

Photoreactive S-Triazine as Crosslinking Agents for UV-Crosslinkable Acrylic Pressure-Sensitive Adhesives

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ABSTRACT: The UV-crosslinking as an established technology has been used in many industrial manufacturing processes. New application and technical specifications of UV-crosslinking lead to continuous development of tailor-made photoinitiators which can efficiently meet specific requirements. A new class of radical reactive photoinitiators

based on s-triazine has been used for crosslinking of acrylic pressure-sensitive adhesives containing double bonds. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3621–3627, 2011

Key words: UV-photoinitiators; s-triazine derivative; polymerization

INTRODUCTION

The UV-initiated crosslinking process is the fundamental of important in advanced technologies, since it is one of the most efficient methods capable to achieve fast and extensive crosslinking of multifunctional oligomers and monomers. Highly photoreactive systems are crosslinked within a fraction of a second exposure to intense UV radiation or laser beams, transforming the liquid resin into a strongly crosslinked solid polymer without the need of additional heat.¹

Industrial applications of UV crosslinkable pressure-sensitive adhesive (PSA) materials have been grown tremendously over the past decade. An entire industry has evolved based on the existence of compounds, which respond to UV radiation. The successive growth of UV crosslinking technologies in a wide variety of industrial products and processes can attribute to the productivity and environmental benefits that result from such technologies.

The UV technology is well established in the market and can be applied to 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 their performance. The combination of patterns with UV-crosslinkable pressure-sensitive adhesives enables the manufacturing of films having areas with different adhesion/cohe-

sion properties and offers novel opportunities to develop innovative tapes with new unique features.^{2,3}

To improve further the performances of these UV-crosslinkable PSAs, pattern crosslinking as a new technology makes it possible to introduce different levels of crosslinking within the same adhesive coating. It results in combination of high cohesion and adhesion areas in the pressure-sensitive adhesive film. To get optimal pressure-sensitive performances with UV-crosslinkable adhesives, it is necessary to find process settings that lead to balanced values of tack, peel, and shear resistance for the aimed application.^{4–6}

The UV-crosslinking of various coatings is based on the photoinitiation of radical and cationic crosslinking reaction. The ultraviolet crosslinking technique is 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, and the outcome of polymerization is critically dependent on the type of the photoinitiator, including its chemical structure and concentration. As it was previously mentioned, a photoinitiator is one of the important and inevitable components in UV crosslinking of pressure-sensitive adhesives.^{7,8} For this reason, the activity of a photoinitiator is one of the more important properties due the important advantages of these adhesives and it must be considered when choosing a photoinitiator.

This group of UV activating crosslinkers known as photoreactive crosslinking agents has a maximum absorption at a wavelength between 330 and 380 nm. Important classes of photocrosslinking agents are chromophoric-substituted bis-(chloromethyl)-s-triazines,⁹ which function simultaneously as photoinitiators and photocrosslinkers (Chart 1).

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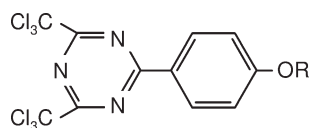


Chart 1 Bis-(chloromethyl)-s-triazine.

For some pressure-sensitive adhesive applications, crosslinking is also required, particularly where it is desired to increase the cohesive strength of the adhesive without unduly affecting its compliance. This can be achieved by using bis-(trichloromethyl)-s-triazines, which act simultaneously as photoinitiator and photocrosslinker.

Light-sensitive halomethyl-s-triazines have been known since the late 1960s.¹⁰ Aryl-trichloromethyl-s-triazines combine with high efficiency as photoacid generators and free radical initiators with facile synthesis.

It is well known that trichloromethyl-substituted s-triazines, such as 2,4,6-tris-(trichloromethyl)-s-triazine undergo a multiple fragmentation upon irradiation with UV light.¹¹ The primary photoproducts are not radicals but dissociate into radicals in a second thermal step as shown in Scheme 1.

