

## Solvent-borne pressure-sensitive adhesives based on acrylic with post-crosslinking performance

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*The technology of solvent-borne pressure-sensitive adhesives (PSA) based on acrylic with post-crosslinking performance has been developed. The new synthesized acrylic PSAs contain monomers with oxirane groups or special monomers with post-crosslinking properties. They are applied for manufacturing of diverse self-adhesive products, such as: mounting tapes, splicing tapes, sign and marking films and structural adhesive tapes.*

**Key words:** acrylic PSA, solvent-borne, post-crosslinking, self-adhesive tapes, structural tapes

## Rozpuszczalnikowe kleje samoprzylepne oparte na poliakrylanach z możliwością dosięciowania

*Opracowano technologię syntezy rozpuszczalnikowych klejów samoprzylepnych opartych na poliakrylanach z możliwością ich dosięciowania termicznego w podwyższonej temperaturze. Nowe kleje samoprzylepne na podstawie poliakrylanów zawierają grupy oksiranowe lub specjalistyczne monomery sieciujące. Po dosięciowaniu termicznym mogą być stosowane do produkcji taśm montażowych, taśm łączących, folii dekoracyjnych oraz adhezyjnych taśm strukturalnych.*

**Słowa kluczowe:** rozpuszczalnikowe kleje samoprzylepne oparte na poliakrylanach, dosięciowanie, taśmy samoprzylepne, taśmy strukturalne

### 1. Introduction

Since their introduction half a century ago, acrylic pressure-sensitive adhesives (PSA) have been successfully used in many fields. They are applied in self-adhesive double-sided, one-sided or carrier-free mounting tapes, splicing tapes, self-adhesive labels, protective films, sign and marking films, as well as medical products, such as band-aid, OP-tapes and biomedical electrodes.

In the last sixty years or so, acrylic PSAs 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 self-adhesive articles and their even larger suppliers now use very expensive equipment to study pressure-sensitive adhesive behavior: tack (initial adhesion), adhesion (peel adhesion) and cohesion (shear strength). These three properties are useful in characterizing the nature of pressure-sensitive adhesives. 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.

The main performance of acrylic PSAs, such as tack, peel adhesion and shear strength, synthesized through co-polymerization process of acrylate monomers are to a large degree determined by the molecular weight of acrylic copolymer, polymerization method and especially by the type and quantity of the crosslinking agents added to the PSAs or crosslinking methods [1].

Although the production of acrylic PSAs in form of solvent-borne, water-borne or solvent-free systems worldwide is characterized by a constantly increasing productivity, up to now a complex publication concerning synthesis, crosslinking and technology of acrylic PSAs has not been published. The similar information regarding the dependence of the main properties of acrylic PSAs on type and amount of used crosslinking agents, or crosslinking methods, are also fragmentary and dissipated and only negligible publications undertake an optimization of the problem of PSA application properties and used crosslinking agents and crosslinking methods.

A target of this work was the development of solvent-borne acrylic pressure-sensitive adhesives with

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high application performances through a selection among the most efficient crosslinking agents and the best crosslinking methods. This work brought to development a technology of a wide palette manufacturing of acrylic PSAs and self-adhesive articles with post-crosslinking potential [2].

Acrylic pressure-sensitive adhesives with post-crosslinking potential can be synthesized using the reaction between carboxylic and epoxid groups into polymer backbone at high temperatures, or by the use of monomers with crosslinking properties.

## 2. Thermal crosslinkable acrylic PSA with post-crosslinking potential

The term PSA with post-crosslinking potential means that the adhesive may be crosslinked to a final state of adhesive and cohesive properties at higher temperatures by the use of heat. In the assembly of automotive components, e.g., automobile trim, a pre-made component may be bonded to the body by means of a high performance adhesive. Useful adhesives must be conformable to the bonding surfaces, must be initially tacky, and must adhere to such substrates as paint surfaces and oily metal. The adhesive layer may be applied to the structural member prior to heating in a paint curing oven; it must demonstrate high temperature resistance and high adhesiveness. Ideally the adhesive would be initially pressure-sensitive and would crosslink upon exposure to temperatures normal to paint curing oven, permanently bonding the component to the structure member or sealing a seam between adjacent structural members, yet remaining flexible [3].

