ZBIGNIEW CZECH*), MAGDALENA URBALA

Institute of Organic Chemical Technology
Technical University of Szczecin
ul. Pułaskiego 10, 70-322 Szczecin, Poland

UV-crosslinked acrylic pressure-sensitive adhesive systems containing unsaturated ethers

Summary — A new class of acrylic pressure-sensitive adhesives (PSA), containing oxirane groups [formula (VII)], were developed. PSA systems obtained from butyl acrylate, glycidyl methacrylate and acrylic acid were modified with selected unsaturated allyl, vinyl or 1-propenyl ethers [formulas (I)—(VI)] in amounts of 1.0 to 5.0 wt. %. Then they were cured (using UV lamp) in the presence of 1.0 wt. % of cationic photoinitiator Irganocure 261 at room temperature and air atmosphere for 3 min. The tack, adhesion to glass and cohesion values of the cured PSA samples were measured. The effects of the type and concentration of unsaturated ether monomers used on these properties were evaluated. It was found that vinyl and 1-propenyl ethers were the most UV reactive crosslinking monomers while allyl ethers deteriorated PSA properties. The most advantageous values of adhesion, cohesion and tack were obtained for the samples containing 2 wt. % of vinyl or 1-propenyl ether. The results of investigations showed also that increase in crosslinking time, under UV radiation, caused faster increase in cohesion of the samples modified with vinyl ethers in comparison with those modified with 1-propenyl ones.

Key words: polyacrylic pressure-sensitive adhesives, unsaturated ethers, cationic initiated UV-crosslinking, tack, adhesion, cohesion.

POLIAKRYLANOWE KLEJE SAMOPRZYLEPNE ZAWIERAJĄCE ETERY NIENASYCONE SIECIOWANE ZA POMOCĄ PROMIENIOWANIA UV

Streszczenie — Opracowano nową klasę poliakrylanowych klejów samoprzylepnych (PSAs) zawierających grupy oksiranowe [wzór (VII)]. PSAs otrzymane z akrylanu butylu, metakrylanu glicydylu oraz kwasu akrylowego modyfikowano za pomocą wybranych nienasyconych eterów allilowych, winylowych i 1-propylenowych [wzory (I)—(VI)] w ilości od 1,0 do 5,0 % mas. i sieciowano w obecności 1,0 % mas. kationowego fotoinicjatora Irganocure 261 w temperaturze pokojowej, w atmosferze powietrza w czasie do 3 min używając lampy UV. Otrzymane próbki usieciowanych PSA badano mierząc ich kleistość (lepność, ang. *tack*) (rys. 1), adhezję do szkła (rys. 2) oraz kohezję (rys. 3) i oceniano wpływ na te właściwości rodzaju oraz ilości użytych nienasyconych monomerów eterowych. Stwierdzono, że najbardziej UV-reaktywnymi monomerami sieciującymi były etery winylowe i 1-propylowe, natomiast etery allilowe wpływały niekorzystnie na właściwości PSA. Najlepsze wartości adhezji, kohezji i kleistości uzyskano w przypadku próbek zawierających ok. 2 % mas. eterów winylowych i 1-propylenowych. Badania wykazały również, że wzrost czasu sieciowania za pomocą promieniowania UV powoduje szybszy wzrost kohezji próbek PSA modyfikowanych eterami winylowymi niż modyfikowanych eterami 1-propylenowymi (rys. 4).

Słowa kluczowe: poliakrylanowe kleje samoprzylepne, nienasycone etery, kationowe sieciowanie UV, kleistość, adhezja, kohezja.

The UV initiated crosslinking of pressure sensitive adhesives (PSA) is one of the most rapidly developing fields in the entire coating and self-adhesives industry. Industrial applications of photoreactive PSA have grown tremendously over the past decade. UV technology is well established in the market and allows the production of a wide range of UV-crosslinking PSAs with interesting features (Table 1). They are used in self-adhesive tapes, labels and protective films as well as in dermal dosage systems for pharmaceutical applications, in biomedical electrodes, the assembly of automotive parts, toys, electronic circuits and keyboards. The low toxicity, cheapness, speed, control and ease of formulation and operation are some of the main advantages of this technology [1—5].

