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Synthesis and modification of biodegradable pressure-sensitive adhesives based on acrylic

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ABSTRACT

New pressure-sensitive adhesives (PSAs) based on solvent-borne acrylic copolymer containing butyl acrylate, 2-ethylhexyl acrylate and acrylic acid have been synthesized. After special modification using ethoxylated amines and neutralizing agents they can be used as water-soluble PSAs for manufacturing of biodegradable various self-adhesive products as water-soluble partially biodegradable labels, OP-tapes and biomedical electrodes.

Synteza i modyfikacja biodegradowalnych klejów samoprzylepnych na bazie poliakrylanów

STRESZCZENIE

Dokonano syntezy nowych rozpuszczalnikowych poliakrylanowych klejów samoprzylepnych na bazie kopolimerów zbudowanych z akrylanu butylu, akrylanu 2-etyloheksylu oraz kwasu akrylowego. Po modyfikacji przy zastosowaniu etoksylowanych amin oraz związków neutralizujących otrzymano rozpuszczalne w wodzie kleje samoprzylepne, mogące znaleźć zastosowanie do produkcji rozpuszczalnych w wodzie częściowo biodegradowalnych etykiet, taśm operacyjnych oraz elektrod biomedycznych.

1. INTRODUCTION

The controversy within the industry as to which materials should be considered biodegradable continues unabated. Several of the materials in question include polyolefin-based compositions and polymers containing aromatic groups. Microorganisms have difficulty using these materials in their metabolism. Part of the current debate is defining an acceptable period of time for the biodegradation to be completed. Almost all carbon-based materials biodegrade given an acceptable period of time.

This report includes modified acrylic polymers in form of pressure-sensitive adhesives (PSAs) that producers market as not fully but acceptable biodegradable. Most producers define a fully biodegradable polymer as a polymer that is completely converted by microorganisms to carbon dioxide, water and humus. In the case of anaerobic biodegradation, carbon dioxide, methane, and humus are the degradation products.

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 view 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, Lohmann and Ashland invested in solvent-borne water-soluble acrylic PSAs. 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 self-adhesives based on acrylics which all companies already developed or is currently developing are characterized 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 copolymer composition and modifying the synthesized acrylic polymers (Fig. 1) [5].

State-of-the-art technology in the field of water-soluble PSA based on acrylic comprises more than 50 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 ethoxylated amines and neutralizing agents.

