

Zbigniew Czech¹*, Urszula Głuch¹, Arkadiusz Kowalski¹, Joanna Ortyl²

UV-crosslinkable s-triazine containing acrylic pressure-sensitive adhesives

The present report is related to synthesis of UV-crosslinkable acrylic pressure-sensitive adhesives (PSA) by solvent-borne polymerization. New synthesized photoreactive acrylic PSA have been tested according main properties of self-adhesives such as tack, peel adhesion and shear strength.

Key words: acrylic PSA, UV-crosslinkable, polymerization, s-triazine, photoreactivity, tack, peel adhesion, shear strength.

Sieciowalne promieniowaniem UV samoprzylepne kleje poliakrylanowe zawierające s-triazyny

Przedstawiony artykuł opisuje syntezę sieciowalnych promieniowaniem UV poliakrylanowych klejów samoprzylepnych zawierających s-triazyny. Otrzymane w wyniku syntezy nowe fotoreaktywne poliakrylanowe kleje samoprzylepne zostały zbadane pod kątem swoich podstawowych właściwości, jak lepność (tack), adhezja oraz kohezja.

Słowa kluczowe: poliakrylanowe kleje samoprzylepne, sieciowanie UV, polimeryzacja, s-triazyny, fotoreaktywność, lepność, adhezja, kohezja.

1. Introduction

Acrylic pressure-sensitive adhesives are standing used for manufacturing of wide range self-adhesive products, such as mounting tapes, labels, sign and marking films, protective films, masking and splicing tapes, and various medical products, such as pads, OP-tapes and biomedical electrodes [1]. The properties, which are essential in characterizing the nature of PSAs comprise: tack (initial adhesion), peel adhesion (adhesion), and shear strength (cohesion). The first measures the adhe-

sive's ability to adhere quickly, the second its ability to resist removal through peeling, and the third its ability to hold in position when shear forces are applied [2].

Industrial applications of UV-crosslinkable PSA and self-adhesive materials have grown tremendously over the past decade. An entire industry has evolved based on the existence of chemicals, which respond to UV radiation. The growing success of UV crosslinking technologies in a wide variety of industrial products and processes can be attributed to the productivity and environmental benefits that result from such technologies. UV

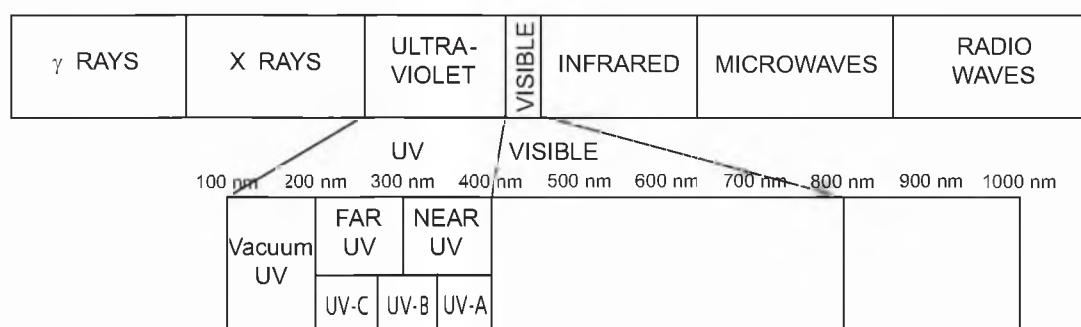


Figure 1. Electromagnetic spectrum
Rysunek 1. Widmo fal elektromagnetycznych

¹ West Pomeranian University of Technology, Faculty of Chemical Engineering, Pułaskiego 10, 70-322 Szczecin.

² Cracow University of Technology, Institute of Organic Chemistry and Technology, Warszawska 24, 31-155 Kraków.

