CZASOPISMO TECHNICZNE Ch
WYDAWNICTWO POLITECHNIKI KRAKOWSKIEJ

z. 2-Ch/2008
ISSN 0011-4561
ISSN 1897-6298

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BIODEGRADABLE ACRYLIC PRESSURE-SENSITIVE ADHESIVES

BIODEGRADOWALNE SAMOPRZYLEPNE KLEJE POLIAKRYLANOWE

Abstract

Biodegradable water-soluble pressure-sensitive adhesives (PSA) based on acrylic are still something of a speciality. They are synthesized from typical acrylate monomers such as soft 2-ethylhexyl acrylate (2-EHA) or butyl acrylate (BA), hard monomers as methyl acrylate (MA) or ethyl acrylate (EA), hydroxylated acrylates as 2-hydroxyethyl- or 2-hydroxypropyl acrylate and vinyl carboxylic acid suitable for water solubility and crosslinking reaction, as acrylic acid (AA) or ß-acryloiloxypropionic acid (BCEA). After synthesis the water-soluble acrylic PSA are modified through addition of water-soluble plasticizers, water-soluble ethoxylated amines, and special soft or hard resins, and neutralized in the presence of potassium hydroxide. After this procedure the water-soluble acrylic PSA are crosslinked using different external crosslinking agents.

Keywords: biodegradation, water-soluble, acrylic, pressure-sensitive adhesives (PSA), crosslinking

Streszczenie

Biodegradowalne rozpuszczalne w wodzie poliakrylanowe kleje samoprzylepne mają obecnie szerokie zastosowanie w wielu aplikacjach. Są one otrzymywane z typowych monomerów akrylanowych, takich jak: monomery obniżające temperaturę zeszklenia polimeru: akrylan 2-etyloheksylu (2-EHA) oraz akrylan butylu (BA) oraz monomery podwyższające kohezję, takie jak akrylan metylu (MA) lub akrylan etylu (EA), a także monomery funkcyjne, jak np. akrylan 2-hydroksyetylu, akrylan 2-hydroksypropylu oraz karboksylowe kwasy winylowe, jak np. kwas akrylowy (AA) lub kwas ß-akryloilooksypropionowy (BCEA). Po syntezie rozpuszczalne w wodzie akrylanowe (PSA) są modyfikowane przez dodatek wodorozcieńczalnych plastyfikatorów, etanoloamin, specyficznych żywic zmiękczających i utwardzających oraz związków neutralizujących (KOH). Zmodyfikowane są sieciowane przez zastosowanie odpowiednich czynników sieciujących.

Słowa kluczowe: biodegradacja, kleje wodorozcieńczalne, akrylany, kleje samoprzylepne, sieciowanie

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1. Introduction

Biodegradable water-soluble pressure-sensitive adhesives are a very interesting novel group of polymers with self-adhesive properties. The research and development of these polymers is quite an interesting scientific terrain with full innovation and exciting further development in this area is expected. A challenging area of biodegradable water-soluble PSA application constitutes their use for water-dispersible labels and medical devices like surgical tapes and biomedical electrodes. Acrylic biodegradable water-soluble PSA characterized by high mechanical and thermal performances are not commercially available on the market. Their composition, synthesis method and technical details are described in a great number of patents and are hidden from producers [1–5].

Biodegradable water-soluble self-adhesives are known in the art of natural products such as dextrin, gelatine, casein or starch, or in the art of synthetic products such as polyvinyl alcohol. Under dry conditions, however, this type of products lacks elasticity and viscosity, showing no pressure-sensitive adhesive properties. These typical natural water-soluble adhesives have disadvantages such as little thermal strength and little resistance to ageing. On the one hand, a large number of natural or synthesized polymers, by their nature, have no adhesive properties, whilst on the other hand, the adhesive tapes industry resorts to raw materials which are produced in large quantities and therefore at a low cost. It is not necessary to develop new base polymers, but rather it is sufficient to selectively modify the polymers selected according to the commercial criteria. An unusual and interesting challenge is that of giving a pressure-sensitive adhesive a certain water-solubility, which depends greatly on the hydrophilic properties of the groups incorporated into the polymer chain [6].

2. Selection of suitable acrylate monomers

The preferred choice for the manufacture of biodegradable water-soluble acrylic pressure-sensitive adhesives are commercially available tackifying acrylic acid alkyl esters with C_4 to C_{12} carbon atoms in the alkyl group together with other comonomers such as vinyl carboxylic acid or water-soluble hydroxyalkyl acrylates. The most important members of this class of substances are listed in the overview below [7].