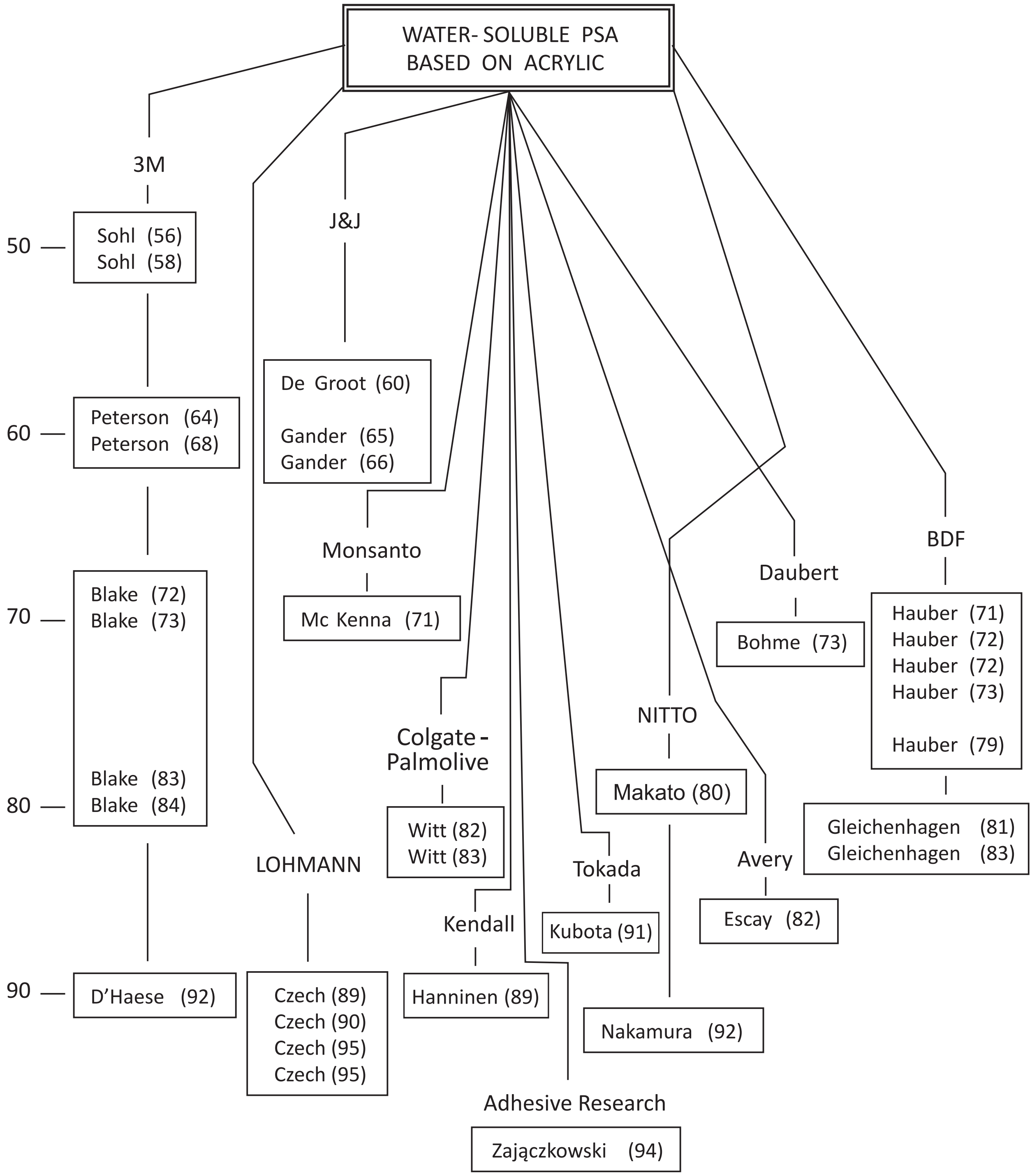

Figure 1. History of the development area of water-soluble PSAs

3. SYNTHESIS AND MODIFICATION OF SOLVENT-BORNE ACRYLIC PSA

Acrylic monomers

The basic acrylic PSAs were synthesized in solvent ethyl acetate (BASF) at the boiling temperature about 77°C using butyl acrylate, 2-ethylhexyk acrylate and acrylic acid (all monomers available from BASF) and 0.1 wt.% radical thermal initiator AIBN (Union Carbide). The water-soluble acrylic PSA containing between 20 and 80 wt. % butyl acrylate and 2-ethylhexyl acrylate (soft monomers) and between 80 and 20 wt.% acrylic acid (water-soluble monomer with crosslinking centers). Figure 2 shows the water-solubility of acrylic copolymers at diverse pH-values.

Figure 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

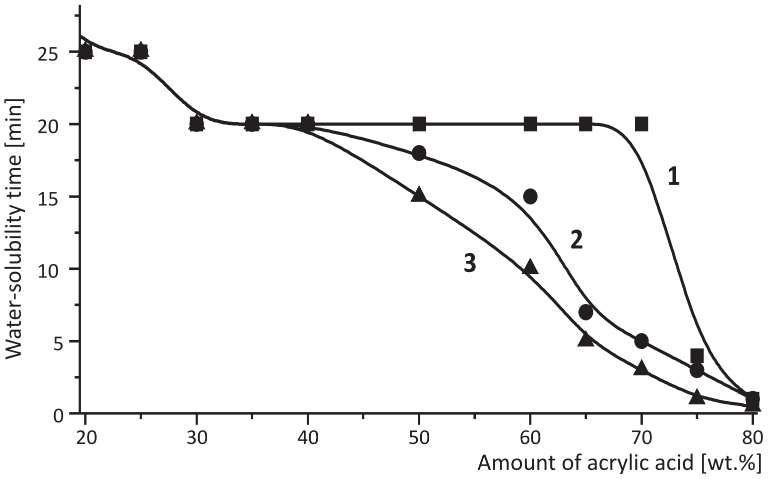

Figure 2. The influence of acrylic acid amount in the polymer on its water solubility time: 1 – pH = 8.0 – pH = 9.5 – pH = 11

polymers containing more than 30 wt.% of acrylic acid in evaluated pH-areas.

