

# PHOTOREACTIVITY ADJUSTMENT OF ACRYLIC PSA

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Received: January 23, 2007

**Abstract.** This article describes the methods of photoreactivity adjustment of diverse kinds of acrylic pressure-sensitive adhesives. The need to replace solvent containing systems, which still have maintained a large market share in various areas, results in a further push of innovations in the development of photoreactive hot melt and the low viscosity systems acrylic pressure-sensitive adhesives. As opposed to the classical solvent containing or to the aqueous systems, the photoreactive hot melt or low viscosity systems provides the following advantages as reduction of environmental impacts to a minimum, saving of energy costs, no drying channel, high coating speed, and production possibility of thick self-adhesive product carrier-free tapes. From the photoreactivity adjustment of acrylic PSAs, the results according to their main performances as tack, adhesion and cohesion were observed for main chain modification using copolymerizable unsaturated photoinitiators. Photoreactivity adjustment of acrylic PSAs through the side chain modification using additionable photoinitiators is technically very complicated, because so many photoinitiators are not available on the market. Normally vinylation of polymer chain demands the addition of conventional unsaturated photoinitiators with high migration rate of toxic photolytic substances after UV-crosslinking. In this case the amelioration of important PSA properties is very doubtful.

## 1. INTRODUCTION

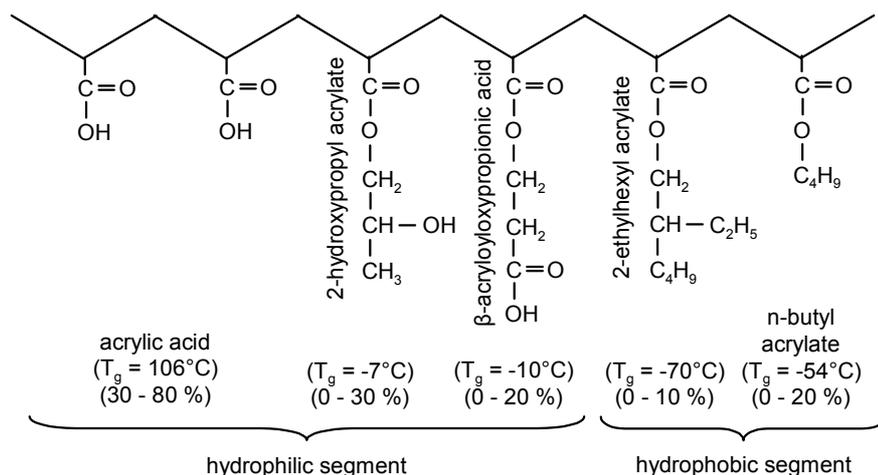
Although one of the first known examples of light induced cross-linking and polymerisation dates back to Egypt over 400 years ago, the scientific interest in UV crosslinkable systems developed only in the 1940s when the first patent was granted for unsaturated polyester styrene inks that polymerised readily under UV light. The basic pressure-sensitive adhesive solvent based, water based or solvent free polymers for the production of self-adhesive tapes, labels and layers are usually acrylics (Fig. 1), natural or synthetic rubbers, silicones, polyesters, polyurethanes or polyethers. Normally these polymers are not photoreactive.

The idea of replacing the conventional solvent based, water based or solvent free crosslinking systems with photoreactive UV crosslinkable systems became very attractive to manufacturing industries [1,2].

However, it is only in the past 20 years that the use in particular of the very reactive mono or multifunctional acrylic pressure-sensitive adhesives (PSA) has resulted in a growing market for UV radiation crosslinkable products, finding uses in the fields of automobile, building, labels, protective films, electronics, medical applications, printing and the optics industry. The range of UV crosslinkable articles produced by 3M, Beiersdorf, Nitto,

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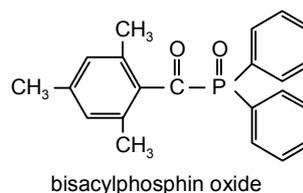
**Fig. 1.** Acrylic basic polymers for photoreactive pressure-sensitive adhesives.

Lohmann, Orafol, *etc.* provides all the benefits of the UV crosslinkable systems and is a result of considerable work devoted to formulating high performance, well-defined products that could meet the specific requirements of a given application [3] (Fig. 1).