In recent years, there have been many achievements in the synthesis and photochemical studies of photoini-

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*) Corresponding author; e-mail: psa_czech@wp.pl

tiators, monomers, prepolimers and PSA polymers' structures with more desirable properties, such as high reactivity in photocrosslinking process and high quality of polymer films obtained [6—10]. Acrylates are known to be among the most reactive monomers polymerizing by free radical mechanism. The final main properties of UV-crosslinked acrylic polymers depend primarily on the chemical structure of the functionalized chain segment. The acrylic PSA compositions can be UV-crosslinked by adding of unsaturated crosslinking agents that react with a reactive groups present in the polymer. The multifunctional vinyl, allyl and 1-propenyl ethers are very attractive cationic UV-crosslinking agents. The unsaturated ethers are electron rich olefins that undergo very fast and easy cationic photopolymerization. They can also be polymerized under radical conditions with acrylates and electron deficient olefins [11—13].

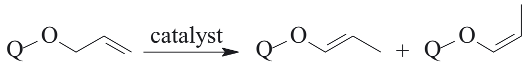
Table 1. European market of photoreactive resins and photoinitiators

Year	Turnover, mln USD	Turnover growth rate, %
1996	304.3	—
1997	327.6	7.6
1998	352.7	7.7
1999	381.0	8.0
2000	413.3	8.4
2001	445.7	7.8
2002	484.7	8.7
2003	523.9	8.1
2004	570.7	8.9
2005	617.6	8.2

The multifunctional allyl ethers are a well-known and potentially inexpensive class of monomers that are readily prepared by a variety of simple synthetic methods from readily available inexpensive starting materials by O-allylation of alcohols, diols and polyols by allyl halides under phase transfer catalysis conditions [eq. (1)] [14].

$$\mathrm{Y{-}(OH)_n + CH_2{=}CH{-}CH_2{-}X \xrightarrow{Bu_4N^+HSO_4^-;\ NaOH} (CH_2{=}CH{-}CH_2)_{n-a}{-}O{-}Y{-}(OH)_a} \qquad (1)$$

The vinyl and 1-propenyl ethers are, perhaps, the most reactive monomers yet prepared, easily undergoing cationic photopolymerization in the presence of conventional cationic initiators (Y^+) such as Lewis or Brönsted acids. The vinyl ethers derivatives are commercially available monomers for photocuring but their usual syntheses are inconvenient. Normally vinyl ethers do not homopolymerize under radical conditions, but they do react with acrylate radicals forming copolymers [11]. On the other hand, the mono-, di- and multifunctional 1-propenyloxy monomers ethers could be very reactive in radical and cationic polymerization processes initiated by UV irradiation, but they are not in mass production yet. These compounds could be easily and efficiently synthesized by the catalytical double-bond isomerization of appropriate allyl ethers in the presence of transition metals complexes (TMC). The example is a synthesis of multifunctional 1-propenyl ethers described by eq. (2).



(2)

Q = $\mathrm{HO(CH_2)_n}$-, $\mathrm{CH_2CH{=}CH{-}O{-}Y}$- (Y = $\mathrm{-CH_2-}$, $\mathrm{-(CH_2CH_2)_n-}$, $\mathrm{-CH_2CH{=}CHCH_2-}$), $\mathrm{Me_3Si}$-, $\mathrm{(CH_2{=}CHCH_2O)_3Si}$-,...,

TMC catalysts are usually based on Rh, Ru or Ir, but most popular of them are the phosphine ruthenium(II) complexes, *e.g.* $\mathrm{[RuClH(CO)(PPh_3)_3]}$, $\mathrm{[RuCl_2(PPh_3)_3]}$, $\mathrm{[RuH_2(PPh_3)_4]}$, $\mathrm{[RuH_2(CO)(PPh_3)_3]}$. Application of homogeneous ruthenium complexes as catalyst precursors let achieve quantitative yield and selectivity of reaction in mild and solventless conditions [15—18].

Cationic UV-crosslinking acrylic PSA shows excellent oxidation resistance [19], which allows working during the crosslinking process without an inert gas atmosphere, in the presence of an air.

In this publication, new cationic UV-crosslinked acrylic PSA systems including modeling the vinyl, allyl and 1-propenyl ethers as liquid crosslinking agents are described. The synthesized acrylic PSA containing pendant oxirane groups in the polymer chain and cationic photoinitiator have been used.

EXPERIMENTAL

Materials

Butyl acrylate (BA), and acrylic acid (AA) were available from BASF (Germany).

Glycidyl acrylate (GA) were purchased from Nitto (Japan).