Suitable crosslinking agents

As it can be stated from tested water-soluble acrylic PSA, the increasing of crosslinker concentration shows a positive influence on the PSA cohesion but influences negatively very important parameter water-solubility. The water-solubility of acrylic PSAs containing between 20 and 40 wt.% of acrylic acid was evaluated using two suitable non hydrolyzed crosslinkers: aluminium acetylacetonate [6] (AlACA) from Du Point and zirconium acetylacetonate (ZrACA) from Wacker (Fig.3). After exceeding a threshold of 0.5 wt.% of AlACA or 0.5 wt.% of ZrACA the water solubility of crosslinked acrylic PSA decreases. As can be supposed from the Fig. 4, an acceptable level of water-solubility of about 300 s (5 min) for acrylic PSA containing from 30 to 40 wt.% acrylic acid guaranties even 1.5 wt. % AlACA.

Using of water-soluble 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)

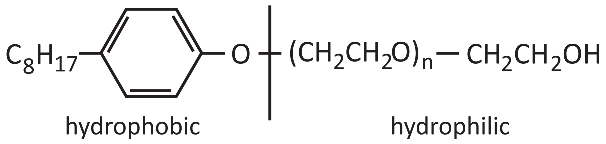

Figure 4. Chemical structure of ethoxylated octylphenol

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.

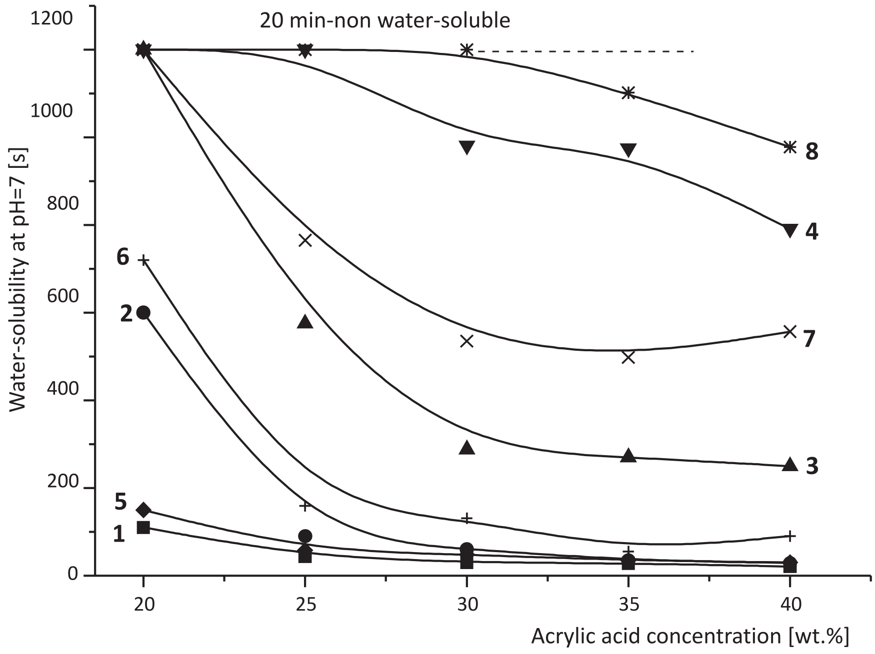

Figure 3. Effect of crosslinkers AlACA and ZrACA on water-solubility of acrylic PSA at pH=8: 1 – 0.5 % AlACA, 2 – 1 % AlACA, 3 – 1.5 % AlACA, 4 – 2 % AlACA, 5 – 0.5 % ZrACA, 6 – 1 % ZrACA, 7 – 1.5 % ZrACA, 8 – 2 % ZrACA

Suitable 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 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.

Figure 6 shows the influence of ethoxylated amine Ethoduomeen T/25 concentration on thermal resistance and temperature resistance time of synthesized water-soluble acrylic PSA, crosslinked

