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Photoreactive UV-crosslinkable acrylic pressure-sensitive adhesives containing type-II photoinitiators

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ABSTRACT

UV-crosslinking is an established technology used in many industrial manufacturing processes. New applications and technical specifications of UV technologies stimulate the continuous development of photoinitiators that can efficiently meet specific requirements. A typical class of radical-reactive type-II photoinitiators has been used for the UV-initiated crosslinking of acrylic pressure-sensitive adhesives (PSAs).

The activity of type-II photoinitiators such as: benzophenone derivatives, thioxanthone derivative, antraquinone derivative and fluorenone (without tertiary amine as a co-initiator) in the photoreactive UV-crosslinkable acrylic pressure-sensitive adhesives was described. The effect of the type-II photoinitiators on the acrylic PSA properties (tack, peel, and shear strength) was summarized.

1. Introduction

The number of industrial applications of UV-crosslinkable pressure-sensitive adhesive (PSA) materials has grown tremendously over the past decade. UV radiation is now widely used in industrial processes. UV equipment, which includes UV lamps and UV lasers, emits light in the UV region of the electromagnetic spectrum (from 100 to 400 nm). The growing success of UV-crosslinking technologies in a wide variety of industrial processes can be attributed to the productivity and environmental benefits that result from such technologies. UV technologies are well established in the market and allow the production of a wide range of UV-crosslinkable PSAs with interesting features. The balance between adhesive and cohesive strengths within the crosslinked coatings is critical for their performance [1–3].

To obtain 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 specific application [4–6]. The photoinitiator is therefore one of the key components in UV-crosslinking systems. The outcome of the polymerization process is critically dependent on the photoinitiator characteristics, including its chemical nature and concentration [7,8]. For this reason, the activity of a photoinitiator is one of the most important properties to be considered. The advantages of UV-crosslinking over thermal crosslinking include rapid network formation (in a fraction of a second using high-intensity light sources) and the utilization of heat-sensitive substrates. There are two basic categories of radical photoinitiators: The first group involves type-I photoinitiators [9], which undergo a direct photofragmentation process in the excited state to form free radicals. The second group involves type-II photoinitiators [10], which undergo a primary process of hydrogen-atom abstraction from the environment (R-H) (this may be the resin itself or a solvent) to produce a ketyl radical. The intermolecular H-abstraction photoinitiators include benzophenone and its derivatives, such as xanthone, thioxanthone, and 4,4′-bis-(*N*,*N*′-dimethylamino)benzophenone, as well as benzil and quinines [11].

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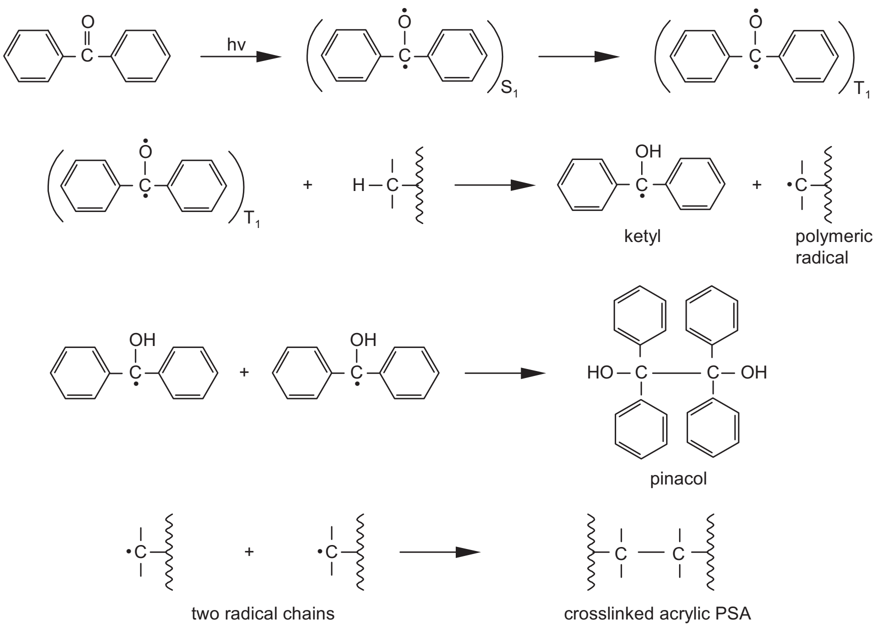


Fig. 1. Hydrogen atom abstraction and photocrosslinking of an acrylic PSA using benzophenone.