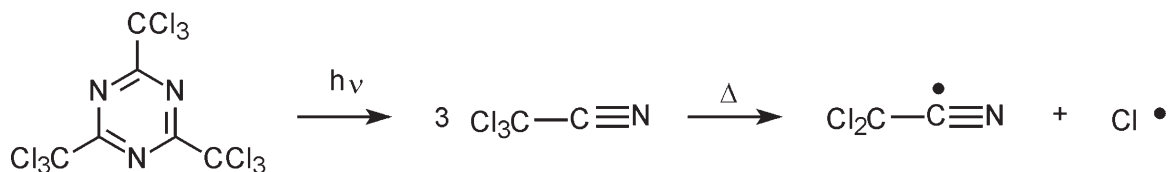
Direct fragmentation of carbon-chloride bond in the triazine derivative is the major photochemical pathway for radical formation.¹²

Among few examples of UV or near visible photoinitiators, the substituted bis-(trichloromethyl)-s-triazine derivatives are widely mentioned in the patent literature, alone or in the presence of the sensitizers or/and co-initiators, such as titanocene, peroxide/amine, or mercaptan.¹³⁻¹⁵

The most important application of trichloromethyl-substituted triazines is also combinations with various types of dyes as sensitizers. For example, high-speed photoinitiating systems sensitive to a visible light were developed on the basis of initiating systems, using cyanine or merocyanine dyes or 3,3'-carbonyl(coumarine) derivatives.¹⁶⁻¹⁸

EXPERIMENTAL PART

The following experiments were carried out to study the influence of different photoreactive crosslinking agents based on s-triazine on the main performance of solvent-borne acrylic pressure-sensitive adhesives,



Scheme 1 Free radicals formation from s-triazine after irradiation with UV light.

such as tack, peel adhesion (adhesion), shear strength (cohesion), and shrinkage.

The influence of the crosslinking agents or crosslinking methods is usually determined in relation to the reaction time and to the concentration versus adhesion properties, considering the properties, such as tack, adhesion, cohesion, and shrinkage. The three of the first properties were determined by standard A.F.E.R.A. (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 (shear strength). Administrative address: 60, rue Auber-94408 Vitry Sur Seine Cedex, France.

The coating weight (thickness of the layer) of dry pressure-sensitive adhesives after the removal of the organic solvent influences essentially their tack, peel adhesion, and shear strength. The base weight of the adhesive layer covering the polyester foil was 60 g/m².

The viscosity of the investigated solvent-borne acrylics pressure-sensitive adhesives was determined by a Rheomat RM 189 (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 chromatography (Unicam 610, J and W DB-1 column, FID detector and integrator Unicam 4815).

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

The evaluated photoreactive UV-crosslinked pressure-sensitive adhesives were cured with a ultraviolet light lamp U 350M-I-DL from IST Company with a UV-A wavelength between 315 and 380 nm.

The UV-exposure can be measured using an integrating radiometer (Dynachem™ Model 500, available from Dynachem Corp., 2631 Michelle Drive, Tustin, CA 92680).

RESULTS AND DISCUSSION

Basic acrylic pressure-sensitive adhesive (PSA)

All starting materials such as acrylate monomers, solvent, and AIBN were technical grade and were used without further purification unless otherwise noted.

TABLE I
Investigated *s*-triazine Photoreactive Crosslinkers

Photoinitiator	Chemical formula	Chemical name
XL-353		2,4-Bis-(trichloromethyl)-6-(4-methoxyphenyl)- <i>s</i> -triazine
BMP-s-T		2,4-Bis-(trichloromethyl)-6-(3,4,5-tri-methoxyphenyl)- <i>s</i> -triazine
BN-s-T		2,4-Bis-(trichloromethyl)-6-(1-naphthyl)- <i>s</i> -triazine
BMN-s-T		2,4-Bis-(trichloromethyl)-6-[1-(4-methoxynaphthyl)]- <i>s</i> -triazine
MOST		2,4-Bis-(trichloromethyl)-6-(<i>p</i> -methoxystyryl)- <i>s</i> -triazine

Other photoreactive crosslinking agents were synthesized in the laboratory scale with about 98% of purity.

