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**THERMAL DEGRADATION OF PLASTICIZERS
RESISTANT ACRYLIC PRESSURE-SENSITIVE
ADHESIVES****TERMICZNA DEGRADACJA SAMOPRZYLEPNYCH
KLEJÓW POLIAKRYLANOWYCH ODPORNÝCH
NA DZIAŁANIE PLASTYFIKATORÓW****Abstract**

Pressure-sensitive adhesives (PSA) containing, among others, methyl acrylate and their copolymers are plasticizers resistant and are used for different PVC applications, especially for marking and signing products. The thermal degradation of copolymers based on butyl acrylate-methyl acrylate-acrylic acid used as acrylic pressure-sensitive adhesives, especially for bonding of plasticizer containing substrates, has been investigated at isothermal 250°C using pyrolysis-gas chromatography (P-GC). The degradation run process, as well as the kind and amount of the pyrolysis products, give the relevant information about the thermal degradation of acrylic adhesives and a mechanism of pyrolysis degradation. It was observed that during the pyrolysis of butyl acrylate-methyl acrylate-acrylic acid copolymers from unsaturated monomers as methyl acrylate, methyl methacrylate, butyl acrylate and butyl methacrylate were formed. During the side-chain of butyl acrylate-methyl acrylate-acrylic acid-copolymer degradation the presence of methyl alcohol and butyl alcohol was observed.

Keywords: pressure-sensitive adhesives (PSA), acrylic, thermal degradation, pyrolysis, pyrolysis product

Streszczenie

Poliakrylanowe kleje samoprzylepne zbudowane między innymi z akrylanu metylu i jego kopolimerów są materiałami odpornymi na działanie plastyfikatorów. Pozwala to na ich zastosowanie w różnych aplikacjach PVC, a w szczególności do produkcji folii dekoracyjnych i banerów. Wielu informacji o składzie i rodzaju zastosowanego kleju dostarcza piroliza. Piroliza pozwala również określić mechanizm termicznej degradacji klejów samoprzylepnych. W poniższym artykule przedstawiono wyniki badań nad termiczną degradacją samoprzylepnych klejów poliakrylanowych zbudowanych na bazie akrylanu butylu-akrylanu metylu-kwasu akrylowego, używanych głównie w łączeniu materiałów z materiałami zawierającymi plastyfikatory lub plastyfikowanych materiałów ze sobą. Degradację termiczną prowadzono izotermicznie w temperaturze 250°C w połączeniu z chromatografią gazową (P-GC). Stwierdzono, że w czasie pirolizy tych kopolimerów tworzą się nienasycone monomery, takie jak: akrylan metylu, metakrylan metylu, akrylan butylu oraz metakrylan butylu. Zaobserwowano również powstawanie alkoholu metylowego i butylowego, powstających w wyniku rozerwania łańcuchów bocznych kopolimeru.

Słowa kluczowe: kleje samoprzylepne, akrylany, degradacja termiczna, piroliza, produkty pirolizy

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1. Introduction

Pressure-sensitive adhesives (PSA) are polymeric materials used to bond other materials, mainly on their surfaces through adhesion and cohesion. Adhesion and cohesion are phenomena which may be described thermodynamically and chemically, but actually they cannot be measured precisely. The difference between pressure-sensitive adhesives and other adhesives, such as contact adhesives, is in the permanent surface stickiness of the pressure-sensitive adhesives before, or after, the application. Pressure-sensitive adhesives can be applied in the form of solvent-borne, water-borne (dispersions) and solvent-free systems. The European market of PSA in 2006 was 446,000 tons [1, 2].

