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ORIGINAL PAPER

Influence of selected photoinitiators type II on tack, peel adhesion, and shear strength of UV-crosslinked solvent-borne acrylic pressure-sensitive adhesives used for medical applications

Zbigniew Czech · Agnieszka Kowalczyk · Janina Kabatc · Jolanta Świderska · Lu Shao · Yongping Bai

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Abstract This article describes the photoreactive UV-crosslinkable solvent-borne acrylic pressure-sensitive adhesives (PSA) containing unsaturated copolymerizable photoinitiators and their synthesis. The solvent-borne acrylic PSA were synthesized in ethyl acetate as a solvent, and the copolymerizable photoinitiators type II, known as hydrogen abstractors, were incorporated into acrylic polymer chain during conducted radical polymerization process. The synthesized solvent-borne acrylic PSA containing different unsaturated photoinitiators were investigated to evaluate their relevant and significant properties such as tack, peel adhesion, and shear strength after UV exposure.

Keywords Acrylic PSA · Copolymerizable photoinitiators · UV crosslinking · Tack · Peel adhesion · Shear strength

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Z. Czech (✉) · A. Kowalczyk
Institute of Chemical Organic Technology, West Pomeranian University of Technology, Pułaskiego 10, 70-322 Szczecin, Poland
e-mail: psa_czech@wp.pl

J. Kabatc
Faculty of Chemical Technology and Engineering, University of Technology and Life Sciences, Seminaryjna 3, 85-326 Bydgoszcz, Poland
e-mail: nina@utp.edu.pl

J. Świderska
Non-Public Health Center, Bolesława Śmiałego 28, 70-348 Szczecin, Poland

L. Shao · Y. Bai
Department of Polymer Science and Engineering, Harbin Institute of Technology, Harbin 150001, People's Republic of China

Introduction

Since their introduction half a century ago, pressure-sensitive acrylic adhesives (PSA) have been successfully applied in many areas. They are used in self-adhesive tapes, labels, protective films, and sign and marking films as well as in dermal dosage systems for pharmaceutical applications, in plaster, self-adhesive hydrogels, and in biomedical electrodes.

The acrylic PSA are manufactured as solvent-borne, water-borne, and solvent-free systems.

An acrylic PSA as dispersions, polymer solution or solvent-free systems, in which the polymer chains are crosslinked only by hydrogen bridges, can be stressed cohesively to only a limited degree. A small concentration of crosslinking agent changes it already to a PSA, which has strongly pronounced mechanical and thermal properties. This does not necessarily apply to acrylic PSA dispersions, which form the coating in several steps. The evaporation of water in the first step causes the shrinkage of the extremely high polymeric particles generated by the emulsion polymerization until they touch each other. Then, capillary forces occur which additionally compress the particles, deform them, and finally melt together to a homogeneous consistency. This is then a polymeric layer produced, which actually does not require crosslinking any more. However, there are important application areas, for which an additional crosslinking is desired or even necessary [1].

To reach the PSA crosslinking, several of the most important multifunctional chemical compounds with suitably reactive groups, or very efficient suitable chemical methods, are used as the following list illustrates: multifunctional unsaturated monomers [2], monomers with crosslinking properties [3], metal chelates [4], polycarbodiimides [5], polyfunctional propylene imines [6], amino resins [7], and especially UV crosslinking [8].

It is well known that components of acrylic pressure-sensitive adhesive systems, which are not chemically linked, can migrate into the PSA surface of the finished coating. This phenomenon is called bleeding or chalking if these components are resins, fillers, plasticizers, conventional photoinitiators, and photolytical by-products of photoinitiators after UV exposure. The initiator molecules do not react completely and only a fraction of the photolytically generated radicals become part of the polymer network, while other radicals recombine to form secondary products. These effects usually degrade gloss, adhesion, and skin irritation and can interfere with many applications. Extractability of photoinitiator by-products by food in contact with these adhesive coatings excludes their use for food-packaging materials. UV-crosslinkable acrylic pressure-sensitive adhesive systems need photoinitiators to start the radical crosslinking reaction [9].

The most typical directions, however, are in the development of functionalized chromophores of type I and type II initiators, for e.g., acrylated, vinylated, allylated, acrylamidated, or vinyloxylated (Fig. 1).