## 3. Epoxy-acrylate blend thermal crosslinkable pressure-sensitive adhesives

These kinds of PSAs are synthesized using typical alkyl acrylate monomers, such as 2-ethylhexyl acrylate, octyl acrylate or butyl acrylate, and glycidyl methacrylate (GMA) in the concentrations between 30 and 50 wt.%, and acrylic acid (AA) in concentrations between 5 and 10 wt.%. The best organic solvents for the synthesis of acrylic thermal crosslinkable pressure-sensitive adhesives containing oxirane groups were the mixtures from ethyl acetate and acetone. As conventional crosslinking agent was aluminum acetylacetonate (AlACA) in amount of 0.1 wt.% used. The self-adhesive layers as carrier-free tapes are only "light" crosslinked in the dry-

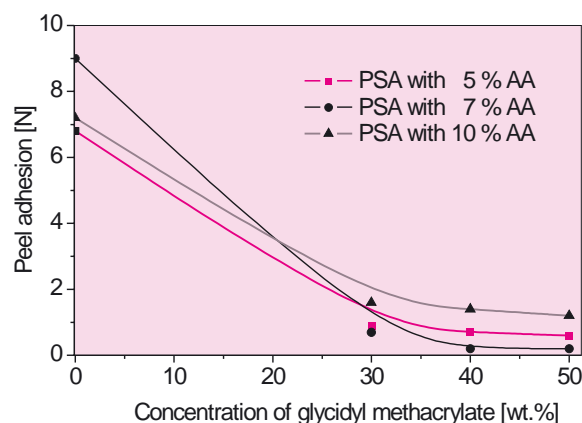


Figure 1. Effect of glycidyl methacrylate amount on the peel adhesion for acrylic PSAs containing various concentration of acrylic acid

Rys. 1. Wpływ stężenia metakrylanu glicydylu na adhezję poliakrylanowych klejów samoprzylepnych zawierających różne ilości kwasu akrylowego

ing canal at about 105°C after remove of polymerization medium and stabilizer.

The diagram (Fig. 1) illustrates how the influence of acrylic acid amount on the peel adhesion according to AFERA 4001 depends on the glycidyl methacrylate content.

Varying the acrylic acid and glycidyl methacrylate concentration offers an interesting possibility of influencing the peel adhesion. A relatively very low peel adhesion level was observed for glycidyl methacrylate in amounts between 40 and 50 wt.%. The highest values of peel adhesion, but on the very low level, was registered for acrylic PSA with 10 wt.% of acrylic acid.

The crosslinking of acrylic PSA layers containing oxirane groups from GMA and carboxylic group from AA can be reached at higher temperatures between 100 and 180°C (Fig. 2).

The controlling and course of the thermally initiated chemical crosslinking were determined by quantitative differential scanning calorimetry (DSC) in the temperature range between 20 and 250°C [4]. The temperatures and heat flows associated with transitions in self-adhesives as a function of temperature or time in a controlled nitrogen atmosphere were measured. This technique provides quantitative and qualitative information on chemical changes that involve exothermic crosslinking process. Fig. 2 demonstrates the DSC ability to detect the crosslinking process in a thermosetting acrylic PSA containing 10 wt.% AA and 40 wt.% GMA. Having known the heat reaction of 100 % unreacted non-crosslinked acrylic PSA, universal analysis calculated automatically heat of the crosslinking reaction. For this maximal heat reaction the optimal crosslinking temperature is calculated. For the investigated acrylic PSA layer with 10 wt.% AA and 40 wt.% GMA the maximum of heat reaction for about 150°C was observed.

The pressure-sensitive carrier-free tapes thus obtained were subjected to the following main tests, be-

