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## 2-Vinyloxykarbonyloxymethyl antraquinone as a new unsaturated photoinitiator for UV-cured acrylic pressure-sensitive adhesives

### RAPID COMMUNICATION

**Summary** — Modern UV-curing technology requires efficient and very effective photoinitiators. The best technological solution is the use of unsaturated photoinitiators incorporated into the polymer chain during the synthesis of a pressure-sensitive adhesive (PSA) and being active in its UV-curing. In this work the unsaturated photoinitiator based on antraquinone [VCMA, formula (I)], in amounts from 0.1 to 2.0 wt. %, was used in the syntheses of photoreactive PSA made of 2-ethylhexylacrylate, methyl acrylate and acrylic acid. The obtained photoreactive polyacrylic adhesives, coated onto polyester films, were cured by UV lamp. Adhesion and cohesion of PSA were determined, dependently on photoinitiator concentration and UV curing time. It was found that high values of adhesion and cohesion were reached when photoinitiator concentration was about 0.5 wt. % and curing time about 2.5–3 min. Photoreactive polyacrylic adhesives, described and characterized in the article, synthesized with use of 2-vinyloxykarbonyloxymethyl antraquinone as photoinitiator, can be used in the wide range of technical and medical pressure-sensitive products.

**Key words:** photoreactive polyacrylic pressure-sensitive adhesive, unsaturated photoinitiator, UV-curing, adhesion, cohesion

### 2-WINYLOOKSYKARBONYLOOKSYMETYLOANTRACHINON JAKO NOWY NIENASYCONY FOTOINICJATOR STOSOWANY DO SIECIEWANYCH ZA POMOCĄ UV SAMOPRZYLEPNYCH KLEJÓW POLIAKRYLANOWYCH

**Streszczenie** — Nowoczesna technologia sieciowania przy użyciu promieniowania UV wymaga zastosowania wydajnych wysokoefektywnych fotoinicjatorów. Zdecydowanie najlepszym rozwiązaniem technologicznym jest zastosowanie nienasyconych fotoinicjatorów, wbudowanych w trakcie syntezy kleju samoprzylepnego (PSA) w łańcuch polimeru a następnie biorących aktywny udział w jego sieciowaniu za pomocą UV. W pracy wykorzystano nienasycony fotoinicjator na bazie antrachinonu [VCMA, wzór (I)], który w ilościach od 0,1 do 2,0 % mas. zastosowano do syntezy fotoreaktywnego PSA zbudowanego z akrylanu 2-etylohyksylu, akrylanu metylu oraz kwasu akrylowego. Otrzymane fotoreaktywne kleje poliakrylanowe po powleczeniu na folię poliestrową sieciowano lampą UV. Określono adhezję i kohezję usieciowanych PSA w zależności od stężenia fotoinicjatora oraz czasu sieciowania pod lampą UV (rys. 1–4). Stwierdzono, że wysokie wartości adhezji i kohezji osiągnięto stosując stężenia fotoinicjatora rzędu 0,5 % mas., a czasy sieciowania rzędu 2,5–3 min. Opisanie i scharakteryzowane w artykule fotoreaktywne kleje poliakrylanowe otrzymane z zastosowaniem jako fotoinicjatora 2-winyloksykarbonyloksymetyloantrachinonu mogą być stosowane do produkcji szerokiego asortymentu technicznych i medycznych produktów samoprzylepnych.

**Słowa kluczowe:** fotoreaktywny samoprzylepny klej poliakrylanowy, nienasycony fotoinicjator, sieciowanie UV, adhezja, kohezja.

UV-induced crosslinking is a rapidly expanding technology in the pressure-sensitive adhesives' area, resulting from its main advantages such as interesting crosslinking technology in the case of solvent-borne, water-borne and solvent-free acrylic pressure-sensitive adhesives (PSA)

[1–3]. This crosslinking process found an interesting application for producing self-adhesive articles, based on photoreactive PSA systems used in the coating industry for mounting tapes, decorative films, labels, protective films, assembly, and hygiene and medical materials.