Tackifying alkyl acrylates (Tab. 1) C_4–C_{12} alkyl acrylates supply the initial adhesion owing to the low glass transition temperature (T_g). They reduce the glass transition temperature T_g of the polymer and give it tack and adhesion.

Table 1

Tackifying alkyl acrylates

Monomer	T_g [°C]
n-octyl acrylate	–80
2-methylheptyl acrylate	–72
2-ethylhexyl acrylate	–70
isooctyl acrylate	–70
butyl acrylate	–54

The glass transition temperature T_g is the main criterion for the self-adhesive properties of the polymers. It is characteristic for homopolymers, but provides interesting information about the usability of the chosen monomers for synthesis and potential application for manufacturing of self-adhesive articles.

Hardening monomers (Tab. 2) such as methyl acrylate or ethyl acrylate are included to provide internal strength and improve plasticizer resistance.

Table 2

Hardening alkyl acrylates

Monomer	T_g [°C]
ethyl acrylate	–24
methyl acrylate	+6

Vinyl carboxylic acids (Tab. 3) give the PSA water-solubility and improve the adhesion to polar substrates with high surface energy. They raise the glass transition temperature T_g and create active crosslinking centres to ameliorate the shear strength.

Table 3

Vinyl carboxylic acids

Monomer	T_g [°C]
β-acryloyloxypropionic acid	–10
acrylic acid	+106
vinylphosphonic acid	+137

Hydroxyalkyl acrylates (Tab. 4) give the PSA hydrophilicity and water-solubility. They decrease the glass transition temperature T_g of the synthesized water soluble copolymers.

Table 4

Hydroxyalkyl acrylates

Monomer	T_g [°C]
2-hydroxyethyl acrylate	–15
2-hydroxypropyl acrylate	–7

The biodegradable water-soluble copolymer may be comprised of monomers of about 40 to 70 weight percent of C_4–C_{12} alkyl acrylates, about 20 to 50 weight percent of vinyl carboxylic acids, and the rest of hydroxyalkyl (meth)acrylates. Preferred are, for example, butyl acrylate or 2-ethylhexyl acrylate, ethyl acrylate, acrylic acid and 2-hydropropyl acrylate.

3. Synthesis of biodegradable water-soluble PSA

Biodegradable water-soluble PSA are generally prepared by the polymerization of a high level of hydrophilic monomers (Fig. 1) and, after synthesis, modified with various types of water-soluble plasticizers, tackifiers and neutralization of the carboxylic groups, are compounded with water-soluble additives and metal hydroxides [8–10].

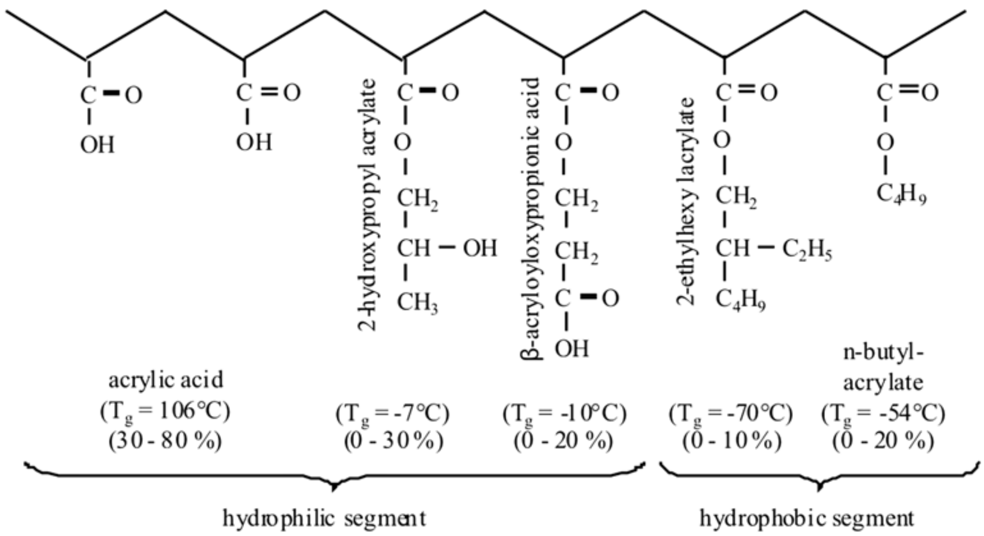

Fig. 1. Polymer chain of water-soluble acrylic PSA

Rys. 1. Łańcuch wodorozcieńczalnego akrylanu (PSA)

The hydrophilic monomers containing functional groups improve the specific adhesion to various substrates and create active crosslinking centres.

