Biodegradable acrylic pressure-sensitive adhesives and their application

Zbigniew Czech*
Agnieszka Butwin*
Marta Wesołowska*

The technology of solvent-borne water-soluble biodegradable acrylic pressure-sensitive adhesive (PSA) has been developed. The novel acrylic PSA based on butyl acrylate and acrylic acid can be used after special modification for production of biodegradable self-adhesive products as water-dispersable labels, OP-tapes and biomedical electrodes.

Key words*: biodegradable acrylic PSA, labels, OP-tapes, biomedical electrodes*

Biodegradowalne poliakrylanowe kleje samoprzylepne i ich zastosowanie

Opracowano technologię syntezy rozpuszczalnych w wodzie biodegradowalnych poliakrylanowych klejów samoprzylepnych. Nowe kleje poliakrylanowe syntetyzowane z akrylanu butylu i kwasu akrylowego stosowane są po modyfikacji do produkcji biodegradowalnych etykiet samoprzylepnych, taśm operacyjnych oraz samoprzylepnych elektrod biomedycznych.

Słowa kluczowe*: biodegradowalne poliakrylanowe kleje samoprzylepne, etykiety, taśmy operacyjne, bioelektrody*

1. Introduction

Over the last decade, the performance and availability of biodegradable polymers has developed strongly, driven by increasing interest in sustainable development, desire to reduce dependence upon finite resources and changing policies and attitudes in waste management. Most of the biodegradable polymers on the market or in development are based on renewable raw material feedstocks from agriculture or forestry. Although biodegradable polymers have been commercialized for over 30 years, this niche market is beset with a variety of roadblocks led by high prices and lack of an industrial infrastructure to deal with these materials.

Although the term „biodegradable polymers" is well known, there are no universal standards in place, and in many instances, the fate of these materials in composting media is unclear. In addition, the major drivers for growth in the North America stem from mandated legislation, which may not develop for some time. Consumption is provided for the North America, but there is considerable information on both Western European and Japanese products, technologies, markets and companies, because biodegradable polymers need to viewed on a global scale.

Conventional adhesives and pressure-sensitive adhesives based on synthetic polymers such as rubbers, polyamides, polyesters, silicones or acrylics and self-adhesive products used synthetic polymers persist for many years after disposal are not biodegradable. Built for the long haul, these polymers seem inappropriate for applications in which polymers are used for short time periods and then disposed. In contrast, biodegradable polymers disposed in bioactive environments degrade by the enzymatic action of microorganisms such as bacteria, fungi, and algae. Their polymer chains may also be broken down by no enzymatic processes such as chemical hydrolysis. Biodegradable polymers are often derived from plant processing of atmospheric CO_2. Biodegradation converts to CO_2, CH_4, water, biomass, humic matter, and other natural substances. They are thus naturally recycled by biological processes [1-4].

2. Solvent-borne water soluble acrylic PSA

Several years ago companies 3M, Beiersdorf (BDF), Nitto and Lohmann invested in solvent-borne water-soluble acrylics. These are distinguished by many features including excellent ageing resistance, thermal resistance and consistency of the properties of tack, bonding strength and shear strength. The water-soluble acrylic based self-adhesives which all companies already developed or is currently developing are characterised by excellent thermal strength and complete water-solubility over a wide pH-spectrum. Although the possibilities of the acrylic components, acrylate monomers, have been more or less exhausted as far as the chemical structure is concerned, nevertheless there is wide scope for formulations by varying the

* Institute of Chemical Organic Technology, Szczecin University of Technology, Szczecin, Poland

