

# CROSSLINKING OF PUR-PSA WATER-BORNE SYSTEMS

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**Abstract.** Since their introduction in the 1930s, polyurethanes have been successfully applied in many fields. They are used for insulation in construction and in mechanical engineering, for the installation of door and window frames, even in the field of medicine. Water-borne polyurethane pressure-sensitive adhesives (PUR-PSA) represent a relatively new self-adhesive group used for the production of self-adhesive tapes, labels, and protective films. A very interesting scientific area is the crosslinking process of novel water-borne polyurethane pressure-sensitive adhesives synthesized from hydroxylated polybutadiene, hydroxylated benzophenones, diisocyanates, polypropylene glycols with high molecular weight and dicarboxylic acids.

## 1. INTRODUCTION

In many chemical industry sectors, environmental factors are the main driving force for the increase of research, development, production and application. In the last ten years or so, polyurethane pressure-sensitive adhesives have made tremendous strides from what was virtually a black art to what is now a sophisticated science. So much so that both the few larger manufacturers of pressure-sensitive adhesive articles and their even larger suppliers now use very expensive equipment to study pressure-sensitive adhesive behavior: tack, adhesion, and cohesion [1].

Four properties that are useful in characterizing the nature and structure of pressure-sensitive ad-

hesives are tack, peel adhesion (adhesion), shear strength (cohesion), and shrinkage. The first measures the adhesive's ability to adhere quickly, the second its ability to resist removal by peeling, and the third its ability to hold in position when shearing forces are exerted (Fig. 1). Shrinkage phenomenon is attributed to the formation of a three-dimensional, covalently crosslinked network during crosslinking, which reduces intermolecular distances between the monomers used to form the crosslinked network [2].

The performance of pressure-sensitive adhesives, such as tack, peel, shear, and shrinkage, based on polyurethanes synthesized through polyaddition of suitable monomers and formulated in water, are to a large degree determined by the molecular weight of the polyurethane polymer, synthesis method and

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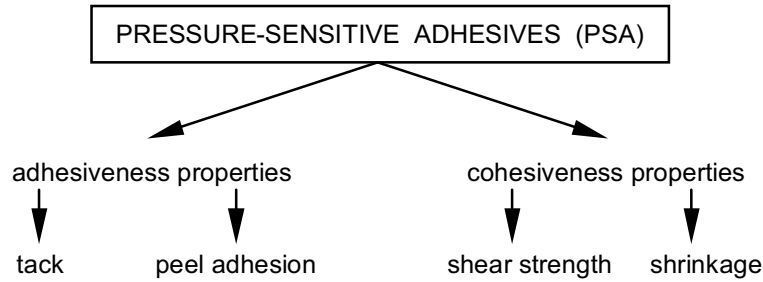


Fig. 1. Main properties of pressure-sensitive adhesives.

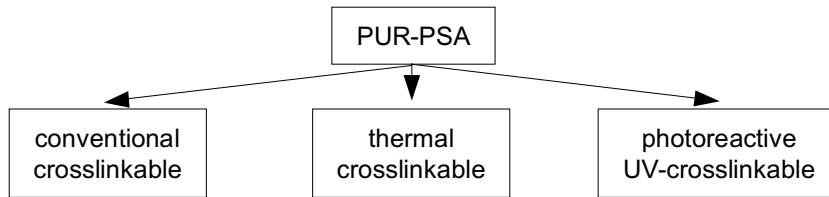


Fig. 2. Kind of water-borne polyurethane PSA.

especially by the type and quantity of the crosslinking agents added to the water-borne PUR-PSA [3].

## 2. KIND OF WATER-BORNE POLYURETHANE PSA

The pure polyurethane polymer in water normally exhibits lower levels of tack and peel adhesion (adhesion) and comparable shear strength (cohesion) compared to typical water-borne acrylics. Tackification of the PUR-systems is very complicated and desired to increase tack and peel adhesion, but it reduces cohesion. In this case, aging of the tackifier may cause brown spots or overall yellowing of the dispersion adhesive. However, since water is much less expensive than solvents and also the solids content of water-based acrylics is higher, they are more economical in use, which is important in the competitive paper label and packaging tape markets. Applications are usually limited to indoor use as the water resistance of these adhesives is limited, although improvements are made continuously [4].

Drying water-based systems can be very fast, particularly when the web (e.g. release paper or release adhesive film) allows high temperature. Explosion hazards do not exist. However, wetting of

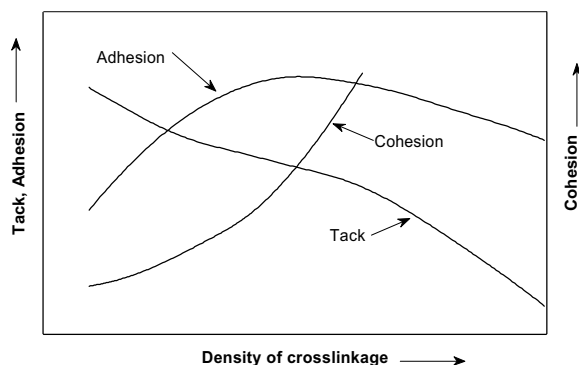
the web is often a tricky problem and much work is carried out in the area of wetting agents to improve this whilst minimizing effects on performance.

