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**UTILIZATION OF SELECTED ACRYLIC PRESSURE-
-SENSITIVE ADHESIVES BY THERMAL PYROLYSIS****PIROLITYCZNA UTYLIZACJA WYBRANYCH
SAMOPRZYLEPNYCH KLEI AKRYLOWYCH****Abstract**

Acrylic pressure-sensitive adhesives (PSA) in the form of solvent-borne, water-borne or solvent-free formulations are synthesized from typical acrylate monomers such as 2-ethylhexyl acrylate (2-EHA), butyl acrylate (BA), methyl acrylate (MA) and unsaturated carboxylic acids such as acrylic acid (AA). After polymerization as dried adhesive layers with or without carrier they are applied for manufacturing or a wide range of self-adhesive materials such as double-sided, one-sided or transfer mounting tapes, splicing tapes, labels, protective films, sign and marking films, masking tapes or diverse medical surgical tapes. The pyrolysis of commercial acrylic PSA based on typical alkyl acrylates and acrylic acid and the use of gas chromatography for the identification of formed thermal degradation products is very important for their utilization and eventual further recycling. During the pyrolysis the formation of carbon dioxide, olefins, alcohols, corresponding acrylates and methacrylate was observed.

Keywords: acrylic pressure-sensitive adhesives (PSA), pyrolysis, thermal degradation products, gas chromatography, utilization, recycling

Streszczenie

Poliakrylanowe kleje samoprzylepne (PSA) w postaci klejów rozpuszczalnikowych, dyspersji wodnych oraz klejów bezrozpuszczalnikowych są syntezowane z typowych monomerów akrylanowych, takich jak: akrylan 2-etyloheksylu oraz butylu, metakrylanów oraz nienasyconych kwasów karboksylowych, jak kwas akrylowy. Kleje samoprzylepne po polimeryzacji wraz lub bez nośnika są używane do wyrobu szerokiej gamy materiałów samoprzylepnych, takich jak: jedno i dwustronne taśmy klejące, etykiety, powłoki ochronne, taśmy maskujące lub różnorodne taśmy medyczne. Piroliza przemysłowych PSA opartych na typowych akrylanach alkilowych i kwasie akrylowym, w połączeniu z chromatografią gazową w celu identyfikacji pirolizatu, jest istotną techniką utylizacji lub drogą do ewentualnego ponownego ich wykorzystania. Stwierdzono, że w trakcie pirolizy powstają takie produkty, jak: ditlenek węgla, olefiny, alkohole oraz odpowiednie akrylany i metakrylany.

Słowa kluczowe: akrylanowe kleje samoprzylepne (PSA), piroliza, degradacja termiczna, chromatografia gazowa, utylizacja, recycling

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1. Introduction

Acrylic pressure-sensitive adhesives (PSA) are nowadays predominantly manufactured by polymerization from a wide selection of monomers with unsaturated acrylic groups, often with low levels of other unsaturated monomers having pendant functional groups in organic solvent or water in the presence of an initiator, such as organic peroxides or azo compounds. For the manufacture of acrylic pressure-sensitive adhesives, primarily tackifying common acrylic acid esters are preferred with C₄–C₁₂ and hard acrylic acid esters with C₁–C₂ carbon atoms in the alkyl moiety together with other comonomers. The composition of acrylate polymers that are inherently pressure-sensitive is a combination of soft (low T_g), hard (high T_g) and functional monomers as acrylic acid [1–2].

Commercial acrylic PSA contain typical soft and hard monomers, as well as the types of functionality that can be incorporated into the polymer. The tack and the peel properties are impacted by the soft or low glass transition temperature monomers such as 2-ethylhexyl acrylate or *n*-butyl acrylate. The harder monomers, such as methyl acrylate or ethyl acrylate are included to provide internal strength and plasticizer resistance. The carboxylic group containing a monomer such as acrylic acid is incorporated into the balanced monomers for specific adhesion to desired substrates and to provide sites in the form of active centres for crosslinking and ameliorating of synthesized PSA cohesion [3].

The most important requirements for a pressure-sensitive adhesive, such as high tackiness (adhesion by touch), high cohesion (inner stability), high stickiness (adhesion), UV, solvent and temperature stability are fulfilled by acrylics in an outstanding way. Acrylic PSA offer several advantages such as excellent ageing characteristics and resistance to elevated temperatures and polymeric plasticizers, exceptional optical clarity due to the polymer compatibility and non-yellowing.