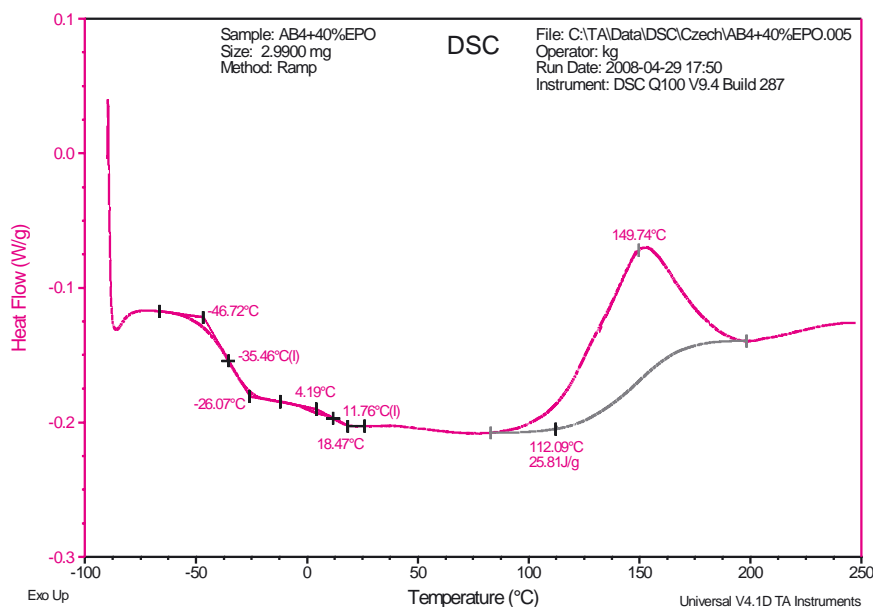


Figure 2. Thermodynamic characteristic of acrylic PSA containing 40 wt.% of GMA

Rys. 2. Termodynamiczna charakterystyka poliakrylanowego kleju samoprzylepnego zawierającego 40 % wag. GMA

fore and after thermal crosslinking in order to evaluate the performance as either a seam sealing or structural bonding adhesive [5].

## Aluminum T-peel

A carrier-free tape samples is placed between two strips of 13.5 mm × 200 mm × 0.125 mm anodized aluminum, leaving an adhesive free 25 mm tab at each end of each aluminum strip. The assembly is rolled down with a 6.8 kg roller, one pass in each direction, and the samples then conditioned for 1 to 2 hours at room temperature. The tabs are bent back at 90°C in opposite directions and respectively clamped in the upper and lower jaws of a tensile testing machine. The jaws are separated at a rate of 300 mm/minute, nothing both the average force required to effect separation as well as the maximum force at adhesive failure.

## Film strength and film elongation

A dumbbell-cut sample according to ASTM D-412 of the adhesive was connected to the jaws of an Instron and the jaws separated at a rate of 51 cm per minute. The force at film break and the % elongation at break were recorded. This test was performed on both the crosslinked and uncrosslinked tape samples as initiated.

## Properties of epoxy-acrylate crosslinked PSAs

The synthesized acrylic PSAs containing 10 wt.% acrylic acid (AA) and adequately 30, 40 and 50 wt.% glycidyl methacrylate (GMA) in form of carrier-free tapes are 10 minutes thermal crosslinked at tempera-

tures between 100 and 160°C. In Table 1 were shown shear strength values measured at room temperature (RT) and at 70°C for thermal crosslinkable PSAs.

Table 1. Cohesion values of thermal crosslinked acrylic PSAs measured at 20°C and 70°C

Tabela 1. Wartości kohezji sieciowanych termicznie samoprzylepnych klejów poliakrylanowych mierzone w 20°C oraz w 70°C

GMA	T <sub>c</sub> [°C]	Shear strength at 20°C [N]	Shear strength at 70°C [N]
30 wt.%	100	45 min af	> 48 h
	120	45 min af	> 48 h
	140	30 min af	> 48 h
	160	not measured (adhesion-free)	not measured (adhesion-free)
40 wt.%	100	6 h af	> 48 h
	120	4 h af	> 48 h
	140	2 h af	> 48 h
	160	not measured (adhesion-free)	not measured (adhesion-free)
50 wt.%	100	2 h 40 min af	> 48 h
	120	2 h 40 min af	> 48 h
	140	2 h 40 min af	> 48 h
	160	not measured (adhesion-free)	not measured (adhesion-free)

T<sub>c</sub> – thermal crosslinking temperature, af – adhesive failure

The eminent significant cohesive properties of thermal crosslinkable acrylic PSAs containing epoxide and carboxylic groups can be controlled by the ratio of GMA/AA. An additional benefit from using these PSAs in a quasi epoxy adhesive is their excellent shear strength (cohesion) at high temperatures and high thermal resistance. As it can be seen in Table 1, it is very difficult to predict the maximum of the shear strength range for thermal crosslinked acrylic PSA layers. In

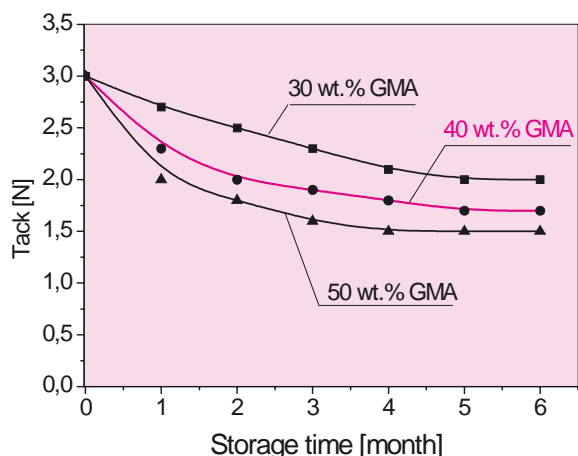


Figure 3. Tack performance of thermal crosslinkable acrylic PSAs with various content of GMA during the storage

