

UV-CROSSLINKABLE SOLVENT-FREE PSA SYSTEMS

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INTRODUCTION

Acrylics dominate the world of pressure-sensitive adhesives (PSA), contributing about 40% of all PSA products. Within the acrylic segment, about 25% of products are solvent-borne, and the rest are primarily water-borne. A small number of products, 3...5%, are photoreactive solvent-free acrylic systems. Solvent-free pressure-sensitive adhesives that require physical crosslinking upon cooling exhibit a low melt viscosity, a high heat resistance, and are typically applied as hot melts. UV crosslinkable pressure-sensitive adhesive hot melts (HMPSA) have successfully been used for labels, tapes, and medical products for several years. Although the number of UV crosslinkable raw materials available is limited, formulations of these materials have introduced a wide range of new adhesives [1...3].

UV CROSSLINKABLE SOLVENT-FREE TECHNOLOGIES AND THEIR FORMULATION

Today, most UV crosslinkable solvent-free PSA compositions are based on any of four acrylic polymer systems: hot melt acrylic PSA, warm melt acrylic PSA, low viscosity acrylic PSA, and acrylic syrups (**Figure 1.**).

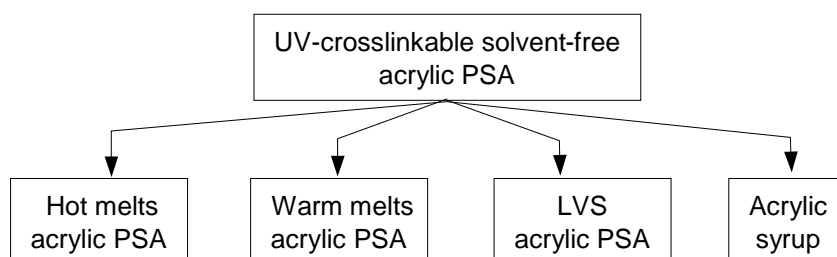


Figure 1. Photoreactive solvent-free acrylic PSA systems.

The currently available hot melt and warm melt acrylic systems include an unsaturated photoinitiator photoreactive group in the polymer chain, incorporated during PSA synthesis. Systems based on low viscosity acrylic PSA and acrylic syrup require an additional photoinitiator [4].

The distinguishing features of these photoreactive solvent-free acrylic PSA systems, particularly from the perspective of the end user, are summarized in **Table 1.**

Table 1. Comparison of the various solvent-free UV crosslinkable acrylic PSA systems

Photoreactive PSA system	Acrylic hot melt	Acrylic warm melt	Acrylic LVS	Acrylic syrup
Loop Tack	Very good	Very good	Very good	Very good
Peel adhesion	Very good	Very good	Very good	Very good
Shear strength at RT at 70°C	Very high High	Very high High	Very high High	Very high Very high
UV-reactivity	Very high	High	High	Very high
Odor from photoinitiator	Non measurable	Non Measurable	Exceptional	Exceptional
Transparency	Exceptional	Exceptional	Exceptional	Exceptional
Modification	Moderate	Moderate	Good	moderate

The summary shows that none of these technologies delivers a performance superior to solvent-borne systems.

ACRYLIC HOT MELT PSA CONTAINING A PHOTOINITIATOR WITHIN THE POLYMER CHAIN

Photoreactive acrylic hot melt PSA are commercially available raw materials for the production of pressure-sensitive adhesive tapes, labels, and medical products. They are processed as hot melts with a very high viscosity, exceeding 100 Pa·s at room temperature. During a coating process, an acrylic hot melt is applied directly to a carrier or a siliconized paper or film in preparation for subsequent transfer by heating to temperatures of 130...140°C, at which point the hot melt liquid adhesive displays a viscosity acceptable for processing. After coating onto the carrier, the acrylic film is crosslinked by UV irradiation using a commercially available UV lamp (**Figure 2.**), thereby achieving the required adhesive performance.



Figure 2. UV lamp with transmission belt

Photoreactive acrylic PSA can be processed using standard coating equipment for preparing synthetic rubber hot melts, such as common slot-die or roll systems. These systems are readily available for the production of typical self-adhesive materials and can be modified by installing UV lamps. Standard mercury medium pressure vapor lamps have an appropriate emission spectral profile in the UV-C range, 220...280 nm, which is required for the efficient UV-initiated crosslinking of photoreactive acrylic hot melts. The acrylic polymer backbone of these chemically modified acrylic hot melts includes photoreactive groups. Unlike conventional UV crosslinkable systems, the photoinitiator is not mixed as a separate photoinitiator component; rather, the photoinitiator is incorporated into the polymer backbone via chemical bonding during polymerization [5...7].

The manufacture of photoreactive acrylic hot melts involves routine and common solvent polymerization techniques. Typical organic solvents may be used, including acetone, ethyl acetate, n-hexane, special boiling point petrol (b_p between 60°C and 95°C), methyl ethyl ketone, and toluene. The use of these solvents allows for the synthesis of a solvent-borne acrylic PSA with a high final polymer content between 55 and 85 wt.% (**Figure 3.**) and a controlled high viscosity between 30 and 60 Pa·s, measured at room temperature for PSA systems with a high polymer content [8].