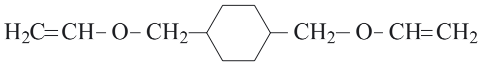
Triarylsulfonium salts with $\mathrm{SbF_6^-}$ anion (Irgacure 261) used as cationic photoinitiator was supplied by Ciba (Germany).

2,2'-azobis-(isobutyronitrile) (AIBN) used as initiator was supplied by TCI (Japan).

The vinyl ethers, *i.e.* divinyl ether of triethylene glycol [Rapi-Cure DVE-3, formula (I)] and 1,4-cyclohexanedimethanol divinyl ether [Rapi-Cure CHVE, formula (II)] are commercially available on the market from ISP (USA).

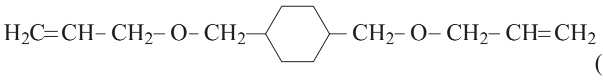
Diallyl ether of triethylene glycol [DAETG, formula (III)], 1,4-cyclohexanedimethanol diallyl ether [CHDAE, formula (IV)], di-1-propenyl ether of triethylene glycol [DPETG, formula (V)], and 1,4-cyclohexanedimethanol

$H_2C{=}CH{-}(O{-}CH_2{-}CH_2)_3{-}O{-}CH{=}CH_2$ (I)



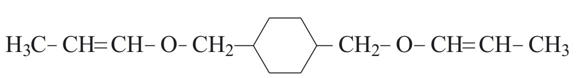
$H_2C{=}CH{-}O{-}CH_2{-}C_6H_{10}{-}CH_2{-}O{-}CH{=}CH_2$ (II)

$H_2C{=}CH{-}CH_2{-}(O{-}CH_2{-}CH_2)_3{-}O{-}CH_2{-}CH{=}CH_2$ (III)



$H_2C{=}CH{-}CH_2{-}O{-}CH_2{-}C_6H_{10}{-}CH_2{-}O{-}CH_2{-}CH{=}CH_2$ (IV)

$H_3C{-}CH{=}CH{-}(O{-}CH_2{-}CH_2)_3{-}O{-}CH{=}CH{-}CH_3$ (V)



$H_3C{-}CH{=}CH{-}O{-}CH_2{-}C_6H_{10}{-}CH_2{-}O{-}CH{=}CH{-}CH_3$ (VI)

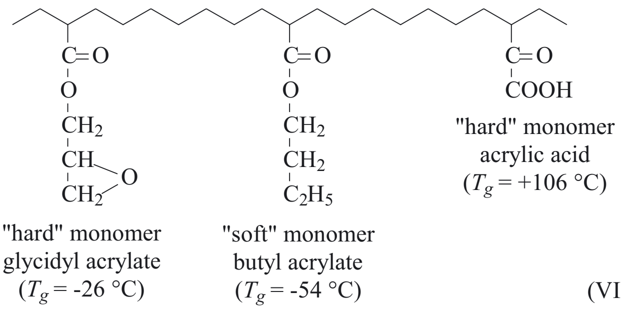
di-1-propenyl ether [CHDPE, formula (VI)] used as liquid crosslinking agents were prepared by the authors.

Synthesis of ethyl acetate-borne acrylic PSA

The acrylic PSA was synthesized from 80 wt. % of BA, 15 wt. % of GA and 5 wt. % of AA at boiling temperature of the solvent (ethyl acetate) in the presence of 0.1 wt. % of AIBN. Polymerization process was carried out for 6 h to reach 50 wt. % of solid content of acrylic polymer.

Modification, coating and UV-crosslinking of synthesized acrylic PSA

The synthesized acrylic PSA containing oxirane groups in the polymer chain [formula (VII)] was mixed with 1.0 wt. % of Irgacure 261, unsaturated vinyl, allyl or 1-propenyl ethers in concentrations between 1.0 to 5.0 wt. % in relation to the acrylic content, cast with knife coater on 36 μm polyester film Hostaphan RN from Hoechst (Germany) with coat weight of 60 g/m^2. Next, the compositions were cured within 3 min with an ultraviolet light (lamp U 350-M-I-DL from IST Company) with UV-A wavelength between 315 to 400 nm at constant UV dose of 300 mJ/cm^2. The UV-radiation was measured using an integrating radiometer UVIMAP^{TM} UM 365 L-S manufactured by Electronic Instrumentation & Technology, Inc. (USA).



(VII)

Methods of testing

The acrylic PSAs were tested by measuring such properties as: tack, peel adhesion (adhesion) and cohesion (shear strength). These properties were determined by standard AFERA (Association des Fabricants Europeens de Rubans Auto-Adhesifs) procedures. Exact details can be found in AFERA 4015 (tack), AFERA 4001 (peel adhesion) and AFERA 4012 (cohesion) or in [20].