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

technology is well established in the market and allows the production of a wide range of UV-crosslinkable pressure-sensitive adhesives with interesting features. The balance between adhesive and cohesive strengths within the crosslinked coatings is critical for the performance of

the UV-PSA. The combinations of photoinitiators with UV-crosslinkable adhesives enable the manufacturing of films having different adhesion/cohesion properties and offers novel opportunities to develop innovative tapes with new unique features [3-4].

The UV radiation spectrum used for the crosslinking of pressure-sensitive adhesives comprises the wavelengths between 100 and 400 nm as shown in Fig. 1 is practically subdivided into UV-A (315–400 nm), UV-B (280–315 nm) and UV-C (200–280 nm). For the manufacturing of radiation crosslinked PSA acrylics the UV-A band width between 315 and 400 nm is used. A shorter wavelength can show the same deterioration to pressure-sensitive adhesives as would occur from exposure to sunlight and so should be screened out.

The UV-crosslinking of various photoreactive adhesive layers is based on the photoinitiation of radical and cationic crosslinking reaction. The ultraviolet crosslinking technique allows for the use of a photoinitiator to be added to the pressure-sensitive adhesive system. The photoinitiator is therefore one of the key components in a UV-crosslinking, including its chemical nature and the amount. As previously mentioned, a photoinitiator is one of the important and necessary constituents in UV crosslinking of pressure-sensitive adhesives [5-6]. For this reason, the activity of a photoinitiator is one of the more important properties that must be considered when choosing a photoinitiator, due to the important advantages of these adhesives. The concentration depends on the type of photoinitiator, but it is typically 1 to 3% of the weight of the polymer. This photoinitiator breaks down under the UV radiation to yield free radicals, which act as the trigger to the crosslinking mechanism. The selection of a particular photoinitiator for use in a composition is generally made on the basis of the solubility, rate of reaction, activating wavelength, and intended use of the photoinitiator [7]. In recent years, there have been many new developments in the synthesis and photochemical studies of novel photoinitiator molecules with more desirable properties such as higher activity coupled with greater speed and low migration rate to the surface of the cured coating, in order to ameliorate shear strength and minimize toxicity where food contact is important [8-11].

1.1. s-Triazines as photosensitive crosslinking agents

For some pressure-sensitive adhesive applications crosslinking is also required, particularly where it is desired to increase the shear strength of the adhesive without unduly affecting its compliance. This can be achieved using trichloromethyl-s-triazines, which can be used as photoinitiator and photocrosslinker that have absorption maxima in the UV-A area at the wavelength of about 330 to 380 nm [12]. UV-sensitive halomethyl-s-triazines have been known since the late

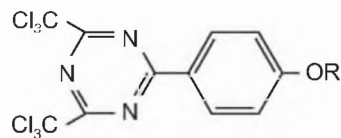


Figure 2. Bis(chloromethyl)-s-triazine
Rysunek 2. Dichlorometylo-s-triazyna

1960's [13]. The aryl-trichloromethyl-s-triazines combine high efficiency as photoacid generators and free radical initiators with facile synthesis. They may be obtained in a one-step reaction by cotrimerization of the corresponding aromatic nitrile with two moieties of trichloroacetonitrile in the presence of hydrogen chloride and Friedel-Crafts catalysts like $AlBr_3$, $AlCl_3$ and BF_3 . This group of UV activating crosslinkers has an absorption maximum at a wavelength between 330 and 380 nm. Important classes of photocrosslinking agents are chromophoric substituted bis(chloromethyl)-s-triazines (Fig. 2) [14].

