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Water-borne pressure-sensitive adhesives based on polyurethanes

The technology of water-borne pressure-sensitive adhesives (PSA) based on polyurethanes has been developed. The new synthesized polyurethane PSAs are synthesized using polyols, hydroxylated polybutadiene, carboxylic containing hydroxyl groups and aliphatic, aromatic or cycloaliphatic isocyanates. They are applied for manufacturing of diverse self-adhesive products, such as: mounting tapes, splicing tapes, sign and marking films, labels and protecting films.

Key words: pressure-sensitive adhesives, water-borne polyurethanes, self-adhesive properties, peel-adhesion, shear strength

Wodne dyspersyjne poliuretanowe kleje samoprzylepne

Opracowano technologię syntezy wodnych dyspersyjnych klejów samoprzylepnych na podstawie poliuretanów. Nowe samoprzylepne kleje poliuretanowe otrzymywane są przez poliaddycję mieszanin komponentów zawierających poliole, hydroksylowany polibutadien, hydroksylowany kwas karboksylowy oraz alifatyczne, aromatyczne lub cykloalifatyczne diizocyjaniany.

Słowa kluczowe: kleje samoprzylepne, dyspersje poliuretanowe, właściwości samoprzylepne, adhezja, kohezja

1. Introduction

Since their industrial introduction half a century ago, pressure-sensitive adhesive has been successfully applied in many fields. They are used in self-adhesive tapes, labels, sign and marking films and protective films as well as in medical dosage systems for dermal pharmaceutical applications and by the manufacturing of biomedical electrodes. Three properties which are useful in characterizing the nature of pressure-sensitive adhesives are tack, peel (adhesion) and shear (cohesion). Tack, peel adhesion and shear strength of pressure-sensitive adhesives based on organic polymers are to a large degree determined by the polymerization method, molecular weight of polymer, and especially by the type and quantity of the crosslinking agents or crosslinking methods. For commercially used PSA systems with excellent performances are preferred synthetic polymers based on acrylics, rubber, silicones, polyurethanes, polyesters and polyethers (Fig. 1).

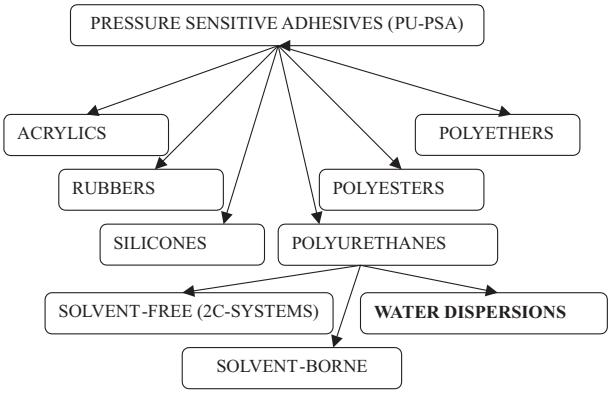

Figure 1. *Polymer types for manufacturing of pressure sensitive adhesives*
Rys. 1. *Polimery stosowane do wytwarzania klejów samoprzylepnych*

2. Water-borne polyurethane pressure-sensitive adhesives

Water-borne polyurethane pressure-sensitive adhesive fulfil many of the industry's most severe requirements in terms performance, environment and easy of practical application. They have been widely used in self-adhesives, sealants and electrical products owing to its low glass transition temperature (T_g) between -40 and -60 °C, hydrophobicity, acid-based resistance and excellent dielectric properties. In many industries, the research, development and application on the coating technology area having a lower chemical impact on occupational health and environment is warmly welcomed especially when it is accompanied with robust application conditions and high standards of performance. As a matter of fact, the water-borne polyurethane polymers fulfil many of these preoccupations and are gradually dominating the market in view to corn ply with the forth-

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coming reduction of volatile organic compounds. Water-borne polyurethanes can offer excellent performance among the water-borne polymer family, the polyurethane water dispersions benefit over the last few years from a continuously growing attention by the market that recognises their high performance and strong potential from soft and rubber properties to right thermoplastic or after cured to thermoset materials. As an example, in recent important publications about polyurethane technology, especially water-dispersible products based on polyurethanes the authors describe the versatility of polyurethane water dispersions technology. Polyurethane chemistry is known for providing high performance in water-borne systems. One of the standard polyurethane adhesive raw materials is diisocyanate which has been a key raw material for the preparation of water-borne adhesive systems for packaging, footwear and automotive applications [1-3].