Rys. 3. Zmiana lepności sieciowanych termicznie poliakrylanowych klejów samoprzylepnych w czasie składowania w zależności od zawartości GMA w kleju

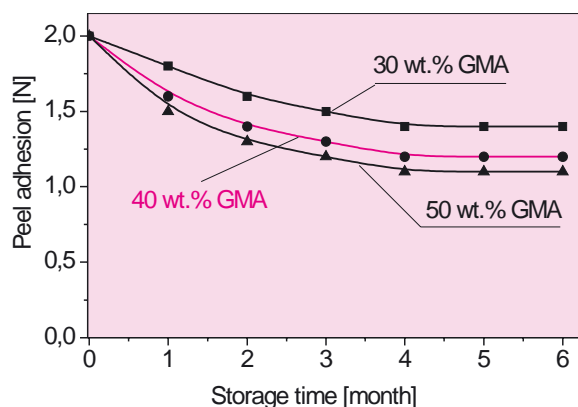


Figure 4. Peel adhesion performance of thermal crosslinkable acrylic PSAs with various content of GMA during the storage

Rys. 4. Zmiana adhezji sieciowanych termicznie poliakrylanowych klejów samoprzylepnych w czasie składowania w zależności od zawartości GMA w kleju

general, cohesion at 20°C grows with the increase of GMA concentration, however, the overcrosslinking for the self-adhesive layers crosslinked at 160°C appears. The samples crosslinked at 160°C were tack- and adhesion-free, the measurement of shear strength was in this case not possible. The overcrosslinking problem is the result of the completely crosslinking reaction between oxirane and carboxylic groups into acrylic polymer layer.

Control of the tack, peel adhesion and shear strength stability of thermal crosslinkable acrylic PSAs containing between 30 and 50 wt.% GMA (oxirane groups) and 10 wt.% acrylic acid (carboxylic groups) can be evaluated on typical substrates such as steel or aluminum during applications after storage of 6 months.

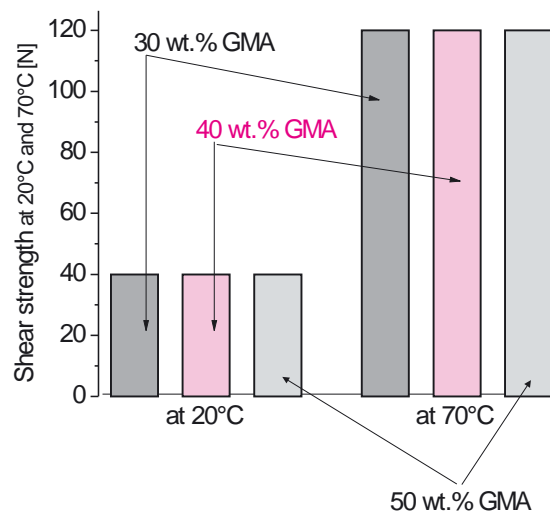


Figure 5. Shear strength of thermal crosslinkable acrylic PSAs with various content of GMA during the storage

Rys. 5. Zmiana kohezji sieciowanych termicznie poliakrylanowych klejów samoprzylepnych mierzonej w 20°C oraz 70°C w zależności od zawartości GMA w kleju

The stability of investigated mentioned properties such as tack (AFERA 4015), peel adhesion (AFERA 4001) and shear strength (AFERA 4012) explicated as ageing performance during 6 months was presented in Figs. 3-5.

As can be seen from mentioned diagrams the tack and peel adhesion of investigated thermal crosslinkable acrylic PSAs containing between 30 and 50 wt.% GMA and 10 wt.% AA are reduced during storage for about 50 % in compare with beginning values, measured directly after coating. Generally, the incorporating of GMA into acrylic polymer chain reduces tack and peel adhesion of thermal crosslinkable acrylic PSAs. Fig. 5 shows that the shear strength tested by applications at room temperature and at 70°C reached the highest cohesion values.

The development of thermal crosslinkable acrylic PSAs with post crosslinking potential characterized by excellent cohesion typical for structure adhesives is relatively straightforward. Such a formulation of synthesized acrylic PSAs have to utilize chemistries which ensure that the adhesives first wet and adhered well (low tack and peel adhesion) and then after thermal crosslinking gives the required mechanical properties following the optimum specified crosslinking temperature.