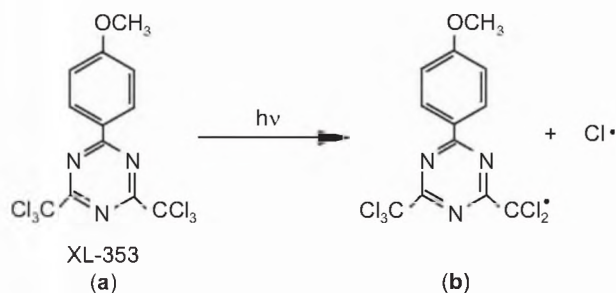


Figure 3. Mechanism of s-triazine photoreactive crosslinker photolysis

Rysunek 3. Mechanizm fotolizy s-triazynowego fotoreaktywnego środka sieciującego

The efficiency of bis-trichloromethyl-s-triazines as photoinitiators in radically initiated photocrosslinking systems, as well as photoacid generators, may be explained and described by the mechanism outlined in Fig. 3. Electronically excited fragments (a) suffer homolytically transformation to the radical (b) and chlorine radical.

2. Experimental

The UV-crosslinking investigations were conducted using the pressure-sensitive adhesives synthesized from 65 wt.% of 2-ethylhexyl acrylate, 30 wt.% of methyl acrylate and 5 wt.% of acrylic acid mixture in organic solvent ethyl acetate. For the polymerization 0.1 wt.% of thermal initiator 2,2'-azo-bis-diisobutyronitrile (AIBN) was used. The content of s-triazine photoreactive crosslinkers amounted to 0.2–2.0 wt.% with respect to the used initial monomers.

The polymerization process was carried out under the following conditions:

- addition of the blend of monomers containing AIBN into ethyl acetate before the polymerization (amount of reactor charge) ······ 30 wt. %
- dosage time of residual monomers with residual AIBN ······ 3 h
- time of post-reaction ······ 5 h
- polymer content ······ 50 wt. %
- dilution step ······ with isopropanol

After dilution with isopropanol, the synthesized solvent-borne acrylic pressure-sensitive adhesive was characterized by the following main parameters:

- amount of solid materials ······ 45 wt. %
- viscosity ······ 5.3 Pa·s
- weight average molecular weight \bar{M}_w ······ 468 000
- number average molecular weight \bar{M}_n ······ 236 000
- polydispersity $P_d = \bar{M}_w/\bar{M}_n$ ······ 1,98

The viscosity of the investigated solvent-borne acrylics pressure-sensitive adhesives was determined with a Rheomat RM 189 from Rheometric Scientific, with spindle No 3 at 23°C.

The amount of solid materials was found according to DIN EN 12092, the residual of monomers were measured with gas chromatograph Unicam 610, J&W DB-1 column, FID detector and integrator Unicam 4815.

The molecular weight studies were performed in tetrahydrofuran with a liquid chromatograph LaChrom system: RI Detector L-7490 and LaChrom UV Detector L-7400 from Merck-Hitachi, equipped with a PLgel 10⁶Å column from Hewlett-Packard.

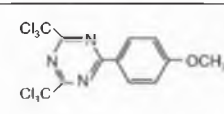
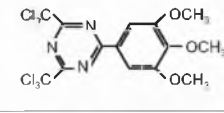
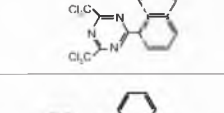
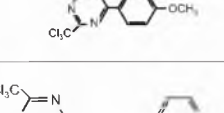
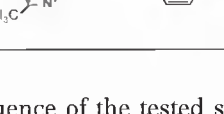
The pressure-sensitive adhesive layers coated on 25 µm thick polyester film Hostaphan RN from Kalle Chemie (Germany) must be dry, free from polymerization solvents and residual monomers. It is the aim to examine the performance of the tested crosslinked adhesives with a constant temperature. The solvent-borne acrylics PSA coated on polyester film were dried for 10 min at 105°C. The base coating weight of the adhesive layer covering the foil was about 60 g/m². The dried PSA layers were crosslink using UV radiation from UV lamp Aktiprint-mini-18-2 from Technigraf (Germany) and UV-dose was measured using UV integrator from the same company. The dried UV-crosslinked PSA layer was covered with dehesive silicone paper 95 g/m² from Laufenberg (Germany). Before the test, the adhesive-coated strips were stored for 7 days at room temperature and 50 % relative humidity. 3 samples were tested and the given value of tack, peel adhesion and shear strength was the arithmetic mean of the results obtained.