The following experiments were conducted using standard solvent-borne acrylic PSA synthesized from 61.7 wt % of 2-ethylhexyl acrylate, 33 wt % of methyl acrylate, 5 wt % of acrylic acid, and 0.3 wt % 1,6-hexanedioldiacrylate in ethyl acetate as a solvent at the boiling point temperature about 77°C. 2,2'-Azo-bisdiisobutyronitrile (AIBN) in the amount of 0.1 wt % was used as the thermal initiator to start radical polymerization.

The polymerization process was conducted under the following conditions:

- Addition of monomers blended with AIBN into ethyl acetate before the polymerization (reactor charge) 50 wt %
- Dosage time of residual monomers with residual AIBN 1 h
- Time of postreaction 5 h

The final synthesized solvent-borne basic acrylic pressure-sensitive adhesive, after addition of isopropyl alcohol as a stabilizer, was characterized by the following important properties:

- Amount of solid materials 40 wt %
- Viscosity 5.7 Pa s
- Concentration of residual monomers < 0.3 wt %
- Weight average molecular weight M_W 675,000 Dalton
- Number average molecular weight M_n 303,000 Dalton
- Polydispersity $P_d = M_W/M_n$ 2.23

Photoreactive crosslinking based on *s*-triazine

Table I presents the examples of *s*-triazine photoreactive crosslinking agents tested.

The influence of the tested *s*-triazine photoreactive crosslinking agents (ranging from about 0.2 to 3.0 wt %) 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 Figures 1–3.

It was unequivocally shown (Fig. 1) that the investigated photoreactive *s*-triazine crosslinkers in amounts up to 1.4 wt % BMP-s-T and XL-353, and up to 1.2 wt % BN-s-T and BMN-s-T, increase the tack of UV-crosslinked solvent-borne acrylic pressure-sensitive adhesives. The maxima of tack were observed for about 0.8 wt % of the aforementioned

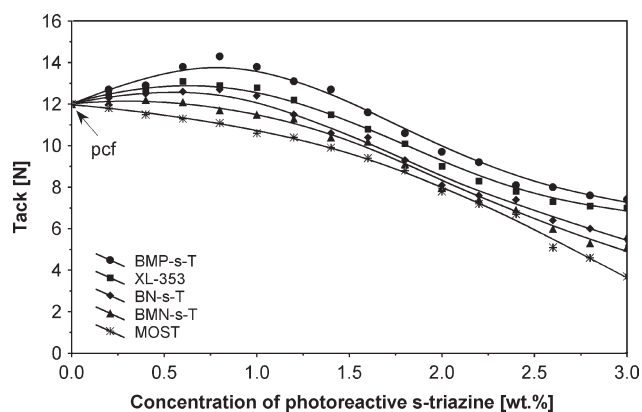


Figure 1 Tack of UV-crosslinked acrylic PSA as a function of *s*-triazine photoinitiator concentration.

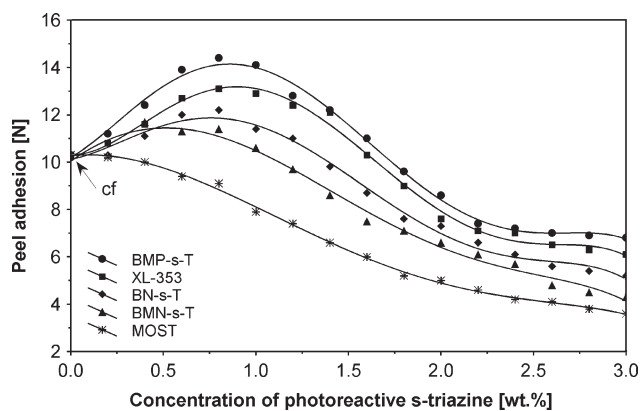


Figure 2 Peel adhesion of a UV-crosslinked acrylic PSA as a function of the s-triazine photoinitiator concentration.

photoreactive crosslinking agents. The use of most of photoreactive s-triazine crosslinkers influences the tack values negatively. Perhaps the free radicals yielded after UV exposure are 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 in the Figure 2 show that the photoreactive s-triazine crosslinkers increase the peel adhesion of UV-crosslinked acrylic PSAs. They were little bit more efficient than by use of other previously tested photoinitiators. Similar to the tack measurements, the peel adhesion maxima were noticed for about 0.8 wt % of the examined s-triazine photoinitiator BMP-s-T. The use of MOST failed.