Water containing polyurethane PSA can also in the future be an unabandonable constituent of particularly efficient water-soluble PSA technology. The development of the typical crosslinkable, thermal crosslinkable and UV-crosslinkable PUR-PSA (Fig. 2) is directed towards improving present technologies for broader use and for new applications.

## 3. TARGET OF CROSSLINKING

The physical, mechanical, and chemical properties of PSA based on polyurethanes, such as tack, adhesion, cohesion, and shrinkage, are determined by the kind and amount of crosslinking agents that are added to the PUR-polymer. It is known that polyurethane polymers, which are uncrosslinked or crosslinked only by hydrogen bonds, have insufficient thermo-mechanical stability and are practically useless as high performance PSA.

The crosslinking can be considered as a critical factor in the formulation of a PSA, concerning the application stage. The crosslinked connections generated extensively inhibit the mobility of the polymer molecules due to chemical bonds in the network of the polymeric PSA. A crosslinked PSA can



**Fig. 3.** General effects of crosslinking on PSA properties.

therefore no longer melt. Perhaps it becomes somewhat softer at increased temperature, but does not melt. It rather undergoes decomposition above a certain temperature.

With the aid of chemical bonds, an increase in cohesion may be accomplished during the drying of the PSA coating. Logically, the tackifying properties of the PSA coating, such as tack and adhesion decrease (Fig. 3) [5].

### 3. CONVENTIONAL CROSSLINKABLE POLYURETHANE PSA

The properties of water-dispersible polyurethane pressure-sensitive adhesives, synthesized by the addition of hydroxylated polybutadiene (HTPB), polypropylene glycol (PPG), dimethylolpropionic acid (DMPA), and isophorone diisocyanate (IPDI), catalyzed by dibutyltin dilaurate (DBTDL) in the absence of a solvent at about 85 °C for 2 h under nitrogen atmosphere, are formulated by the kind and quantity of the crosslinking agent added to the self-adhesive. It is necessary to achieve inter-chain crosslinking for heat resistance, because the pressure-sensitive adhesive polymers are operating in the region above their glass transition temperature.

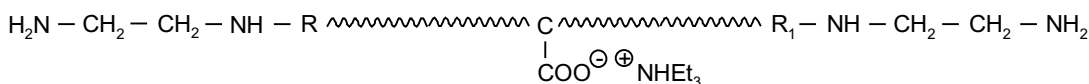
Therefore, without crosslinks, the polymer would readily flow under heat, losing all cohesive strength. The crosslinking also builds water and chemical resistance, as well as final adhesive properties to enhance die cutting, slitting and roll stability [6].

Additional to physical crosslinking, the polyurethane PSA is also linked by hydrogen bonds when the water is removed after coating. Additionally, van der Waals forces should be mentioned, which are noticeable in all PSAs being free of crosslinking agents and are more or less connecting the molecule chains by secondary valence forces in a narrow spaced network. The hydrogen bonds also belong to secondary valence crosslinking and are based on a dipole-dipole attraction of polar groups such as COOH, -CONH<sub>2</sub> or -OH. If, therefore, such polar groups are present at certain distances in an overall non-polar PSA, the chains are more strongly connected at places where such groups are present in comparison to those where they are not. This causes the characteristic features of crosslinking. The polar groups used affect one another and generate hydrogen bonds. The hydrogen bonding existing between polymer chains in PSA systems is fully reversible.

Water-borne polyurethane polymers whose chains are not only crosslinked via hydrogen bonds or inter penetrating systems (IPN) can hardly be cohesively loaded. But a few tenths of a percent of crosslinking agent make it a pressure-sensitive adhesive having good mechanical and thermal properties.

The synthesized polyurethane polymer is neutralized with triethylamine (TEA) and the polyurethane dispersion of the bulk in water was performed at high-speed stirring. Afterward, ethylenediamine (EDA) was added to the dispersion that was kept to complete the chain-extension reaction between the amino groups of the chain extender and the NCO end groups of the polyurethane polymer (Fig. 4).

There are several different chemistries that are employed to achieve the water-borne polyurethane polymer crosslinking. A list of the more common chemistries employs the following suitable derivatives [7]:



**Fig. 4.** Chemical structure of the polyurethane aqueous PSA dispersions.

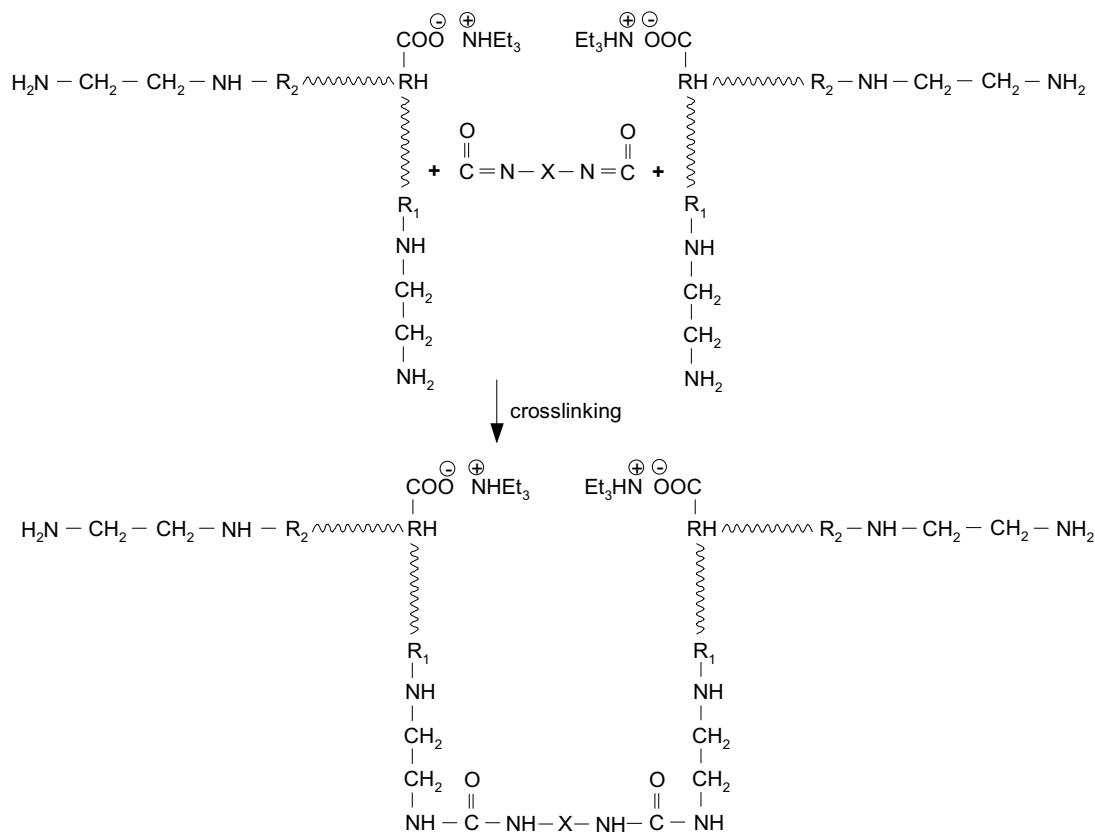


Fig. 5. Crosslinking of water-borne PUR-PSA using multifunctional isocyanates.

- multifunctional isocyanate crosslinking agents;
- polycarbodiimides.

The influence of the crosslinking agent is determined in relation to the reaction time and concentration versus the adhesion property under consideration, of the parameters: tack, adhesion, cohesion, and shrinkage. The PUR dispersion containing a crosslinker was coated onto the polyester film. The basis weight of the adhesive layer covering the film amounted to 60 g/m<sup>2</sup> dry polymer.

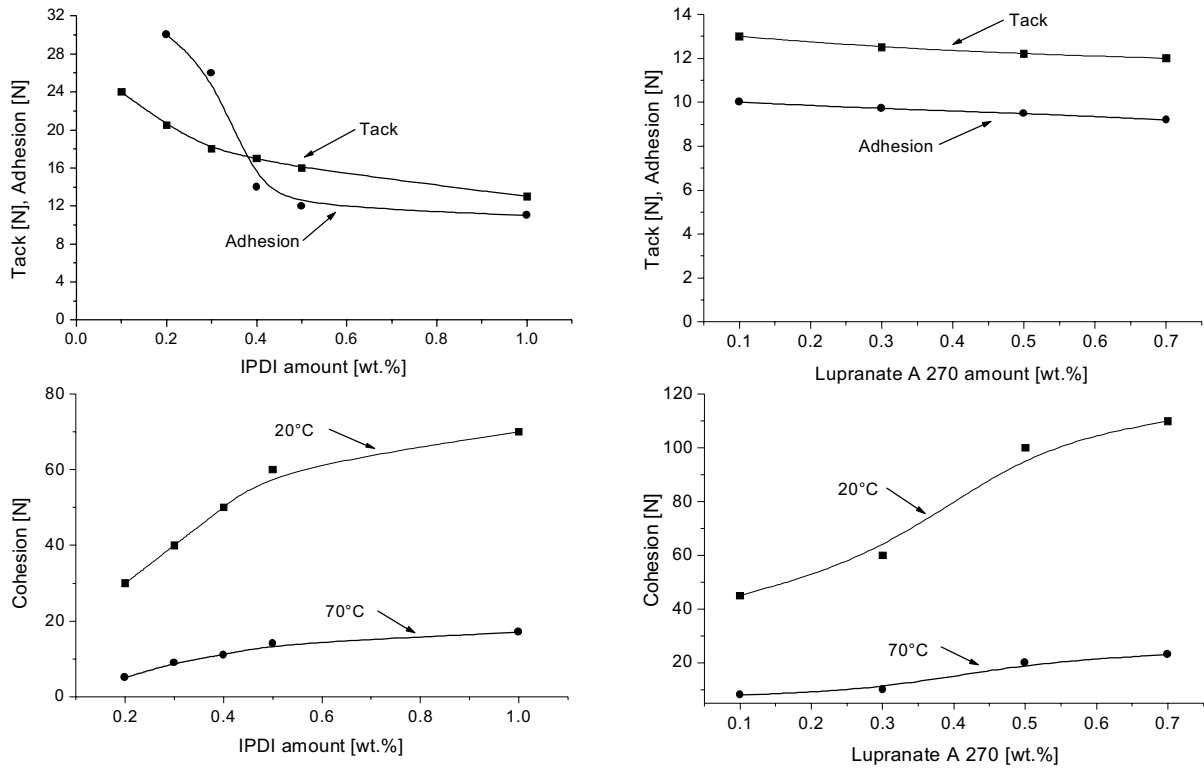
The main properties of investigated PUR-PSA: tack, peel adhesion, and shear strength are determined by standard AFERA (Association des Fabricants Européens de Rubans Auto-Adhésifs). Exact details are found in AFERA 4001 (adhesion), AFERA 4012 (cohesion), and AFERA 4015 (tack). Adresse administrative: 60, rue Auber-94408 Vitry Sur Seine Cedex.