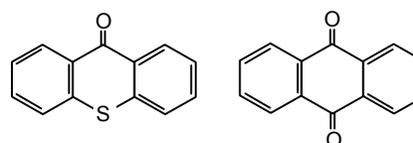
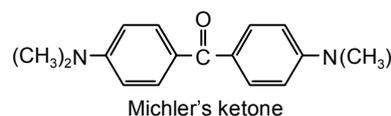
First of all very interesting for industrial applications are acrylic PSA characteristic through by excellent adhesive (tack and peel adhesion) and cohesive (shear strength) properties, excellent thermal and ageing performances.

### 1.1. Basic chemistry of UV crosslinking

The basic principle of photoreactive UV crosslinkable adhesives is the conversion of light energy into chemical energy. This energy conversion takes place through the use of chemical species photoinitiators which, upon absorption of a particular wavelength of light, photochemically produce reactive radicals or ions capable of initiating a rapid chain reaction. With the use of commercial available photoinitiators (Fig. 2) or novel photoinitiators synthesised at the Szczecin University of Technology (Fig. 3) and of commonly available light sources (UV lamps, UV lasers) it can be calculated that as many as  $10^{19}$  initiating species per second can be generated. It is therefore not surprising that the UV crosslinkable systems on the market today can harden so rapidly-sometimes in less than one second [4].



Examples of type I photoinitiators

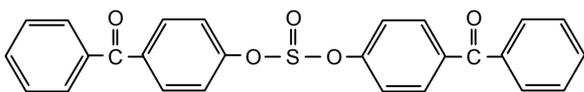


Examples of type II hydrogen atom abstracting photoinitiators

**Fig. 2.** Commercial photoinitiator groups.

The typical UV crosslinkable formulation contains two basic components:

- Photoinitiator(s) that must effectively absorb the indirect light and produce initiating radicals with a high efficiency
- PSA based on acrylic bearing at least reactive unsaturations or photoreactive centres, that can



**Fig. 3.** Novel synthesised conventional photoinitiators.

crosslink to generate the polymeric network (Fig. 4).

Other relevant components, e.g. plasticizers, tackifiers, resins, adhesion promoters, *etc.* are typically also present.

The choice of photoinitiator is of prime importance in light induced polymerisation, since it directly governs the rate of crosslinking. A suitable photoinitiator system must first present a high initiation efficiency. This means that it must have a high absorption in the emission range of the UV source and the excited states thus formed must have both a short life time to avoid quenching by oxygen or monomer molecules and split into active radicals with the highest possible quantum yield. Also the photoinitiator must be soluble in the self-adhesive polymers used and not affect the nature of the crosslinked PSA-colour, toxicity, degradation [5].

## 1.2. Acrylic pressure-sensitive adhesives

The difference between pressure-sensitive adhesives and other adhesives, such as contact adhe-

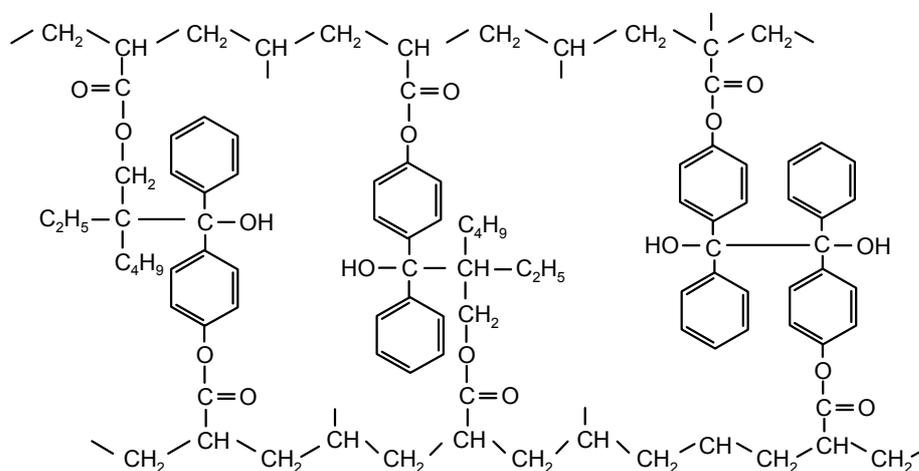
sives, is in the permanent surface stickiness of the pressure-sensitive adhesives before, or after, the application.