The experiments were conducted in order to study of UV-initiated crosslinking process of photoreactive acrylic pressure-sensitive adhesives contained s-triazine on their main important properties, such as tack, peel adhesion and shear strength. These properties of UV-crosslinked PSA layers were tested according to international norm A.F.E.R.A. 4015 (tack), 4001 (peel adhesion) and 4012 (shear strength).

Examples of examined s-triazine photoreactive crosslinking agents for acrylic pressure-sensitive adhesives are presented in Table 1.

Table 1. Investigated s-triazine photoreactive crosslinkers

Tabela 1. Badane s-triazynowe fotoreaktywne środki sieciujące

s-Triazine	Chemical formula	Chemical name
XL-353		2,4-bis-trichloromethyl-6(4-methoxyphenyl)-s-triazine
BMP-s-T		2,4-bis-trichloromethyl-6(3,4,5-trimethoxyphenyl)-s-triazine
BN-s-T		2,4-bis-trichloromethyl-6(1-naphthyl)-s-triazine
BMN-s-T		2,4-bis-trichloromethyl-6[1-(4-methoxynaphthyl)]-s-triazine
MOST		2,4-bis-(trichloromethyl)-6-p-methoxystyryl-s-triazine

The influence of the tested s-triazine photoreactive crosslinking agents (ranging from about 0.2 to 3.0 wt. % according to acrylic polymer amount) on solvent borne acrylic pressure-sensitive adhesive properties, such as tack, peel adhesion and shear strength, at 100 mJ/cm² UV dose after 3 min UV-crosslinking time is presented in Figs. 4-6.

It was unequivocally shown (Fig. 4) that the tested photoreactive s-triazine crosslinkers in amounts up to 1.4 wt. % BMP-s-T and XL-353, and up to 1.2 wt. %

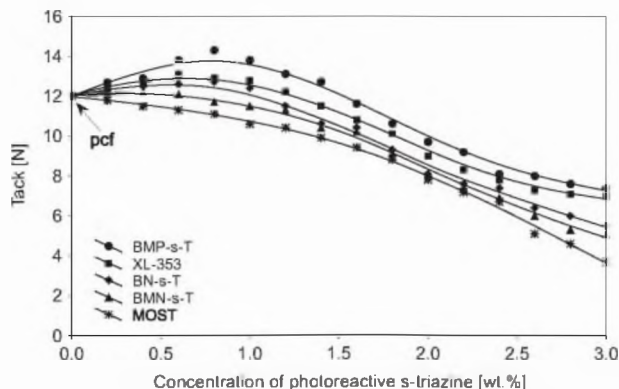


Figure 4. Tack of UV-crosslinked acrylic PSA as a function of s-triazine photoinitiator concentration

Rysunek 4. Lepność sieciowanych UV akrylowych PSA w funkcji stężenia fotoinicjatora s-triazynowego

BN-s-T and BMN-s-T, increase the tack of UV-crosslinked acrylic pressure-sensitive adhesives. The maxima of tack were observed for about 0.8 wt.% of the aforementioned photoreactive crosslinking agents. The use of MOST influences the tack values negatively. Perhaps the free radicals yielded after UV exposure is converted into a polymer chain through the double bonds in the MOST structure, which is possible due to the short distance between the neighboring polymer chains.

The peel adhesion results from the Fig. 5 show that the photoreactive s-triazine crosslinkers increase the peel adhesion of UV-crosslinked acrylic PSAs from about 10 N to more than 14 N for BMP-s-T. Similarly to the tack measurements, the peel adhesion maxima were noticed for about 0.8 wt.% of the examined s-triazine photoinitiators. The use of MOST failed.