Such functionalized chromophores will themselves either co-react with the crosslinked acrylic PSA or are capable of copolymerization to produce acrylic self-adhesive copolymers, which are not extractable. The above-mentioned functionalized unsaturated photoinitiators have also been prepared.

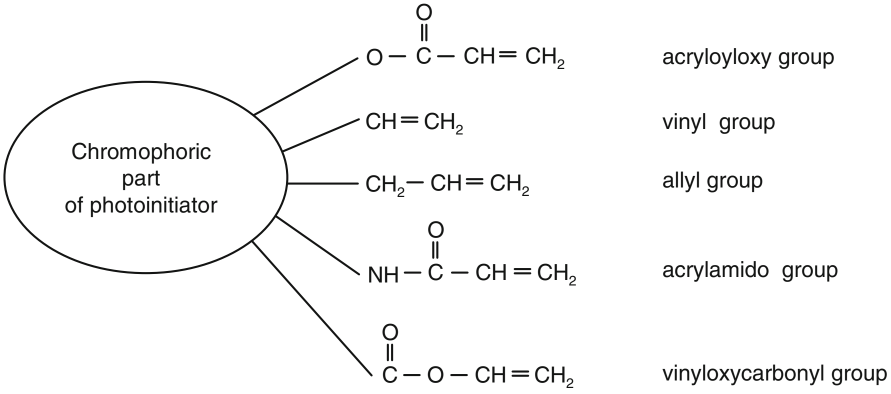


Fig. 1 Examples for copolymerizable photoinitiators structure [10]

Copolymerizing the unsaturated photoinitiator into the backbone of the acrylic pressure-sensitive adhesive copolymer allows crosslinking of the acrylic PSA with ultraviolet radiation, after formation of the copolymer. Furthermore, incorporation of the unsaturated copolymerizable photoinitiators into the acrylic polymer backbone, before the crosslinking thereof, greatly increases the efficiency of the crosslinking obtainable by inclusion of the photoinitiator monomer in the adhesive, as compared with the addition of an aromatic ketone compound which is not initially copolymerized into the copolymer. Because of increased efficiency, only small amounts of unsaturated copolymerizable photoinitiator monomer are needed to achieve useful degrees of crosslinking.

Performed polymer structures that crosslink directly under the influence of ultraviolet energy require special photosensitive groups to effect network formation (Fig. 2) [11].

The unsaturated photoinitiator type II (no presence of by-product after UV crosslinking) is now part of the polymer chain and is, therefore, nonmigratory. The attached photoinitiator gives no harmful by-products on curing and, therefore, presents no problem with toxicity. After UV-initiated crosslinking by using of photoinitiators type II, known as hydrogen abstractors, are formed no photolytically by-products.

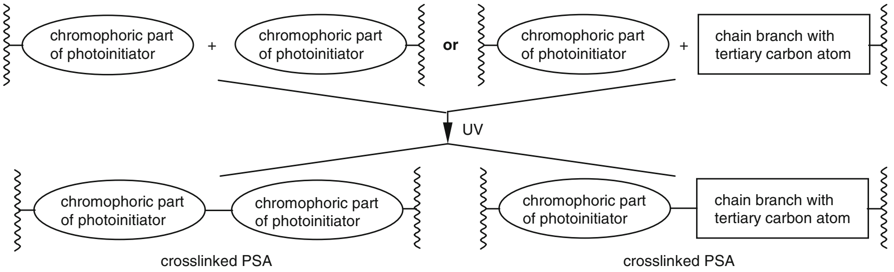


Fig. 2 UV crosslinking using of unsaturated photoinitiators incorporated into polymer chain

Experimental

In the set of experiments, it has been investigated how copolymerizable unsaturated hydrogen atom abstractor photoinitiators containing acryloyloxy groups influence tack, peel adhesion, and shear strength of UV-crosslinked solvent-borne acrylic pressure-sensitive adhesives. The evaluated unsaturated H-abstractor photoinitiators are incorporated during typical solvent polymerization into the acrylic polymer chain. These compounds are listed in Table 1.

The aforementioned compounds were tested for photoreactivity and application, as photoreactive internal crosslinking agents, after incorporating into the polymer chain. Their efficiency and properties are determined after copolymerization.

