of the concentration of different copolymerizable benzophenone photoinitiators on the viscosity and molecular weight of the synthesized PSA are illustrated in Fig. 1 and 2, respectively.

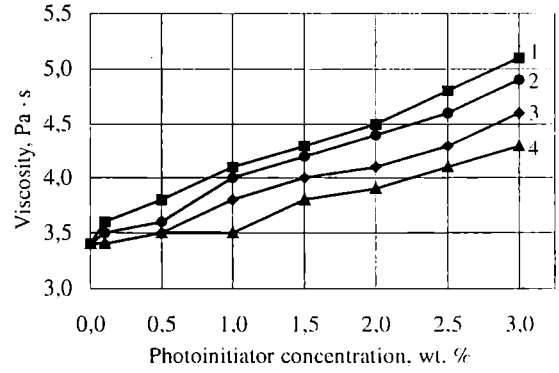


Fig. 1. Effect of photoinitiator kind and concentration on PSA viscosity; 1 — ABP, 2 — AEBP, 3 — ABBP, 4 — AHBP

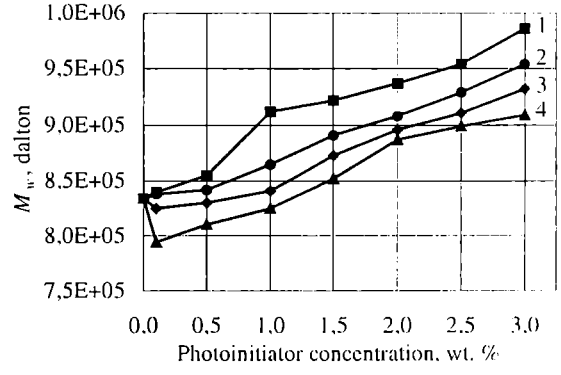


Fig. 2. Effect of photoinitiator kind and concentration on PSA molecular weight M_w; curves description as in Fig. 1

The following conclusions can be inferred from experimental results:

— the increase in unsaturated benzophenone amount corresponds with the increase in PSA viscosity,

— the increase in unsaturated benzophenone amount increases the molecular weight of PSA,

— from the investigated unsaturated benzophenones the highest values of PSAs viscosities and molecular weights were given by benzophenones with shorter organic chain (ABP, AEBP).

Shrinkage

The influence of the concentration of different unsaturated benzophenone photoinitiators on PSA shrinkage, at the same cross-linking time (60 s), is shown in Fig. 3. Figure 4 shows the influence of cross-linking time on

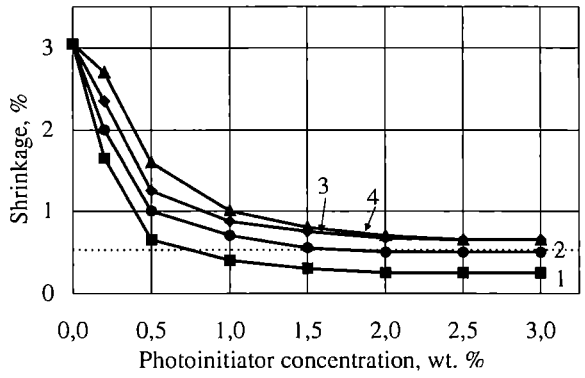


Fig. 3. Shrinkage dependence on photoinitiator kind and concentration (cross-linking time 60 s); curves description as in Fig. 1, dotted line — low shrinkage level

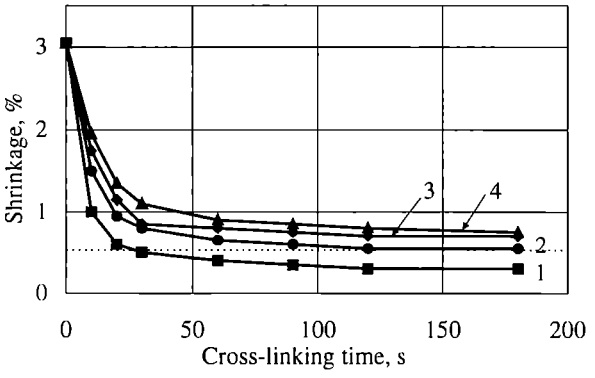


Fig. 4. Shrinkage dependence on cross-linking time (concentration of photoinitiator 1 wt. %); curves description as in Fig. 1, dotted line — low shrinkage level

shrinkage of PSA by the selected concentration of unsaturated benzophenones (1.0 wt. %). So with the increase in photoinitiator concentration and curing time, shrinkage at the beginning rapidly decreases and then stabilizers on the level far lower than initial one.

In general the use of unsaturated benzophenones as photoinitiators offers an interesting alternative to the other methods of reducing the shrinkage of PSA coated on PVC films. The best results with respect to shrinkage are observed in the case of ABP. For the sample with about 0.75 wt. % of ABP the shrinkage of PSA was lower than 0.5% and exactly shrinkage <0.5% is a criterion required by consignee of synthesized PSA with high performance for PVC surfaces. Similarly low value of shrinkage is obtained in the case of using 1 wt. % of ABP for curing time 30 s.

CONCLUSIONS

From the investigated unsaturated benzophenone photoinitiators, the best results concerning the shrinkage were obtained for 4-acryloyloxy benzophenone. Using of this photoinitiator in the amount as low as 0.75 wt. % guarantees the satisfying value of shrinkage reaching just for curing time 60 s. For the other photoinitiators used, higher concentrations of them are needed to reach similarly low shrinkage value for curing time 60 s. However, for their concentrations equal to 1.0 wt. % the prolongation of curing time up to 180 s is not sufficient to reach shrinkage value <0.5%.

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