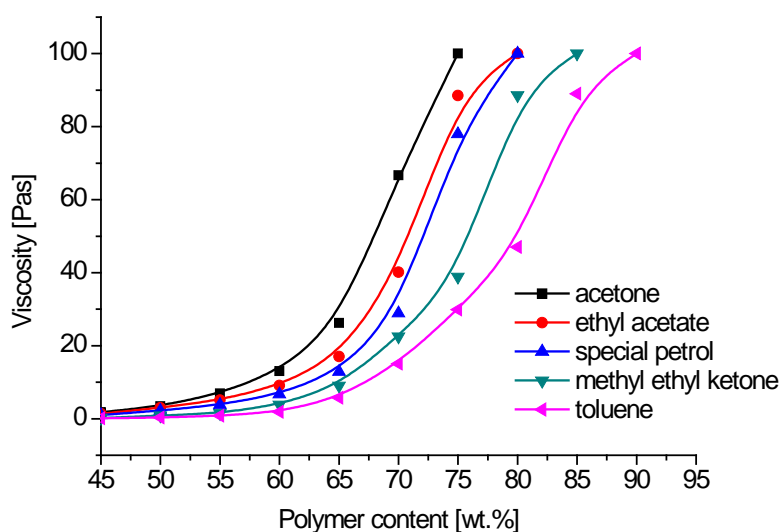


Figure 3. Viscosities of the solvent-borne acrylic PSA as a function of the polymer content

It is eminently important to determine the viscosity limit that permits the removal of polymerization medium from the PSA solution without thermal degradation. The solvent-free polymeric mass should melt at temperatures below 140°C. Above this temperature, acrylic polymers begin to thermally degrade. The selection of suitable organic solvents depends on the polymer solubility and the polymerization mechanism. Controlled synthetic methods are suitable for the preparation of high-performance photoreactive solvent-borne pressure-sensitive adhesives with high molecular weights between 150 000 and 350 000 Da.

The customer demand for solvent-free PSA systems and radiative crosslinking techniques has increased because these approaches offer high efficiencies and low processing costs associated with

the UV sources. UV radiation processing has several other advantages, including high line speeds that improve production speeds and can be used with solvent-free environmentally friendly formulations. The ratio of the peel adhesion to the shear strength in a UV crosslinkable acrylic-based hot melt PSA can be varied within certain limits by controlling the amount of UV energy applied to a self-adhesive film coating. Photoreactive films become more cohesive as the amount of radiant energy applied is increased, whereas the film adhesion and tack decrease with increasing radiant energy (**Figure 4**).

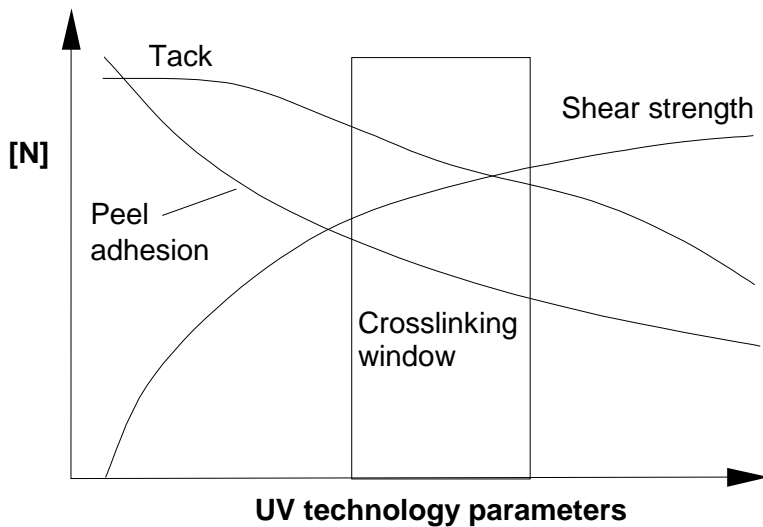


Figure 4. Properties of radiation crosslinked acrylic PSA as a function of the UV dose

These properties result from the crosslinking reaction that occurs upon exposure of the polymer layer to UV radiation. Photoinitiators absorb the UV radiation and generate free radicals or reactive species that initiate UV crosslinking upon cleavage or intermolecular reactions. UV crosslinking approaches are advantageous in that they allow for precise temporal and spatial control over the crosslinking process, which occurs selectively within the illuminated areas. These advantages, together with the costs and environmental considerations, are the main reasons why the use of UV crosslinkable adhesives has increased over time. The technique continues to attract attention in a variety of sectors, as indicated by the numerous patent applications that have been filed recently describing novel applications of the technology. A crucial motivation for developing high-performance UV crosslinkable acrylic PSA has been to ensure excellent adhesion to a variety of substrates. In this regard, the absence of solvent for resin formulations is certainly a disadvantage relative to solvent-borne acrylic PSA. One limitation of the use of UV crosslinking in PSA applications is that because crosslinking only occurs in illuminated areas, regions of the assembly must be transparent to UV radiation [9].