The arcylic PSA of medical grade were synthesized during radical polymerization of monomers' mixture composed of 69.0 and 70.9 wt% 2-ethylhexyl acrylate (2-EHA), 25% methyl acrylate (MA), 4% acrylic acid (AA) and between 0.1 and 2.0 wt% of unsaturated photoinitiators type II (see Table 1) in ethyl acetate as a solvent at boiling point. 2,2′-Azo-bis-diisobutyronitrile (AIBN) in a concentration of 0.1 wt% was used as a radical starter. The next part of monomers' mixture was added into polymerization reactor during 2 h at performed post-reaction time about 6 h (due to the decrease of the free monomers concentration). The monomers 2-ethylhexyl acrylate (2-EHA), methyl acrylate (MA), and acrylic acid (AA) were purchased from BASF (Germany). Thermal starter AIBN and copolymerizable photoinitiators type II (Table 1) are available from ChemCycle (Germany).

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

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.

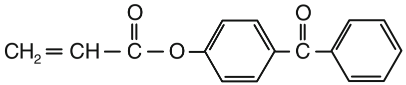
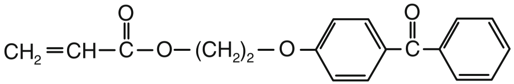
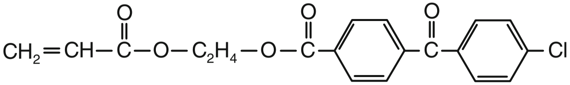
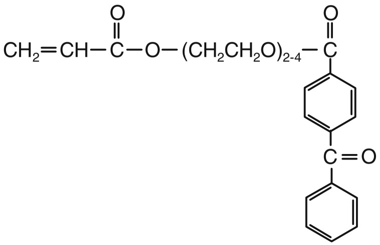
The number average molecular weight, weight average molecular weight, and molecular weight distribution studies were performed in tetrahydrofuran with a liquid chromatography LaChrom system: RI Detector L-7490 and LaChrom UV Detector L-7400 from Merck-Hitachi, equipped with a PLgel 10^6 Å column from Hewlett-Packard.

The UV-inducted crosslinking process was performed using a ultraviolet light lamp U 350-M-I-DL from IST Company with a UV-A wavelength between 315 and 380 nm. The UV exposure was measured using an integrating radiometer Dynachem$^{\mathrm{TM}}$ Model 500, available from Dynachem Corporation, 2631 Michelle Drive, Tustin, CA 92680.

The representative solvent-borne acrylic pressure-sensitive adhesives, synthesized with different amounts of ABP, were coated at a coating weight of 60 g/m^2 solid content onto a smooth layer of polyester film, and after drying for 10 min at ca. 105 °C the adhesives were crosslinked by UV radiation using mentioned UV lamp with 1 min UV-crosslinking time and by 800 mJ/cm^2 UV dose.

The influence of the ABP photoinitiator on UV-initiated crosslinking of photoreactive-synthesized acrylic PSA is usually determined in relation to the photoinitiator concentration, UV-crosslinking time, and UV dose to the significant

Table 1 Evaluated H-abstractor acroyloyloxy-photoinitiators type II

Acroyloyloxy- photoinitiator	Chemical formula	Chemical name
ABP		4-Acryloyloxybenzophenone
AEBP		4-Acryloyloxyethoxy benzophenone
ACCP		4-Acryloyloxyethoxy carbonyl-4′-chlorobenzo-phenone
Uvecryl P36		Mixture of 4-acryloyloxy-oligoethylenoxy carbonyl-benzophenones

PSA properties such as tack, peel adhesion, and shear strength. The three first 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 (shear strength). Administrative address: 60, rue Auber-94408 Vitry Sur Seine Cedex, France.

Results and discussion

Viscosity of synthesized acrylic PSA containing unsaturated photoinitiators type II

The viscosity of the synthesized solvent-borne acrylic PSA is determinate to the concentration of unsaturated photoinitiators type II which are incorporating into polymer chain during radical polymerization (Fig. 3).