As it is shown in Fig. 1, photoinitiators of this type abstract H atoms from the environment (R-H) (this may be an acrylic PSA) to produce a benzophenone ketyl radical [12].

In this paper, the activity of different radical-reactive type-II photoinitiators in the UV-initiated crosslinking of acrylic pressure-sensitive adhesives (PSAs) was presented. The influence of a structure of type-II photoinitiators under studies on the main performance of solvent-borne acrylic PSAs was also described. The main purpose of our studies was to find the balance between the following properties: tack, peel and shear resistance of UV-crosslinkable adhesives.

2. Experimental

Various experiments were carried out to study the influence of different type-II photoinitiators (H abstractors) on the main performance of solvent-borne acrylic PSAs. We investigated properties such as tack, peel adhesion (adhesion) and shear strength (cohesion). The base weight of the adhesive layer covering the polyester foil was 60 g/m^2.

The influence of the crosslinking agents or crosslinking methods is usually determined in relation to reaction time and concentration versus adhesion properties, considering the properties tack, adhesion and cohesion, which 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.

The evaluated photoreactive PSAs were crosslinked using an ultraviolet-light lamp of the type Aktiprint-mini 18-2 (Technigraf). The UV exposure was measured with an integrating radiometer (Dynachem™ Model 500, available from Dynachem Corporation).

2.1. Basic acrylic PSA

The experiments were conducted using a standard solvent-borne acrylic PSA, synthesized from a mixture of 2-ethylhexyl acrylate (65 wt.%), methyl acrylate (30 wt.%), and acrylic acid (5 wt.%) in the organic solvent ethyl acetate at the boiling point temperature (about 77 °C) and in the presence of 2,2'-azo-bis-diisobutyronitrile (AIBN, 0.1 wt.%)—according to the monomer concentration—used as a thermal initiator to start radical polymerization. All the starting materials, such as acrylate monomers, solvent, AIBN and type-II photoinitiators, were technical-grade reagents used without further purification (unless otherwise noted).

The final synthesized solvent-borne basic acrylic PSA was characterized by the following important properties:

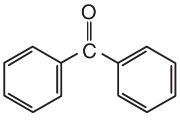
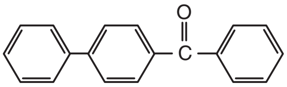
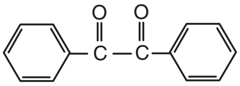
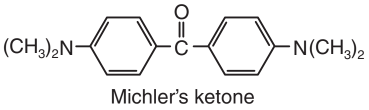
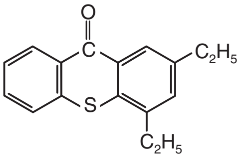
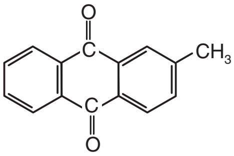
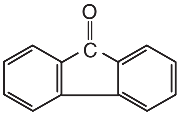
Amount of solid materials	45 wt.%
Viscosity	11,7 Pa·s
Concentration of residual monomers	<0.3 wt.%
Weight average molecular weight M_W	708,000 Da
Number average molecular weight M_n	369,000 Da
Polydispersity $P_d = M_W/M_n$	1.92

2.2. Hydrogen abstractors as reactive type-II photoinitiators

Examples of the tested type-II photoinitiators are shown in Table 1.

The hydrogen abstractors mentioned in Table 1 were tested as photoreactive crosslinkers for solvent-borne

Table 1
Tested intermolecular hydrogen abstractors.

Photoinitiator (Supplier)	Chemical formula	Chemical name
BP (Transol)		Benzophenone
Trigonal 12 (AKZO)		4-Phenylbenzophenone
BZ (Pflatz & Bauer)		Benzil
MK Michler's ketone (BASF)		4,4'-Bis(*N*,*N*-dimethylamino) benzophenone
Esacure DETX (Lamberti)		2,4-Diethyl thioxanthone
MAQ (American Cyanamide)		2-Methyl anthraquinone
Fluorenone (Rütgerswerke)		Fluorenone

acrylic PSAs without tertiary amine co-initiators (for PSAs used for medical products, the presence of amines is not acceptable). The crosslinking effects of various amounts of these H-abstractor photoinitiators (ranging from about 0.2 to 3.0 wt.%) on tack, peel adhesion, and shear strength (at the same UV dose of 100 mJ/cm^2 and a crosslinking time of 3 min) are presented in Figs. 2–4.