## 4. Acrylic PSA containing monomers with crosslinking properties

Thermal crosslinkable acrylic PSAs using monomers with crosslinking properties are distinguished

from crosslinkable polymers in that the crosslinkable polymers contain a functionality, such as a carboxyl group, which can only be crosslinked by the addition of a co-reactant to the polymer solution. Homogeneously crosslinked systems require crosslinking sites, which are statistically distributed in the polymer chain. Such systems are synthesized by the conventional solvent polymerization of acrylate monomers, which are capable to thermal initiated reaction with carboxyl groups or self-condensation [6].

Such monomers include for example N-methylol acrylamide (N-MAA), N-(iso-butoxymethyl)acrylamide (IBMA), and methyl acrylamidoglycolate methyl ether (MAGME) [7].

The advantages of thermal crosslinkable acrylic PSA systems are their simplicity, economy, and particularly their efficiency. The typical thermal crosslinkable systems, which are typical for self-crosslinked acrylics, contain methylol acrylamide repeating units. Such monomers may release formaldehyde upon crosslink-

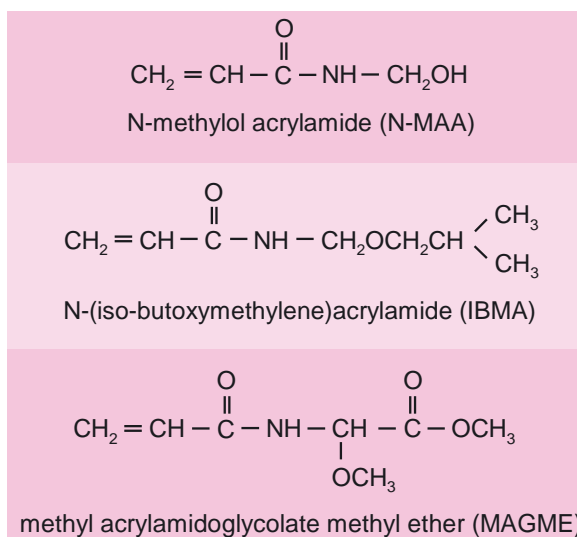


Figure 6. Monomers with crosslinking properties  
Rys. 6. Monomery o właściwościach sieciujących

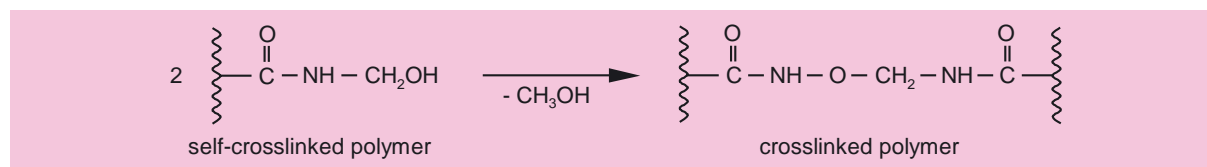


Figure 7. Self-crosslinking reactions by using of N-MAA  
Rys. 7. Reakcja samosieciowania klejów zawierających N-MAA

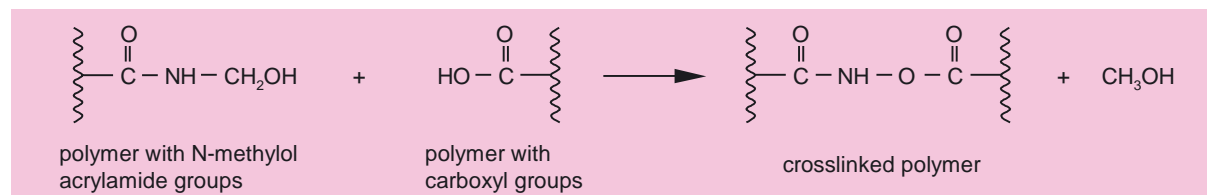


Figure 8. Use of N-methylol acrylamide for the crosslinking of acrylic PSAs  
Rys. 8. Zastosowanie N-MAA do sieciowania poliakrylanowych klejów samoprzylepnych

ing or cause the loss of tack and adhesion. Thus the preferred polymers contain less than 5 wt.% of N-methylol acrylamide monomer units [8].

The aim of this technology was to examine the influence of monomers with crosslinking effect on the fundamental performance characteristics of pressure-sensitive adhesives such as tack, peel adhesion, and shear strength and develop special categories of acrylic PSAs with post-crosslinking potential. This kind of monomers with crosslinking properties have been used in novel solvent-borne acrylic PSA systems [9].