### 3.1. Influence of multifunctional isocyanate crosslinking agents on tack, adhesion, and cohesion

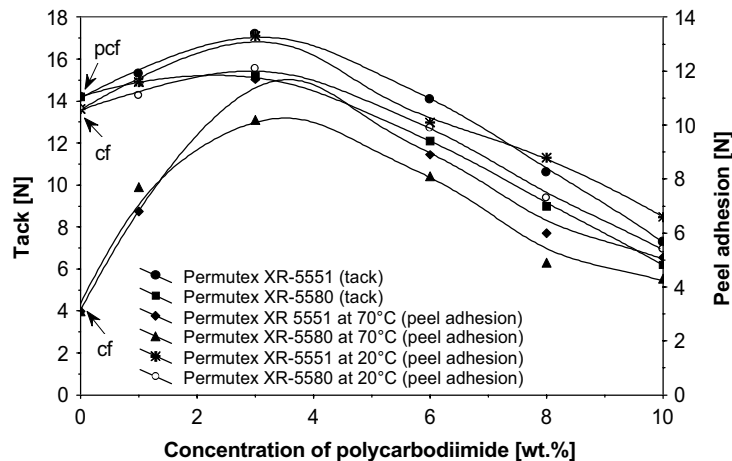
Solventless multifunctional isocyanate crosslinkers are available, based on aromatic, aliphatic, cycloaliphatic, or heterocyclic diisocyanates, which can be dispersed into a water-borne polyurethane formulation. Aliphatic versions are preferred for non-yellowing coatings. In dried coatings, multifunctional isocyanates undergo the normal reactions with active hydrogen atoms of amino groups of the polyurethane polymer chain (Fig. 5).

Typical performance of water-borne PUR-PSA, such as tack, adhesion and cohesion, were tested by the use of polyisocyanate crosslinkers: isophorone diisocyanate (IPDI) and Lupranate A 270 (4,4'-diisocyanatediphenyl methane) (Fig. 6).

The following conclusions can be inferred from the experimental results.



**Fig. 6.** Effect of isocyanate concentration on tack, adhesion and cohesion of crosslinked acrylic dispersions.



**Fig. 7.** Influence of the polycarbodiimides on the tack and peel adhesion of water-borne PUR-PSA.

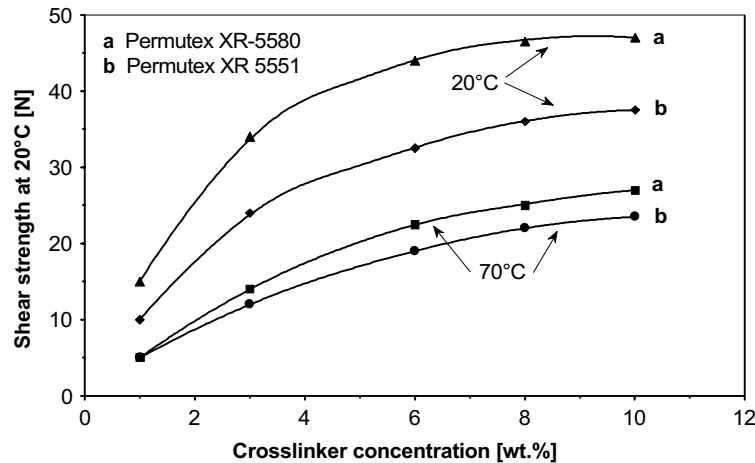
- Cycloaliphatic isocyanate IPDI has a positive influence on the tack and adhesion of PUR dispersions such as that of aromatic Lupranate A 270.

- The use of Lupranate A 270 for crosslinking of dispersions results in excellent cohesion at 20 °C and 70 °C of investigated polyurethane PSA.

### 3.2. Influence of polycarbodiimides on tack, adhesion and cohesion

Several grades of multifunctional carbodiimides have been used in the coating industries, normally supplying the product as 50% active solids in a water-miscible solvent.

The aim here was to examine the influence of polycarbodiimide Permutex XR-5551 and Permutex XR-5580 on the important properties of investigated



**Fig. 8.** Influence of tested polycarbodiimides on the water-borne PUR-PSA cohesion.

polyurethane dispersion. The influence of both of the Permutex crosslinkers' concentration on the PSA tack, adhesion and cohesion are described in the graphs shown in Figs. 7-8.

The uncrosslinked water-borne polyurethane PSA shows low values of tack and peel adhesion along with cohesive failure. After addition of a small amount of the polycarbodiimides, the PUR-PSA begins to crosslink. The PSA structure is now compact, tack, and peel adhesion increases and in the course of the evaluation a maximum of tack and peel adhesion was observed. Finally, at higher concentrations of polycarbodiimides the tack and peel adhesion levels were reduced.