Films formed by water-dispersible polyurethane pressure-sensitive adhesives become more cohesive as more crosslinking agent is applied, while their tack and peel adhesion decrease. To achieve optimal pressure-sensitive performance with crosslinked adhesives, it is necessary to find process settings that lead to balanced values of tack, peel adhesion and shear strength for the preferred application. Polyurethane PSA coatings, in general, provide excellent chemical, solvent, and abrasion resistance, as well as toughness combined with good low-temperature flexibility. There are various ways of combining a wide variety of diisocyanates, dihydroxyl carboxylic acids and suitable polyols. The extraordinarily diverse chemistry of polyurethanes has also contributed to the development of efficient pressure-sensitive adhesives. However this applies only to a limited degree to PSA where the number of patent publications and references to the manufacturing of aqueous polyurethane PSA dispersions is relative great. Ready for coating water-borne polyurethane pressure-sensitive adhesives are seldom commercial available on the market. With the aqueous polyurethane PSA dispersion products we are stepping on rather unknown terrain-at least so far, almost nothing on this subject has been published, even though this adhesive system would offer an attractive formulation spectrum at raw material costs which are still lower than those of acrylic dispersion [4-6].

Polyurethane adhesives are particularly known for forming bonds with excellent green strength, plasticizer resistance and durability. As environmental legislation limits the further use of water-borne systems, there has been a rapid growth in the area of aqueous polyurethanes (Fig. 2). Reasons for the increasing trend to aqueous adhesives systems are the ecological and economical aspects.

1. Ecological aspects
- superior working hygiene during handling
- higher working safety during handling
- health precaution for the end product

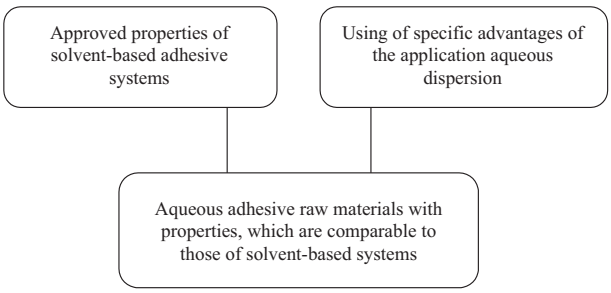


Figure 2. *Target for the development of water-borne adhesive raw materials*
Rys. 2. *Kierunki badań nad rozpuszczalnymi w wodzie materiałami klejącymi*

2. Economical aspect
- lower investment costs (no solvent recovery)
- high solid content than by solvent-based systems

3. Polyurethane water-borne PSA versus acrylic dispersions

Regarding the chemical nature of polyurethane, the water-borne polyurethanes are applied with higher solids content, compared to the solvent-based polyurethanes, because their viscosity does not depend on the molecular weight of the polyurethane, as is in the case of solvent-borne polyurethanes [7].

Table 1. *Properties of acrylic and polyurethane water-borne systems [8]*
Tabela 1. *Właściwości systemów poliakrylanowych i poliuretanowych rozpuszczalnych w wodzie [8]*

Water-borne acrylic PSAs	Water-borne polyurethane PSAs
Advantages	
• Hydrolysis resistance	• Water and moisture resistance
• UV resistance	• UV resistance
• Oxidation resistance	• Moderate cohesion at higher temperatures
• Easier modification	• Good water vapour permeability
• High tack and adhesion values	• Presence of ionomeric groups
• High molecular weight	
• Price: < 4 €/kg (dry)	
Drawbacks	
• Problems with crosslinking	• Hydrolysis sensitive
• Low cohesion value at higher temperatures	• Moderate to low tack and adhesion values
• No water and moisture resistant	• Low molecular weight
• Presence of emulsifier	• Price: 5-7 €/kg (dry)