The numerous advantages of solvent-based acrylic PSA have led to their wide use in the manufacture of self-adhesive products. Solvent-based acrylic pressure-sensitive adhesives represent in Europe more than 45% of the total PSA produced (Fig. 1).

Other groups of PSA are based on natural and synthetic rubbers, silicones, polyurethanes, polyesters and polyether.

The concept of utilization of acrylic pressure-sensitive adhesive waste materials by thermal pyrolysis is based on well-tested techniques and runs with the least risks. The removed thermal degradation products of acrylic PSA such as acrylate and methacrylate monomers, alcohols, alkenes and other organic products can be used for the synthesis of PSA and other derivatives. One undoubtedly positive aspect of utilization of acrylic pressure-sensitive adhesive waste materials is not only in harmony with the increasing concerns for the environment, but they even make a decisive contribution to reducing the strain on the environment [4–6].

Gas Chromatography (GC) is a universal separation technique of complex mixtures by thermal degradation of acrylic PSA. GC is commonly used to analyze mixtures for identification and quantification. Various ancillary GC techniques such as headspace/GC, pyrolysis/GC, and other multidisciplinary techniques are available to conduct this concept [7].

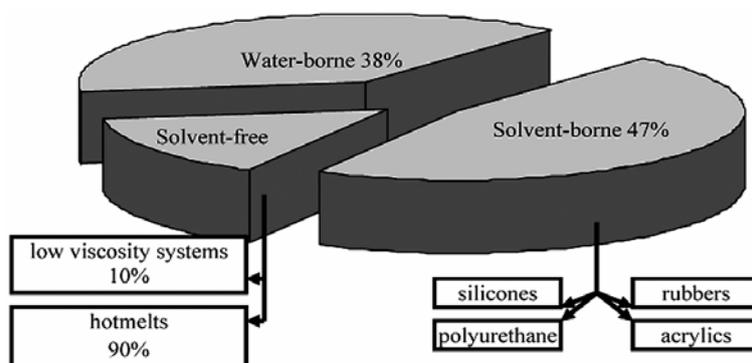


Fig. 1. Raw materials and market share for manufactured PSA in Europe

Rys. 1. Udział surowców w rynku i produkcji PSA w Europie

2. Experimental

For pyrolysis trials the necessary acrylic copolymers were synthesized from 95 wt.% alkyl acrylate and 5 wt.% acrylic acid (AA) in ethyl acetate using 0.1 wt.% radical starter AIBN. All the monomers, the radical starter AIBN and organic solvent ethyl acetate were purchased from BASF (Germany).

The polymerization process was carried out under the following conditions:

- dosage time of monomers and AIBN: 1 h
- time of post-reaction: 6 h
- polymer content: 50 wt.%

The synthesized solvent-borne acrylic copolymers were characterized by the following viscosities (Tab. 1), measured at room temperature.

As evaluated acrylic PSA characterized by viscosity of 8.3 Pa·s at 50 wt.% solid content, a copolymer containing the following acrylate monomers was pyrolysed:

- methyl acrylate: 10 wt.%
- ethyl acrylate 20 wt.%
- butyl acrylate 30 wt.%
- 2-ethylhexyl acrylate 35 wt.%
- acrylic acid 5 wt.%

Table 1

Viscosity and composition of synthesized acrylic copolymers

Copolymer name	Alkyl acrylate [wt.%]	Acrylic acid [wt.%]	Viscosity [Pa·s]
MA/AA	Methyl acrylate 95	5	11.2
EA/AA	Ethyl acrylate 95	5	9.1
BA/AA	Butyl acrylate 95	5	7.3
2-EHA/AA	2-ethylhexyl acrylate 95	5	5.2

The theoretical structure of synthesized acrylic PSA using commercially available main monomers is shown in Fig. 2.

The most satisfactory conditions for pyrolysis of the investigated acrylic polymers were a temperature of about 500°C for 30 seconds in a helium atmosphere. The expected pyrolysis products of the evaluated acrylic copolymers were introduced using gas chromatograph Unicam 610 (detector: FID, column: quartz capillary column 25 QC2/BP1).

The identification and composition of the tested acrylic copolymers were determined by the comparison of the chromatogram of the sample with chromatograms of known pyrolysis products of the synthesized acrylic copolymer with known composition.