After the addition of small concentrations of polycarbodiimides Permutex XR-5551 and Permutex XR-5580, an amelioration of the PSA properties, like tack and peel adhesion, has been observed for 3 wt.% of either polycarbodiimide. The maxima of tack and peel adhesion are achieved. PSA layers crosslinked with polycarbodiimides are highly tacky and aggressive. After exceeding a threshold of 3 wt.% polycarbodiimide, the tack and peel adhesion levels decrease.

The results show (Fig. 8) that the polycarbodiimides differ in their ability to improve the intended strength of the crosslinked water-borne PUR-PSA. Permutex XR-5580 is a better crosslinking agent than Permutex XR-5551 in this system. In order to reach the shear strength of 50 N at room temperature and 30 N at 70 °C, it is necessary to use about 9 wt.% polycarbodiimide crosslinker Permutex XR-5580.

#### 4. THERMAL CROSSLINKABLE POLYURETHANE PSA

An interesting class of crosslinking agents for the diverse polymers for use at higher temperatures in thermoset coatings, including carboxyl-, hydroxyl- or amine groups, are melamine-formaldehyde resins [8], generally known as amino resins.

They are characterized by their reactive end groups and enable a controlled crosslinking reaction and a precise adjustment of the required adhesive properties. It is their special feature that crosslinking speed is practically zero at room temperature while it increases exponentially above 100 °C. That means that the crosslinking ensues only during the drying of the pressure-sensitive adhesive layer in the drying oven.

The amino resins can be used for the crosslinking of water-borne PUR-PSA at elevated temperatures between 105 and 150 °C. The chemistry of these multifunctional resins is extremely complex and they can be generally classified as fully alkylated, partially alkylated and high imino resins.

Melamine-formaldehyde resins containing high methylol or imino functionality are highly reactive, but prone to self-crosslinking reactions catalysed by free acid groups on the polymer.

The following diagram (Fig. 9.) illustrates how the tack, adhesion and cohesion depend on highly methylated melamine-formaldehyde crosslinker Cymel 303.

As shown in Fig. 9, the increase of amino crosslinker Cymel 303 increases the level of cohesion at 20 and 70 °C. Other properties such as tack and adhesion are reduced. The best results with



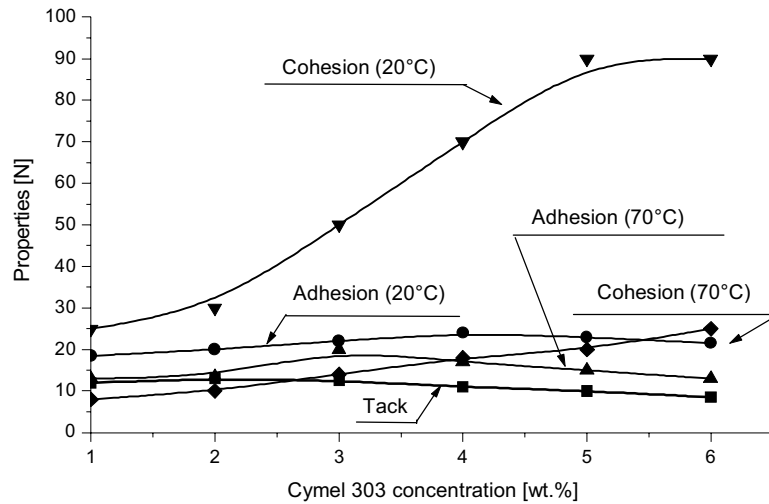


Fig. 9. Properties of crosslinked water-borne PUR-PSA vs. Cymel 303 amount.

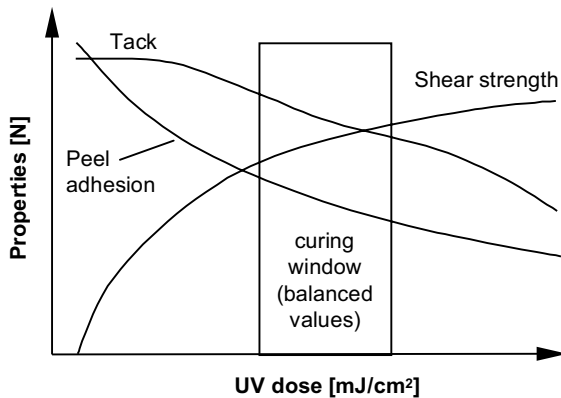


Fig. 10. Tack, peel adhesion and shear strength as a function of UV dose.

respect to the whole performance are observed in the case of about 4%-weight of Cymel 303.

### 5. PHOTOREACTIVE UV-CROSSLINKABLE POLYURETHANE PSA

UV technology is well established in the market and allows the production of a wide range of UV-crosslinkable pressure-sensitive adhesives with interesting features. The balance between adhesive and cohesive strength within the crosslinked coatings is critical for the performance of the UV-PSA. The combination of pattern with UV-crosslinkable adhesives enables the manufacturing of films having zones with different adhesion/cohesion properties and offers novel opportunities to develop innovative tapes with new, unique features [9,10].