Table 2. *Specific adhesion from acrylics and polyurethanes PSA on selected substrates*
Tabela 2. *Adhezja poliakrylanowych i poliuretanowych klejów samoprzylepnych do wybranych podłoży*

Substrate	Surface energy	Peel adhesion [N]					
		at 20°C		at 70°C		at 20°C after 24 h	
	[mN/m]	Acrylic	PU	Acrylic	PU	Acrylic	PU
Al	ca. 1500	21.5	9.0	14.5	7.0	28.0	12.0
Glass	1200	20.3	5.8	12.8	5.1	25.5	15.0
Wood	ca. 80	16.3	10.1	8.2	9.1	18.3	20.1
PA	44	13.0	7.0	6.0	9.6	16.5	8.6
Plexiglas	43	12.5	9.0	5.8	5.4	14.0	9.0
PVC	39	11.8	10.2	5.3	6.0	13.1	4.0
PS	33	11.2	12.1	5.0	8.0	12.3	12.4
EPDM	ca. 30	8.3	12,3	4.2	5.1	6.0	9.2
PP	31	10.1	17.0	6.4	7.2	11.0	15.6
PE	26	7.3	15.5	3.8	7.2	7.5	15.0
Teflon	19	3.0	9.1	1.4	4.3	3.3	4.1

Important difference in the structure of water-borne polyurethane PSA in comparison with typical water-borne acrylic PSA is the presence of polar ionomeric groups, mainly carboxylate or sulphonate, into polymeric chain of PUD. Such ionomeric groups are absolutely necessary for the formation of aqueous dispersions, because they act internal surfactans, and cannot be found or are not necessary in the chain of the acrylic water-borne PSA. By various application sectors using acrylic or polyurethane PSA the decided factor is the specific adhesion of both pressure-sensitive adhesives to diverse substrates available on the market (Tab. 2) [9].

Generally, polyurethane PSA are characterised by excellent adhesion on low energy surfaces such as PP, PP and PTFE (Teflon) and acrylic PSA adhere efficient to high energy surfaces like aluminium or glass [10].

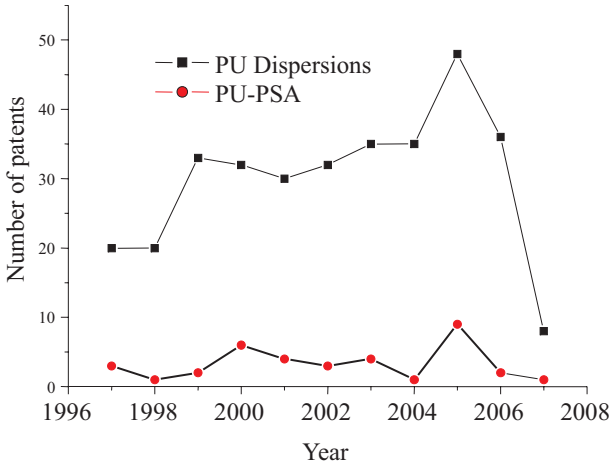


Figure 3. *Patents about water-borne polyurethane adhesives and polyurethane PSAs from 1996 to 2007*
Rys. 3. *Patenty dotyczące rozpuszczalnych w wodzie klejów poliuretanowych oraz poliuretanowych klejów samoprzylepnych w latach 1996 – 2007*

The amount of important patents according to water-borne polyurethane adhesives and water-borne polyurethane pressure-sensitive adhesives (PU-PSA) are illustrated in Fig. 3.

4. Synthesis of the water--borne PU-PSA dispersions

The chemistry and the synthesis process of aqueous PU-PSA illustrate Figure 4.

