

UV-INITIATED CROSSLINKING OF ACRYLIC PRESSURE-SENSITIVE ADHESIVES USING ULTRAVIOLET EXCIMER-LASER

Z. Czech and A. Butwin

Institute of Chemical Organic Technology, West Pomeranian University of Technology, Szczecin, Pulaskiego 10, 70-322 Szczecin, Poland

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Abstract. The crosslinking of acrylic pressure-sensitive adhesives (PSAs), especially for ameliorating of tack, peel adhesion, and shear strength of self-adhesive polymer layers, has been investigated using an ultraviolet excimer-laser and a UV-lamp as ultraviolet (UV) sources. It has been observed that excellent self-adhesive products for manufacturing of self-adhesive materials are received after UV crosslinking of acrylic PSA.

1. INTRODUCTION

Pressure-sensitive adhesives (PSA) are nonmetallic materials used to bond other materials, mainly on their surfaces through adhesion and cohesion. Adhesion and cohesion are phenomena which may be described both thermodynamically and chemically, but they cannot actually be measured precisely. The term PSA has a very precise technical definition and has been dealt with extensively in the chemical literature. New developments in the area of PSA technology have been described in the same literature [1]. The function of PSAs is to ensure instantaneous adhesion upon application of light pressure. The properties which are essential in characterizing the nature of PSAs comprise: tack, peel adhesion, and shear strength. The first property measures the adhesive's ability to adhere quickly, the second - its ability to resist removal through peeling, and the third - its ability to hold in a position when shear forces are applied [2].

The physicochemical and mechanical properties (tack, peel adhesion and shear strength) of PSAs based on acrylic acid esters are determined to a large degree by the type and amount of the

crosslinking agent which is added to the copolymer or to crosslinking methods. The crosslinking can be considered as a critical factor in the formulation of PSA at the application stage [3]. The generated crosslinked connections inhibit extensively the mobility of polymer molecules by chemical bondings in a network of polymeric PSA. Therefore, a crosslinked PSA cannot melt any more.

Industrial applications of UV crosslinkable materials have grown tremendously over the past decade. An entire industry has evolved based on the existence of chemicals which respond to the UV light. 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-lamps are UV sources that emit light in the UV region between 200 to 400 nm. Spectral emissions of common UV-lamps used for UV-crosslinking also contain other wavelengths such as, for example, IR components [4].

The word LASER (Light Amplification by Stimulated Emission of Radiation) reveals a technology existing for about 45 years. A UV-laser is a high

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

Table 1. Excimer laser wavelengths.

Active medium	Wavelength [nm]
ArCl	170
ArF	193
KrCl	222
KrF	248
XeCl	308
XeF	351

energy, monochromatic light source, the application of which in curing is known from stereolithography. Regarding the pressure-sensitive adhesive technology, it is the excimer laser that has the highest chance to be used [5-11]. The excimer laser was invented in 1975 and it is considered the youngest laser with high radiation power when compared to the Nd:YAG-Laser. Excimer lasers are very intense pulsed light sources which radiate UV wavelengths between 170 and 351 nm (Table 1) [6] depending on the noble gas-halogen mixture, and provide high energy, MW-power which is in the ns-range of radiation times.

The electron beam has been used successfully to crosslink polymers, also in crosslinking applications where ultraviolet radiation (UV) does not work well. However, it has not been generally applied to polymerization which mostly converts monomers and therefore requires more time to complete. Most curing applications are done basically for the purpose of hardening a coating which is much like a chemical equivalent of drying. If the material under consideration is a pressure-sensitive adhesive (PSA), then meeting the more demanding physical

property requirements that depend on the polymer structure offers considerable challenges. A high molecular weight, crosslinked network is essential to make a high performance PSA.

The advantage of UV radiation from excimer lasers lies primarily in the tailored UV light spectrum. Compared to commercial UV lamps with spectral UV light, the excimer laser with monochromatic UV light offers significant advantages in the possibility of application of a chemical synthesis of macromolecules, in particular in laser-induced polymerization and laser-initiated crosslinking.

2. EXPERIMENTAL

The investigated solvent-borne acrylic PSAs were synthesized in ethyl acetate from between 63.0 and 64.9 wt.% 2-ethylhexyl acrylate, 30 wt.% methyl acrylate, 5 wt.% acrylic acid and between 0.1 and 2.0 of unsaturated copolymerizable acryloyloxy-photoinitiator in the presence of 0.1 wt.% radical starter AIBN at the temperature of 77 °C. All the components were purchased from BASF in Ludwigshafen (Germany). The unsaturated photoinitiators (Table 2) were available from Chemitec of Hohrhausen (Germany). The same unsaturated photoinitiators were tested by UV-crosslinking of water-soluble acrylic pressure-sensitive adhesives using the UV radiation from a UV lamp [12].