With UV-crosslinkable polyurethane 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 (Fig. 10). The chemistry and the synthesis process of water-borne polyurethane PSAs are illustrated in Fig. 11.

The applied hydroxylated H-abstractors are suitable from the group of multifunctional H-abstractor consists of saturated photoinitiators, which contain at least two photoreactive structures in the molecule and form crosslinks with the polymer chain of the pressure-sensitive adhesives by UV radiation. It is possible to obtain so-called migration-free photoinitiators by specific constructions, e.g. from multifunctional benzophenones, xanthenes, thioxanthenes, anthraquinones, fluorenones or benziles (Fig. 12).

Performed polyurethane polymer structures that crosslink directly under the influence of ultraviolet energy require special photosensitive groups from incorporated hydrogen abstractors to effect network formation (Fig. 13).

The synthesized photoreactive water dispersible polyurethane PSA containing photoreactive benzophenone groups incorporated into the polymer structure as main polymer chain by using dihydroxy benzophenone, or as side chains by the use of monohydroxy benzophenone in a concentration between 0.5 and 3.0 wt.%. (Fig. 14).

The water-dispersible polyurethane pressure-sensitive adhesives were cast with a knife coater at 60 g/m<sup>2</sup> on a polyester film. After drying in an oven for 10 min at ca. 105°C, the adhesive was crosslinked

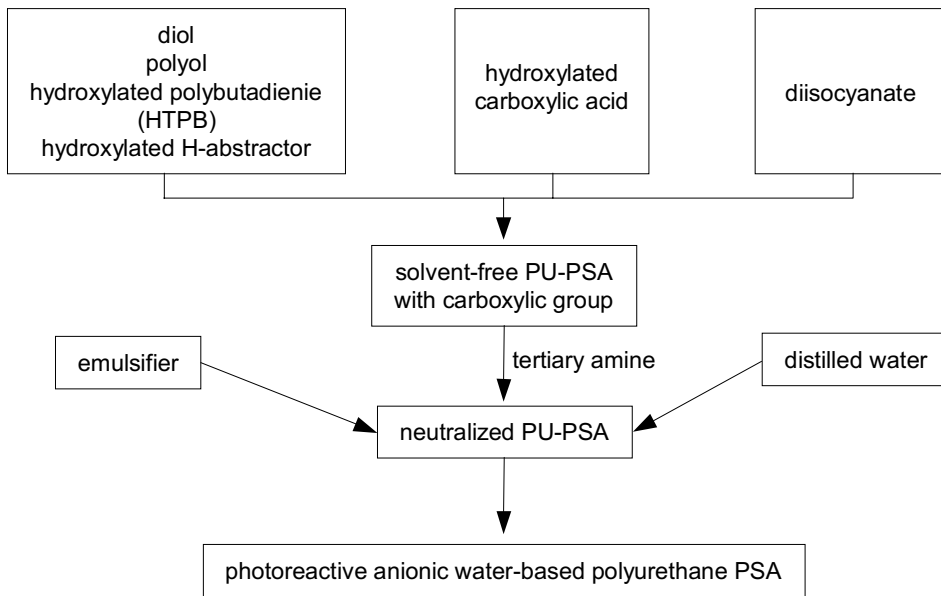


Fig. 11. Synthesis of water-borne photoreactive polyurethane self-adhesives.

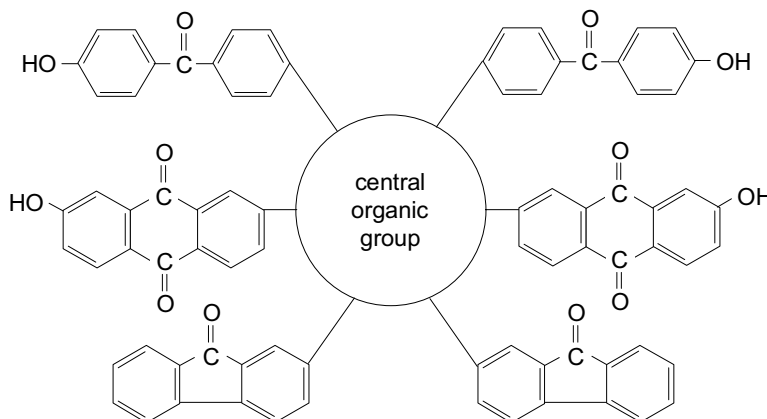


Fig. 12. Multifunctional hydrogen abstractor photoinitiators.