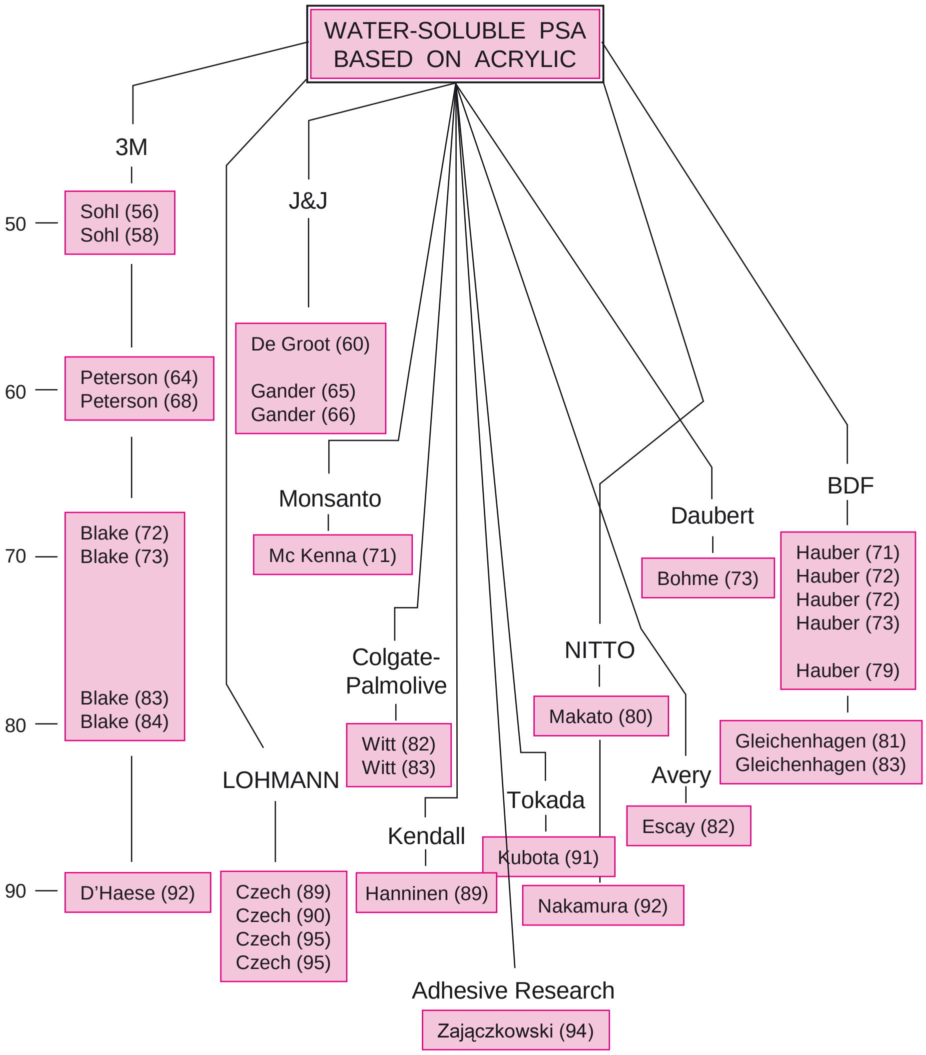

Fig. 1. *History of the development of water-soluble PSA*
Rys. 1. *Historia rozwoju rozpuszczalnych w wodzie klejów samoprzylepnych*

copolymer composition and modifying the synthesized polymers (Fig. 1) [5].

State-of-the-art technology in the field of water-soluble PSA based on acrylic comprises more than 40 patents. Therefore, development work in this area is concentrated on the aspects of monomer and polymerisation media selection, optimising of polymerisation processes, molecular mass and molecular mass polydispersity, kind and method of crosslinking and modification of the water-soluble acrylic pressure-sensitive adhesives.

Synthesized water-soluble acrylic PSA are not directly biodegradable. The biodegradability requires appropriated modification based on application of suitable crosslinking agents, water-soluble plasticizers and neutralizing agents.

3. Experimental section

Monomers

The basic acrylic PSA were synthesized in solvent ethyl acetate (BASF) at the boiling temperature about 77^{o}C using butyl acrylate and acrylic acid (both monomers available from BASF) and 0.1 wt.% radical thermal initiator AIBN (Degussa). The water-soluble

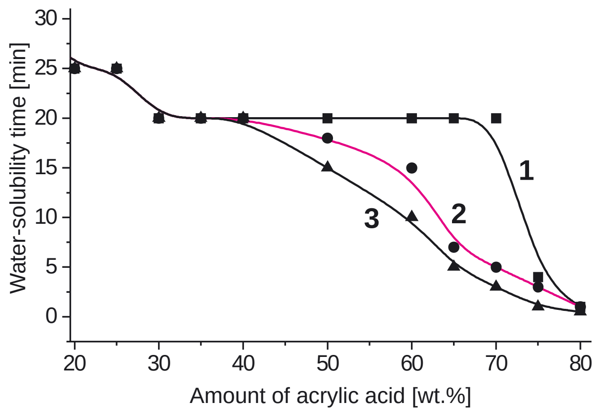

Fig. 2. *The influence of acrylic acid amount in the polymer on its time of water solubility time: 1 – pH = 4; 2 – pH = 7; 3 – pH = 11*
Rys. 2. *Wpływ zawartości kwasu akrylowego w polimerze na jego rozpuszczalność w wodzie przy wartościach pH 4, 7, 11*

acrylic PSA containing between 20 and 80 wt.% butyl acrylate (soft monomer) and between 80 and 20 wt.% acrylic acid (water-soluble monomer with crosslinking centers). Fig. 2 shows the water-solubility of synthesized copolymers at diverse pH-values.