In the giant field of pressure-sensitive adhesives the acrylic pressure-sensitive adhesives make up but a high percentage, and the solvent-borne pressure-sensitive acrylic adhesives with about 200.000 tons per annum in Europe are almost a quantity meaningful within this group. Shortly after World War II copolymers of the higher alkyl acrylates, i.e., the acrylics were introduced into the PSA market. Other types of PSA in use nowadays include silicones, vinyl acetate copolymers, poly(vinyl alkyl ether)s, and ethylene-vinyl acetate copolymers, but volumes of these are in many cases relatively small compared to the acrylic polymers [6].

Pressure-sensitive adhesive acrylics can be applied in forms as a solvent-borne, as a water-borne (dispersions) and as a solvent-free system.

Although the solvent-borne pressure-sensitive acrylic adhesives may be dwarfs in terms of quantity, they are giants when considered from the quality point of view. Only by means of these acrylic specialties was it possible to succeed in drafting the present surprisingly efficient generation of double-sided pressure-sensitive adhesive tapes for prominent assembly projects at justifiable cost. Other important applications are for medical products, protective masking films, films for graphics market, and various specialty products [7].

Pressure-sensitive adhesive acrylic solutions are nowadays predominantly manufactured by polymerization from a wide selection of acrylic and methacrylic groups, often with low levels of monomers having pendant functional groups in a reflux-



**Fig. 4.** Polymer network after UV crosslinking.

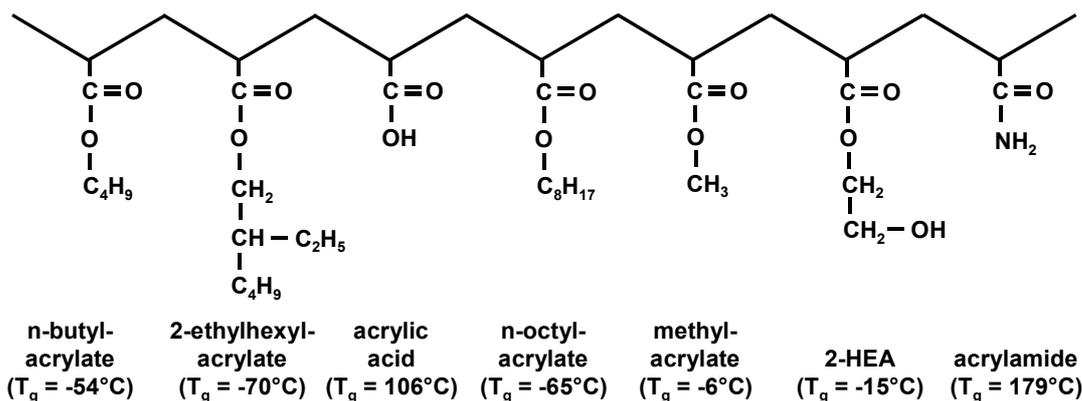


Fig. 5. Architecture of polymer chain of acrylic PSA.

ing organic solvent in the presence of an initiator, such as organic peroxides or azo compounds.

The most important requirements for a pressure-sensitive adhesive, such as high tackiness (adhesion by the touch), high cohesion (inner stability), high stickiness (adhesion), UV, solvent and temperature stability are fulfilled by polyacrylates in an outstanding way.

All kinds of PSA acrylics offer several advantages such as excellent aging characteristics and resistance to elevated temperatures and plasticizers, exceptional optical clarity due to the polymer compatibility and non-yellowing. They also have the highest balance of adhesion and cohesion and an excellent water resistance. Acrylics are harder than rubbers. This can be seen in a less aggressive tack and slower build-up of peel strength. Lower adhesion to non-polar polyolefins is caused by the polar chemistry of acrylics.

### 1.3. The concept of solvent-borne acrylic PSAs design

The versatility of acrylate chemistry is inherently useful in the design of high performance pressure-sensitive adhesives. A broad raw material base and a versatility of polymerization processes lend themselves to design of base polymers with unique properties (Fig. 5).

The glass transition temperature ( $T_g$ ) is the main issue for adhesion properties of various polymers, allowing the selection of raw materials for PSAs applications. It is specific for polymers, but also reveals important information about the suitability of the homopolymers as pressure-sensitive adhe-

sive, which is synthesized from various components. Its value defines the tack of PSAs; a low  $T_g$  is a prerequisite for tacky materials. On the other hand the  $T_g$  alone does not permit to obtain a real image of the adhesive performance. For permanent adherent pressure-sensitive adhesives  $T_g$  ranges from about  $-70^\circ\text{C}$  to  $-25^\circ\text{C}$  [8].