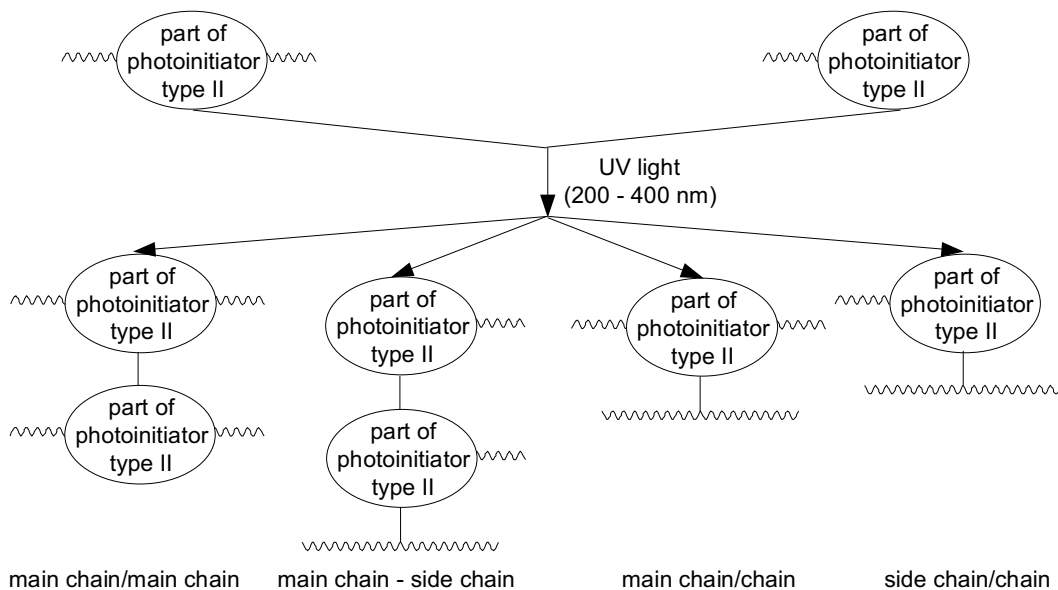


Fig. 13. Polyurethane photocrosslinking by use of H-abstractor photoinitiators incorporated into the polymer chain.



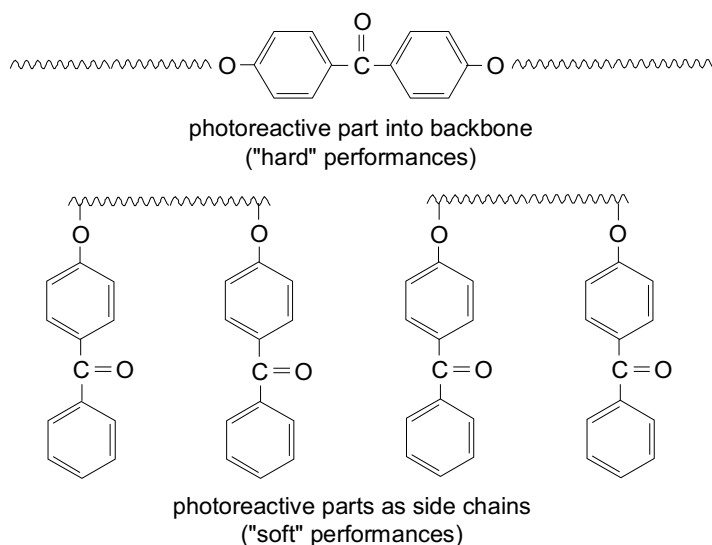


Fig. 14. Structure of the photoreactive aqueous polyurethane PSA.

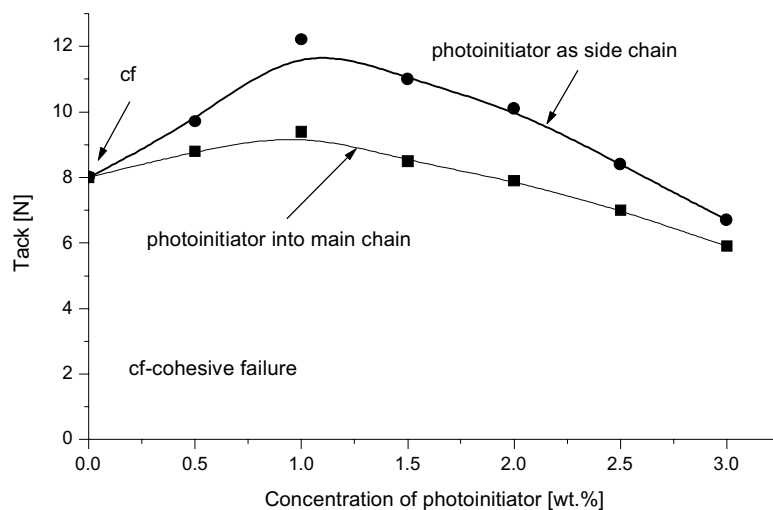


Fig. 15. Tack versus amount of benzophenone photoinitiator.

by ultraviolet light using a  $900 \text{ mJ/cm}^2$  UV source during 3 min of irradiation. The effect of UV-crosslinking of the adhesive by the benzophenone photoinitiators used (concentration ranging from about 0.5 to 3.0 wt.%) on tack, peel adhesion and shear strength for the same crosslinking time of 3 min is illustrated in Figs. 15-17.

These results shown in Figs. 15 and 16 indicate that the best values for tack and peel adhesion of UV-crosslinked water dispersible polyurethane pressure-sensitive adhesives were achieved with the benzophenone photoinitiators type II for about 1.0 wt.% of H-abstractors. Increasing the concentration of photoinitiators incorporated into the polymer chain

leads clearly to deterioration of tack and peel adhesion.

As shown in Fig. 17, both the tested hydrogen abstractor photoinitiators are sufficient to obtain an adequate shear strength improvement of crosslinked PSA acrylics at 20 and 70 °C. The relatively high cohesion was measured with the use of about 3.0 wt.% 4,4'-dihydroxy benzophenone.