The polymerization process was carried out under the following conditions:

- addition of a blend of monomers with AIBN into ethyl acetate before the polymerization (reactor charge amount): 50 wt.%
- dosage time of residual monomers with residual AIBN: 2 h

Table 2. Unsaturated photoinitiator used.

Acryloyloxy-photoinitiator	Chemical formula	Chemical name
ABP		4-acryloyloxy benzophenone
ZLI 3331		2-hydroxy-1-[4-(2-acryloyloxyethoxy)phenyl]-2-methyl-1-propanone
PAC		phenyl-(1-acryloyloxy)-cyclohexyl ketone

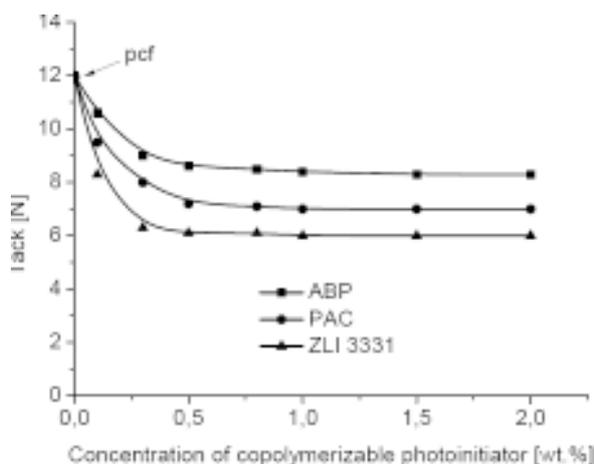


Fig. 1. Tack of an acrylic PSAs containing selected unsaturated photoinitiators after crosslinking using UV excimer-laser.

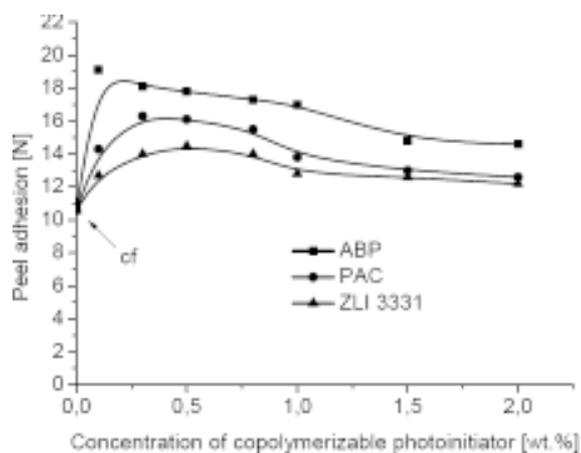


Fig. 2. Peel adhesion of acrylic PSAs containing selected unsaturated photoinitiators after crosslinking using a UV excimer-laser.

- post-reaction time: 5 h
- amount of solid materials (polymer content) 50 wt. %

The UV crosslinking experiments using a UV laser and a UV lamp were conducted using basic acrylic PSAs containing the most efficient unsaturated copolymerizable hydrogen abstraction type photoinitiator, 4-acryloyloxy benzophenone (ABP), and α -cleavage types, 2-hydroxy-1-[4-(2-acryloyloxyethoxy)phenyl]-2-methyl-1-propanone (ZLI 3331) and phenyl-(1-acryloyloxy)-cyclohexyl ketone (PAC), which were incorporated via radical initiated polymerization into the polymeric backbone as photoreactive crosslinking centers.

The solvent-borne UV curable acrylic PSAs containing the above mentioned photoinitiators were coated directly at about 60 g/m² on a polyester film and after drying for 10 min at 105 °C they were crosslinked for 10 s using an ultraviolet excimer-laser LPX 210 from Lambda Physik in Göttingen (Germany) with the following characteristics of the emitted radiation:

emitted pulse UV energy	200 mJ
pulse durations	30 ns
frequency of pulses	10 Hz
number of pulses	100
UV dose	2.7 mJ/cm ²

The evaluated photoreactive UV-crosslinked pressure-sensitive adhesives were cured also with a ultraviolet light lamp U 350-M-I-DL from IST with a UV-A wavelength in the range between 315 to 380 nm. The UV-exposure was measured using an inte-

grating radiometer, Dynachem™ Model 500, available from Dynachem Corporation, 2631 Michelle Drive, Tustin, CA 92680.

The mentioned 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 tests were conducted with the use of the Zwick/Roell Z-25 testing machine.

The peel adhesion was judged and recorded according to the following ratings:

- good-samples that are removed from the test substrate without damaging or leaving residue on the test substrate;
- tear-samples that display too high a peel adhesion to the test substrate, causing test substrate and/or polyester foil backing to tear or delaminate at any peel rate: partially cohesive failure (pcf);
- cohesive failure-samples (cf) that leave adhesive residue on both the polyester film backing and the test substrate.