As it is shown in Fig. 3, the incorporation into polymer chain of unsaturated acryloyloxy-photoinitiators type II such as 4-acryloyloxy benzophenone (ABP), 4-acryloyloxyethoxy benzophenone (AEBP), and 4-acryloyloxyethoxycarbonyl-4′-chlorobenzophenone (ACCP) increases the viscosity of synthesized solvent-borne acrylic pressure-sensitive adhesives (PSA). Only incorporation into polymer chain of unsaturated photoinitiator Uvecryl P 36, built from a benzophenone oligomer mixture, decreases the viscosity of synthesized acrylic PSA. All measured viscosities of acrylic PSA containing between 0.1 and 2.0 wt% of used unsaturated photoinitiators type II are high enough and acceptable for coating process.

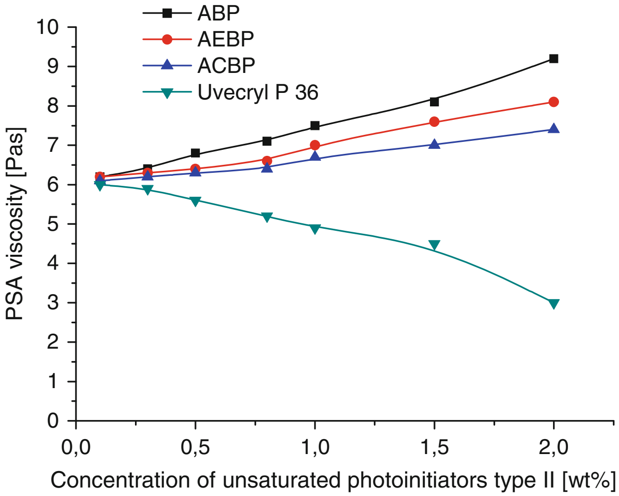


Fig. 3 The viscosity of synthesized acrylic PSA containing unsaturated H-abstractors type II

Table 2 Concentration of residue monomers into synthesized acrylic PSA

Kind of monomer	Concentration (wt%)
2-Ethylhexyl acrylate (2-EHA)	0.05–0.09
Methyl acrylate (MA)	0.01–0.03
Acrylic acid (AA)	0.00
4-Acryloyloxy benzophenone (ABP)	0.00
4-Acryloyloxyethoxy benzophenone (AEBP)	0.00
4-Acryloyloxyethoxycarbonyl-4′-chlorobenzophenone (ACCP)	0.00
Uvecryl P 36	0.00

Determination of free monomers in synthesized acrylic PSA

The free unreacted acrylate monomers in synthesized solvent-borne acrylic pressure-sensitive adhesives were determined using head space GC chromatography. The results of this measurement were presented in Table 2.

The small amount of residue acrylate monomers and unsaturated photoinitiators type II into photoreactive UV-crosslinkable synthesized solvent-borne acrylic PSA predestinates clear kind of acrylic PSA for medical applications.

Molecular weight and molecular weight distribution of synthesized acrylic PSA

The molecular weights M_w, M_n and the polydispersity P_d of synthesized solvent-borne acrylic PSA containing evaluated photoreactive hydrogen atom abstractors as unsaturated photoinitiators in the polymer backbone, are juxtaposed in Table 3.

The molecular weight measurement reveals that the incorporation of the photoreactive H-abstractors: ABP, AEBP, and ACCP during copolymerization into the main polymer chain does not affect the molecular weight the synthesized acrylic PSA or only increase it very little. The greatest growth of M_w, of about 6%, was observed in the case of ABP. A decrease of molecular weight by about 10% was noticed when using unsaturated photoinitiator Uvecryl P 36. From technological point of view, the weight average molecular weight M_W plays more significant role than the number average molecular weight M_n. The measurements of adhesiveness and cohesiveness properties in the case of acrylic polymers applied as pressure-sensitive adhesives shown that M_w influences stronger tack, peel adhesion, and cohesion, after UV-initiated crosslinking, than M_n.

The influence of 2 wt% tested acryloyloxy-photoinitiators type II on the molecular weight of synthesized UV-crosslinkable solvent-borne acrylic PSAs is shown in Fig. 4.

The lower photoinitiating efficiency of 4-acryloyloxyethoxy benzophenone (AEBP) than that of 4-acryloyloxy benzophenone is a result of presence of an alkylene spacer, which inhibits the delocalization of free radical formed.