The shear strength after UV-crosslinking is proportional to the concentration of the photoreactive s-triazines (Fig. 3). During the UV-curing 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 three-dimensional network was created. For all tested s-triazine deriva-

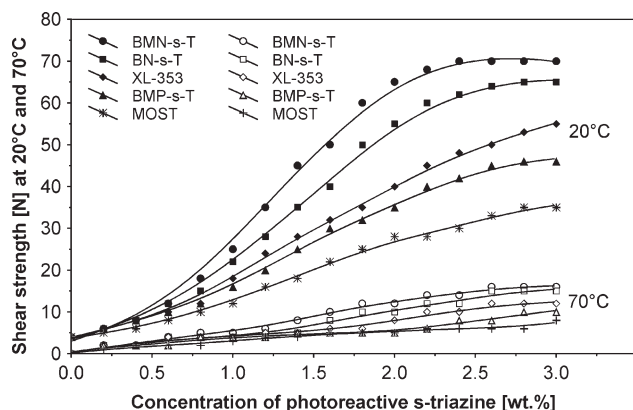


Figure 3 Shear strength of a UV-crosslinked acrylic PSA as a function of the s-triazine photoinitiator concentration.

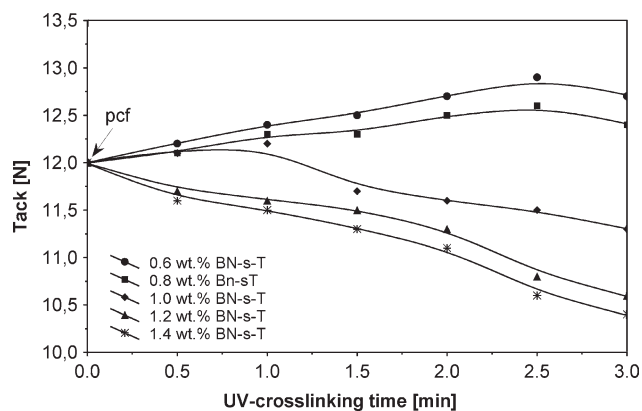


Figure 4 Tack of a UV-crosslinked acrylic PSA as a function of UV-crosslinking time for various concentrations of the photoreactive s-triazine (BN-s-T).

tives, the measured temperature resistance (shear strength at 70°C) was unacceptable.

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 %.

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 and 1.4 wt %, were performed with 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 Figures 4–9.

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. 5). As a result of these

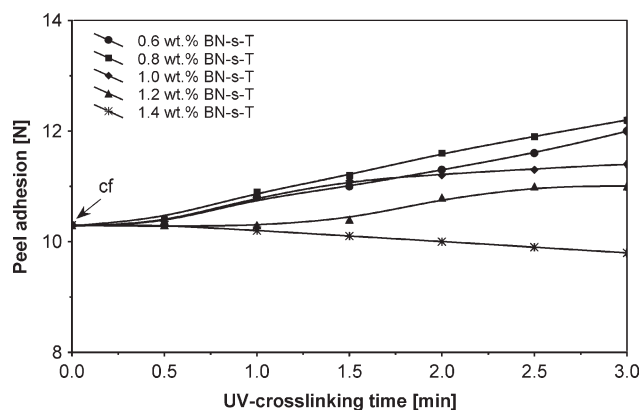


Figure 5 Peel adhesion of a UV-crosslinked acrylic PSA as a function of the UV-crosslinking time for various concentrations of the photoreactive s-triazine (BN-s-T).

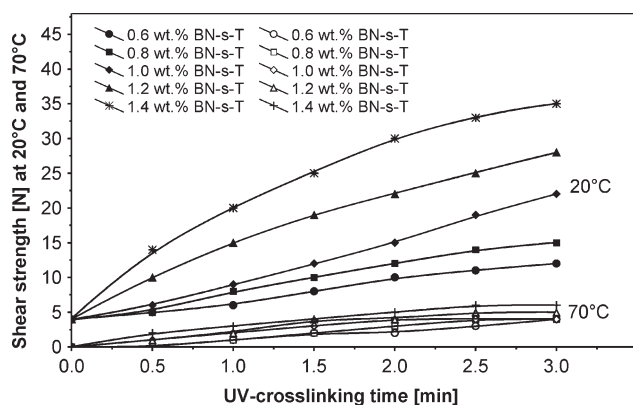


Figure 6 Shear strength of a UV-crosslinked acrylic PSA as a function of UV-crosslinking time for various concentrations of the photoreactive s-triazine (BN-s-T).