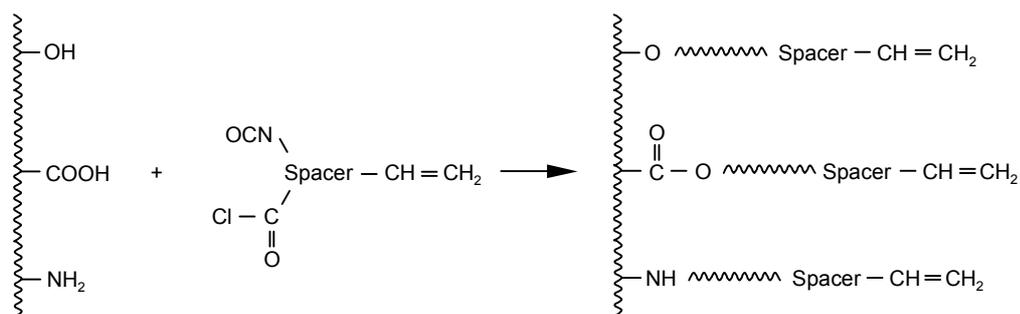
The design parameters utilized to produce high performance solvent-borne or solvent free PSA include: monomer selection, selection of solvents, type of initiators, molecular weight, polymerization methods and crosslinking process.

Specific design parameters are used to achieve desired surface properties of tack and peel in combination with the bulk property of cohesive strength. The balance of these properties is needed for high performance products [9].

## 2. ADJUSTMENT OF PHOTOREACTIVITY

To further improve the performances of these UV-crosslinkable PSAs, pattern crosslinking is a new technology that makes it possible to introduce different levels of crosslinking within the same self-adhesive coating. The result is a combination of high cohesion and adhesion areas in the adhesive layer and is inseparably connected with photoreactivity of acrylic PSA [10].

With photoreactive acrylic PSAs, the ratio of adhesion to cohesion can be varied within wide limits by controlling the amount of UV-dose applied to the adhesive layer after it has been coated. UV-dose can be controlled by adjusting the power of



**Fig. 6.** Introduction of photoreactive groups into a pressure-sensitive adhesive structure.

the lamps and the speed at which the substrate is passed under the lamps in the production plant [11].

Chemically UV-crosslinkable acrylic PSAs consists of polymer backbone molecules that are modified with photoreactive groups. The physico-chemical and mechanical properties of pressure-sensitive adhesives are determined to a high degree by type and concentration of the photoreactivity. Photoreactive adjustment of acrylic PSAs can be conducted by the following procedures [12]:

### 2.1. Vinylation of self-adhesive acrylic polymers

There are many situations in which polymers are reacted with unsaturated compounds to give adhesive components with built in pendant vinyl groups for UV-initiated crosslinking. A typical example for that is the vinylation of hydroxy-, carboxylic- or amino-group containing pressure-sensitive adhesives in an unsaturated architecture (Fig. 6).

The pressure-sensitive adhesives obtained in this way are actually suitable for electron beam crosslinking. For UV crosslinking purposes commercial photoinitiators are added [13].

### 2.2. Side chain modification with additionable photoinitiators

One possibility to introduce photoreactive unsaturated groups consists of synthesizing the solvent-borne pressure-sensitive adhesive first without photosensitive groups and then to introduce them after the polymerization into the polymer structure, by distinct chemical methods. There are many situ-

ations in which adhesives are reacted suitable for addition photoinitiators to give adhesive components with built in pendant, e.g. photoreactive crosslinking places [14].

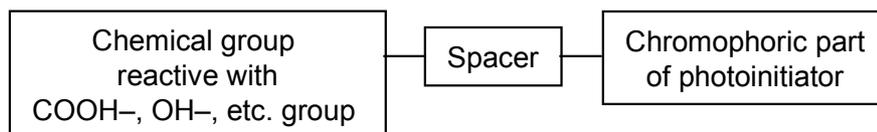
This deals with a new group of photoinitiators. One side of the photoinitiator is a conventional chemical group, which tends to addition reaction or another kind of reaction with the carboxyl or hydroxyl groups of the polymer chain and of the other photoreactive side group (Fig. 7).