3. RESULTS AND DISCUSSION

The influence of the investigated unsaturated photoinitiators (versus their various amounts) on the tested acrylic PSA tack, peel adhesion and shear strength using a UV source excimer-laser is described in the graphs shown in Figs. 1-3.

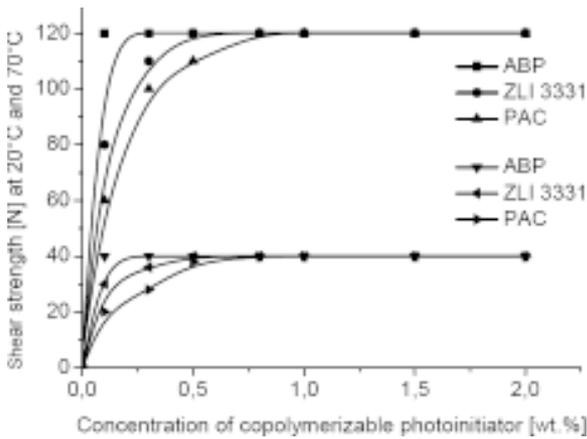


Fig. 3. Shear strength of acrylic PSAs containing selected unsaturated photoinitiators after crosslinking using a UV excimer-laser.

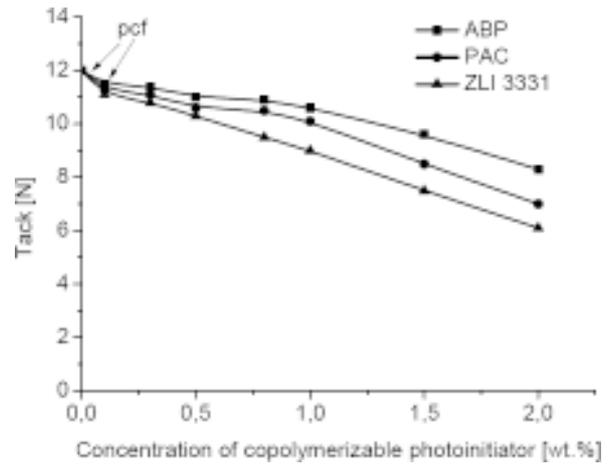


Fig. 4. Tack of acrylic PSAs containing selected unsaturated photoinitiators after crosslinking using a UV lamp.

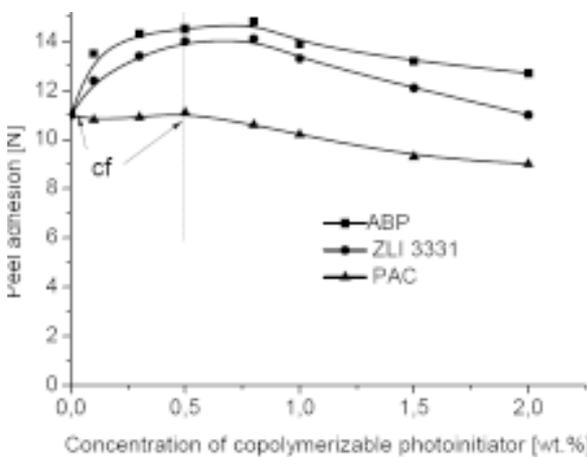


Fig. 5. Peel adhesion of acrylic PSAs containing selected unsaturated photoinitiators after crosslinking using a UV lamp.

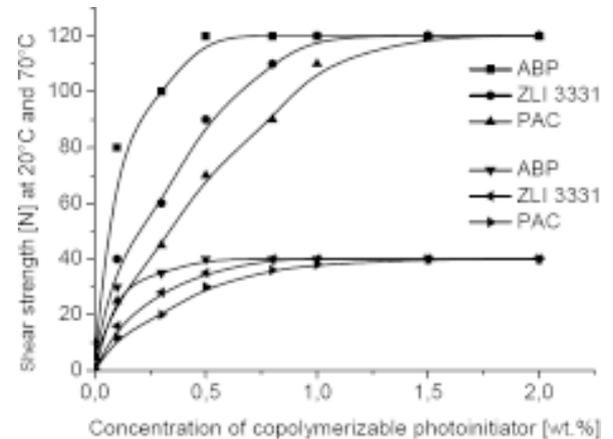


Fig. 6. Shear strength of acrylic PSAs containing selected unsaturated photoinitiators after crosslinking using a UV lamp.