As such monomers N-methylol acrylamide (N-MAA), N-(iso-butoxymethyl)acrylamide (IBMA) and methyl acrylamidoglycolate methyl ether (MAGME) with high glass transition temperatures ( $T_g$ ) of homopolymers:  $T_{g \text{ N-MAA}} = +119^\circ\text{C}$ ,  $T_{g \text{ IBMA}} = +30^\circ\text{C}$ , and  $T_{g \text{ MAGME}} = +78^\circ\text{C}$  were tested (Fig. 6).

The methylol groups of N-MAA are insensitive to free-radical polymerization and readily self-condense upon conventional thermal crosslinking (Fig. 7) and

crosslinking reaction with carboxyl groups of acrylic PSA [10] (Fig. 8).

Performance characteristics of the synthesized pressure-sensitive adhesives, containing the above mentioned crosslinking monomers, are presented in Table 2, and illustrated in Figures 9–11. For 60 g/m<sup>2</sup> thick PSA layers after coating on polyester film and drying 10 min at 105°C tack, peel adhesion at 20°C and 70°C as far as shear strength at 20°C and 70°C were tested.

All three investigated crosslinking monomers have a negative influence on the tack of thermal crosslinkable acrylic PSAs (Fig. 9).

The greatest decrease of tack was noted using N-methylol acrylamide and MAGME. A similar tendency was observed in the case of IBMA. An increase of N-MAA, IBMA and MAGME content decreases the peel adhesion of the thermal crosslinked acrylic PSAs. This effect correlates to the glass transition temperature ( $T_g$ ) of homopolymers synthesized of monomers with crosslinking properties. The higher the  $T_g$  of the respec-

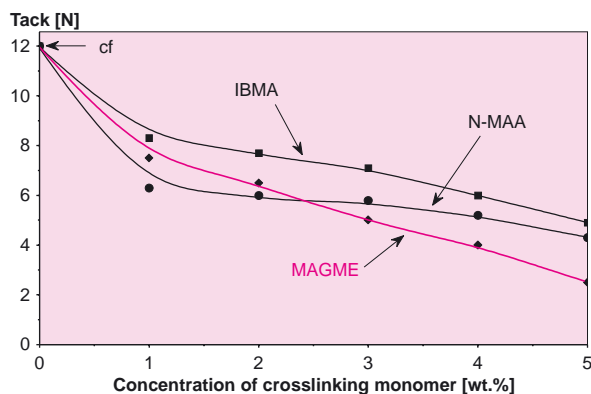


Figure 9. Effect of N-MAA, IBMA and MAGME level on the tack

Rys. 9. Wpływ N-MAA, IBMA oraz MAGME na lepność klejów samoprzylepnych

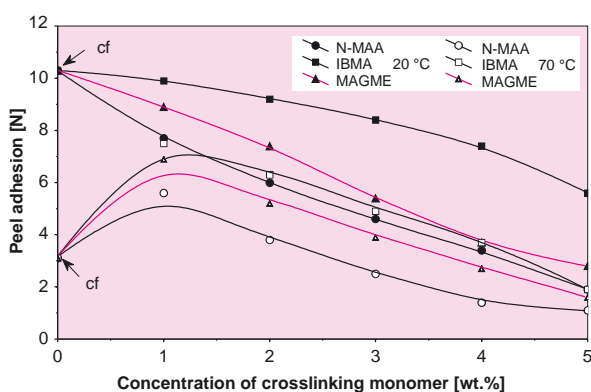


Figure 10. Effect of N-MAA, IBMA and MAGME level on the peel adhesion

Rys. 10. Wpływ N-MAA, IBMA oraz MAGME na adhezję klejów samoprzylepnych

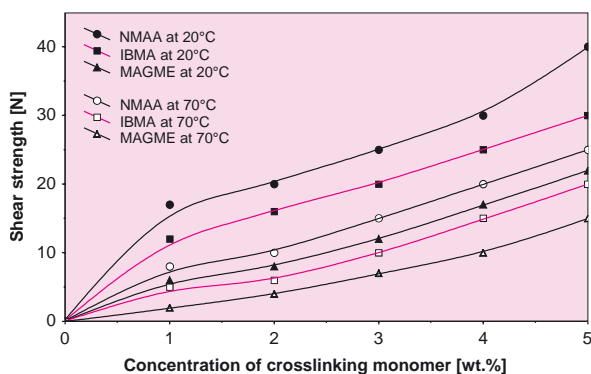


Figure 11. Effect of N-MAA, IBMA and MAGME level on the shear strength

Rys. 11. Wpływ N-MAA, IBMA oraz MAGME na kohezję klejów samoprzylepnych

tive homopolymer ( $T_g$  of N-MAA = +119°C;  $T_g$  of IBMA = +30°C) the lower the tack and peel adhesion of the synthesized pressure-sensitive adhesives.