The quantity of radiation energy applied to an adhesive layer can be expressed as the UV dose, measured in mJ/cm^2 . The UV dose can be controlled by adjusting the power of the lamp and the speed at which a substrate is passed under the lamp in the production plant.

CROSSLINKING MECHANISM OF THE UV CROSSLINKABLE ACRYLIC PSA

The mechanism whereby the photoreactive acrylic PSA crosslink involves the photoreactive benzophenone derivatives incorporated into polymer backbones. This mechanism has been thoroughly investigated and is illustrated schematically in **Figure 5**. [2]. Upon UV exposure, intermolecular benzophenone derivative H-abstractor structures become excited and react by hydrogen abstraction with the neighboring tertiary carbon atoms of the polymer side chains.

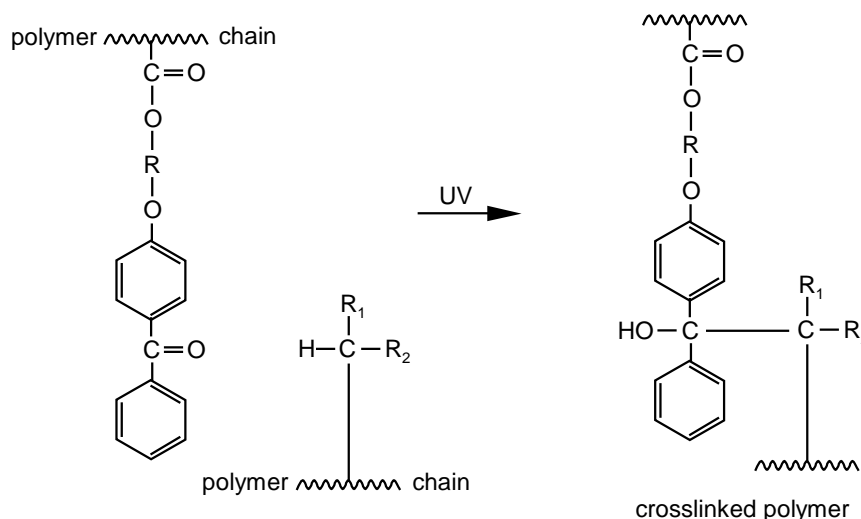
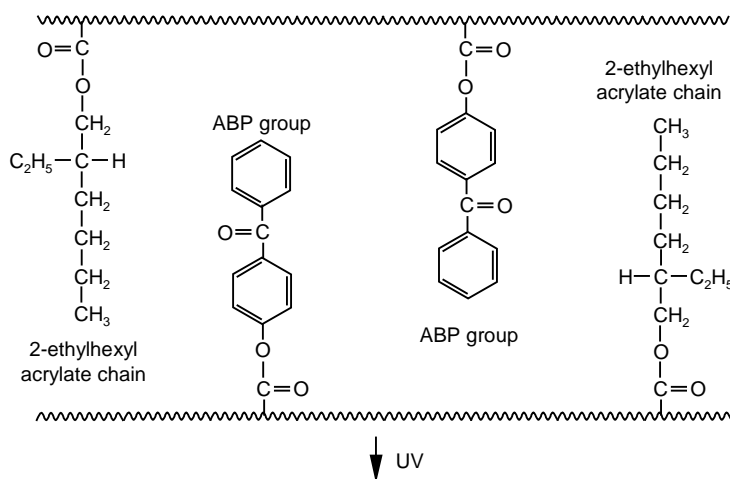


Figure 5. The UV-initiated crosslinking reaction of the acrylic PSA (R = alkylene, R₁, R₂ = alkyl groups)

A particularly important feature of the crosslinking behavior of photoreactive acrylic PSA is that they form crosslinks only at certain polymer chain positions, mainly at tertiary carbon atoms. Other carbon atoms in the polymer backbone do not contribute significantly to crosslinking in UV crosslinkable acrylic adhesives. These chemical properties rely on the chemical structures of the polymer chain and the photoreactive group in the acryloyloxybenzophenone (ABP) (**Figure 6**.) [10].