## 6. CONCLUSIONS

In this study, it was shown that water-dispersible photoreactive UV-crosslinkable polyurethanes have attracted a considerable amount of developmental

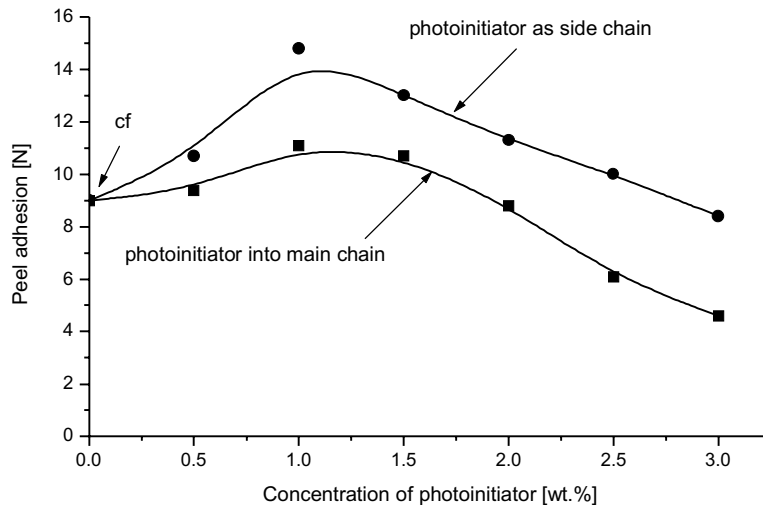


Fig. 16. Peel adhesion versus amount of benzophenone photoinitiator.

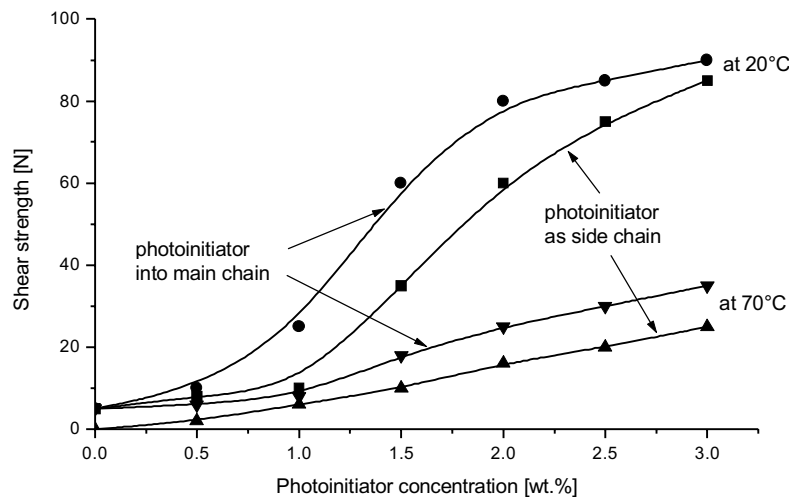


Fig. 17. Shear strength versus amount of benzophenone photoinitiator.

effort for various types of pressure-sensitive adhesives. However, the applications so far have been limited for the production of different self-adhesive products, mainly due to relatively low tack, low peel adhesion and moderate cohesion.

This is unfortunate, because the characteristic photoreactive aqueous polyurethane PSA system properties which cannot be tested by common adhesive article test methods, together with the relatively low raw material costs, should offer enough incentive to more or less re-discover this class of adhesives. Their inherent gentleness to skin, as well as their non-aggressive adherence, makes them predestined for applications in the field of medicine.

Photoreactive water-borne PUR-PSA will not likely take the place of other firmly established PSAs, although there is surely a wide range of pos-

sible new technical applications where this new adhesive type could be of service.

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PUR Faucet Filtration Systems are certified to remove 96% of Mercury. Mercury can make its way into the water system through the erosion of natural deposits along with factory and landfill runoff. According to the EPA, long term exposure to Mercury above regulated levels could lead to kidney damage. [LEARN MORE](#). See full contaminants. PUR Faucet Filtration Systems are certified to remove 99% of Total Trihalomethanes. Disinfection by-products such as Total Trihalomethanes or TTHMs are a result of Chlorine mixing with organic and inorganic materials in the water. If ingested at levels above the r Water-soluble pressure-sensitive adhesives (PSA) based on acrylic acid and carboxymethyl starch (CMS) have been prepared. The tack and peel adhesion to various paper types (newsprint, hygienic) Obtained PSA were completely soluble in water, and the time of water-solubility depended on CMS content, as well as pH value, however it did not exceed 5 min. Keywords. Adhesives Carboxymethyl starch Polysaccharide Pressure-sensitive adhesives Water-soluble polymers. Compared with solventborne systems, traditional waterborne parquet coatings lack various properties such as scuff- and chemical resistance. Several approaches have been investigated in the past to overcome these drawbacks, but many of them were not totally successful. New generations of raw materials for manually applied parquet coatings (waterborne one- and two-component) and industrial application (UV-curing parquet coatings) were developed. The high degree of crosslinking is the main reason for the high shrinkage of such coating systems. This shrinkage often leads to adhesion problems between radiation-cured coatings and the wood substrate. The flexibility, even of high-grade urethane acrylates, does not attain the level of aqueous PUDs.