The high cohesion of acrylic PSAs containing monomers with crosslinking character is based on the

reaction between carboxylic groups from acrylic polymer and the functional groups of those monomers (Fig. 12) or self-condensation reaction within crosslinking monomers (Fig. 13) [1].

Table 2. Performance of acrylic PSA containing crosslinking monomers

Tabela 2. Właściwości poliakrylanowych klejów samoprzylepnych zawierających monomery sieciujące

Concentration of crosslinking monomer [wt.%]	Tack [N]	Peel adhesion [N]		Shear strength [N]	
		20°C	70°C	20°C	70°C
<b>N-MAA</b>					
0	12.0*	10.3*	3.1*	<1	<1
1	6.3	7.7	5.6	18	8
2	6.0	6.0	3.8	20	10
3	5.8	4.6	2.5	25	15
4	5.2	3.4	1.4	30	20
5	4.3	1.9	1.1	40	25
<b>IBMA</b>					
0	12.0*	10.3*	3.1*	<1	<1
1	8.3	9.9	7.5	12	5
2	7.7	9.2	6.3	16	6
3	7.1	8.4	4.9	20	10
4	6.0	7.4	3.7	25	15
5	4.9	5.6	1.9	30	20
<b>MAGME</b>					
0	12.0*	10.3*	3.1*	<1	<1
1	7.5	8.9	6.9	6	<5
2	6.5	7.4	5.2	8	<5
3	5.0	5.4	3.9	12	8
4	4.0	3.7	2.7	15	10
5	2.5	2.8	1.2	20	15

\* cohesive failure

By the use of gas chromatography, traces of by-products like methyl alcohol or isobutyl alcohol were found and a very low amount of formaldehyde too. Crosslinking via functional groups of the investigated crosslinking monomers is achieved under elevated temperatures and/or acidic conditions. Thermal post-cures without the presence of hydrogen ions require 20–30 minutes heating at 150–170°C. Pressure-sensitive adhesives containing crosslinking monomers can be post-crosslinked under milder conditions by the use of combinations of heat and acid catalysts.

For medical applications, in addition to the odor problems due to the presence of free formaldehyde, the dermatological effect may appear a serious problem too.

The exposure of operating personnel and consumers to formaldehyde has been a recent concern of both industry and regulatory agencies.

Because the crosslinking monomers are above all used by applications at higher temperatures, the acrylic PSAs containing the mentioned N-substituted acrylamide derivatives were dried in an oven for 10 min at 145°C [11–12]. This temperature is also used in practice in the coating equipment. Cohesion of the PSA layers

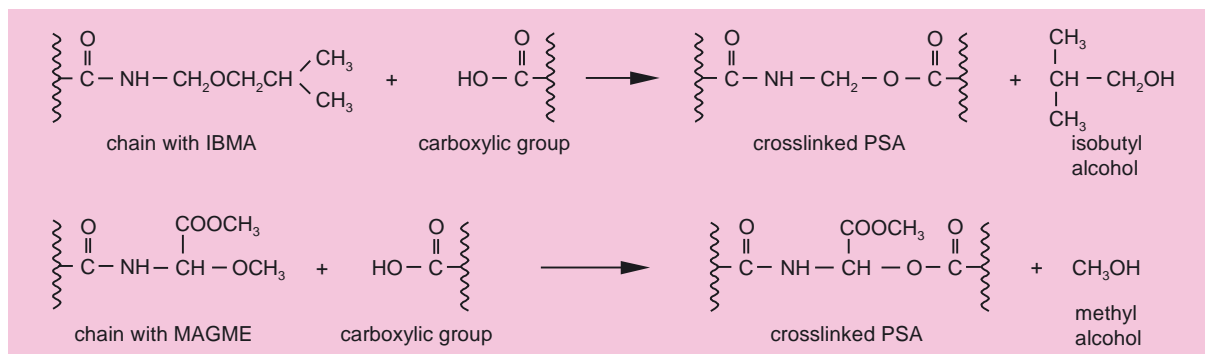


Figure 12. Crosslinking reaction between carboxylic group and N-substituted acrylamides (IBMA and MAGME)  
 Rys. 12. Reakcja sieciowania pomiędzy grupami karboksylowymi oraz podstawionymi akryloamidami (IBMA oraz MAGME)