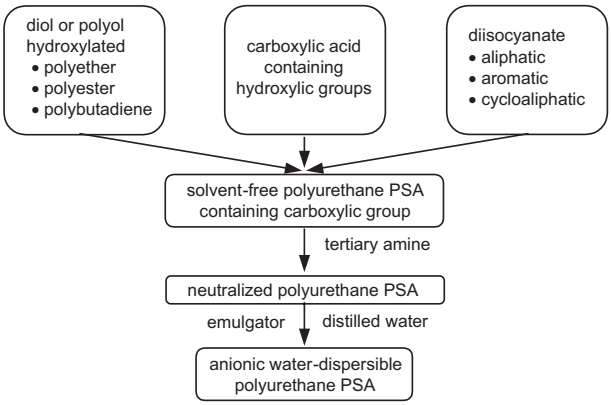
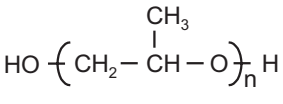


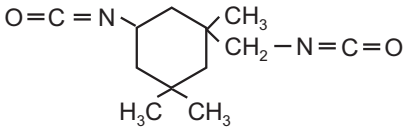
Figure 4. *Synthesis schemas of water-borne polyurethane self-adhesives*
Rys. 4. Schemat syntezy rozpuszczalnych w wodzie poliuretanowych klejów samoprzylepnych

The synthesis of the novel water-borne polyurethane PSAs based on hydroxylated polybutadiene (HTPB), polypropylene glycol (PPG), dimethylolpropionic acid (DMPA) and isophorone diisocyanate (IPDI) catalyzed by dibutyltin dilaurate (DBTDL) was carried out in the absence of a solvent at about 85°C for 2 h under nitrogen

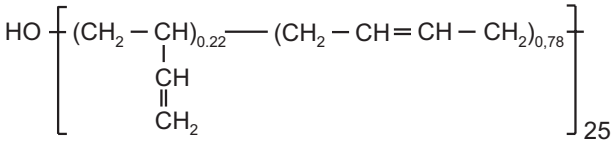


polypropylene glycol (PPG)

$\overline{M}_w$ = 1 010 or $\overline{M}_w$ = 2 000

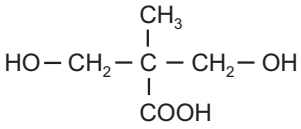


isophorone diisocyanate (IPDI)

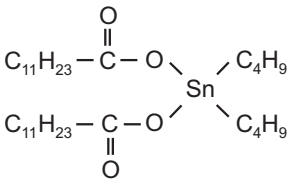


hydroxytelechelic polybutadiene (HTPB)

$\overline{M}_n$ = 1370, $\overline{f}_{OH}$ = 2,45



dimethylolpropionic acid (DMPA)



dibutyltin dilaurate

Figure 5. *The reagents used by the synthesis of water-dispersible polyurethane PSA*

Rys. 5. Reagenty użyte do syntezy dyspergowalnych w wodzie poliuretanowych klejów samoprzylepnych

atmosphere. The mentioned reagents are presented in Figure 5.

After the period, the temperature was reduced to 85°C and aliquots were removed from the bulk for NCO content determination. The synthesized polyurethane polymer neutralization with triethylamine (TEA) was preceded at 50°C for 1 h, the temperature was reduced to 25°C 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 at about 35°C for 1 h to complete the chain-extension reaction between the amino groups of the chain extender and the NCO end groups of the polyurethane polymer. Aqueous polyurethane PSA dispersions with a solid content of about 40 to 60 wt.% were obtained by varying the hydroxylated polybutadiene (HTPB) content from 20 to 50 wt.%, dimethylolpropionic acid (DMPA) from 2 to 6 wt.%.

The isocyanates are very important to introduction of urethane groups into the polymer. Depending on their structure, the final properties of the polymer are influenced. Beside isophorone diisocyanate (IPDI), cycloaliphatic dicyclohexylmethane (HMDI) and aliphatic diisocyanate 2,2,4-trimethyl-hexamethylene diisocyanate (TMDI) are used (Tab.2). The aromatic toluene diisocyanate (TDI) and diphenylene diisocyanate (PPDI) are more difficult to handle. It is result of their high reactivity of water. Some of the newer production processes allow them to be built in.