The relatively long organic spacer between ester group and benzophenone group contributes to a greater possibility of free radical transfer onto the organic spacer by which de facto the molecular weight of solvent-borne acrylic PSA decreases. The

Table 3 Molecular weight and polydispersity of acrylic PSA containing investigated acryloyloxy-photoinitiators type II

Concentration of unsaturated photoinitiator (wt%)	$\bar{M}_\mathrm{w}$	$\bar{M}_\mathrm{n}$	$P_\mathrm{d} = \frac{\bar{M}_w}{\bar{M}_n}$
4-Acryloyloxy benzophenone (ABP)			
0.1	880,000	280,000	3.14
0.3	885,000	275,000	3.22
0.5	893,000	276,000	3.24
0.8	903,000	273,000	3.31
1.0	908,000	278,000	3.27
1.5	916,000	269,000	3.41
2.0	934,000	268,000	3.49
4-Acryloyloxyethoxy benzophenone (AEBP)			
0.1	882,000	295,000	2.99
0.3	881,000	290,000	3.04
0.5	884,000	290,000	3.05
0.8	887,000	286,000	3.10
1.0	891,000	293,000	3.04
1.5	902,000	294,000	3.07
2.0	912,000	302,000	3.02
4-Acryloyloxyethoxycarbonyl-4′-chlorobenzophenone (ACCP)			
0.1	879,000	270,000	3.26
0.3	872,000	273,000	3.19
0.5	880,000	275,000	3.20
0.8	891,000	281,000	3.17
1.0	901,000	288,000	3.13
1.5	901,000	281,000	3.21
2.0	903,000	292,000	3.09
Mixture of 4-acryloyloxyethoxycarbonyl-benzophenone (Uvecryl P 36)			
0.1	878,000	280,000	3.14
0.3	869,000	277,000	3.14
0.5	870,000	271,000	3.21
0.8	862,000	265,000	3.25
1.0	855,000	260,000	3.29
1.5	830,000	255,000	3.25
2.0	790,000	237,000	3.33

commercially available unsaturated photoinitiator Uvecryl P 36 built from a benzophenone oligomer mixture incorporates more slowly in the polymer backbone than other unsaturated mono photoinitiators.

The influence of the above-mentioned unsaturated acryloyloxy H-abstractors in terms of their different concentration on the basis of acrylic PSA properties, such as tack, peel adhesion, and shear strength, is described in the graphs shown in Figs. 5, 6, and 7.

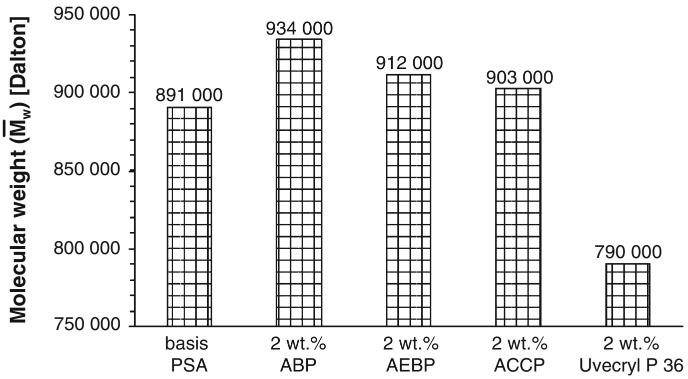


Fig. 4 Influence of the copolymerizable acryloyloxy-photoinitiators type II on acrylic PSA molecular weight M_w

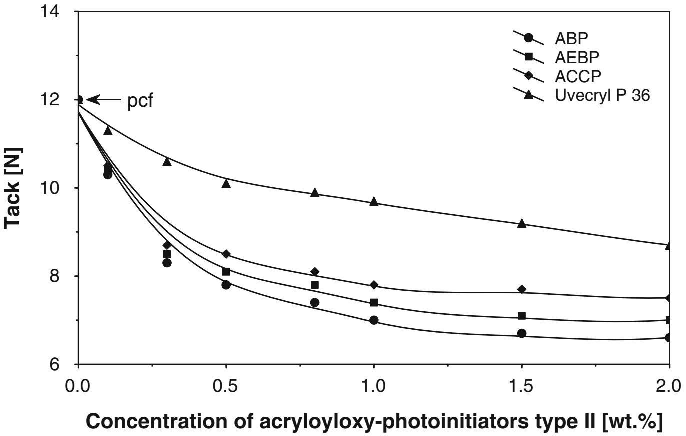


Fig. 5 Influence of acryloyloxy-photoinitiator type II kind and amount on the tack of UV-crosslinked acrylic PSA

The typical dependence of amounts of type II acryloyloxy-photoinitiators tested on the tack of UV-crosslinked acrylic PSAs (Fig. 5) showed that 4-acryloyloxy benzophenone (ABP) was the most efficient H-abstractor (the lowest tack) for the investigated acrylic self-adhesives.