The photoinitiator suitable for addition is generally used in amounts ranging from about 0,01 to 5,0% by weight of the total polymerizable composition. Photosensitive pressure-sensitive adhesives are known where the photoinitiator suitable for addition is incorporated into a UV-crosslinkable composition, which brings about the crosslinking of the adhesive with attendant enhancement of the cohesive strength of the adhesive composition. Examples of these photoreactive photoinitiators include e.g. the hydrogen abstraction with a benzophenone group (Fig. 8) [15].

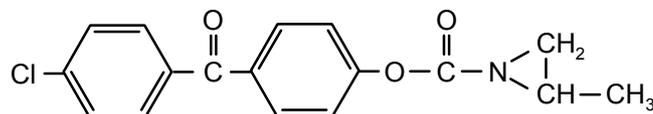
The transformation of the carboxyl group of a pressure-sensitive adhesive takes place after the polymerization by addition reaction in the polymerization media without side products and leads to UV-crosslinkable highly efficient pressure-sensitive adhesives (Fig. 9).

### 2.3. Main chain modification with copolymerizable unsaturated photoinitiators

It is well known that components of pressure-sensitive adhesive systems, which are not chemically



**Fig. 7.** Structure of saturated photoinitiators suitable for addition.



4-chloro-4'-propylene imine carbonyl benzophenone

**Fig. 8.** Example for a photoinitiator tending to addition.

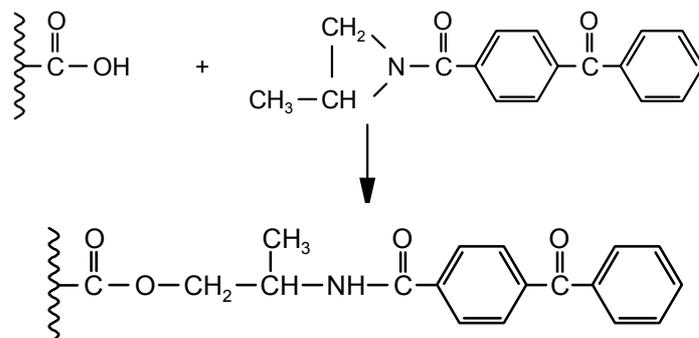
linked, can migrate into the PSA surface of the finished coating. This phenomenon is called bleeding or chalking if these components are pigments, fillers, plasticizers, conventional photoinitiators and by-products of photoinitiators after UV exposure. The initiator molecules do not react completely and only a fraction of the photolytically generated radicals become part of the polymer network, while other radicals recombine to form secondary products [16].

These effects usually degrade gloss, adhesion and mechanical properties 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 initiators to start the radical crosslinking reaction [17].

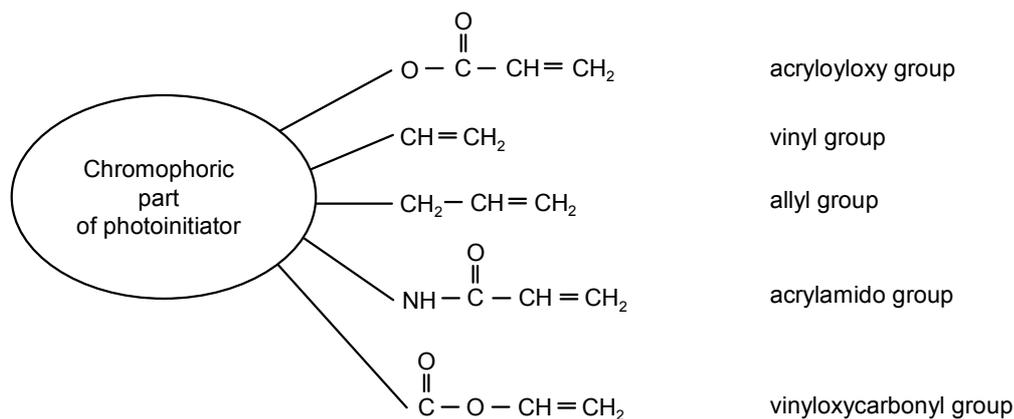
The most typical directions, however, are in the development of functionalized chromophores of type I and type II initiators e.g. acrylated, vinylated, allylated, acrylamidated or vinyloxyated (Fig. 10).

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 [18].