The shear strength of acrylic PSA after UV-crosslinking is proportional to the concentration of the photoreactive s-triazines (Fig. 6). During the UV-curing

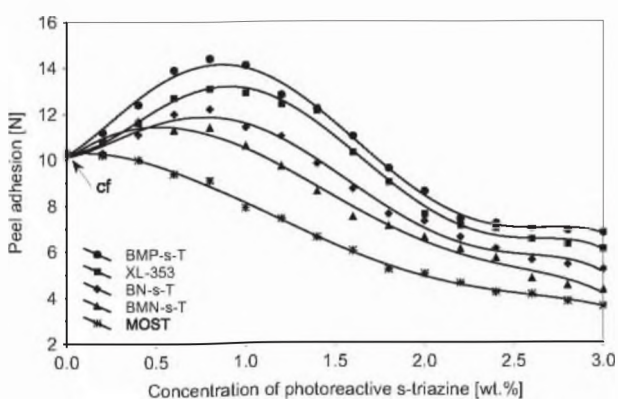


Figure 5. Peel adhesion of UV-crosslinked acrylic PSA as a function of the s-triazine photoinitiator concentration
Rysunek 5. Adhezja sieciowanych UV akrylanowych PSA w funkcji stężenia fotoinicjatora s-triazynowego

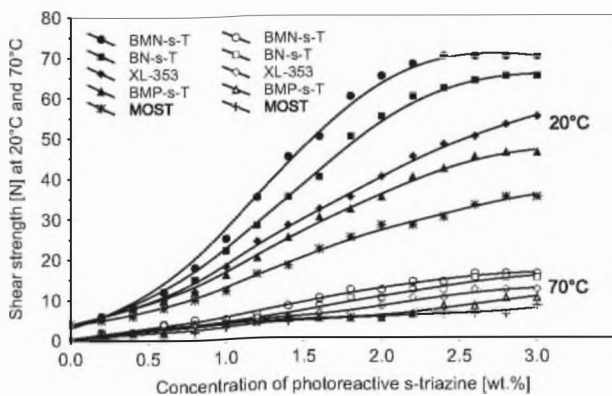


Figure 6. Shear strength of a UV-crosslinked acrylic PSA as a function of the s-triazine photoinitiator concentration

Rysunek 6. Kohezja sieciowanych UV akrylanowych PSA w funkcji stężenia fotoinicjatora s-triazynowego

reaction, the elastomeric acrylic PSA chains react with each other to form chemical crosslinks. At a certain stage, after application of the photoreactive s-triazine crosslinker BMN-s-T, a very strong chemical 3-dimensional network is created. For all tested s-triazine derivatives, the measured temperature resistance (shear strength at 70°C) was on the low level.

For UV technology it is essential to define an operating 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 s-triazine crosslinker can be achieved with BN-s-T, in an amount ranging between 0,6 and 1.4 wt.% according to polymer amount.

The extent of crosslinking is dependent upon the UV-crosslinking time and upon the energy imparted to the PSA layer, which in UV curing is a function of the UV lamp power. The other investigations with UV-crosslinkable acrylic PSAs containing the best selected photoreactive s-triazine crosslinker, BN-s-T, in concentrations between 0.6 to 1.4 wt.%, were conducted by UV-crosslinking times between 30 s and 3 min and by using a UV lamp dose between 50 and 250 mJ/cm². The experimental results of these examinations are presented in Figs. 7–12.

At relatively high concentrations (1.2 and 1.4 wt.%) of BN-s-T, the UV-crosslinked acrylic PSAs become harder and the tack sinks (Fig. 7). As a result of these