4. Crosslinking of biodegradable water-soluble PSA

The mechanical and physio-chemical properties of the biodegradable water-soluble pressure-sensitive adhesives are determined to a great extent by the type and quantity of a crosslinking agent added by modification to the polymerizate. From the comprehensive range of crosslinkers the most important for biodegradable water-soluble PSA will be described.

Metal acetylacetonates with iron-, hafnium- zirconium- and aluminium atoms (Fig. 2) [11] are particularly efficient as crosslinking agents. The addition of alcohol as a stabilizer after the vaporization of which, in the drying chamber together with other solvents, the crosslinking reaction starts spontaneously is characteristic for these crosslinking systems. The crosslinking reaction takes place via the carboxyl groups of the copolymer from vinyl carboxylic acid.

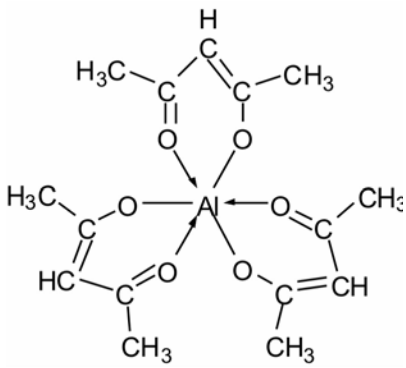

Fig. 2. Chemical structure of aluminium acetylacetonate (AlACA)

Rys. 2. Struktura acetyloacetonianu glinu (AlACA)

Amino resins: Thermal crosslinking agents (crosslinking temperature >100°C) amino resins which can be classified into four main groups: melamine formaldehyde resins, benzoguanamine, glycoluril or urea resins have been on offer in the last year. In order to obtain a crosslinking effect these resins need only weak canalization or none at all. In most cases a low acid value of the acrylic basis is already sufficient, and the reactivity of the alkoxyalkyl groups is relevant for the crosslinking speed (Fig. 3).

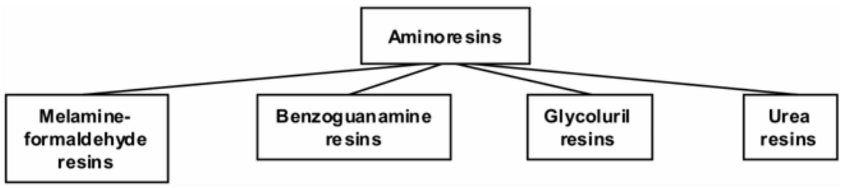

Fig. 3. Kinds of various amino resins

Rys. 3. Rodzaje żywic aminowych

Multifunctional propylene imines are functional 2-methylaziridine derivates (Fig. 4), which act as very reactive low energy crosslinking agents in carboxylated polymers [12].

The high reactivity of propylene imine crosslinkers can be ascribed to ring strain inherent in the terminal aziridine groups [13]. Ring opening is acid catalyzed, proceeding initially via protonation of the tertiary nitrogen atom. Effective utilization of aziridine chemistry is dependent very much upon the availability of an active H^+ to protonate the aziridine ring. Unlike many other products used to crosslink polymer acrylics, temperature is not a major factor in the use of aziridine chemistry. For a crosslinking application the multifunctional propylene imines are added to the final compounded coating just prior to use. These pressure-sensitive adhesive acrylics have a pot life of about 8 to 36 hours. The level of propylene imines used will depend on the desired properties of the finished adhesive coating.

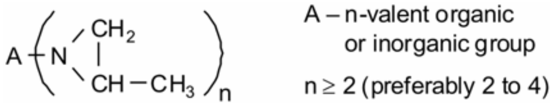

Fig. 4. Chemical formula of multifunctional propylene imine crosslinkers

Rys. 4. Struktura wielofunkcyjnej propyleno iminy sieciującej

5. Modification of biodegradable water-soluble PSA

Higher alkyl esters of acrylic acid provide the resulting copolymers with softness and tackiness. At the same time they make the copolymer hydrophobic and water-insoluble. However, the water-insoluble copolymer can be modified to become water-soluble through neutralization of the carboxyl groups of the copolymer derived from the vinyl carboxylic acid. The latest development trend comprises the synthesis of a polymer from tackifying alkyl acrylate and acrylic acid. The resulting polymer possesses certain water-solubility and a certain tack. A further modification differs in principle from the cases described above only in the proportion of additives, whose quantity or concentration is much smaller in relation to the pure acrylics. This means that the properties of the modified biodegradable water-soluble PSA can be better controlled. The important modification of biodegradable water-soluble PSA is conducted by addition of soft and hard resins, plasticizers and neutralization of carboxyl groups.