Crosslinking with UV radiation immediately leads to a strong decrease in tack (see Fig. 2), and to a general decrease in peel adhesion. The tack decreases with increasing concentration of the type-II photoinitiator. At low photoinitiator contents (about 0.5–1.0 wt.%), the peel adhesion reaches a maximum value. For the two most efficient hydrogen-atom abstractors, namely, Michler's ketone and Trigonal 12, the highest peel adhesion values were observed at 0.8 and 1.2 wt.%, respectively (Fig. 3). Michler's ketone is a specific photoinitiator and functions like a tertiary amine. It is used as a hydrogen donor and not only as a typical hydrogen abstractor. For acrylic PSAs without

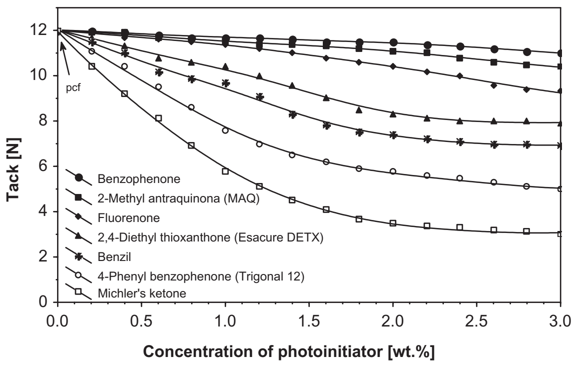


Fig. 2. Tack versus amount of H abstractor.

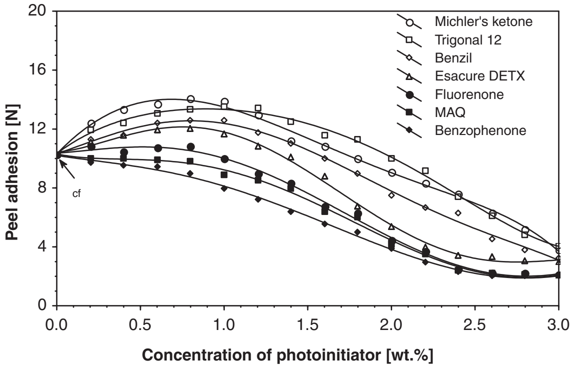


Fig. 3. Peel adhesion versus amount of H abstractor.

addition of photoinitiators, partially cohesive failure (pcf) was observed.

The cohesion of a UV-crosslinked acrylic PSA was measured at 20 and 70 °C. When the adhesive was cured with benzophenone, 2-methyl anthraquinone (MAQ) or fluorenone, cohesive failure (cf) was observed at a relatively low value (at 70 °C). The effect of the photoinitiator concentration on the shear strength is clear: A higher photoinitiator amount leads to a higher cohesion (Fig. 4). Test results obtained for the shear strength reveal that a high cohesion of UV-crosslinked acrylic PSAs can be obtained using Michler's ketone and Trigonal 12 at very high concentrations (about 2–3 wt.%).

In summary, the best H-abstractor photoinitiators of those listed in Table 1 lead to unexpectedly high shear properties and relatively high tack and peel adhesion characteristics of the UV-crosslinked acrylic PSAs.

As it is seen from Figs. 2–4, the effect of photoinitiator Esacure DEXT was not as satisfactory as Michler's ketone. The difference between the activity of both photoinitiators: Esacure DETX and Michler's ketone may came from different rates of hydrogen-atom abstraction/donation.

The UV-crosslinking time determines the tack, peel adhesion and shear strength properties of the resulting UV-crosslinked acrylic PSAs. For further tests, carried out to investigate the effect of the UV-crosslinking time (up to 3 min) on the above-mentioned properties, Michler's ketone was selected at a concentration ranging from about 0.6 to 1.4 wt.%. The results obtained for an acrylic solvent-borne PSA containing Michler's ketone crosslinked at a UV dose of 100 mJ/cm^2 are shown in Figs. 5–7.

The tack of UV-crosslinked acrylic PSAs is very sensitive to variations in crosslinking time and H-abstractor concentration. In general, the surface of the adhesive suffers a tack decrease with increasing concentration of the yielded free radicals.

Fig. 6 presents some results obtained for the UV-crosslinking of an acrylic PSA containing different amounts of Michler's ketone. The maximum peel adhesion is observed at a photoinitiator concentration of 0.8 wt.% after a curing time of 90 s. The use of 1.2 and 1.4 wt.% Michler's ketone leads to a decrease in the peel adhesion values.