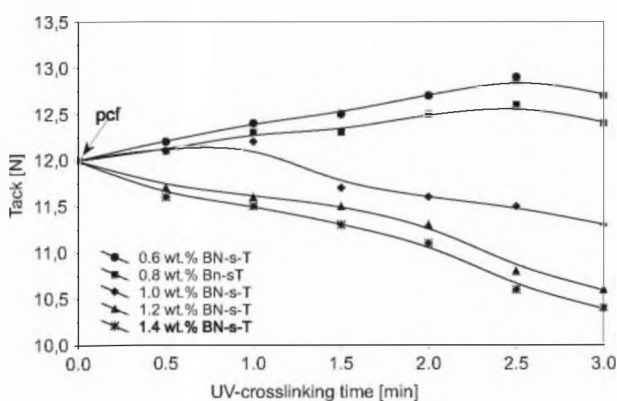


Figure 7. Tack of UV-crosslinked acrylic PSA as a function of UV-crosslinking time for various amounts of the photoreactive s-triazine (BN-s-T)

Rysunek 7. Lepność sieciowanych UV akrylanowych PSA w funkcji czasu sieciowania dla różnych ilości fotoreaktywnej s-triazyny (BN-s-T)

findings, the highest tack value was achieved with 0.6 wt.% photoreactive crosslinker BN-s-T after a UV-exposure of 3 min.

Referring to Fig. 8 above, the peel adhesion increased with irradiation time and was the highest for 0.8 wt.% photoreactive s-triazine crosslinker BN-s-T.

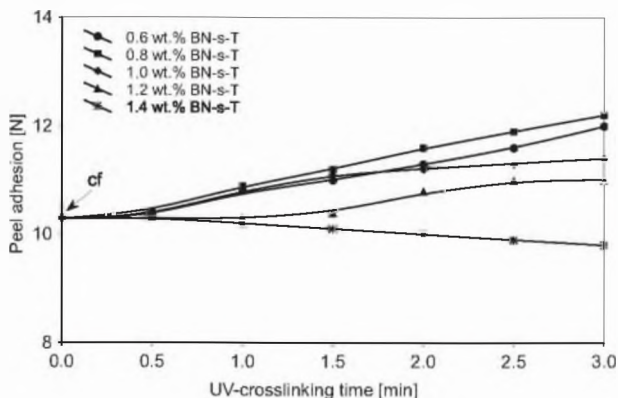


Figure 8. Peel adhesion of UV-crosslinked acrylic PSA as a function of the UV-crosslinking time for various amounts of the photoreactive s-triazine (BN-s-T)

Rysunek 8. Adhezja sieciowanych UV akrylanowych PSA w funkcji czasu sieciowania dla różnych ilości fotoreaktywnej s-triazyny (BN-s-T)

The use of the selected photoreactive s-triazine crosslinker BN-s-T in increased amounts does not yield satisfactory shear strength values, measured at 70°C, after the relatively long UV-crosslinking time of 3 min (Fig. 9). The noticed shear strength at 20°C was of a similar level to the obtained by the use of multifunctional hydro-

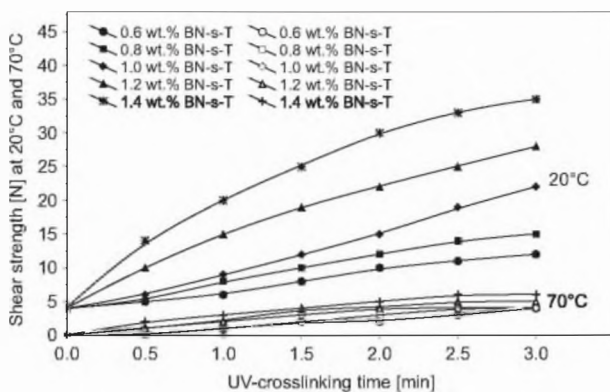


Figure 9. Shear strength of UV-crosslinked acrylic PSA as a function of UV-crosslinking time for various amounts of the photoreactive s-triazine (BN-s-T)

Rysunek 9. Kohezja sieciowanych UV akrylanowych PSA w funkcji czasu sieciowania dla różnych ilości fotoreaktywnej s-triazyny (BN-s-T)

gen atom abstracting photoinitiators. The increase of UV-crosslinking time from 1 min to 3 min allows an increase of the shear strength at room temperature by about 30%.