DISCUSSION OF RESULTS

The most important properties of the photoreactive UV-cured acrylic PSAs such as tack, peel adhesion and cohesion can be controlled by the concentration of photoinitiator, the kind and amount of unsaturated ether (crosslinking agent), the UV dosage and UV-crosslinking time. In the technology of photocuring of polymer films (*e.g.* coatings, adhesives), it is necessary to find process settings that lead to balanced values of tack, adhesion and cohesion for the preferred PSA application. In the case of UV-crosslinked acrylic PSA, the ratio of tack and peel adhesion to shear strength can be varied within wide limits depending on UV radiation dose. The UV-dose can be controlled by adjusting the power of the lamps and/or the speed at which the adhesive is passed under the lamp [1].

Work in this study was focused on the effects of the kind and concentration of the unsaturated vinyl, allyl or 1-propenyl ethers as important crosslinking agents on the properties of synthesized PSA, particulary in order to reach very good adhesion to glass and high cohesion at room and higher temperatures.

Influence of the kind and concentration of the unsaturated ethers

The UV-crosslinking effect on tack of acrylic PSA caused by the unsaturated vinyl, allyl or 1-propenyl ethers using as internal crosslinking agents (ranging from 1 to 5 wt. %) is presented in Fig. 1. Tack was measured on glass after 3 min of UV-crosslinking time with UV dose 800 mJ/cm^2. It was established that the addition of small amounts vinyl ethers *i.e.* Rapi-Cure DVE-3, Rapi-Cure CHVE or 1-propenyl ethers *i.e.* DPETG and CHDPE increased the tack of UV-crosslinked acrylic PSAs (Fig. 1). The maxima of tack were observed for about 2.0 wt. % of the investigated cationic photoreactive crosslinking agents. The use of both allyl ethers *i.e.* DAETG and CHDAE decreased the tack values independently on their amounts.

Similarly to the tack measurements results, the small rise of adhesion values of PSAs with maximum for about

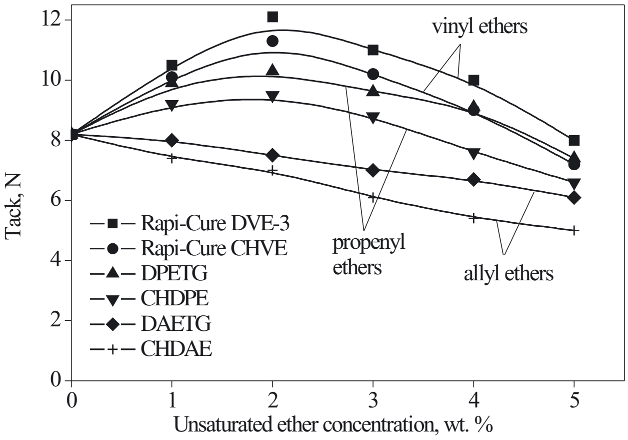


Fig. 1. Effects of unsaturated ether type and concentration on the tack of acrylic PSA

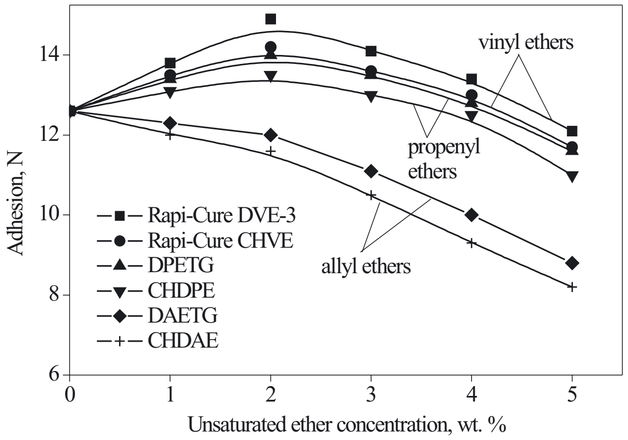


Fig. 2. Effects of unsaturated ether type and concentration on the adhesion of acrylic PSA