Soft resins: A tackifier is an optional additive to the pressure-sensitive adhesive. If present, the tackifier is a resin such as an aromatic hydrocarbon resin or a resin acid compatible with acrylic PSA. Liquid at room temperature, soft resins are particularly suitable for water-soluble acrylic PSA, for example for water-soluble removable products such as labels and OP-tapes, which require a good tack as well as an excellent removability. The peel adhesion, however, decreases distinctly with an increasing concentration of soft resin (Fig. 5).

Adhesion increasing resins: The function of these resins is based substantially on the achievement of a desired surface aggressiveness. Unexpectedly, it was found that the increase in adhering strength is in quite a simple linear correlation to the resins content (Fig. 5).

Plasticizers: Suitable water-soluble plasticizers are, for example, polyoxyethylenes like PEG 200, PEG 300, PPG 300 or PPG 400. No limiting examples of water-soluble plasticizers include a free acid or sodium salt of a complex organic phosphate ester such as poly (oxy-1, 2-ethandiyl), alpha-(nonylphenyl)-omega-hydroxyl-phosphate (Fig. 6) having an oxyethylene content of about 52 weight percent. A preferred amount of water-soluble plasticizers is generally used in an amount from 40 to 100 parts by weight per 100 parts by weight of the acrylic copolymer.

Neutralization of carboxylic groups: To neutralize the acid groups of the acrylic chain using KOH or a secondary or tertiary alkanolamine is very important for ameliorating of water-solubility and biodegradability. It is very advantageous to use ethoxylated alkanolamines (Fig. 7) with HLB (Hydrophilic-Lipophilic Balance) between 10 and 20, determined by a polarity index procedure, in which at least one or preferably several amino hydrogen atoms are replaced by a residue containing one carbon atom.

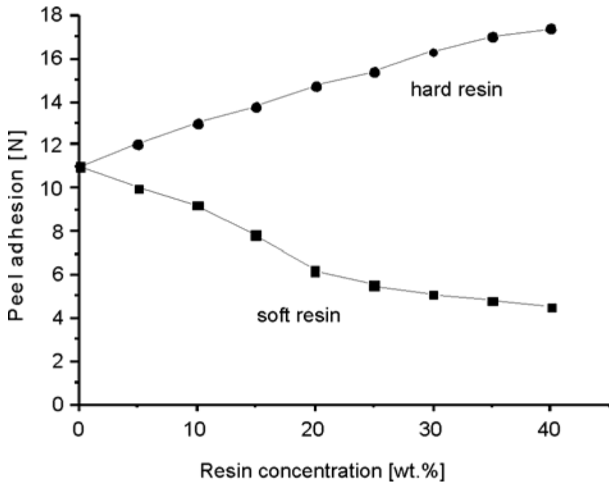

Fig. 5. Peel adhesion versus diverse resin content

Rys. 5. Zależność przyczepności od zawartości odpowiedniej żywicy

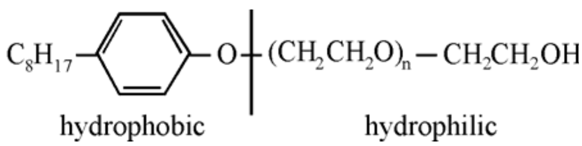

Fig. 6. Chemical structure of ethoxylated octylphenol

Rys. 6. Struktura oksyetyleno para oktylofenolu

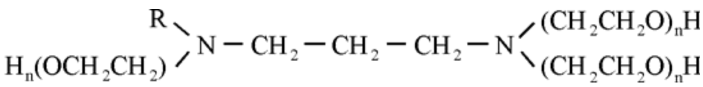

Fig. 7. Chemical structure of ethoxylated alkanolamine

Rys. 7. Struktura oksyetyleno alkanoaminy

Recyclability and biodegradability: The biodegradable water-soluble pressure--sensitive adhesives used for the production of biodegradable labels, OP-tapes and biomedical electrodes are fully recyclable. They reached approx. 60% decomposition on the basis of the chemical oxygen demand (COD) of the test substance within 28 days in the BODIS test, provisional guideline of the German Federal Environmental Agency (UBA). It is therefore classified as partially biodegradable. Further studies are planned in order to assess the biodegradability of water-soluble adhesive labels in the ecosystems (Fig 8).