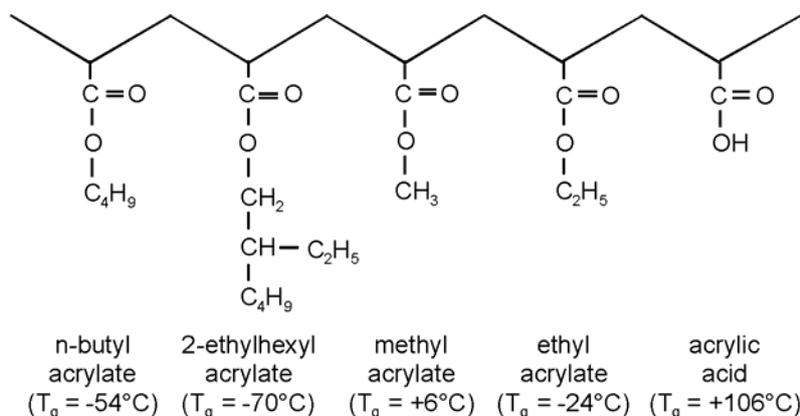


Fig. 2. The chain of acrylic PSA includes main monomers

Rys. 2. Łańcuch akrylanowego PSA zawierającego główne monomery

3. Results and discussion

Figures 3–6 have shown the chromatograms of the thermal breakdown products of acrylic copolymers containing commercially suitable alkyl acrylates and acrylic acid.

The pyrolysis chromatogram of exanimate acrylic copolymer based on methyl acrylate and acrylic acid (Fig. 3) contains three principal peaks. The first is methanol, the second is methyl acrylate and the third is methyl methacrylate corresponding to acrylic acid methyl ester incorporated into the acrylic polymer chain.

The pyrogram of ethyl acrylate-acrylic acid-copolymer shows ethanol, ethyl acrylate and ethyl methacrylate as thermal degradation products.

The peaks in Fig. 5 belong to butanol-1, butyl acrylate and butyl methacrylate. The presence of these three peaks in the pyrolysis chromatogram in thermal degradation process is possibly due to the thermal decomposition of butyl acrylate groups in the side chain. The pyrolysis behaviour of acrylic copolymers is in good agreement with own trials in the quantitative yield of butanol-1, butyl acrylate and butyl methacrylate from the ester.

As chain fragments, from tested acrylic copolymer based on the radical polymerization of 2-ethylhexyl acrylate and acrylic acid, are also observed included suitable monomer in

the liquid phase 2-ethylhexene-1, 2-ethylhexanol-1, 2-ethylhexyl acrylate and 2-ethylhexyl methacrylate (Fig. 6).

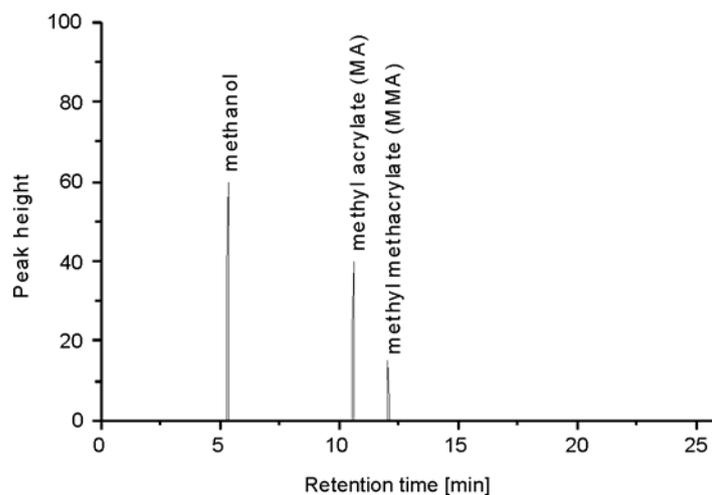


Fig. 3. Chromatogram of the pyrolyzates of acrylic copolymer: methyl acrylate-acrylic acid