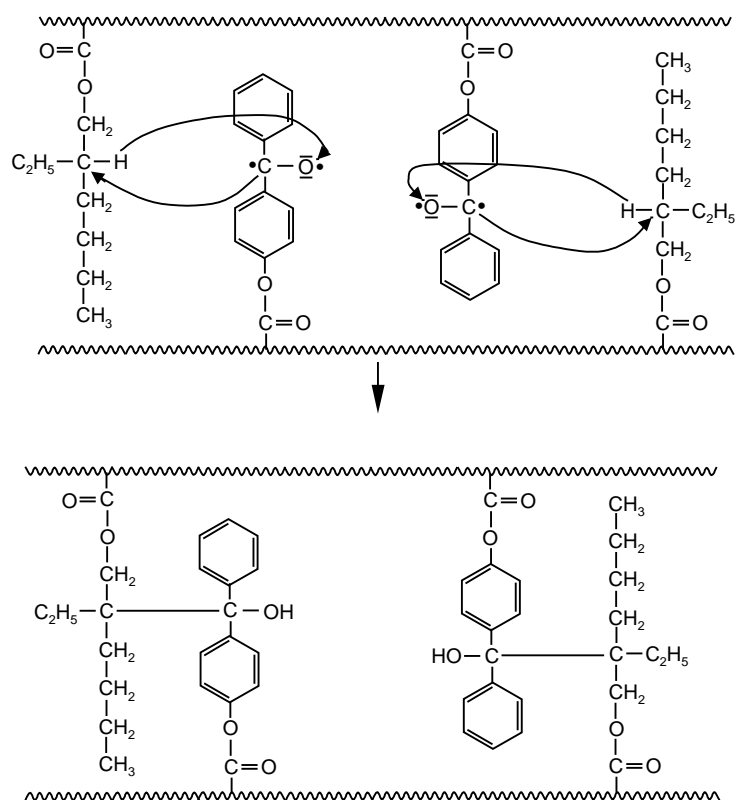


Figure 6. UV crosslinking of an acrylic PSA using the copolymerizable H-abtractor, ABP

The radicals necessary for the crosslinking reaction in the adhesive film are produced by irradiating the photoreactive ABP groups with UV light at a wavelength that is on resonance with the electronic transitions associated with reactive species generation.

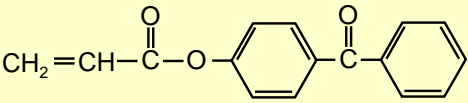
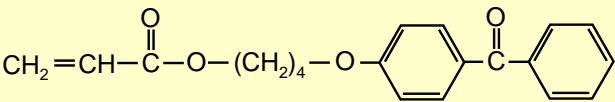
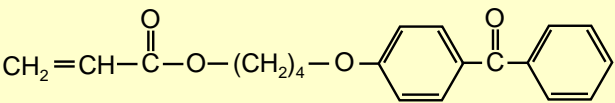
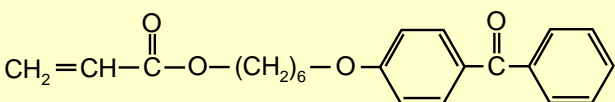
UV crosslinking methods are limited by the high costs associated with synthesizing polymers containing photoinitiators with unsaturated double bonds. No such photoinitiators are currently available on the market, none have been approved by the FDA, and the photoinitiators display significant absorption at UV wavelengths shorter than the absorption bands of acrylic PSA. Additionally, the UV penetration depth is limited, crosslinking can vary nonlinearly with the line speed, and the melt viscosities of solvent-free acrylic PSA are generally less appropriate for coating applications [11].

PROPERTIES OF THE PHOTOREACTIVE ACRYLIC PSA INCORPORATING A VARIETY OF PHOTOINITIATORS

The influence of select unsaturated photoinitiators of type II (hydrogen abstractors) on the properties of synthesized acrylic hot melts was investigated. Acrylic PSA were synthesized using a monomer mixture composed of 65 wt.% 2-ethylhexyl acrylate (2-EHA), 30 wt.% methyl acrylate (MA), and 5 wt.% acrylic acid (AA). During polymerization, copolymerizable benzophenone photoinitiators, such as ABP, 4-acryloyloxyethoxybenzophenone (AEBP), 4-acryloyloxybutoxybenzophenone (ABBP), and 4-acryloyloxyhexoxybenzophenone (AHBP) with different organic spacer chain lengths, were

incorporated into the polymer backbone at concentrations of 0.05...1.0 wt.% (**Table 2.**).

Table 2. Polymerizable photoinitiators of type II used for the synthesis of acrylic PSA

Photoinitiator	Chemical formula	Chemical name
ABP		4-acryloyloxy benzophenone
AEBP		4-acryloyloxyethoxy benzophenone
ABBP		4-acryloyloxybutoxy benzophenone
AHBP		4-acryloyloxyhexoxy benzophenone

The synthesized acrylic PSA were coated at a 60 g/m² coating weight onto a polyester film, then crosslinked using a UV lamp over a range of applied UV doses and UV-crosslinking dwell times. The tack, peel adhesion, shear strength, and shrinkage of the UV-crosslinked self-adhesive layers were evaluated. The influence of crosslinking agents or methods on the adhesion properties of a film (the tack, adhesion, cohesion, and shrinkage) is usually determined in relation to the reaction time

and crosslinking agent concentration. The tack, adhesion, and cohesion were determined using standard A.F.E.R.A. (Association des Fabricants Europeens de Rubans Auto-Adhesifs) procedures. Procedural 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. Shrinkage of the synthesized acrylic PSA was evaluated by applying a coating on siliconized paper. After UV-crosslinking, the films were transferred directly onto a PVC film [12].

RESULTS AND DISCUSSION

Molecular weight as a function of the photoinitiator type and concentration

The polymer molecular weights (M_w : weight average molecular weight; M_n : number average molecular weight; P_d : polydispersity) were measured in tetrahydrofuran using a liquid chromatograph 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 measured molecular weights are presented in **Table 3**.