Fig. 2 makes it evident that the increase of pH-value improves the water solubility of acrylic PSA containing hydrophilic acid into polymer structure. A shorter water-solubility time was observed for polymers containing more than 30 wt.% of acrylic acid in evaluated pH-areas.

Crosslinking agents

As it can be stated from tested water-soluble acrylic PSA, the increasing of crosslinking agent concentration shows a positive influence on the PSA cohesion but influences negatively a very important parameter water-solubility. The water-solubility of acrylic PSA containing between 20 and 40 wt.% of acrylic acid was determined using two suitable non hydrolyzed cross-linkers: aluminium acetylacetonate [6] (AlACA) from Du Pont and zirconium acetylacetonate (ZrACA) from Wacker (Fig.3).

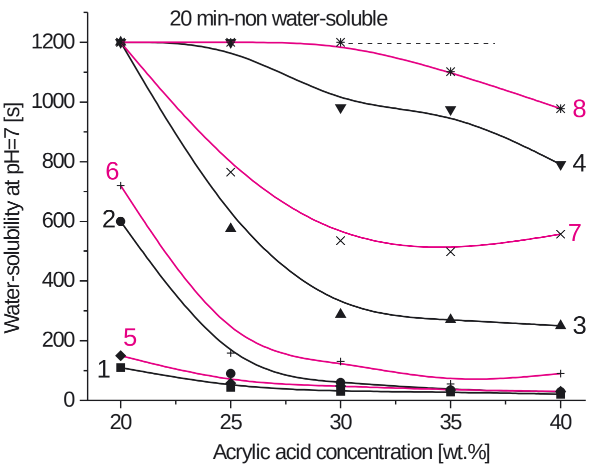

Fig. 3. *Effect of crosslinkers AlACA and ZrACA on water-solubility of acrylic PSA at pH=7: 1 – 0.5% AlACA, 2 – 1% AlACA, 3 – 1.5% AlACA, 4 – 2% AlACA, 5 – 0.5% ZrACA, 6 – 1% ZrACA, 7 – 1.5% ZrACA, 8 – 2% ZrACA*

Rys. 3. *Wpływ związków sieciujących AlACA oraz ZrACA na rozpuszczalność w wodzie poliakrylanowych klejów samoprzylepnych przy pH=7*

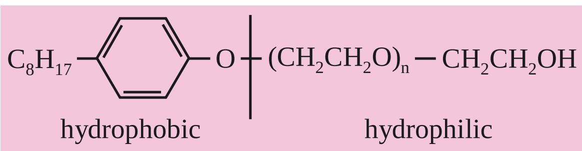

Fig. 4. *Chemical structure of ethoxylated octylphenol*

Rys. 4. *Struktura chemiczna etoksylowanego oktylofenolu*

After exceeding a threshold of 0.5 wt.% of AlACA or 0.5 wt.% of ZrACA the water solubility of cross-linked acrylic PSA decreases. As can be supposed from the Fig. 4, an acceptable level of water-solubility of about 300 s for acrylic PSA containing from 30 to 40 wt.% acrylic acid guaranties even 1.5 wt.% AlACA.

Plasticizers

Suitable water-soluble plasticizers are, for example, polyoxyethylenes like PEG 200, PEG 300, PPG 300 or PPG 400 (BASF or Degussa). No limiting examples of water-soluble plasticizers include a free acid or sodium salt of a complex organic phosphate ester, commercially available under the trademark Gafac PE 510 from Rhone Poulenc or ethoxylated octylphenol (Fig. 4) having an oxyethylene content of about 52 wt.%, available from GAF Corporation under the registered trademark as Igepal CA-520 [7]. A preferred amount of water-soluble plasticizers is generally used in an amount from 40 to 100 wt. parts per 100 wt. parts of the acrylic copolymer.