Rys. 3. Chromatogram pirolizatu kopolimeru akrylan metylu-kwas akrylowy

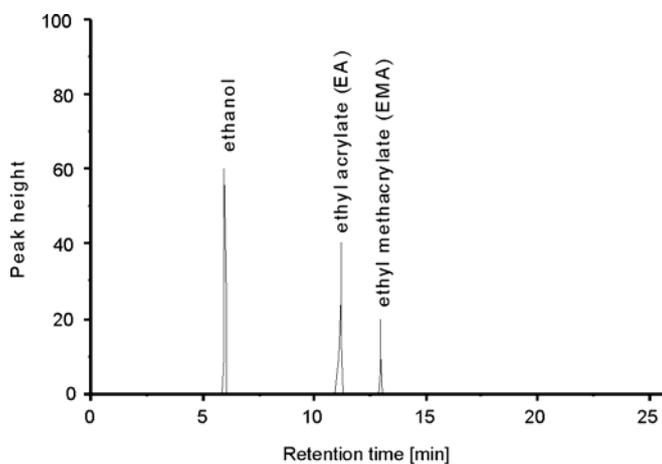


Fig. 4. Chromatogram of the pyrolyzates of acrylic copolymer: ethyl acrylate-acrylic acid

Rys. 4. Chromatogram pirolizatu kopolimeru akrylan etylu-kwas akrylowy

Figure 7 shows the chromatogram of the pyrolyzate of a synthesized acrylic PSA containing all evaluated methyl-, ethyl-, butyl- and 2-ethylhexyl acrylates and acrylic acid.

Comparison of the retention times of the major peaks of various acrylate monomers used for polymerization indicated the presence of four main monomers. The additional present peaks were accounted for by the comparison with the chromatograms of

individually selected synthesized PSA. The analyzed acrylic PSA (Fig. 7) was identified as being composed of methyl acrylate, ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate.

The mechanism of formation of the above mentioned and established liquid breakdown products can be explained on the basis of the characteristic property and thermal resistance of typical acrylic copolymers containing methyl acrylate, butyl acrylate and acrylic acid (Fig. 8).

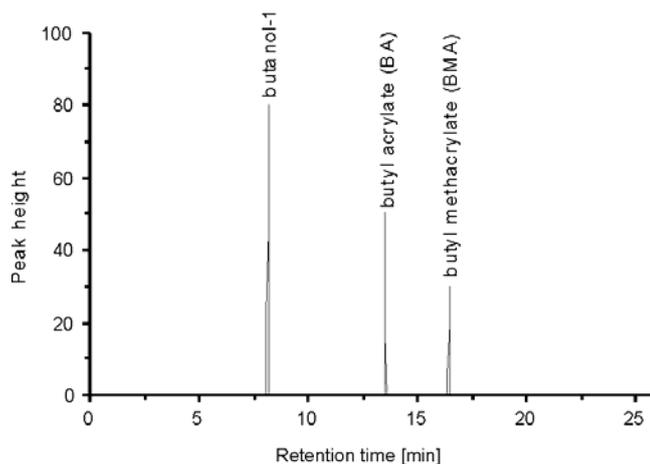


Fig. 5. Chromatogram of the pyrolyzates of acrylic copolymer: butyl acrylate-acrylic acid

Rys. 5. Chromatogram pirolizatu kopolimeru akrylan butylu-kwas akrylowy

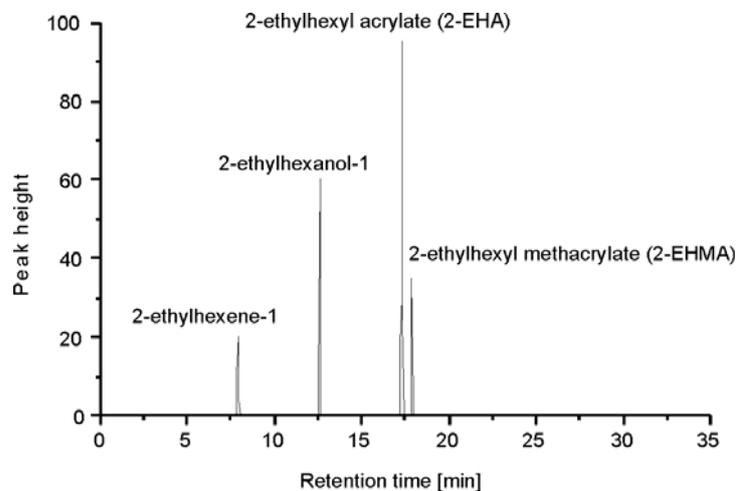


Fig. 6. Chromatogram of the pyrolyzates of acrylic copolymer containing 2-ethyl hexyl acrylate and acrylic acid