Table 3. Molecular weights and polydispersity of the acrylic PSA containing incorporated copolymerizable hydrogen atom abstractor photoinitiators

Concentration of photoinitiator [wt.%]	\bar{M}_w	\bar{M}_n	$P_d = \frac{\bar{M}_w}{\bar{M}_n}$
4-acryloyloxy benzophenone (ABP)			
0.0	280 000	180 000	1.56
0.05	285 000	177 000	1.61
0.1	293 000	176 000	1.66
0.3	303 000	173 000	1.75
0.5	308 000	171 000	1.80
0.7	316 000	169 000	1.87
1.0	334 000	168 000	1.99
4-acryloyloxyethoxy benzophenone (AEBP)			
0.0	280 000	180 000	1.56
0.05	281 000	171 000	1.64
0.1	284 000	166 000	1.71
0.3	287 000	159 000	1.80
0.5	291 000	156 000	1.87
0.7	302 000	154 000	1.96
1.0	312 000	149 000	2.09
4-acryloyloxybutoxy benzophenone (ABBP)			

0.0	280 000	180 000	1.56
0.05	281 000	169 000	1.66
0.1	283 000	161 000	1.76
0.3	285 000	152 000	1.87
0.5	288 000	147 000	1.96
0.7	296 000	143 000	2.07
1.0	307 000	140 000	2.19
4-acryloyloxyhexoxy benzophenone (AHBP)			
0.0	280 000	180 000	1.56
0.05	281 000	167 000	1.68
0.1	282 000	156 000	1.81
0.3	284 000	146 000	1.95
0.5	287 000	142 000	2.02
0.7	293 000	136 000	2.15
1.0	300 000	132 000	2.27

The influences of the copolymerizable photoinitiators on the molecular weight M_w of the synthesized acrylic PSA are shown in **Figure 7**.

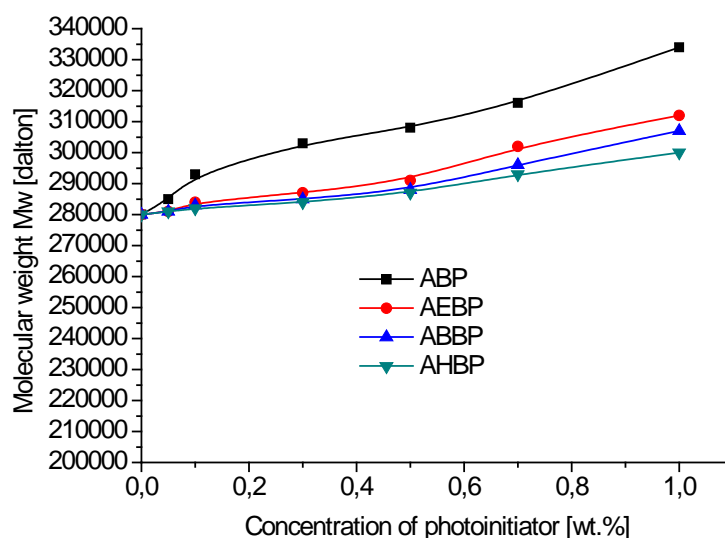


Figure 7. Molecular weights (M_w) of the acrylic PSA as a function of the photoinitiator type and concentration

The experimental results suggest a correlation between the concentration of the unsaturated copolymerizable type II photoinitiator and the molecular weights M_w and M_n of the synthesized acrylic PSA. An increase in the photoinitiator concentration increased M_w and decreased M_n . The highest values of M_w and M_n observed among the acrylic PSA were obtained from adhesives containing ABP incorporated into the polymer chain. Longer organic spacers between the acryloyloxy group and the chromophoric benzophenone groups reduced the value of M_w for the acrylic PSA. An increase in the unsaturated photoinitiator concentration results in a reduced value for M_n in the acrylic PSA (**Figure 8**). The highest values of M_n were measured for ABP.

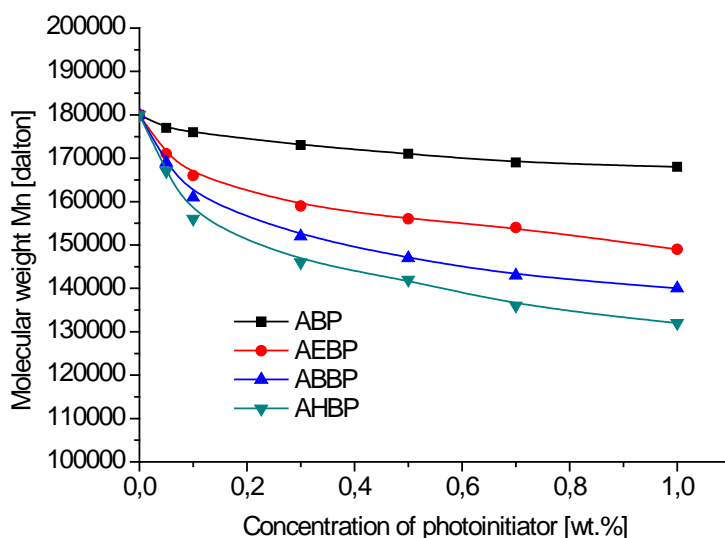


Figure 8. Molecular weight M_n of an acrylic PSA as a function of the photoinitiator type and concentration.