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 Figure 5 above, the peel adhesion increased with irradiation time and was the highest for 0.8 wt % photoreactive s-triazine crosslinker 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. 6). The noticed shear strength at 20°C was of a similar level to the obtained by the use of multifunctional hydrogen 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. 7). With the increase of the UV dose to 250 mJ/cm², the tack of s-triazine free layer and acrylic adhesive containing 1.2 and 1.4 wt % of BN-s-T decreases. The tack maximum

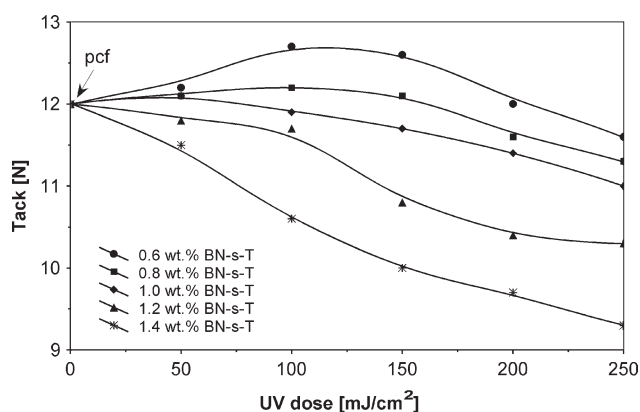


Figure 7 Tack of a UV-crosslinked acrylic PSA as a function of UV dose for various concentrations of the photoreactive s-triazine BN-s-T.

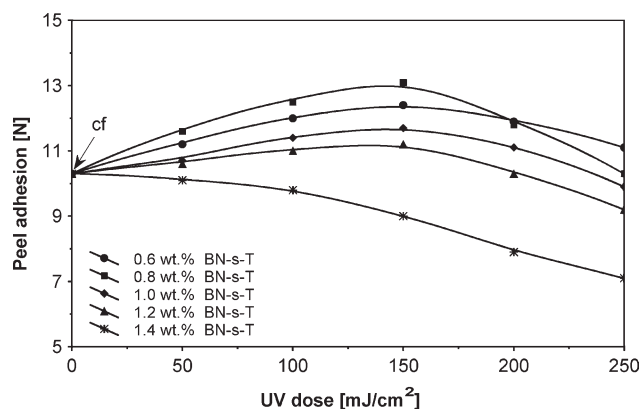


Figure 8 Peel adhesion of a UV-crosslinked acrylic PSA as a function of UV dose for various concentrations of the photoreactive s-triazine BN-s-T.

was found for 0.6 wt % BN-s-T at about 100 mJ/cm² UV dose.

The highest peel adhesion value was indicated for 0.8 wt % BN-s-T at 150 mJ/cm² UV radiation (Fig. 8). 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. 9) 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 an unacceptably low level.

The efficiency of bis-(trichloromethyl)-s-triazines as photoinitiators in free radical initiated photocrosslinking systems, as well as photoacid generators, may be explained and described by the mechanism outlined in Scheme 2.

Electronically excited fragments (a) suffer homolytical transformation to the radical (b) and a chlorine radical, which abstracts hydrogen from a donor