Acrylic copolymers with low glass transition temperature based on alkyl acrylates and unsaturated carboxyl acids are important specialty polymers used as pressure-sensitive adhesives for manufacturing of diverse self-adhesive products such as mounting and masking tapes, splicing tapes, packaging tapes, and sign and marking films [3]. Figure 1 illustrates the plasticizer resistance of typical acrylic PSA as the function of alkyl acrylates, measured as shear strength of the PSA layer on the PVC surface [4]. The increase of alkyl chain length from C_1 (methyl acrylate) to C_{12} (lauryl acrylate) corresponds with the decrease of shear strength of the synthesized solvent-borne acrylic PSA. The plasticizer from a PVC substrate migrates into the crosslinked acrylic layer and deteriorates shear strength. The best plasticizer resistance was achieved using acrylic PSA based on short methyl acrylate. Even methyl acrylate is the main component during the synthesis of plasticizer resistance, however its concentration is between 30 and 40 wt.%.

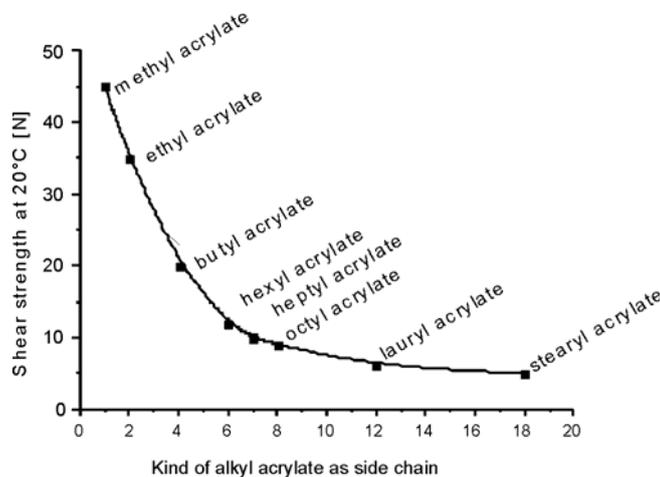


Fig. 1. Influence of kinds of alkyl acrylate on shear strength of the synthesized acrylic PSA tested on the PVC surface containing plasticizer

Rys. 1. Wpływ rodzaju akrylanu alkilu na ścinanie syntezowanych PSA, testy na powierzchni PVC zawierającego plastyfikator

A goal of this work was the investigation of thermal degradation of acrylic PSA based on methyl acrylate/butyl acrylate/acrylic acid using thermogravimetry (TGA) and gas

chromatography (GC). It is very interesting from the practical technological point of view to study the effects of thermal degradation of so much important plasticizer resistant acrylic PSA.

2. Experimental

The necessary acrylic PSA was synthesized from 50 wt.% butyl acrylate (BA), 40 wt.% methyl acrylate (MA) and 10 wt.% acrylic acid (AA) in ethyl acetate using 0.1 wt.% radical starter AIBN. All raw products were available from BASF Germany in Ludwigshafen.

The polymerization process was carried out under the following conditions:

- addition of the monomers blend containing AIBN into ethyl acetate
- amount of reactor charge: 50 wt.%
- dosage time of monomers with solved AIBN: 1 h
- time of post-reaction: 6 h

The synthesized solvent-borne acrylic pressure-sensitive adhesive was characterized by:

- amount of solid materials (polymer content) 50 wt.%
- viscosity 8.1 Pa·s
- concentration of residual monomers < 0.3 wt.%
- weight average molecular weight \bar{M}_w 71 000 Dalton
- number average molecular weight \bar{M}_n 23 000 Dalton
- polydispersity $P_d = \bar{M}_w/\bar{M}_n$ 3.01

This synthesized acrylic copolymer PSA was characterized by thermal and chromatographic methods. Differential scanning calorimetry (DSC) was conducted at a heating rate of 5°C pro min using TA Instruments Inc. model 2100 DSC cell. The thermal degradation experiments were performed by pyrolysis-gas chromatography and pyrolysis-gas chromatography/mass spectrometry techniques following the parameters below:

Gas chromatograph:	Unicam 610
Detector:	FID
Column:	quartz capillary column 25 QC2/BP1
	– length: 25 m
	– diameter: 0.25 mm
Carrier gas:	nitrogen, pressure 0.8 bar
Oven temperature:	temperature program:
	50°C (0 min) to 230°C(32 min)
	heat rate: 10°C/min
Sample:	0.3 µl

The thermal polymer stability was assessed by thermogravimetry (TGA) using TA Instruments Inc. model 2950 TGA unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. A sample of about 10 mg was contained in a platinum sample pan and the TGA cell was swept with nitrogen at 60 ml/min during degradation process. The temperature was ramped at 5°C/min.