Figure 9. Illustrates the influence of the photoinitiator concentration on the polydispersity of the synthesized acrylic PSA.

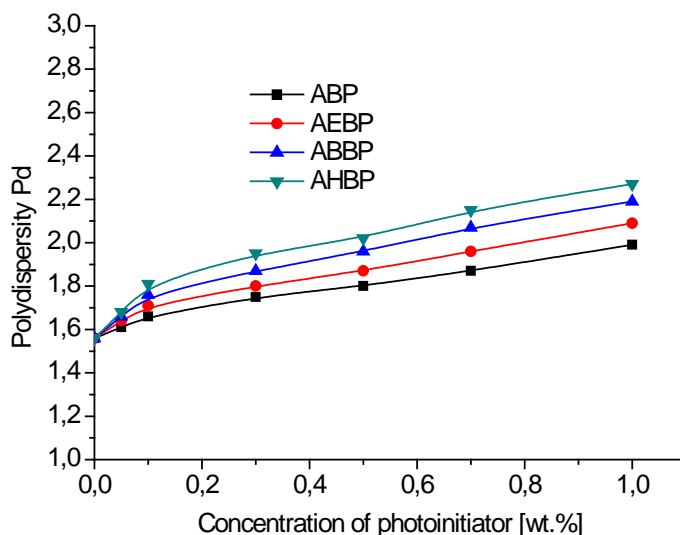


Figure 9. Polydispersity P_d of the acrylic PSA as a function of the photoinitiator type and concentration

An increase in the photoinitiator concentration increased the polydispersity P_d of the synthesized photoreactive acrylic hot melts. Relatively long organic spacers between the ester group and the benzophenone group increased the possibility of free radical transfer onto the organic spacer, which decreased the polydispersity of the acrylic PSA.

Influence of the type and concentration of photoinitiator on film tack

The tack results presented in **Figure 10.** show that the most efficient UV-crosslinking of acrylic PSA (a reduction in tack) was observed for adhesives containing ABP and AEBP.

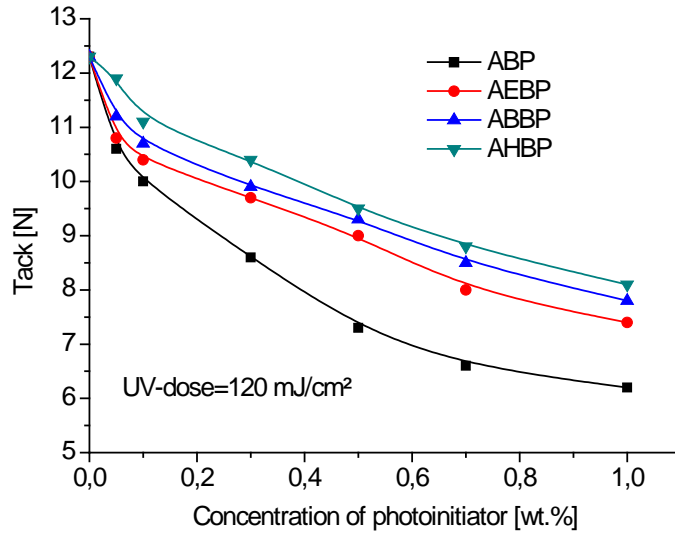


Figure 10. Tack of acrylic PSA films as a function of the photoinitiator type and concentration

Influence of the type and concentration of photoinitiators on film peel adhesion

The peel adhesion of UV-initiated crosslinked acrylic PSA films was measured as a function of the photoinitiator concentration, for a fixed UV dose of 120 mJ/cm². The maximum peel adhesion values observed among all acryloyloxybenzophenones was found to occur at a photoinitiator concentration of 0.1 wt.%. Increasing the photoinitiator concentration beyond 0.1 wt.% decisively reduced the peel adhesion (**Figure 11.**) because unsaturated photoinitiators are less reactive and, therefore, reduce the peel adhesion.

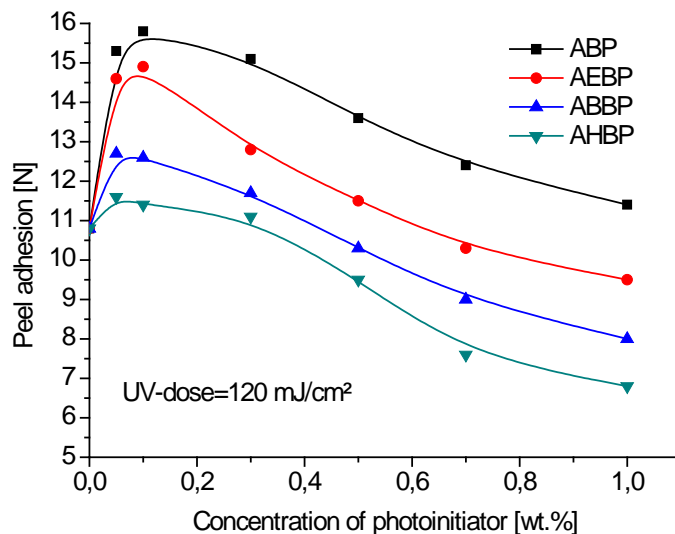


Figure 11. Peel adhesion of an acrylic PSA as a function of the photoinitiator type and concentration