Rys. 6. Chromatogram pirolizatu kopolimeru akrylan 2-etyloheksylu-kwas akrylowy

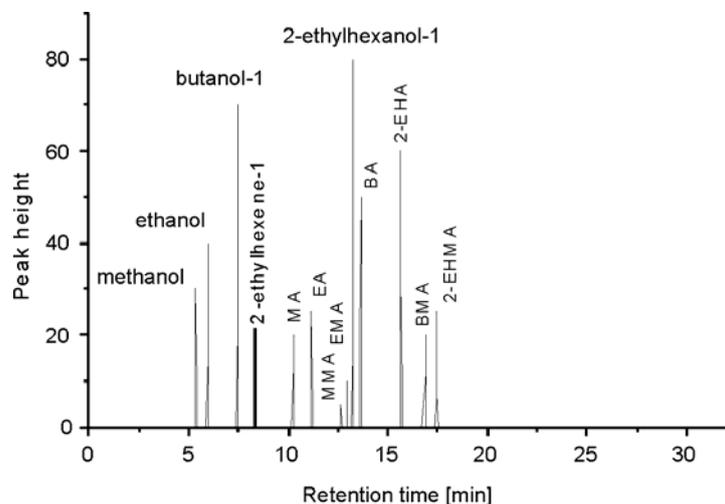


Fig. 7. Pyrolyzates chromatogram of evaluated acrylic PSA based on main commercial alkyl acrylates and acrylic acid

Rys. 7. Chromatogram pirolizatu PSA opartych na głównych akrylanach i kwasie akrylowym

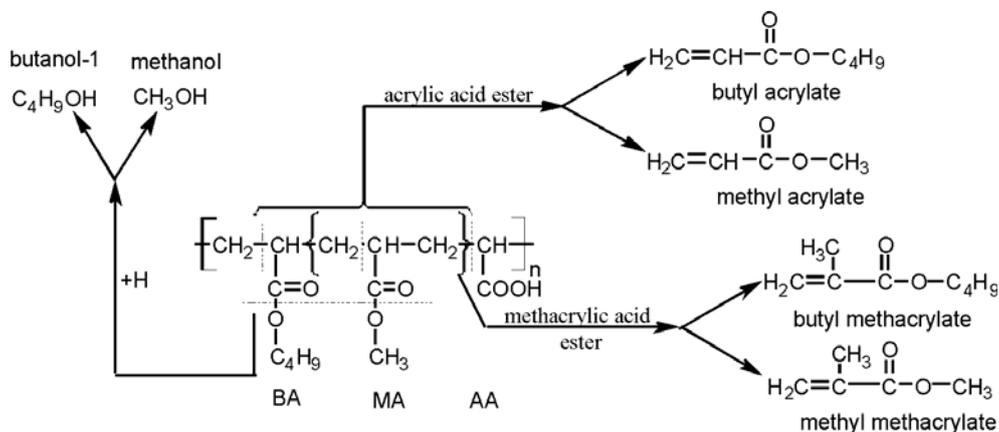


Fig. 8. Forming of alcohols, acrylic and methacrylic monomers during the pyrolysis of acrylic copolymers based on methyl acrylate, butyl acrylate and acrylic acid

Rys. 8. Mechanizm tworzenia monomerów akrylanowych w trakcie pirolizy kopolimeru opartego na akrylanie metylu, akrylanie butylu i kwasie akrylowym

4. Conclusions

Gas chromatography, coupled with a controlled thermal degradation of the pyrolysis technique, provides a rapid method for the identification of PSA based on acrylate and

methacrylate copolymers. The investigated acrylic PSA can be pyrolyzed and the pyrolyzates can be fed directly into a gas chromatograph by the use of a gas sampling valve. Chromatographing the complete pyrolyzate allows for the separation and identification of thermal degradation by-products such as corresponding olefins, alcohols and monomers and the same esters of acrylic and methacrylic acid.

The gas chromatography method can also be used for the semi-quantitative determination of acrylate and methacrylate monomers in different mixtures of polymers. This technique may be proved useful in solving problems connected with the production of acrylic polymers and for the monitoring and analysis of commercial articles containing developed and ready-to-use acrylic materials. The applicability of this method to the analysis of other types of polymers is being investigated. The thermal degradation products from the acrylic PSA wastes can be separated by the distillation and removed by polymerization plant.

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