Neutralizing agents

To neutralize the acid groups of the acrylic chain, LiOH, KOH, NaOH or a secondary or tertiary alkanolamine may be used. It is very advantageous to use alkanolamines (Fig. 5) with HLB (Hydrophilic-Lipophilic Balance), between 10 and 20, determined by

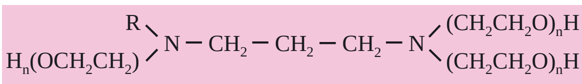

Fig. 5. *Chemical structure of neutralised ethoxylated alkanolamines*

Rys. 5. *Struktura chemiczna etoksylowanych alkanolamin*

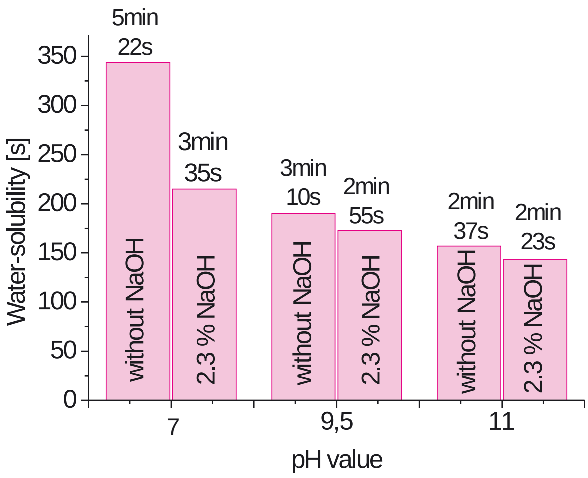

Fig. 6. *Influence of the NaOH amount on the water--solubility at diverse pH values*

Rys. 6. *Wpływ ilości NaOH na rozpuszczalność w wodzie przy różnych wartościach pH* a polarity index procedure [8] in which at least one or preferably several amino hydrogen atoms are replaced by a residue containing one carbon atom.

Very important and technological preferred is the using of conventional neutralizing agents as NaOH. Fig. 6 presented the influence of NaOH concentration and pH-values on water solubility of modified developed water-soluble acrylic PSA containing 40 wt.% acrylic acid, crosslinked with 1.5 wt.% AlACA and modified with 60 wt.% PEG 200.

The best water-solubility of novel developed modified acrylic PSA was observed with increasing of pH value for 2.3 wt.% NaOH.

4. Biodegradability of novel water-soluble modified acrylic PSA

The biodegradable water-soluble pressure-sensitive adhesives and their products like labels, OP-tapes and biomedical electrodes are fully recyclable. They are 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) [9]. 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. 7).

The rate of biological decomposition of the adhesive of water-soluble labels 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

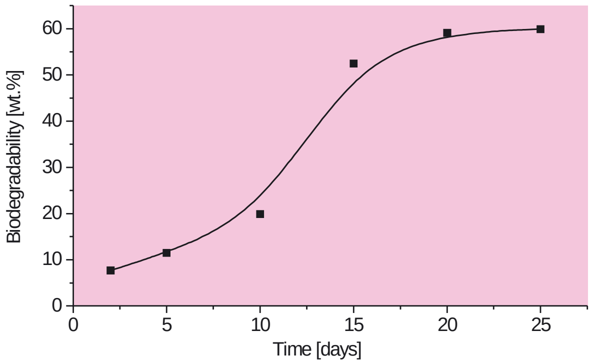

Fig. 7. *Biodegradability of water-soluble labels*
Rys. 7. *Biodegradowalność wodorozpuszczalnych etykiet*

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 water-soluble labels is approximately three-quarters finished 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.

5. Application of water-soluble biodegradable acrylic PSA

Water-soluble biodegradable acrylic pressure-sensitive adhesives are very interesting new group of polymers with self-adhesive properties. Water-soluble biodegradable acrylic PSA with high mechanical and thermal performance are not commercially available on the market. They are applied for the manufacturing of diverse technical self-adhesive products, such as self-adhesive labels and used in medical applications in OP-tapes and biomedical electrodes production.

Water-soluble adhesive labels

This relatively new product is composed of water-soluble acrylic PSA and water-dispersible carrier materials. The water-soluble labels are characterized by excellent adhesion on various materials, such as steel, glass, porcelain, wood, cardboard, PVC, ABS, good adhesion on the low-energy substrates, such as PE or PP, constant adhesive strength over a long period, and printability with conventional printing processes.

Since, up to now adhesive labels have been manufactured with adhesives which are insoluble in water, such as rubbers, dispersions or polyester, they can scarcely be reused as raw material for paper production. The new adhesive labels can be recycled. They have of completely water-soluble acrylic based PSA and water-dispersible carrier systems.