3. Results and discussion

The stability of the acrylic PSA containing butyl acrylate, methyl acrylate and acrylic acid was investigated by thermogravimetry (Fig. 2).

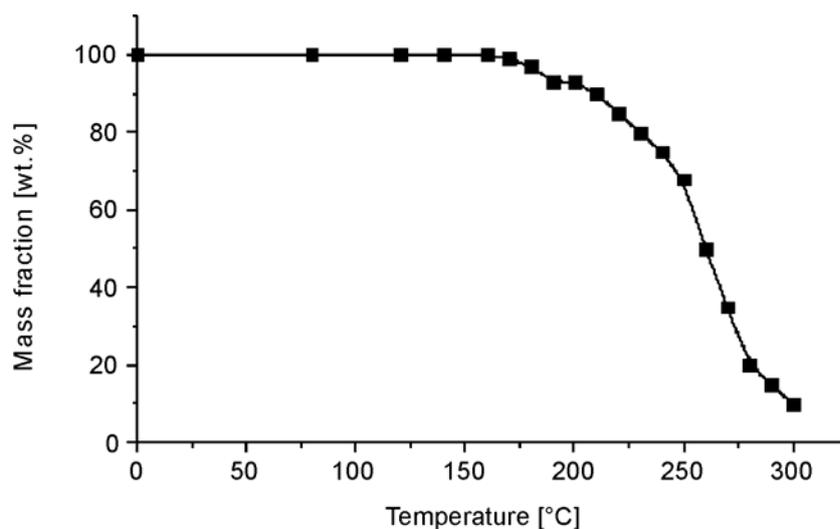


Fig. 2. Thermal degradation of methyl acrylate/butyl acrylate/acrylic acid-copolymer

Rys. 2. Degradacja termiczna kopolimeru akrylan metylu/akrylan butylu/kwas akrylowy

As it can readily be seen, the thermal degradation degree of butyl acrylate–methyl acrylate–acrylic acid–copolymer increases with temperature increasing, reaches 20 wt.% initial mass at about 260°C. The evaluated acrylic PSA was thermally stable to about 160°C. Gaseous, liquid and insoluble pyrolysis products were formed during the thermal degradation. Figure 3 shows the pyrolysis chromatogram of MA/BA/AA-copolymer (Fig. 4).

The pyrolysis chromatogram of the evaluated acrylic PSA (Fig. 3) contains seven principal peaks. The first is butene-1 from butyl acrylate and the second is methanol from methyl acrylate. The next peaks belong to butanol-1, methyl acrylate, methyl methacrylate, butyl acrylate and butyl methacrylate.

The decomposition of simple side chain esters almost certainly occurs by way of a six-membered ring transition state, which for acrylic – in the case of butyl acrylate component – is represented in Fig. 5.

The presence of a butane-1 peak in the pyrolysis chromatogram at higher pyrolysis temperatures is possibly due to the thermal decomposition of acrylate groups in the side chain. The pyrolysis behaviour of acrylic is in good agreement with our trials in the quantitative yield of an olefin (butane-1) from the ester. Because of the isolation of the acrylate ester group in the chain, the decomposition probably occurs in isolated groups. This mechanism, as opposed to the formation of acrylic anhydride which has been reported in [5] (Fig. 6), is further supported by the absence of water from the chromatogram at the used column.