Table 3. *Diisocyanates used by synthesis of aqueous polyurethane adhesives*

Tabela 3. *Diizocyjaniany stosowane do syntezy wodnych klejów poliuretanowych*

Diisocyanate	Polymer content [wt.%]	Viscosity [mPa·s]	Remarks
IPDI	45	210	stable > 12 months
HMDI	40	110	stable > 12 months
TMDI	55	3200	stable > 12 months
TMDI	60	8400	stable > 12 months

All synthesized water-borne polyurethane pressure-sensitive adhesives (PU-PSA) are characterized through an acceptable pot-life at least of 12 month. The excellent stable water-borne PU-PSA with very high solid content between 50 and 60 wt.% were synthesized using aliphatic diisocyanate 2,2,4-trimethyl-hexamethylene diisocyanate (TMDI). High solid aqueous PU-PSAs are specified as high viscosity PU-PSAs water dispersions (Fig. 6). Their practical acceptable viscosity allows their directly coating on dehesive carrier without

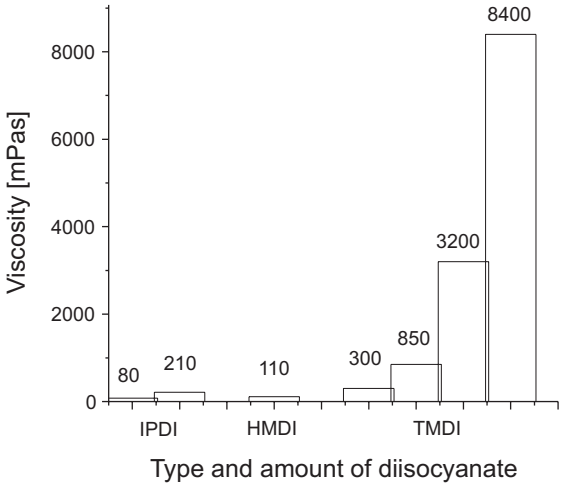


Figure 6. *Viscosity of synthesized water-borne PU-PSA*

Rys. 6. *Lepkość zsyntetyzowanych poliuretanowych klejów samoprzylepnych rozpuszczalnych w wodzie*

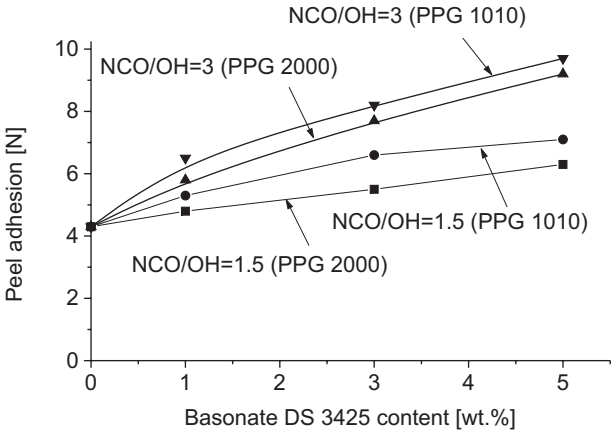


Figure 7. *Effect of multifunctional isocyanate Basonate FDS 3425 amount on the peel adhesion of polyurethane PSA*

Rys. 7. *Wpływ dodatku wielofunkcyjnego izocyjanianu Basonate FDS 3425 na adhezję poliuretanowych klejów samoprzylepnych*

addition of usually wetting and thickener agents. This phenomenon influences the main investigated properties of PSA such as tack, peel adhesion and shear strength tremendous positively.