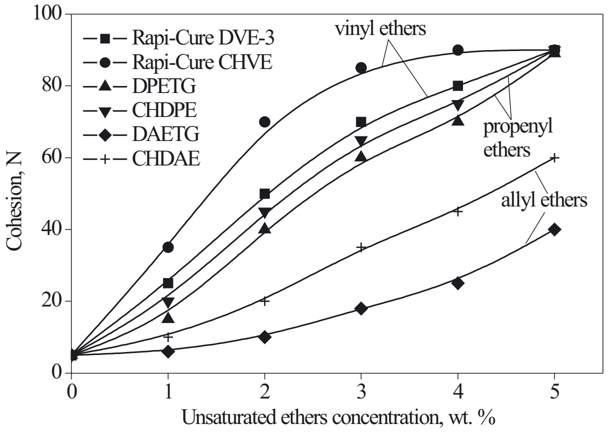


Fig. 3. Effects of unsaturated ether type and concentration on the cohesion of acrylic PSA

2.0 wt. % of vinyl or 1-propenyl ethers was observed (Fig. 2). The attempt to use the allyl ethers as crosslinking agents had failed, because increase in their concentrations caused decrease in adhesion.

The cohesion values of ethers-free PSAs, measured at temp. 20 °C, are about 0.5 N. As it is shown in Figure 3 the introduction of unsaturated ethers into acrylic PSAs improved the cohesion of UV-cured adhesive products in all cases. The PSAs cohesion values are proportional to the concentration of the unsaturated ethers. The best cohesion values were noticed for use of vinyl ethers, but especially Rapi-Cure CHVE. It is generally acknowledged that during the UV-curing, the elastomeric acrylic PSA chains containing oxirane groups react with each other to form chemical crosslinking. It is likely that after application of the photoreactive unsaturated ethers and UV-curing a very strong chemical 3-dimensional network at a certain stage is created.

For UV technology it is essential to define an operation window, where the acrylic PSA exhibits good tack, good adhesive properties and sufficient mechanical resistance. The combination of these main different properties in an acrylic PSA layer containing a photoreactive unsaturated ether can be achieved with vinyl or 1-propenyl ethers in an amount of about 2.0 wt. %.

Influence of the UV-crosslinking time

The extent of crosslinking is dependent also on the UV-crosslinking time and the amounts of radiant energy applied to the adhesive film after it has been coated. Further study on photoreactive acrylic PSAs containing the best selected unsaturated ethers in concentration about 2.0 wt. % were performed with UV-crosslinking times between 30 s and 3 min at constant UV lamp dose of 800 mJ/cm^2. The effect of UV-crosslinking time on the cohesion of PSA system modified with vinyl or 1-propenyl ethers, measured at 20 °C, is shown in Fig. 4. Similarly to previous results the used vinyl ethers are more reactive as crosslinking agents than the 1-propenyl ether. The result of higher reactivity is more rapid increase in cohesion of the samples obtained with increase in crosslinking time. An excellent cohesion value, 90 N at 20 °C was observed after 2 min of UV-crosslinking time for sample prepared using 2.0 wt. % of Rapi-Cure CHVE.

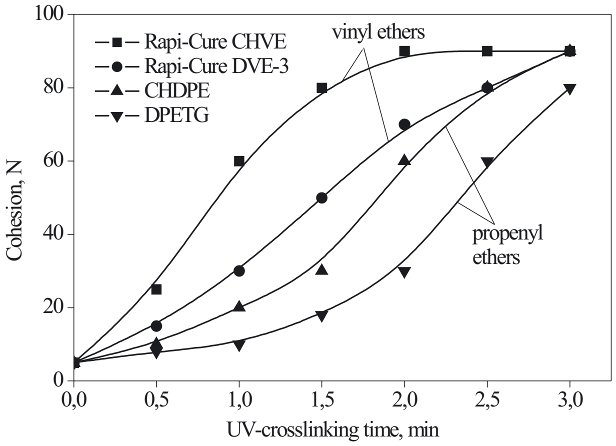


Fig. 4. Effects of UV-crosslinking time and unsaturated ether type on cohesion of acrylic PSA

CONCLUSIONS

From the investigations presented, it would be appear that such unsaturated crosslinking agents as vinyl or 1-propenyl ethers show the requisite reactivity necessary and useful in such high crosslinking speed applications as coatings and production of cationic UV-crosslinked acrylic PSAs. In the tested acrylic PSAs the photoreactivity of the evaluated vinyl and 1-propenyl ethers was superior to allyl derivatives. This kind of the developed photoreactive acrylic PSAs can be used in wide variety of materials including glass, ceramics, poly(vinyl chloride) or ethylene-propylene rubber.

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