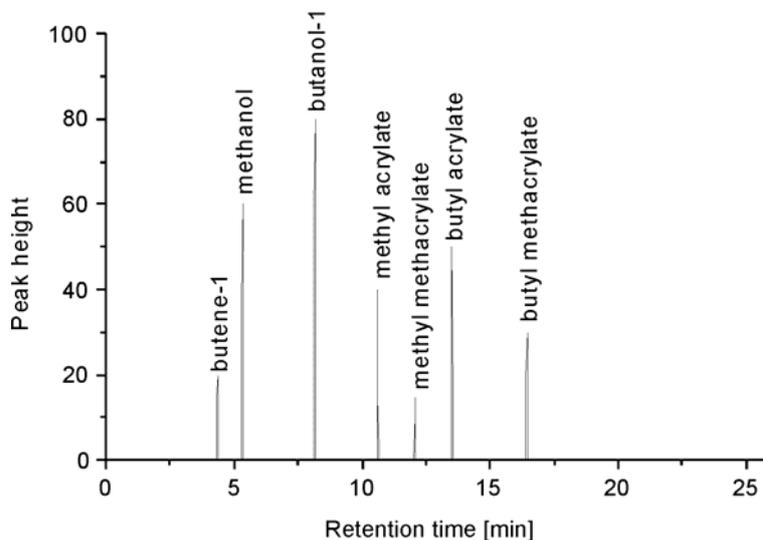


Fig. 3. Pyrolysis chromatogram of PSA based on methyl acrylate, butyl acrylate, and acrylic acid

Rys. 3. Chromatogram pirolizatu PSA opartego na akrylanie metylu, akrylanie butylu i kwasie akrylowym

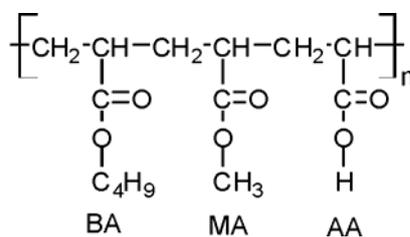


Fig. 4. Acrylic PSA copolymer based on methyl acrylate, butyl acrylate and acrylic acid

Rys. 4. Struktura kopolimeru opartego na akrylanie metylu, akrylanie butylu i kwasie akrylowym

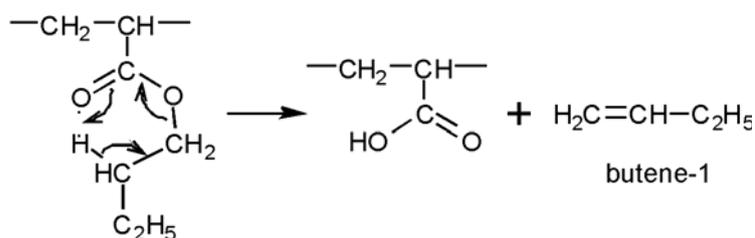


Fig. 5. Formation of alkene butene-1 by pyrolysis of PSA containing butyl acrylate

Rys. 5. Mechanizm powstawania 1-butenu w trakcie pirolizy PSA zawierającego akrylan butylu

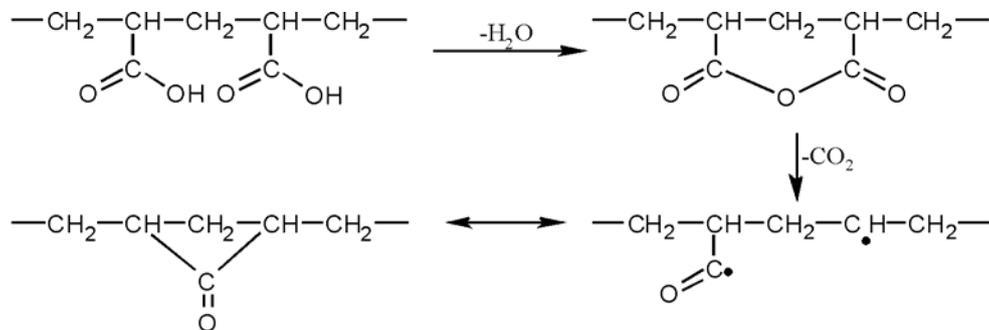


Fig. 6. Thermal degradation of polymer containing carboxyl groups

Rys. 6. Mechanizm degradacji termicznej polimeru zawierającego grupy karboksylowe