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. Further, incorporation of the unsaturated copolymerizable photoinitiators into the acrylic polymer backbone, before the crosslinking



**Fig. 9.** Transformation of carboxyl groups using the photoinitiator with propylene imine group tending to addition reaction.



**Fig. 10.** General examples for copolymerizable photoinitiators.

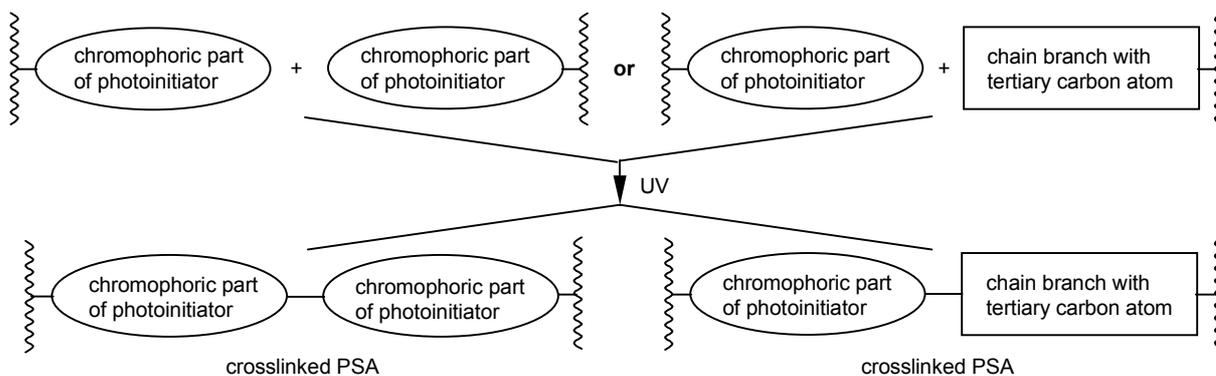
thereof, greatly increases the efficiency of the crosslinking obtainable by inclusion of the photoinitiator monomer in the adhesive, as compared with addition of an aromatic ketone compound which is not initially copolymerized into the copolymer. Because of increased efficiency, only small amounts of unsaturated copolymerizable photoinitiator monomer are needed to achieve useful degrees of crosslinking [19].

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

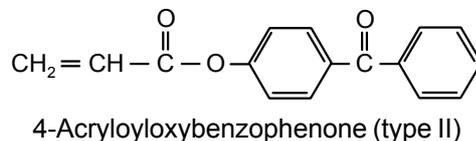
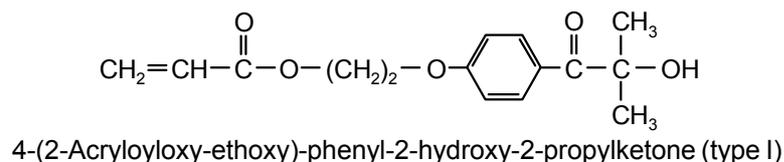
The most important unsaturated photoinitiators suitable for polymerisation are shown in Fig. 12.

Normally the used additives interfere with the reaction of the crosslinking position in the polymer by getting placed between these positions. Furthermore they can react with the incorporated photoinitiator despite of their UV transparency. They additional consumption of photoinitiator decreases the effect of the UV crosslinking [20].

In some applications it is of advantage to add primarily UV inert tackifiers to the photoreactive acrylic pressure-sensitive adhesives such as hydrated colophonium derivatives, terpene phenolic resins or hydrocarbon resins in the amount up to 30 wt.%. Furthermore pigments which contain UV gaps, or inert plasticizing homopolyacrylates can be considered [21].



**Fig. 11.** Photocrosslinking by use of unsaturated photoinitiators incorporated into polymer chain.



**Fig. 12.** Typical photoinitiators suitable for polymerisation.

### 3. PERFORMANCE ADJUSTMENT OF PRESSURE-SENSITIVE ADHESIVES

The most important properties of the UV-crosslinked acrylics pressure-sensitive adhesives, such as tack, peel adhesion and shear strength, can be controlled by the UV dosage. The UV-dose can be controlled by adjusting the power of the lamps and/or the speed at which the substrate is passed under the lamps in the production plant. The solvent-borne UV-crosslinkable acrylic PSA is coated directly and after removing the solvents the adhesive film is crosslinked by UV-irradiation and in a transfer process, depending on the carrier material, to produce the adhesive properties as required. With the pressure-sensitive adhesive layers starting at about 60 g/m<sup>2</sup>, which are primarily used for the manufacture of double-sided pressure-sensitive adhesive tapes, a tendency of hardening can be observed. The high UV-doses are obtained at production speeds of about 200 m/min, if 6 or more UV-lamps with an output power of about 200 W/cm each are used [22].