Medical OP-tapes

An interesting application for pressure-sensitive water-soluble adhesives tapes is for securing sheets and other covering materials used in hospital sector operating theatres. The special composition of the water-soluble acrylic PSA allows such pressure-sensitive adhesive tapes to be used even on hydrophobic, low energy textiles cotton cloths coated with polyfluorocarbon resins. The acrylic PSA used for securing operating theatre linen must be largely moisture-resistant, insoluble in cold water and must be have a gentle adhesive strength on the skin plus hypoallergenic properties. The

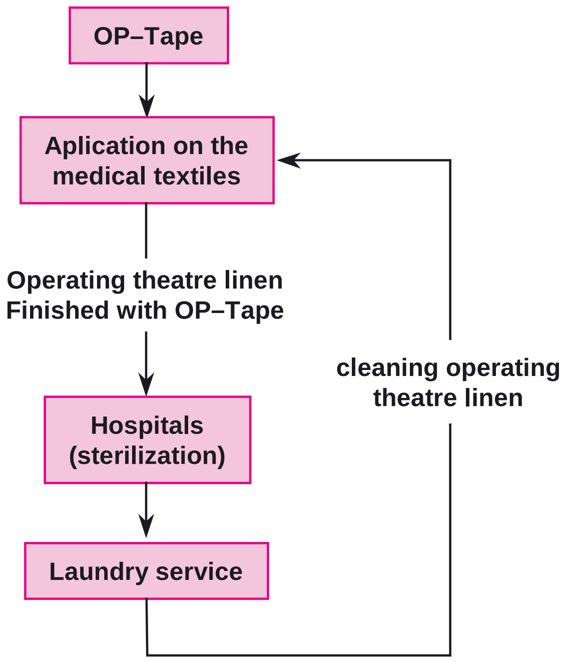

Fig. 8. *Circulation of reusable operating theatre linen*
Rys. 8. *Obieg taśm operacyjnych wielokrotnego użytku*

complete water-solubility of the adhesive, and thus the complete dispersibility of the OP-tape, is reached above 60 to 70^{o}C and in the alkaline pH range (pH > 9) is the target. For this application the availability of water-soluble carrier materials is also demanded [10-11].

Due the growing environmental problems reusable operating theatre linen is becoming increasingly important throughout Europe. The number of hospitals which employ reusable lining is rising constantly and laundries, sterilisation services or laundry rental are becoming central to the overall hospital philosophy. This market for reusable medical systems of this kind is expanding very rapidly.

The textile materials are used with OP-tapes specially developed for the medical sector and fixed after steam sterilisation during 20 min at 121^{o}C on the skin of the patient. After use, the OP-tape is removed without residue during the washing process (alkaline range about 65^{o}C) from the textile, the pressure-sensitive adhesive dissolved and the support completely dispersed (Fig. 8). The biochemical degradation of OP-tape is approximately three-quarters finished 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.

Biomedical electrodes

The term "biomedical electrode" as used hereinafter means an electrode for establishing an electrical connection between the skin of a living body and an electromedical apparatus [12].

For a considerable time now the market has been dominated by electrically conductive thick adhesive layers or hydrogels. Many biomedical electrodes are known in the art, they use electro-conductive materials such as conductive creams, pastes, and gels that incorporate natural polymers such as karaya gum, so as to provide good contact between the skin surface and the electrode and reduce electrical resistance across the skin-electrode interface. New developed water-soluble biodegradable acrylic PSA conductive materials are placed between the skin and the electrode plate. The following large-area biomedical electrodes are well-known.

TENS (Transcutaneous Electrical Nerve Stimulation) electrode coupling media is produced from low to medium concentration of sodium chloride in the hydrogel sheets. It is used as a disposable interface between a "standard" reuse able carbon electrode and the skin.

ESU (Electro-Surgical Unit) electrode is produced from low ionic hydrogel sheet. The dispersive radio frequency return electrode application is a perfect conductive/adhesive application. The biological inertness of the hydrogel assures that local skin reactions.

EKG (electrocardiogram) are the polyethylene oxide hydrogel-based electrodes. They have the widest variety of specific use applications, made possible by the ability to produce hydrogels of specific ionic strength.

DEFIBRILLATION. The defibrillator pad is produced from a sheet with medium ions. The pad is usually used as a conductive media for the application of large amounts of electricity (voltage and current) and also used as a sensing electrolyte for EKG monitoring through the same electrodes.

BIO-FEEDBACK. The Bio-Feedback electrode is produced from a high concentration ionic gel sheet. They are used with a wide variety of home and clinical electrodes, and permits immediate signal reception.