The elimination of water is necessary for anhydride formation. The probability of anhydride formation is also minimized by the space concentration of acid groups along the copolymer backbone. The possible formation of the anhydride, followed by chain decomposition, limits the general application of this method to random copolymers not containing large amounts of block-polymerized methyl- and butyl acrylate. It was observed that both dehydration and decarboxylation are first order reactions, the latter being much slower than the former and it was found that water and carbon dioxide were the only volatile pyrolysis products in the range between 170 and 240°C. The competition between dehydration and decarboxylation reactions is very important.

The forming mechanism of methanol and butanol-1 in terms of the proportion of monomer units involved is illustrated in Fig. 7.

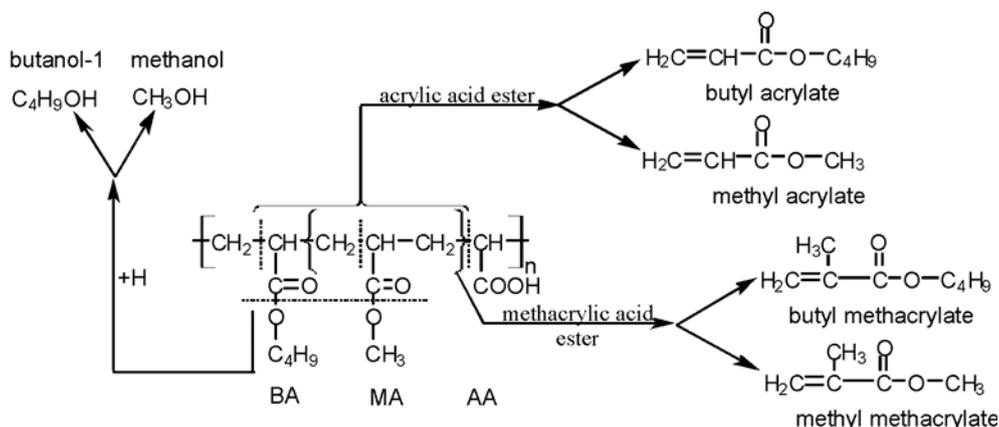


Fig. 7. Forming of alcohols, acrylic and methacrylic monomers during the thermal degradation of investigated acrylic PSA

Rys. 7. Mechanizm tworzenia się alkoholi oraz monomerów akrylanów i metakrylanów w trakcie degradacji termicznej PSA

Chain fragments from the evaluated MA/BA/AA copolymer are also included the corresponding acrylate and methacrylate as methyl acrylate and methyl methacrylate or butyl acrylate and butyl methacrylate.

4. Conclusions

The composition of the thermal degradation products of investigated acrylic pressure-sensitive adhesives (PSA) with high plasticizer resistance was observed at high temperatures, using the pyrolysis process. The characteristics of the formed olefins and alcohols corresponding to used acrylate monomers are very similar, so that one may reasonably presume that they are formed in quite a distinct ester decomposition process. Olefin production almost inevitably implies the formation of carboxyl groups or carboxyl radicals whose decomposition could yield carbon dioxide. Thus carbon dioxide production should be expected to occur concurrently or subsequent to olefin production in a ratio carbon dioxide/olefin not greater than unity. However, since carbon dioxide production generally exceeds that of olefin, there is probably a third ester decomposition reaction operating. The alkoxy radicals formed in the gas phase have a stability similar to that of a methyl radical. Thus it may be expected that alcohol elimination reactions will be less likely to occur in polymers with fewer β -hydrogen atoms in the ester group.

A comparable pyrolysis reaction of investigated PSA would give methyl acrylate, methyl methacrylate, butyl acrylate and butyl methacrylate.

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