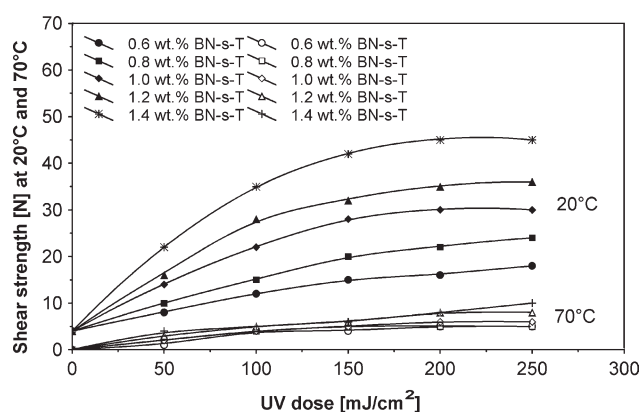
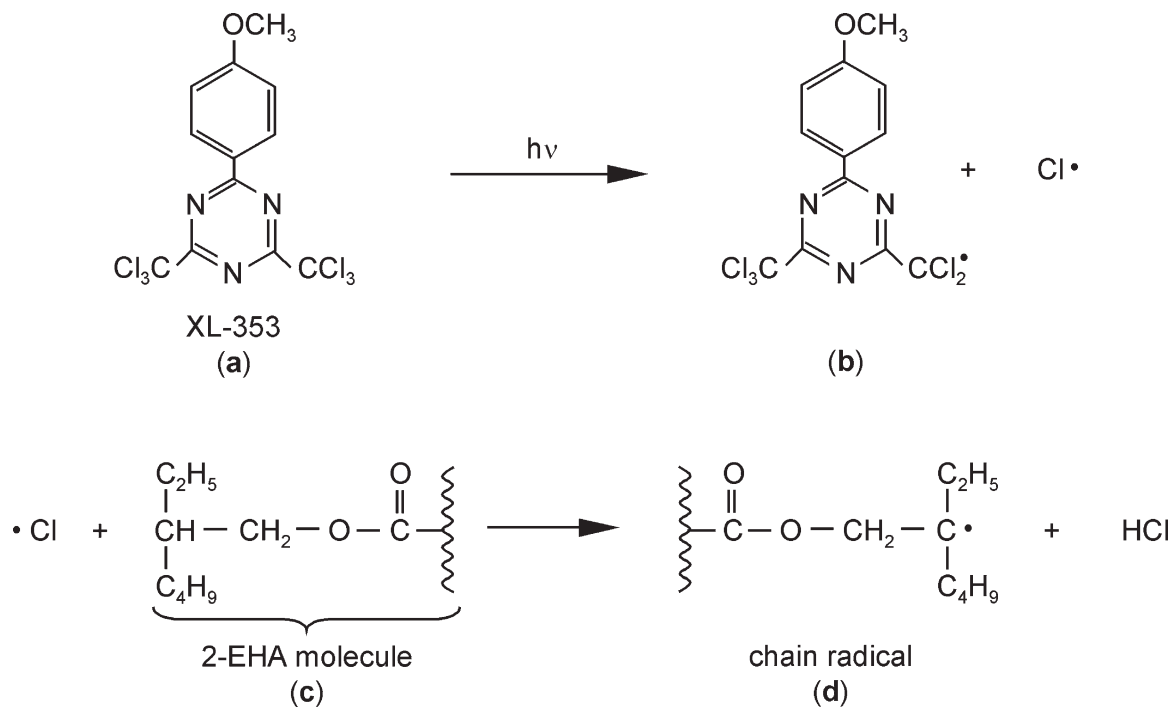


Figure 9 Shear strength of a UV-crosslinked acrylic PSA as a function of UV dose for various concentrations of the photoreactive s-triazine BN-s-T.