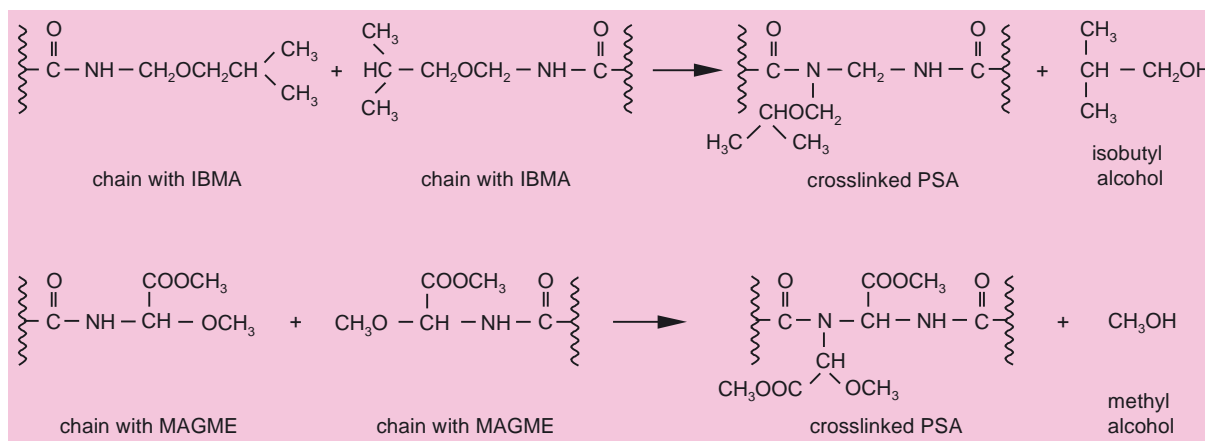


Figure 13. Self-condensation crosslinking reactions by application of crosslinking monomers acryl amide derivatives (IBMA and MAGME)  
 Rys. 13. Samokondensacja jako reakcja sieciowania z udziałem pochodnych akryloamidu (IBMA oraz MAGME) jako monomerów sieciujących

was measured as shear strength after crosslinking at 70°C (Fig. 14).

From the observed experimental results concerning the shear when using crosslinking monomers based on N-substituted acrylamide derivatives at elevated temperatures, it can be concluded that the best thermal reactive monomer crosslinker is N-methylol acrylamide. Compared with IBMA and MAGME, N-MAA provided the highest cohesion in all cases. The adhesive properties like tack and peel adhesion are a little bit poorer than by the application of IBMA or MAGME. The monomer with crosslinking properties N-methylol acrylamide has a practical importance as a second crosslinker for the production of self-adhesive acrylic pressure-sensitive adhesives with post-crosslinking effect at high temperatures and has been used for the industrial production of solvent-borne water-soluble acrylic PSAs.

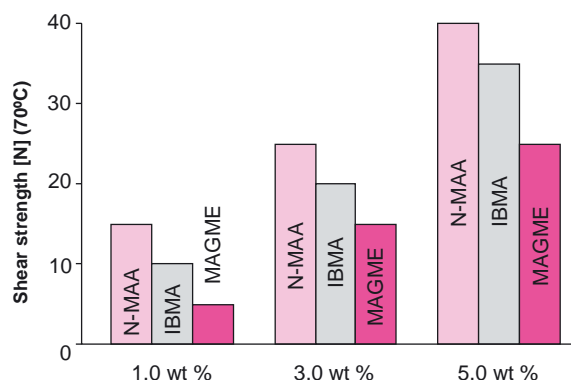


Figure 14. Influence of crosslinking monomer concentration on the cohesion at 70°C, after crosslinking at 145°C

Rys. 14. Wpływ stężenia monomerów sieciujących na kohezję mierzoną w 70°C po usieciowaniu kleju w 145°C

## 5. Summary

Acrylic pressure-sensitive adhesives with post-crosslinking potential can be replacing conventional crosslinkable acrylic PSAs using for manufacturing of

self-adhesive products with extremely high shear performance. An addition of monomers with crosslinking properties gives the best balance between adhesives and shear performance. All the thermal crosslinkable acrylic PSAs must quickly adhere to tested substrates.

The developed thermal crosslinkable acrylic PSA with post-crosslinking potential are characterized by excellent balance between tack and peel adhesion, extremely high cohesion at higher temperatures, and controlled crosslinking reaction. Novel thermal crosslinkable PSA based on acrylics will play a major role in manufacturing of creative new generation self-adhesive materials. Differential scanning calorimetry (DSC) is very interesting method to control the run of crosslinking process of thermally crosslinkable PSA systems.

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