Fig. 7 illustrates the relationship between crosslinking time and shear strength for a UV-crosslinked acrylic PSA at different Michler's ketone concentrations. It should be noted that an almost linear relationship exists between the experimental cohesion values and the UV-crosslinking time. During UV-crosslinking, free radicals are formed which are used to link the polymer chains. The UV-crosslinking time directly determinates the shear strength of the acrylic adhesive.

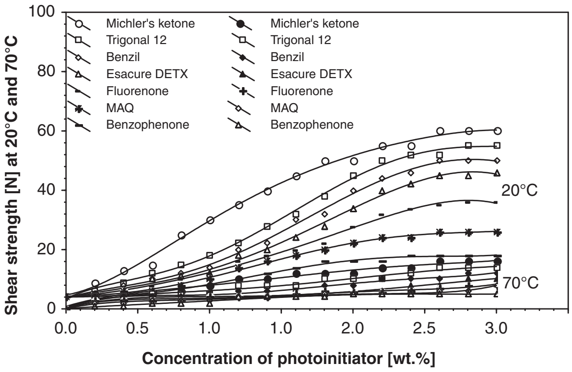


Fig. 4. Shear strength versus amount of H abstractor.

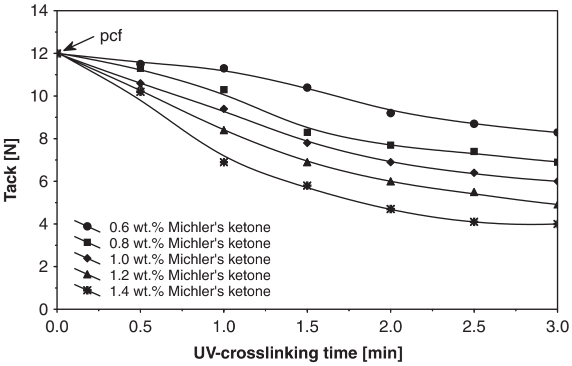


Fig. 5. Effect of the UV-crosslinking time on the tack of tested acrylic PSAs containing different amounts of Michler's ketone.

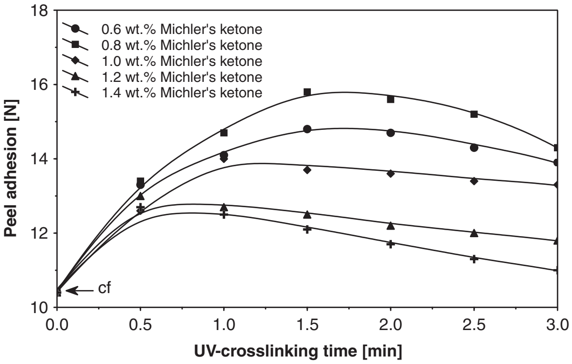


Fig. 6. Effect of the UV-crosslinking time on the peel adhesion of tested acrylic PSAs containing different amounts of Michler's ketone.

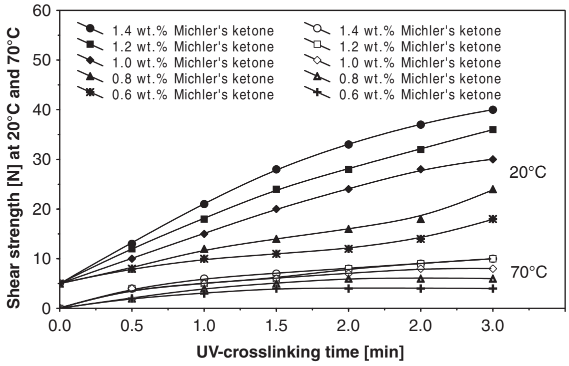


Fig. 7. Effect of the UV-crosslinking time on the shear strength of tested acrylic PSAs containing different amounts of Michler's ketone.

The influence of the UV dose (varied between 50 and 250 mJ/cm^2) on the tack, peel adhesion, and shear strength properties of an acrylic PSA crosslinked using Michler's ketone at different concentrations (between 0.6 and 1.4 wt.%) is presented in Figs. 8–10.

At higher UV doses, the acrylic PSAs are more crosslinked, the surface tack properties are reduced (Fig. 8), and the peel adhesion reaches a maximum for an energy density between 100 and 150 mJ/cm^2 (Fig. 9). The fact that we observe plateau behavior for the tack at UV doses above 150 mJ/cm^2 is interesting because an even stronger variation of the dose leads to essential changes in the peel adhesion.