The idea of using a photoinitiator suitable for copolymerization, in the process of UV induced crosslinking of acrylic PSA, evolved about 30 years ago. Later developments in this area of photoreactive PSA suitable for radiation curing focused on this idea again and resulted in more than 150 patents [4–8], which described the concept and application of unsaturated photoinitiators suitable for polymerization and the PSA containing photoinitiators.

The basic principle of UV crosslinking of PSA is the conversion of UV energy into chemical energy. This energy conversion takes place through the use of chemical species (photoinitiators) that, upon absorption of a particular wavelength of light, produce photochemical reactive radicals capable to initiate a rapid chain reaction. The photoinitiator is therefore one of the key components in UV-crosslinking, and the outcome of such a polymerization is critically dependent upon the choice of the photoinitiator, including its chemical nature and the amount [9].

Crosslinking of photoreactive acrylic PSA coatings with UV light has good environmental features. The advantages are, primarily, high material-, energy- and workspace saving process, as well as the complete elimination of solvents in hotmelt systems. These new UV-crosslinkable acrylic PSA tailored by the incorporation of unsaturated photoinitiators have well defined characteristics and can be customised with designed-in properties, including a combination of excellent peel values and high cohesion properties.

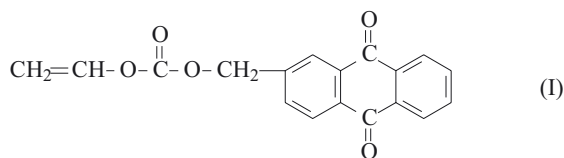
The most important features of the crosslinked acrylic PSA, such as tack, adhesion and cohesion, can be controlled by the concentration of photoinitiator, UV-crosslinking time and UV dosage. The crosslinking of PSA with ultraviolet light can be done directly after the application.

A target of this work was the testing of very effective synthesized unsaturated anthraquinone photoinitiator [10] for manufacturing of solvent-borne acrylic PSA showing high application performance.

## EXPERIMENTAL

### Materials

2-Ethylhexyl acrylate, methyl acrylate and acrylic acid were available from BASF (Germany), 2,2'-azo-diisobutyronitrile (AIBN) was purchased from TCI (Japan), ethyl acetate was purchased from Shell (The Netherlands), and the unsaturated photoinitiator 2-vinyl-oxycarbonyloxymethyl anthraquinone (VCMA) [Formula (I)] was synthesized by Planatol (Germany).



### Synthesis of photoreactive acrylic PSA

For the crosslinking trials the model solvent-borne PSA samples were synthesized using a 65 wt. % of 2-ethylhexyl acrylate, 30 wt. % of methyl acrylate and 5 wt. % of acrylic acid and unsaturated photoinitiator VCMA in concentration between 0.1 and 2.0 wt. % in relation to polymer amount. The solvent-borne polymerization was conducted 4 h in the presence of 0.1 wt. % of AIBN at boiling temperature of ethyl acetate, at 50 wt. % of solid content of acrylic polymer.

### Coating and UV-crosslinking

The tested photoreactive solvent-borne acrylic PSA samples containing unsaturated photoinitiator VCMA incorporated into the polymer backbone were cast with knife coater on 25  $\mu\text{m}$  polyester film Hostaphan RN from Hoechst (Germany) with coat weight of 60  $\text{g}/\text{m}^2$ . Then the material was dried for 10 min at 105  $^\circ\text{C}$  and after drying crosslinked with an ultraviolet light (lamp U 350-M-I-DL from IST Company) with UV-A wavelength between 315 to 380 nm, using different crosslinking time. The UV-exposure has been measured using an integrating radiometer Dynachem<sup>TM</sup> Model 500, available from Dynachem Corporation.

### Method of testing of UV-crosslinked acrylic layers

The two main properties were determined by standard AFERA (Association des Fabricants Europeens de Rubans Auto-Adhesifs) procedures. Exact details can be found in AFERA 4001 (adhesion) and AFERA 4012 (cohesion).

#### Adhesion

The adhesion, measured as peel adhesion is expressed by the force required to remove a coated flexible PSA sheet material from a test panel, measured at a specific angle of 180 $^\circ$ , and rate of removal.