#### 3.1. UV lamps (polychromatic)

The remaining required investment is the modification of the coating machine with UV-lamps. UV-lamps are UV sources that emit light in the UV region between 200 to 400 nm. The crosslinking with ultraviolet light can be done directly after the application or after passing a cooling zone. UV-lamps are categorized as low, medium and high pressure UV-lamps.

Mercury lamps (low, medium, high pressure) are used with powers between 80 to 120 W/cm, which includes UV stations with six and more UV lamps as state of the art with a power of 120 to 260 W/cm. This type of UV-lamp possesses the right wave-length bands in their emission spectrum as needed for an efficient UV-crosslinking of photoreactive pressure-sensitive adhesives. Spectral emissions of common UV lamps for this application also contain other wavelengths for example IR components [23].

#### 3.2. UV laser (monochromatic)

The word LASER (Light Amplification by Stimulated Emission of Radiation) reveals a technology existing for about 45 years. In 1990 Japan with 43% shares the world market of laser systems with USA 31%, and Western Europe 26%. The reason for the distribution is found in part in the historical introduction of systems but primarily in the various application fields, which the laser types have conquered [24].

With UV-crosslinked acrylic PSA, the ratio of tack and peel adhesion to shear strength (cohesion) can be varied within wide limits, by controlling the amounts of radiant energy applied to the adhesive film after it has been coated. Films formed by UV-crosslinked acrylic adhesive become more cohesive as more radiant energy is applied, while their tack and peel adhesion decrease. This effect is the result of the crosslinking that takes place when the film is exposed to UV light. The effect of the UV radiation dose [mJ/cm<sup>2</sup>] on the adhesive properties and cohesion is shown schematically in Fig. 13.

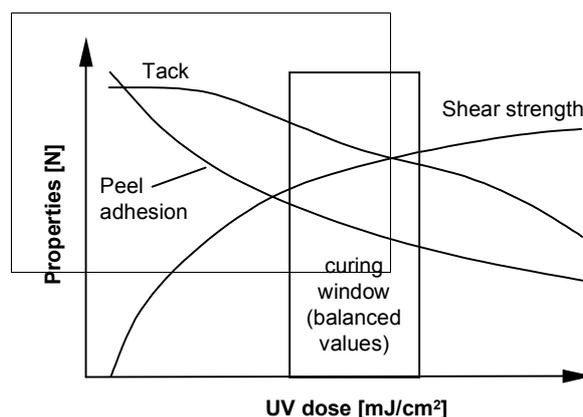


Fig. 13. Tack, peel adhesion and shear strength as a function of UV dose.

As it seems from the Fig. 13, all curves pass through a “curing window” within the same range of UV doses, and this “curing window” represents optimum conditions for the curing. To achieve optimal pressure-sensitive performance with UV-crosslinkable adhesives, it is necessary to find process settings that lead to balanced values of tack, peel adhesion and shear strength for the preferred application. Considering that a UV-cured PSA coating exhibits good adhesion and medium cohesion, and a well-cured one good cohesion and medium adhesion (Fig. 13), it might be interesting to succeed in introducing different levels of curing with the same adhesive film [25].

#### 4. CONCLUSIONS

Environmental protection has been a major issue in our society. The green movements from individual consumers as well as from the government bodies will continue to force the industry to change. The pressure is expected to intensify. Novel developed photoreactive solvent-free acrylic pressure-sensitive adhesives will also in future be an unabandonable constituent of industrial efficient self-adhesive products produced with low energy

costs (Table 1). Novel photoreactive solvent-free acrylic PSAs are applied as montage tapes, labels, protective films, medical OP-tapes and biomedical electrodes [26,27]. For the next 5 years there are predictions of 20% growth rate for the photoreactive solvent-free sector [28].

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Table 1. Comparison of energy costs.

Type of coating	Conventional coating + drying channel Solvent acrylics	Dispersions	MHPSA (coating + UV-crosslinking)
Energy/m <sup>2</sup> [%]	100	90	33

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