As it is illustrated in Fig. 10, increasing the UV dose has a positive effect on the cohesion of UV-crosslinked acrylic PSAs. If higher levels of Michler's ketone are used, the shear strength increases because more free radicals suitable for the crosslinking process are generated.

In summary, the best balance between the investigated acrylic PSA properties (tack, peel adhesion, and shear strength) was registered for Michler's ketone (as the type-II photoinitiator) at concentrations of about 0.8 and 1.2 wt.%.

The maximum peel adhesion was achieved at photoinitiator concentration equal 0.8 wt.% after a curing time of 90 s for energy density between 100 and 150 mJ/cm^2. Following increase of Michler's ketone concentration leads to a decrease in the peel adhesion values.

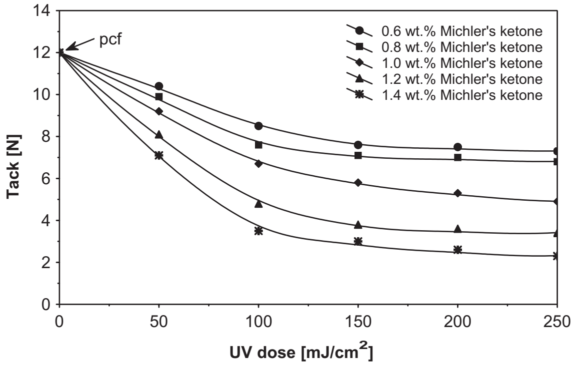


Fig. 8. Effect of UV dose on tack of acrylic PSA crosslinked with different amounts of Michler's ketone.

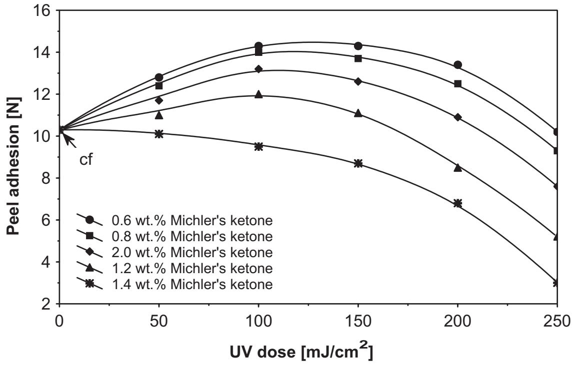


Fig. 9. Effect of UV dose on peel adhesion for acrylic PSAs crosslinked with different amounts of Michler's ketone.

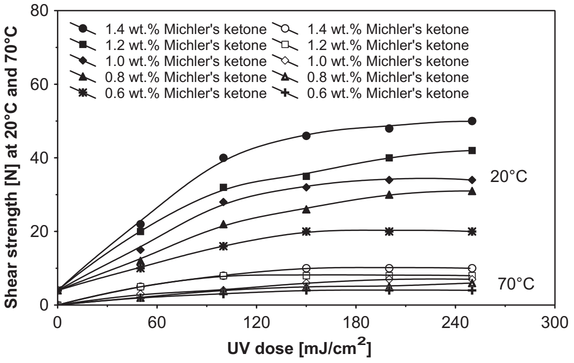


Fig. 10. Effect of UV dose on shear strength for acrylic PSAs crosslinked with different amounts of Michler's ketone.

3. Conclusions

The following conclusions can be drawn from our experiments on intermolecular hydrogen-atom-abstraction type-II photoinitiators:

- There is a clear dependence of the shear strength of UV-crosslinked acrylic PSAs on the photoinitiator concentration.
- An increase in the photoinitiator concentration reduces the tack of the UV-crosslinked acrylic adhesives. The peel adhesion reaches its maximum value at a type-II photoinitiator concentration of about 0.5–1.0 wt.%.
- Among the hydrogen-atom abstractors examined, the best performance was observed for Michler's ketone, a benzophenone derivative. Comparative studies between UV-crosslinked acrylic PSAs containing selected type-II photoinitiators and Michler's ketone showed slightly improved behavior of the ketone-containing UV-crosslinkable basic self-adhesives.
- UV-crosslinkable acrylic PSAs containing Michler's ketone can be used to manufacture self-adhesive materials in the form of mounting tapes, masking tapes or a wide range of sign and marking films.

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