A sample of PSA-coated material 1-inch (about 2.5 cm) wide and about 5-inch (about 12.7 cm) long is bonded to a horizontal target substrate surface of a clean steel test plate at least 12.7 cm in firm contact. A 2 kg hard rubber roller is used to apply the strip. The free end of the coated strip is doubled back nearly touching itself so the angle of removal was 180 $^\circ$ . The free end is attached to the adhesion tester scale. The steel test plate is clamped in the jaws of a tensile testing machine Zwick 1445, which is capable to move the plate away from the scale at a constant rate of 300 mm per minute.

#### Cohesion

The cohesion, measured as shear strength is a measure of the cohesiveness or internal strength of an adhesive. It is based upon the value of force required to pull an adhesive strip from a standard flat surface in a direc-

tion parallel to the surface to which it has been affixed with a definite pressure, according to AFERA 4012, at room temperature and at 70 °C. It is measured in Newtons for 4 h load times. Each test is conducted on from two adhesive-coated strips applied to a standard stainless steel panel in a manner such that at 2.5 cm × 2.5 cm portion of the strip is in fixed contact with the panel with one end of the strip being free.

## RESULTS AND DISCUSSION

### Influence of a photoinitiator (VCMA) concentration on adhesion and cohesion of acrylic PSA

The representative solvent-borne acrylic PSA samples, synthesized with different amounts of investigated anthraquinone-photoinitiator were crosslinked for 3 min by UV radiation using 1000 mJ/cm<sup>2</sup> UV dose.

The influence of amount of the above mentioned unsaturated photoinitiator on the basic acrylic PSA properties, like adhesion and cohesion, is shown in Figures 1 and 2.

An increase in the concentration of the investigated unsaturated photoinitiator VCMA first causes significant increase in adhesion while from about 0.4 wt. % causes its gradual drop (Fig. 1). Maximum occurring is

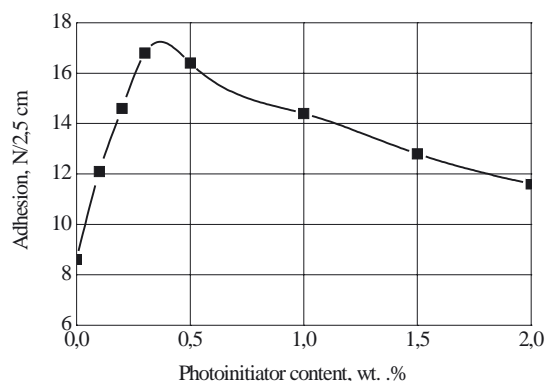


Fig. 1. Influence of photoinitiator content on adhesion of acrylic PSA, measured at 20 °C

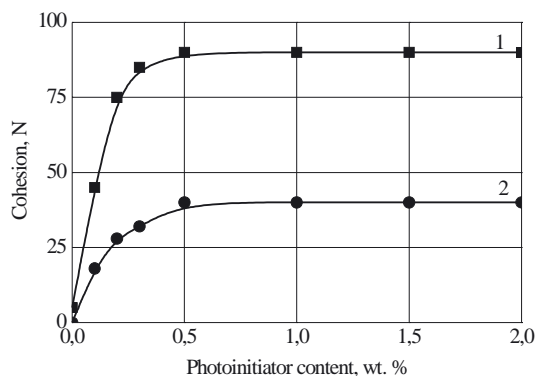


Fig. 2. Influence of photoinitiator content on cohesion of acrylic PSA, measured at: 1 — 20 °C, 2 — 70 °C

consequence of the effect of “light” crosslinking using VCMA.

The cohesion results (measured at 20 °C and 70 °C) presented in Fig. 2 show that the increase in unsaturated anthraquinone-photoinitiator content in an acrylic PSA polymers chains strongly raises, unexpectedly their cohesion after UV exposure but only in the range up to 5 wt. % of VCMA. Further increase in VCMA concentration does not influence the cohesion values.

### Influence of UV-exposure time on adhesion and cohesion

Further investigations with different exposure times of UV radiation and at 1000 mJ/cm<sup>2</sup> UV dose were carried out. The UV-crosslinking time effect on adhesion of the acrylic PSA obtained using various amounts of photoinitiator was illustrated in Fig. 3.