From the water-borne PU-PSA as raw materials for self-adhesive products was selected self-adhesive polyurethane as the formulation containing 2.0 wt.% DMPA, 20.0 wt.% Voranol 1010, 5.0 wt.% HTPB, 7.0 wt. % IPDI, 0.4 wt.% DBTL, 1.0 wt.% TEA, 60 wt.% distilled water, 0.2 wt.% EDA and 4.4 wt.% emulsifier Dowfax. The selected PU-PSA was crosslinked with multifunctional isocyanate Basonate FDS 3425 and coated with 60 g/m^2 on polyester film and dried 10 min at 110°C. The resulted adhesive layers were tested on tack, peel adhesion (adhesion) and shear strength (cohesion) according to the AFERA methods (Association des Fabricants Europeens de Rubans Auto-Adhesifs) procedures (Figs. 7-8). Exact details can be found in AFERA 4001

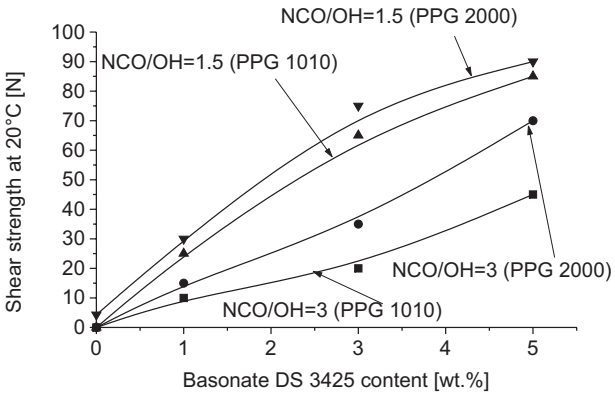


Figure 8. *Effect of concentration of Basonate FDS 3425 on shear strength of polyurethane PSA*

Rys. 8. *Wpływ stężenia Basonate FDS 3425 na kohezję poliuretanowych klejów samoprzylepnych*

(peel adhesion), AFERA 4012 (shear strength) and AFERA 4015 (tack). Administrative address: 60, rue Auber-94408 Vitry Sur Seine Cedex, France.

Figure 8 shows the thermal resistance of developed water-borne PU-PSA crosslinked using three investigated multifunctional isocyanate crosslinkers. In conclusion, multifunctional isocyanate Basonate FDS 3425 is very good crosslinking agents for self-adhesive layers based on water-borne PU-PSA.

5. Conclusions

In this study, it was shown that it is possible to prepare novel water-borne polyurethane pressure-sensitive adhesives (PU-PSA) using hydroxylated polybutadiene as self-adhesives for protective films. The synthesized water-borne self-adhesive polyurethanes ware stable for over 6 months. The versatility of the chemistry provides wide technical perspectives and allows very soft to hard chemical architectures. The increase of HTPB content and PPG amount with higher molecular weight increased the apparent viscosity of the end-products, the thermal resistance and the mechanical resistance of polymer films. Developed water-borne polyurethane PSAs are characterized by low tack, low adhesion and excellent cohesion after crosslinking with selected multifunctional isocyanates as crosslinking agents. Selected water-borne PU-PSA composition containing 2.0 wt.% DMPA, 20.0 wt.% Voranol 1010, 5.0 wt.% HTPB, 7.0 wt.% IPDI, 0.4 wt.% DBTL, 1.0 wt.% TEA, 60 wt.% distilled water, 0.2 wt.% EDA and 4.4 wt.% emulsifier Dowfax. Those kinds of water-borne self-adhesive polyurethanes crosslinked with Basonate FDS 3425 are very well suitable as self-adhesives for manufacturing of protective films. Protective films containing developed PU-PSAs are characterized by excellent removability and stability of removability level.

6. Summary

The ever-changing high performance pressure-sensitive adhesive market continues to expand and present new challenges. To date, the industry has seen strong growth in traditional applications, and the emergence of new applications. Chemistry of the polymers with self-adhesive properties has taken on an added dimension with the introduction of various raw materials, polymerization technique and crosslinking methods. This expansion of the water-borne PU-PSA technology ensures that the future performance and environmental requirements will be met. New developed aqueous PU-PSA dispersions are the best product in this class of PU-PSA. They are characterized by excellent properties, leading to an interesting application for the manufacturing of the family of removable and repositionable self-adhesive materials. Removable and repositionable pressure-sensitive adhesives based on PU-PSA water dispersions will play a major role in the development

and production of new generation of removable memo notes, paper and foil labels.

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