Influence of the type and concentration of a copolymerizable photoinitiator on the shear strength at 20°C and 70°C

The incorporation of unsaturated type II photoinitiators based on benzophenones into an acrylic polymer structure strongly influenced the shear strength of the resulting UV-crosslinked acrylic PSA films (**Figure 12.**). Higher concentrations of the copolymerized photoinitiator produced a higher network density upon UV exposure, leading to higher cohesive forces than are observed in conventional photoinitiator systems. The highest shear strength values were observed for 0.3 wt.% ABP and for 0.5 wt.% AEBP at 20°C and 70°C. Both of the acryloyloxy photoinitiators increased the cohesion to an equal extent.

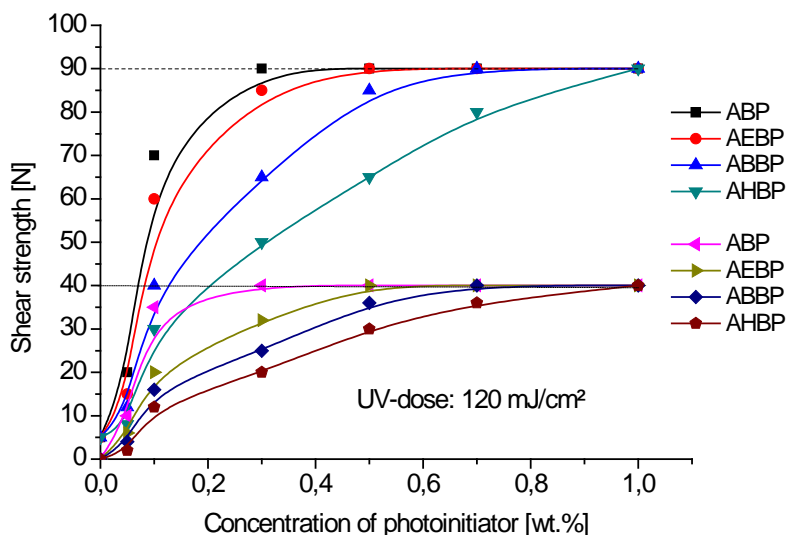


Figure 12. Shear strength of an acrylic PSA at 20°C and 70°C as a function of the photoinitiator type and concentration

Influence of the type and concentration of copolymerizable photoinitiator on film shrinkage

Prior to crosslinking, the PSA polyacrylates were separated according to their characteristic van der Waals radii. Upon crosslinking, the intermolecular distances decreased due to the formation of covalent bonds between monomers, which produced the desired highly crosslinked PSA material. The reduction in the intermolecular distances created internal stress throughout the crosslinked network, as manifested by reduced PSA adhesion to both the substrate and the object attached thereto. Shrinkage was measured as the percentage or millimeter dimensional changes observed in a crosslinked PSA film coating on a PVC foil attached to a glass surface and heated for 1 week at 70°C. The other properties of films that displayed shrinkage values greater than 0.5% or 0.5 mm were neglected [13...15]. The influences of the type and concentration of unsaturated type II photoinitiators on shrinkage for a fixed UV dose, 120 mJ/cm², are shown in **Figure 13.**

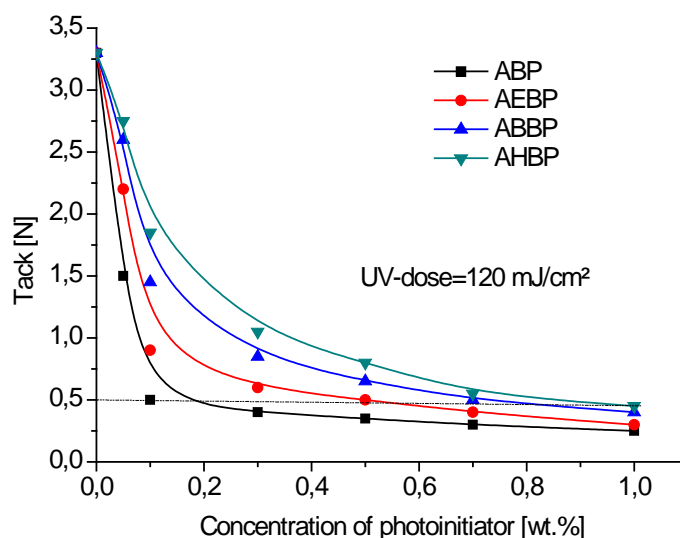


Figure 13. Shear strength of an acrylic PSA at 20°C and 70°C as a function of the photoinitiator type and concentration.

In general, type II copolymerizable photoinitiators offer an efficient method for reducing shrinkage in acrylic PSA film coatings on PVC films. The best results, with respect to shrinkage, were observed in the case of ABP. The acrylic PSA containing 0.3 wt.% ABP were characterized by very low shrinkages < 0.5%.