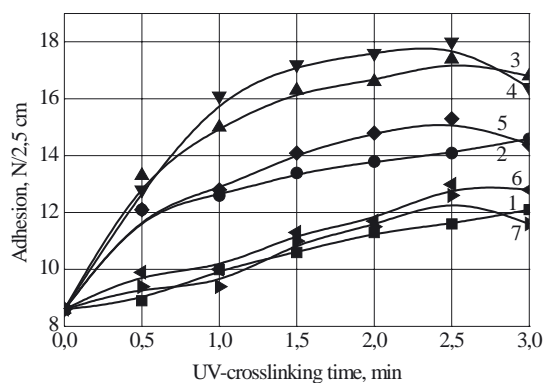


Fig. 3. Influence of the UV exposure time on adhesion (measured at 20 °C) of acrylic PSA obtained using photoinitiator content (in wt. %): 1 — 0.1, 2 — 0.2, 3 — 0.3, 4 — 0.5, 5 — 1.0, 6 — 1.5, 7 — 2.0

Dependence of peel adhesion on both VCMA concentrations and fixed UV-curing times are not monotonic. For all VCMA concentrations not smaller than 0.2 wt. % the peel adhesion maxima were observed between 2 and 2.5 min of UV exposure. It is clear from the courses of curves relating to various photoinitiator contents, that adhesion grows with increase in content up to about 0.3–0.5 wt. % and then drops. Summarizing the effects of both factors one can find that the best adhesion values were achieved for 0.3 and 0.5 wt. % of VCMA at 2.5 min of UV-crosslinking time.

As commonly observed in the field of UV-cured acrylic PSA, the cohesion varies with the UV-crosslinking time and the concentration of unsaturated photoinitiator. The higher degree of crosslinking, resulting from extended ultraviolet exposure and increasing VCMA content, is reflected in higher cohesion. A plot of cohesion performance versus UV-curing time for chosen concentrations of VCMA (Fig. 4) shows that a level of about

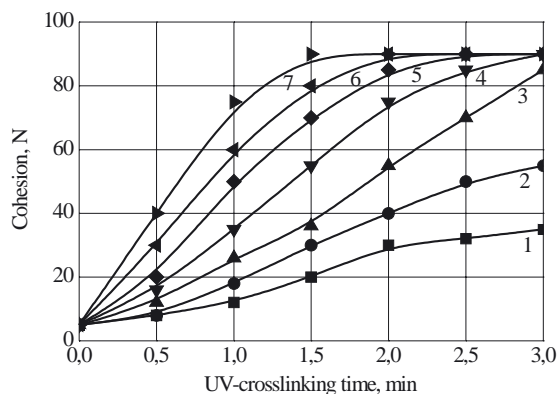


Fig. 4. Influence of the UV exposure time on cohesion (measured at 20 °C) of acrylic PSA obtained using photoinitiator content (in wt. %): 1 — 0.1, 2 — 0.2, 3 — 0.3, 4 — 0.5, 5 — 1.0, 6 — 1.5, 7 — 2.0

0.5 wt. % of copolymerizable photoinitiator VCMA has been sufficient to reach relatively high value (about 90 N) of cured acrylic PSA after 3 min of UV exposure. Increase in VCMA content let shorten curing time needed to reach the similar cohesion value (e.g. use of 2.0 wt. % of VCMA shortens curing time to 1.5 min).

#### CONCLUSIONS

The synthesized photoreactive acrylic pressure-sensitive adhesives containing VCMA incorporated into the

polymer chain are characterized by very good balance between adhesion and cohesion. Such PSA show excellent properties, leading to an interesting applications for the production of masking tapes, PVC sign and marking films. Unsaturated photoinitiators studied here are for more expensive than their conventional saturated counterparts, but they may offer advantages over the conventional photoinitiators, such as greater reactivity, caused probably by the positive inductive effect of the oxycarbonyloxy group. These unsaturated photoinitiators are innovative tailor-made solutions and can be competitive in the future.

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