An increase in concentration of the investigated acryloyloxy-photoinitiators, from 0.1 to 2.0 wt%, can lead to a bigger effect on peel adhesion than in the case of tack (Fig. 6). This is a consequence of the effect of "light" crosslinking using H-abstractors and small amounts of adhesive layer for peel adhesion. In comparison with acrylic PSAs without photoinitiators, the peel adhesion values of about 10 N (cohesive failure) reach a maximum for about 0.1 wt% of the evaluated acryloyloxy-photoinitiators type II. For higher concentrations of the evaluated photoinitiators the peel adhesion decreases. The most efficient and the best acryloyloxy-photoinitiators of type II turned out to be ABP.

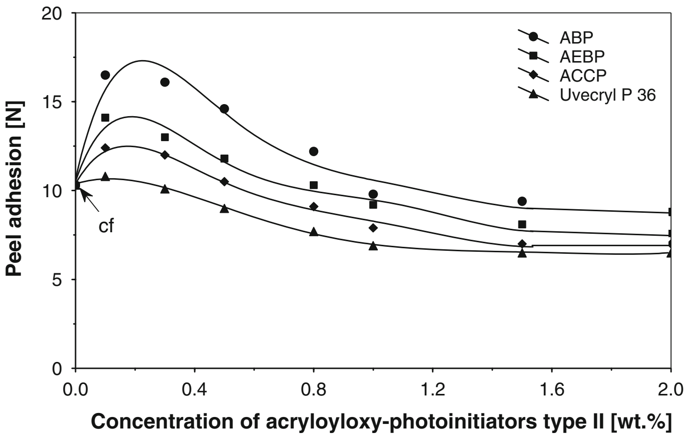


Fig. 6 Influence of acryloyloxy-photoinitiator type II kind and amount on the peel adhesion of UV-crosslinked acrylic PSA

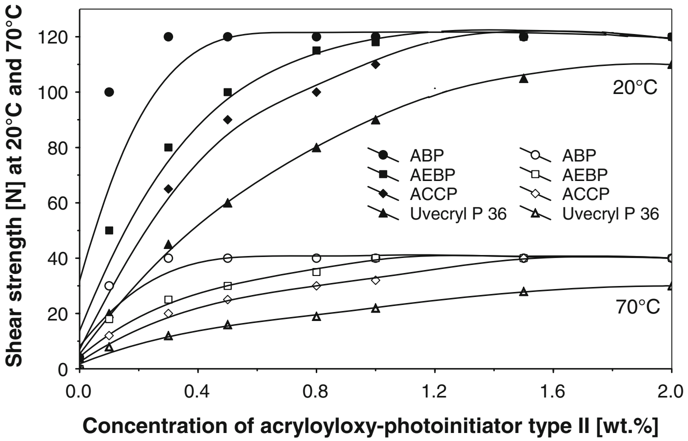


Fig. 7 Influence of acryloyloxy-photoinitiator type II kind and amount on the shear strength of UV-crosslinked acrylic PSA

The shear strength results in Fig. 7 show that the incorporation of unsaturated acryloyloxy-photoinitiators of type II into an acrylic PSA polymer chain strongly raises, unforeseen, their cohesion after UV exposure. This observed shear strength increase is incomparably meaningful as by using other previous investigated photoinitiators. The highest efficiency of hydrogen atom abstracting photoinitiators containing acryloyloxy groups was obtained for ABP. Even small contents of ABP (0.1 and 0.3 wt%) gave UV-crosslinked acrylic PSAs with outstanding shear strength values.