As can be seen in Fig. 1, for all the acrylic PSAs containing the selected copolymerizable photoinitiators a continuous tack drop after UV crosslinking using excimer-laser was observed. The most striking tack drop was observed for relatively small photoinitiator amounts ranging to about 0.3 wt.%. For uncrosslinked acrylic PSA layer a partially cohesive failure (pcf) was observed.

The peel adhesion results obtained for all the tested unsaturated photoinitiators show an influence of the kind of photoinitiators and their concentration in the synthesized acrylic adhesives. UV initiated crosslinking of acrylic PSA containing ABP preceded quickly when an excimer-laser was used. The highest peel adhesion value was noticed for 0.1 wt.% unsaturated H-abstractor ABP (Fig. 2).

Similar cohesion results, measured at 20°C, after a UV excimer-laser exposure, have been obtained with all acrylic PSAs containing the tested copolymerizable photoinitiators (Fig. 3). A faster and more complete crosslinking has been achieved by setting the photoinitiator amounts above 0.1 wt.% ABP, above 0.5 wt.% ZLI 3331 and above 0.8 wt.% PAC. The observed shear strength results at 70 °C have turned out to be the maximal measured values for similar photoinitiator contents.

The best optimal pressure-sensitive performances with UV excimer-laser radiation crosslinkable adhesives, i.e. the balanced values of tack, peel adhesion and shear resistance for the intended application in the investigated solvent-borne acrylic pressure-sensitive adhesives containing more

photoreactive selected copolymerizable photoinitiators have been noticed for ABP.

The UV-crosslinking effect with the use of UV lamp of acrylic PSAs containing tested unsaturated photoinitiators: ABP, ZLI 3331, and PAC (ranging from about 0.1 to 2.0 wt.%) on tack, peel adhesion, and shear strength at 20 °C and 70 °C by the UV dose of 900 mJ/cm² with a UV-crosslinking time of 3 min is illustrated in Figs. 4–6.

Uncrosslinked solvent-borne acrylic PSAs show tack and peel adhesion along with a partially cohesive failure (pcf) or a cohesive failure (cf). As shown in Fig. 1 and Fig. 4, a greater change in the tack has been observed for UV-initiated crosslinking with the use of an excimer-laser. In the case of peel adhesion measurements (Fig. 2 and Fig. 5), the higher maxima of peel adhesion of about 19 N have been observed for acrylic PSAs crosslinked with the use of an excimer-laser. Photoreactive acrylic PSAs begin to crosslink after a small amount of UV radiation. The PSA structure is now compact, the tack decreases and the peel adhesion increases and a peel adhesion maximum is observed in the course of evaluation. Finally, the tack and peel adhesion levels are reduced at higher concentration of unsaturated photoinitiators. The tack of UV-crosslinked acrylic pressure-sensitive adhesives is very sensitive to the crosslinking time and unsaturated photoinitiator amount variations. In general, the adhesive surface suffers a decrease in the tack with an increase of the yielded free radicals, and this is observed by increasing the copolymerizable photoinitiator concentration.

As can be seen in Figs. 3 and 6, the UV crosslinked acrylic pressure-sensitive adhesives build cohesive strength, tested at 20 °C and 70 °C, with an increase in the photoinitiator concentration. Comparative examples with a UV excimer-laser and a UV lamp as the UV radiation source show that the shear strength of the crosslinked PSAs is much higher by application of excimer-laser than that achieved by the UV crosslinking of photoreactive acrylic layers crosslinked under a UV lamp. Above all, the highest peel adhesion and shear strength values are measured for 4-acryloyloxy benzophenone (ABP). An excellent peel adhesion and shear strength has been achieved for 0.1 wt.% ABP. As can be seen from all figures, the application of an excimer-laser ameliorates the main properties of acrylic self-adhesives. The superiority of the UV excimer laser compared to the UV lamp used as the crosslinking medium is obvious. It should be noted that an almost clear relationship exists be-

tween the monochromatic ultraviolet excimer-laser light and the polychromatic UV light emitted from a UV lamp.

4. CONCLUSIONS

The best results for the relevant properties of pressure sensitive adhesives such as tack, adhesion and cohesion in the investigated copolymerizable photoinitiators incorporated during the synthesis of solvent-borne acrylic PSAs have been given by 4-acryloyloxy benzophenone. The highest values of tack, adhesion and cohesion have been observed at a concentration about 0.1 wt.% of 4-acryloyloxy benzophenone (ABP). The unsaturated ABP produces a higher level of radicals immediately after the UV curing process, as well as after a prolonged exposure to UV, than most of the common photoinitiators. Having passing the level of about 2.7 mJ/cm² the tack drop is very slow. The investigated photoreactive solvent-borne UV excimer-laser crosslinkable acrylic PSAs can be used for manufacturing of high performance self-adhesive products such as mounting tapes, labels, masking tapes or sign and marking films.

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