APPLICATIONS OF UV-CROSSLINKALBE SOLVENT-FREE ACRYLIC PSA SYSTEMS

The properties of crosslinked solvent-based acrylic PSA, including tack, peel adhesion, shear strength, and shrinkage, were evaluated according to test procedures established in the industry. The properties are reported as the average result of three independent measurements. In the event that major deviations were observed, the measurements were repeated. High-performance solvent-borne acrylic PSA used in PSA applications are distinguished by their very high shear strength (120 N at 20°C, 40 N at 70°C). PVC applications require a shrinkage of less than 0.5%, a high tack, and a maximum peel adhesion.

Medical tapes

Skin is a complex organ with a very rough surface. Skin is composed of two layers. The lower layer is the dermis containing two major proteins, collagen and elastin, that form a matrix to support the outer layer, called the epidermis. Skin varies considerably with gender, age, ethnicity, location on the body, and ambient conditions. It is also a structurally weak surface. The top layer, called the stratum corneum, is made of cells that migrated from the base of the epidermis and are in the process of being sloughed off as the skin renews and replenishes itself. The body sheds roughly 10 million cells per day, or about 10 thousand per minute during walking. Skin turns over completely in about 20...30 days. Sweat and natural oils are exuded from the pores, which can lead to gradual debonding of an adhesive [14...15].

The surface energy of skin is low, and adhesion may be compromised by contamination with water, oils, salts, and loose debris (**Table 4.**). These considerations limit surface contact and impose an

upper limit on the adhesion that may be achieved [6]. Adhesion bond failure occurs mostly in the stratum corneum.

Table 4. Skin has a low-energy surface

Material	Critical surface-energy [mN/m]	Polar [%]
Skin	25...29	40
Polyethylene	31	3
Teflon	18	0.2
Water	72	68

Ideal adhesives are characterized as very soft, high in peel, permeable to moisture, and capable of exhibiting a slight creep at body temperature to permit rebonding. Although this combination of features is difficult to attain in a single adhesive, the formulation of acrylic PSA provide a new approach with high potential. Acrylic PSA for skin must display a combination of traits that differ from general-purpose adhesive products. Because medical devices are applied to a body that is compromised by acute, chronic, or systemic conditions, it is important that none of the adhesive components are aggravating to the system. Toxic components that can be absorbed through broken or compromised skin must be excluded, and any compounds that result in allergic sensitization, response, or acute chemical irritation must be avoided [16].

Industrial tapes

Industrial tapes require a high glass transition temperature T_g in solvent-free acrylic PSA after UV-initiated crosslinking to provide high SAFT values. Mounting tapes used in the automobile industry must also display good resistance to heat, a high shear strength, and good adhesion to nonpolar surfaces. In most cases, industrial tapes are required for permanent plastic-to-plastic or plastic-to-metal bonds, and they must withstand standard operational temperatures in the automobile industry.

Self-adhesive labels

The softness, clarity, and UV stability of the UV-crosslinked acrylic PSA described above are benefits to graphic label applications. Nearly all self-adhesive labels currently used for label printing, with the exception of high-monomer plasticized PVC carriers, can be produced using UV crosslinkable acrylic hot melt PSA; however, the higher costs associated with the raw materials compared with the costs of solvent- and water-borne systems may initially limit the adoption of the new technology to specialized applications in the PSA label sector. Some interesting applications include labels used as closures, removable labels, and labels that are resistant to heat and moisture.

CONCLUSIONS

Research and development in the area of novel high-quality photoreactive hot melt acrylic PSA include adhesives containing unsaturated copolymerizable type II photoinitiators. The balance between UV- and PSA-technologies is an important factor in the manufacture of high-efficiency

photoreactive acrylic PSA systems. Novel UV crosslinkable acrylic PSA can overcome the challenges associated with fulfilling the demands of removable applications. By formulation, application, UV-crosslinking level, or a combination of these industrially important parameters, customers can achieve tailor-made solutions to stay innovative and competitive. The properties of acrylic PSA can be adjusted right up to the crosslinking stage. There is currently no such thing as a standard UV crosslinkable acrylic PSA. Because chemical reactions occur during crosslinking, a good understanding of the process, chemistry, and the interactions between the two is needed to make a consistent product. The overall best performances of UV-crosslinked acrylic PSA containing copolymerizable acryloyloxy-photoinitiators were achieved using H-abstractor ABP. The ABP was undoubtedly the most efficient photoinitiator among all acryloyloxy-photoinitiators tested. ABP was a very efficient copolymerizable photoinitiator. Concentrations of 0.1...0.3 wt.% ABP were sufficient to reach a peel adhesion maximum and to reach a very high cohesion of 90 N. Further increasing the ABP concentration decreased the tack and peel adhesion of UV-crosslinked acrylic PSA and simultaneously tremendously improved the shear strength. Novel UV crosslinkable acrylic hot melt PSA combine the economic advantages of hot melt coating technologies with the high-performance characteristics of acrylic chemistry, including excellent aging resistance, optical transparency, and heat resistance.

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