The conducted trials have shown that a suitable unsaturated photoinitiators, such as 4-acryloyloxy benzophenone (ABP) and 4-acryloyloxyethoxy benzophenone (AEBP) functioning as H-abstractor, can positively influence shear strength, as well

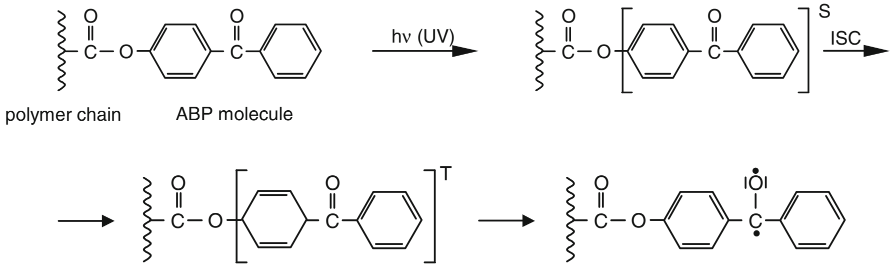


Fig. 8 Forming of free radicals using ABP

as peel adhesion of UV-crosslinked solvent-borne acrylic pressure-sensitive adhesives.

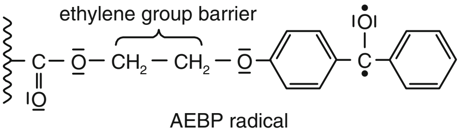
It should be noted from the performed investigations that an almost clear relationship exists between the tested tack, peel adhesion, and shear strength values of UV-crosslinked solvent-borne acrylic pressure-sensitive adhesives and the application of acryloyloxy-photoinitiators of type II. From the mentioned evaluated unsaturated photoinitiators, the best performance was achieved when using 4-acryloyloxy benzophenone (ABP) and 4-acryloyloxyethoxy benzophenone (AEBP) in all conducted trials.

In case of the tested hydrogen atom abstractor acryloyloxy-photoinitiators (for example ABP) compared with other evaluated acryloyloxy-photoinitiators of type II, this phenomenon can be explained by a longer "living time" of formed radicals from ABP in a triplet state (Fig. 8).

The exceptionally high efficiency of 4-acryloyloxy benzophenone (ABP) as copolymerizable photoinitiator in comparison with the other tested unsaturated H-abstractors such as 4-acryloyloxyethoxy benzophenone (AEBP) and 4-acryloyloxyethoxycarbonyl-4′-chloro-benzophenone (ACCP), is attributed among others to a short molecule of ABP and with it a short distance between both crosslinked polymer chains after UV radiation. The photoreactivity of ACCP, comparable with AEBP is lower, because the chlorine atom shortens the radicals "living time" by the so-called "heavy atom effect". Certainly, the lower reactivity of AEBP in comparison to ABP is because of the presence of ethylene groups in the photoinitiator structure as shown in Fig. 9.

The photoinitiators acting as H-abstractors possess alkylene or alkyleneoxy groups between ester moiety and radical on the alpha-carton atom of aromatic ring. These barrier groups are the reason for weakening the induction effect and the reduction of the H-abstractors crosslinking activity.

Fig. 9 Ethylene group barrier in photoinitiator AEBP



Extraordinarily high shear strength at 20 and 70 °C and high peel adhesion in case of the use of 4-acryloyloxy benzophenone (ABP) and 4-acryloyloxyethoxy benzophenone (AEBP) have this unsaturated H-abstractor predestined for a wide range of applications. Solvent-borne UV-crosslinkable acrylic PSA containing ABP and AEBP are characterized by very low concentration of residue monomers and excellent adhesive main performance which enabled their applications in medicine leading to an interesting application for the production of medical self-adhesive products.

Conclusion

Comparative performance studies of photoreactive UV-crosslinkable solvent-borne acrylic pressure-sensitive adhesives (PSA), containing the most outstanding acryloyloxy-photoinitiators type II such as 4-acryloyloxy benzophenone (ABP), 4-acryloyloxyethoxy benzophenone (AEBP), 4-acryloyloxyethoxycarbonyl-4′-chloro-benzophenone (ACCP), and Uvecryl P 36 built from a benzophenone oligomer mixture crosslinked with UV radiation, showed the clear superiority of acrylic PSA balance properties with 0.3 wt% unsaturated photoinitiator ABP or 0.5 wt% AEBP. The performance of this kind of UV-crosslinkable acrylic PSA is dependent on the used UV dose and UV-crosslinking time. The developed photoreactive acrylic PSA wich is incorporated into polymer chain copolymerizable photoinitiators type II are characterized by absence of residue monomers and photolytically by-product after UV-initiated crosslinking and are suitable for wide range of medical applications.

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