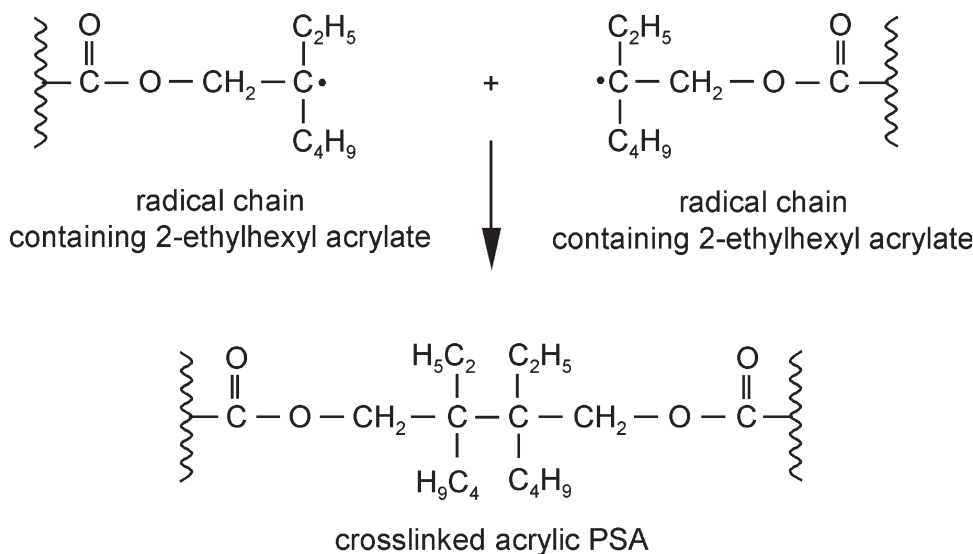
Scheme 2 Mechanism of *s*-triazine photoreactive crosslinker photolysis.

(c) resulting in the formation of hydrogen chloride and the radical (d). Although hydrochloric acid serves as the catalyst in chemical amplification systems, the chain radical (d) may be used to start a chain crosslinking reaction (Scheme 3).

CONCLUSIONS

These photosensitive compounds, in spite of very effectiveness for use in the photocrosslinking of pressure-sensitive adhesives and ameliorating the adhesive properties (tack and peel adhesion) liberate

hydrogen chloride 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



Scheme 3 UV-crosslinking of acrylic pressure-sensitive adhesives by use of photoreactive *s*-triazines.

for BMP-s-T; and the best balance of properties of tack, peel adhesion, and shear strength for BN-s-T. Chromophore-substituted trihalomethyltriazine compounds are preferred as photoreactive crosslinking agents for the UV-crosslinked coating of adhesives with improved tack and peel adhesion, and with moderate cohesion at room temperature.

References

1. Oldring, P. K. In *Chemistry and Technology of UV and EB Formulation for Coatings; Inks and Paints*, Ed.; SITA Technology Ltd: London, 1991; Vol.1-4.
2. Matijasic, C. *Adhesives Age* 2002, 12, 129.
3. Bisges, M. *Adhesives Age* 2002, 11, 34.
4. Czech, Z. *Int J Adhes Adhes* 2004, 24, 119.
5. Czech, Z.; Urbala, M.; Martysz, D. *Polym Adv Technol* 2004, 15, 387.
6. Czech, Z.; Martysz, D. *Int J Adhes Adhes* 2004, 24, 533.
7. Czech, Z.; Milker R. *Farbe und Lack* 2004, 110, 18.
8. Czech, Z. *Polimery (Warsaw)* 2003, 47, 375.
9. Vesley, G. W.O. Pat. 93/13149 (1992) 3M.
10. Vesley, G. W.O. Pat. 81/02262 (1982) 3M.
11. Reiser, A. *Photoreactive Polymers*; Wiley: New York, 1989; Vol.112.
12. Buhr, G.; Dammel, R.; Lindley, C. R. *Polym Mater Sci Eng* 1989, 61, 269.
13. Grotzinger, C.; Burget, D.; Jacques, P.; Fouassier, J. P. *Macromol Chem Phys* 2001, 202, 3513.
14. Hoechst, A. H. Eur Pat. EP 364735 (1990).
15. Kawabata, M.; Kimoto, K.; Takimoto, Y. Eur Pat. EP 211615 (1987).
16. Ishikawa, S. I.; Iwasaki, M.; Tamoto, K.; Umehara, A. Eur. Pat. Appl. 109,291 (Prior. 12.11.82) to Fuji Photo Film Co.
17. Umehara, A.; Kondo, S.; Tamoto, K.; Matsufuji, A. *Nippon Kagaku Kaishi* 1984, 192, 1; Umehara, A.; Kondo, S.; Tamoto, K.; Matsufuji, A. *Chem Abstr* 100(20): 165332f.
18. Kabatc, J.; Zasada, M.; Pączkowski, J. *J Polym Sci Part A: Polym Chem* 2007, 45, 3626.