All this electrodes are tested to determine its electrical responses for use as medical electrodes according to the proposed standards for ECG disposable electrodes by AAMI (The Association for the Advancement of Medical Instrumentation). Furthermore, these electrodes must be hypoallergenic. Contact to the skin must be adjustable within a certain range and removal of the electrodes must be gentle and cause discomfort.

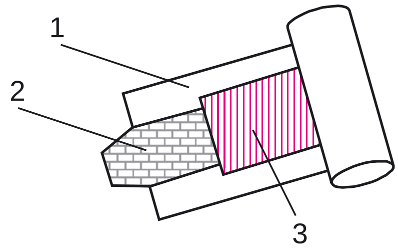

Fig. 9. *Design of new biomedical electrode; 1 – carrier, 2 – electrically conductive film, 3 – acrylic PSA*
Rys. 9. *Konstrukcja nowych elektrod biomedycznych; 1 – nośnik, 2 – folia przewodząca, 3 – poliakrylanowy klej samoprzylepny*

New biomedical electrodes (Fig. 9) consist of an electrically conductive foil (1), a contact (2) and an electrically conductive pressure-sensitive adhesive (3), which is applied over the surface of the electrically conductive foil.

New biomedical electrodes have a transparent, electrically conductive, highly elastic and hypoallergenic layer of pressure-sensitive adhesive based on acrylic. The gentle adhesion of the hydrophilic layer on the skin is unimpaired by skin moisture or sweet. The adhesive and cohesive strength of the electrically conductive adhesive layer is also sufficient to ensure that the electrodes remain fully functional throughout the prescribed duration of application. The acrylic adhesive layers, in which crosslinking takes place at room temperature, contains soft resin, (poly)electrolyte and a moisturizer.

5. Summary

Several developed classes biodegradable PSA have a positive role to play in advancing the modern industries move towards greater sustainability by reducing environmental impacts over their life cycles. This role is likely to become more significant in the future. Water-soluble, modified acrylic pressure-sensitive adhesives will play a major role in the production of biodegradable water-soluble labels, medical OP-tapes, biomedical electrodes and similar products still in the development stage. Important prerequisites for the market success of such materials are adaptation to new paper formulations and expansion of the product range to include a wide variety of medical products, such as operating theatre tapes and novel biomedical electrodes.

References

1. *Gross R. A., Kaira B., Science, 2002, 297, 803.*
2. *Bastoli C., Macromol. Symp., 1998, 135, 193.*
3. *Lunt J., Polym. Degrad. Stab., 1998, 59, 145.*
4. *Buchanan C. M., J. Environ. Polym. Degrad., 1996, 4, 179.*
5. *Loclair H., Dissertation: „Synthese und Anwendung von lösemittelhaltigen wasserlöslichen Haftklebstoffen auf Polyacrylatbasis", Szczecin University of Technology, Szczecin, 2007.*
6. *USA Patent 4, 569, 960, 3M, 1984.*
7. *Czech Z., „Vernetzung von Haftklebstoffen auf Polyacrylatbasis", Ed., Szczecin University of Technology, Szczecin, 1999.*
8. *Technical Data „Ethoxylated Amines", Akzo Chemie, Holland (2001)*
9. *Czech Z., „Wasserlösliche Haftklebemassen auf Polyacrylatbasis und ihre Anwendung", Swiss Bonding'95, Rapperswill, Switzerland (1995), 131--148*
10. *WO 93/03106, Czech Z., Milker R., Nissing P., Wehmann J., 1992.*
11. *EP 0 701 822, Czech Z., Sander D., 1995.*
12. *EP 0 413 301, Czech Z., Lindner E., 1990.*

INSTYTUT INŻYNIERII MATERIAŁÓW POLIMEROWYCH I BARWNIKÓW
ODDZIAŁ ZAMIEJSCOWY
ELASTOMERÓW I TECHNOLOGII GUMY
05-820 PIASTÓW ul. HARCERSKA 30
d. Instytut Przemysłu Gumowego „STOMIL"

oferuje pośrednictwo w organizowaniu:
- konferencji,
- sympozjów,
- spotkań: producentów surowców i maszyn stosowanych w przetwórstwie kauczuków i gumy; firm handlowych i dystrybutorów.

Instytut posiada odpowiednie bazy danych.
Dysponuje salą konferencyjną z wyposażeniem. Ceny do negocjacji.

Kontakt: Teresa Jędrzejak, tel. (0 22) 723 60 25 wew. 264, t.jedrzejak@ipgum.pl