The effect of varying the UV dose on the tack of UV-crosslinked acrylic adhesives is demonstrated with reference to a standard acrylic PSA without s-triazine photoinitiators (Fig. 10). With the increase of the UV

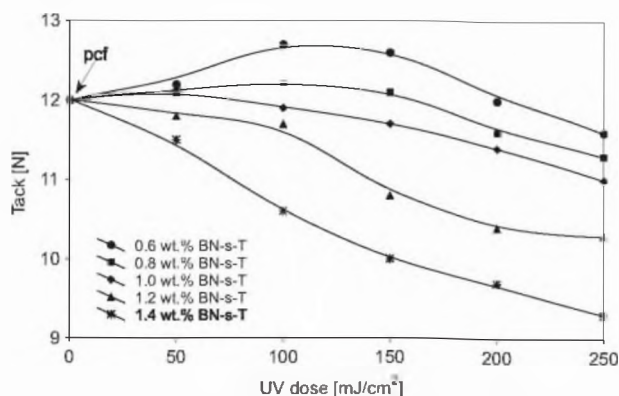


Figure 10. Tack of UV-crosslinked acrylic PSA as a function of UV dose for various amounts of the photoreactive s-triazine (BN-s-T)

Rysunek 10. Lepność sieciowanych UV akrylanowych PSA w funkcji dawki promieniowania UV dla różnych ilości fotoreaktywnej s-triazyny (BN-s-T)

dose to 250 mJ/cm², the tack of s-triazine acrylic adhesive containing 1.2 and 1.4 wt.% of BN-s-T decreases. The tack maximum was found for 0.6 wt.% BN-s-T and 100 mJ/cm² UV dose.

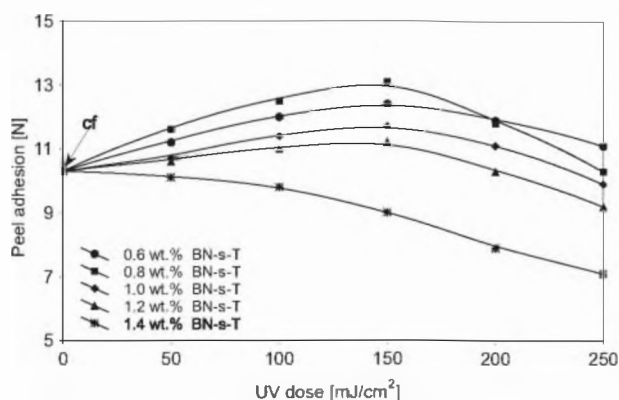


Figure 11. Peel adhesion of UV-crosslinked acrylic PSA as a function of UV dose for various amounts of the photoreactive s-triazine (BN-s-T)

Rysunek 11. Adhezja sieciowanych UV akrylanowych PSA w funkcji dawki promieniowania UV dla różnych ilości fotoreaktywnej s-triazyny (BN-s-T)

The highest peel adhesion value was indicated for 0.8 wt.% BN-s-T at 150 mJ/cm² UV radiation (Fig. 11). After application of this UV power, the investigated peel adhesion of UV-crosslinked pressure-sensitive acrylic adhesives decreases.

The shear strength results at 20°C show that the cohesion of UV-crosslinked acrylic PSAs (Fig. 12) is proportional to the amount of the photoreactive crosslinker BN-s-T used and to the UV dose. The achieved cohesion values at 20°C were similar, or slightly better to those

obtained in the case of multifunctional H-abstractors. The cohesion at 70°C was on a very low level.