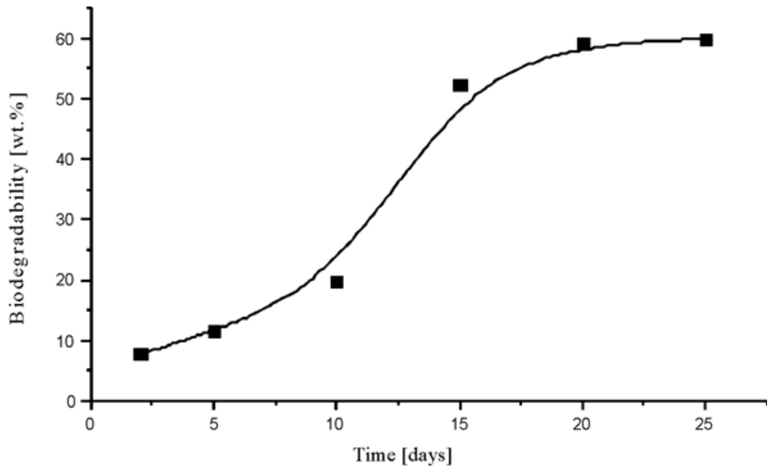

Fig. 8. Biodegradability of water-soluble labels

Rys. 8. Biodegradowalność wodorozcieńczalnych etykiet

The rate of biological decomposition of the adhesive of OP-tapes was determined via the biochemical oxygen demand by measuring the O_2 partial pressure. The latter process not only provides a measure of the rate of oxidative degradation of the organic constituents at the microbiological level, but also provides evidence of the kinetics of decomposition via the corresponding curve shape. The calculation factor used for the rate of degradation is the chemical oxygen demand (7,800 mg O_2/l) determined experimentally by the potassium dichromate method, which can be taken as a measure of the complete mineralization of the organic substance contained in the product. The biochemical degradation of OP-tape is in approximately three-quarters accomplished after a period of twelve days. The end point of microbiological decomposition of the chemically oxidizable constituents is reached after approximately 23 to 25 days under the selected test conditions and is approx. 57%, which allows the adhesive tested to be classified as satisfactorily biodegradable.

6. Outlook

Biodegradable water-soluble, modified acrylic pressure-sensitive adhesives will play a very important role in the manufacturing of biodegradable water-soluble labels, medical OP-tapes, biomedical electrodes and similar products still in the research and development stage. Important prerequisites for the market success of such special biodegradable water--soluble labels are an adaptation to new paper formulations, and surfaces, and expansion of the product range to include a wide variety of medical products, such as operating theatre tapes and biomedical electrodes.

References

[1] M i l k e r R., C z e c h Z., *New trends and applications for water-soluble PSA*, Conference AFERA, Brüssel, Belgium 2002, 29.

[2] C z e c h Z., *Biologisch abbaubare, wasserlösliche Haftetiketten und OP-Tapes*, Polimery, Środowisko, Recykling, Międzyzdroje 1955, 133.

[3] US Patent 2, 838, 421, 3M, 1956.

[4] DE 21 42 770, Beiersdorf, 1971.

[5] EP 0 379 932, Lohmann, 1990.

[6] M i l k e r R., *Synthesis and Application of Solvent-borne Water-soluble Pressure-sensitive Acrylic Adhesives*, Coating, 7, 275, 2004.

[7] M i l k e r R., C z e c h Z., *Redispergierbare Spleißbänder*, Adhäsion, 4, 32 1990.

[8] C z e c h Z., P e ł e c h R., *Use of pyrolysis and gas chromatography for the determination of acrylic acid concentration in acrylic copolymers containing carboxylic groups*, Polymer Testing, 27, 870, 2008.

[9] C z e c h Z., B a r t k o w i a k A., *Biologisch abbaubare wasserlösliche Haftklebstoffe auf Polyacrylatbasis*, Kautschuk Gummi Kunststoffe, 57, 284, 2004.

[10] M i l k e r R., C z e c h Z., *Development trends in PSA systems*, Workshop on Functional Materials FMA 2004, Athens 2004, 11.

[11] *Vernetzung von Haftklebstoffen auf Polyacrylatbasis*, Ed., Szczecin University of Technology, 1999.

[12] EP 0 206 669 3M, 1986.

[13] EP 0 544 183 3M, 1992.

[14] US Patent 4, 569, 960, 3M, 1984.