In conclusion, these photosensitive compounds, although very effective for use in the photocrosslinking of pressure-sensitive adhesives and amelio-

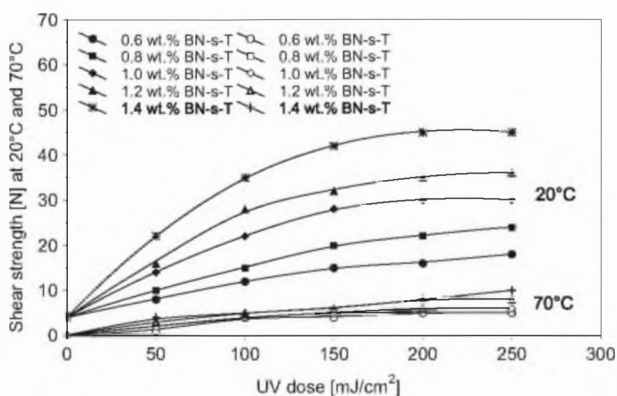


Figure 12. Shear strength of a UV-crosslinked acrylic PSA as a function of UV dose for various amounts of the photoreactive s-triazine (BN-s-T)

Rysunek 12. Kohezja sieciowanych UV akrylanowych PSA w funkcji dawki promieniowania UV dla różnych ilości fotoreaktywnej s-triazyny (BN-s-T)

rating the adhesive properties (tack and peel adhesion) liberate hydrogen chloride (Fig. 3) as by-product (following hydrogen abstraction by chlorine radicals which are responsible for initiating the crosslinking). Hydrogen chloride characterized by its pungent odor acts as a good oxidizing agent and can convert numerous metals to their metal chlorides. HCl gas getting in contact with moist solvents forms hydrochloric acid droplets in the water vapor atmosphere of the surrounding air. This provokes corrosion of the dryer and coating equipment. From the large variety of examined photoreactive s-triazine crosslinking agents, the highest shear strength level was noticed for BMP-s-T; and the best balance of properties of tack, peel adhesion and shear strength for BN-s-T.

3. Outlook

The crosslinking process of photoreactive acrylic pressure-sensitive adhesives has recently attracted considerable attention, due to their practical and potential application in various industrial branches to comprehensive self-adhesive technical and medical products. A wide variety of different photoreactive crosslinking agents based on s-triazine and their influence on the most important properties of acrylic PSAs, such as tack, peel adhesion and shear strength have been investigated. Through these investigations, a better understanding was achieved of the ameliorating of acrylic pressure-sensitive adhesive, such as tack, peel adhesion and shear strength. Chromophore-substituted trihalomethyltriazine compounds are preferred as photoreactive crosslinking agents for the UV-crosslinked coating of acrylic pressure-sensitive adhesives characterized by improved tack and peel adhesion, and with moderate cohesion at room temperature. These types of photoreactive acrylic PSA containing s-triazine can be used for manufacturing of wide range of self-adhesive materials like labels, sign and marking films and protective films.

References

1. Benedeck I., „Developments in Pressure-Sensitive Products”, Taylor & Francis a CRC Press Book, 2006.
2. Wicks Z., Jones F., Pappas S., Wicks D., „Organic Coatings”, A John Wiley & Sons Inc., New Jersey, 2007.
3. Matijasic C., *Adhes. Age* 2002, **12**, 29-32.
4. Bisges M., *Adhes. Age* 2002, **11**, 34.
5. Czech Z., Milker R., *Farbe und Lack* 2004, **110**, 18-20.
6. Czech Z., *Polimery*, 2003, **XLVIII**, 375-377.
7. Czech Z., Butwin A., „Fotoinitiatoren und ihre Schrumpfwirkung”, *Adhäsion Kleben & Dichten* 2009, **3**, 28-34.
8. Czech Z., Patent DE 44 33 290, 1994, Lohmann.
9. Czech Z., Patent DE 44 47 615, 1994, Lohmann.
10. Czech Z., Patent DE 195 01 025, 1995, Lohmann.
11. Czech Z., Patent DE 195 01 024, 1995, Lohmann.
12. Vesley G., F., Patent US, 4 330 590, 1982, 3M.
13. Vesley G., F., Patent WO 81/02262, 1982, 3M.
14. Vesley G., WO 93/13149, 1992, 3M.