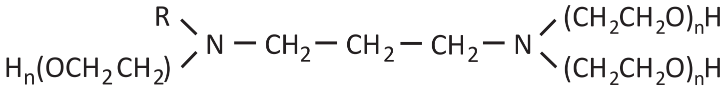

Figure 5. Chemical structure of neutralised ethoxylated alkanolamines

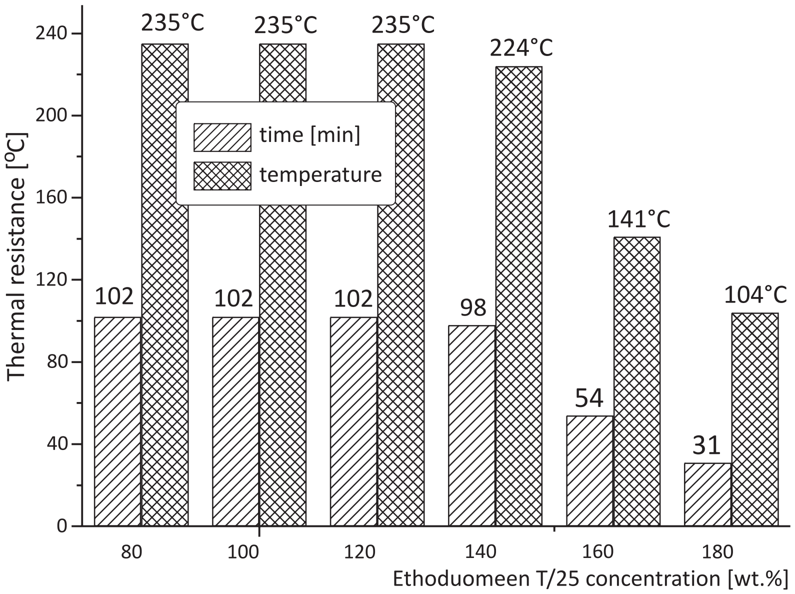

Figure 6. Thermal resistance of water-soluble acrylic PSA versus Ethoduomeen T/25 concentration

using 1.5 wt.% AlACA and modified with 80 wt.% Igepal CA-520.

The best balance according to thermal resistance and temperature resistance time has been observed by the use of about 150 wt.% Ethoduomenn T/25.

Ethoxylated amine Ethoduomeen T/25 has three functional groups which can react with carboxylic groups from acrylic acid incorporated into polymer chain during polymerization process. The additional crosslinking of water-soluble acrylic PSAs (Fig. 7) improved thermal stability and ameliorated their biodegradability.

Very important and technological preferred is the using of conventional neutralizing agents as NaOH. Fig. 8 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 sub-

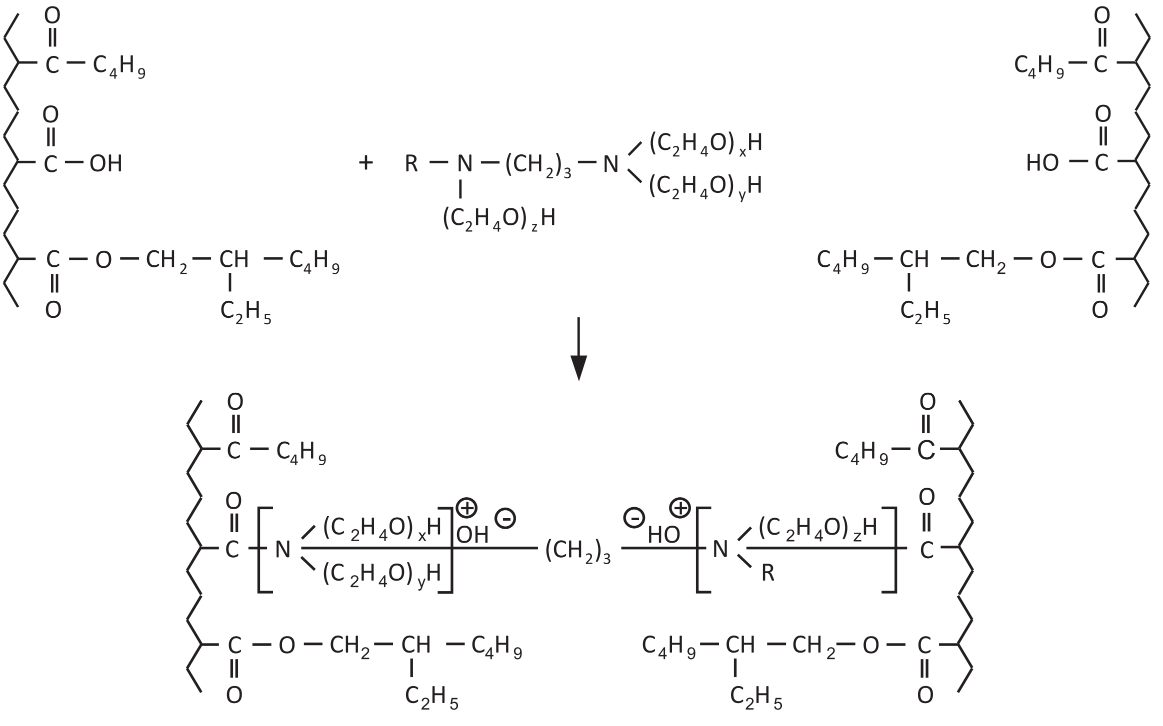

Figure 7. Crosslinking of investigated acrylic PSAs using Ethoduomeen T/25

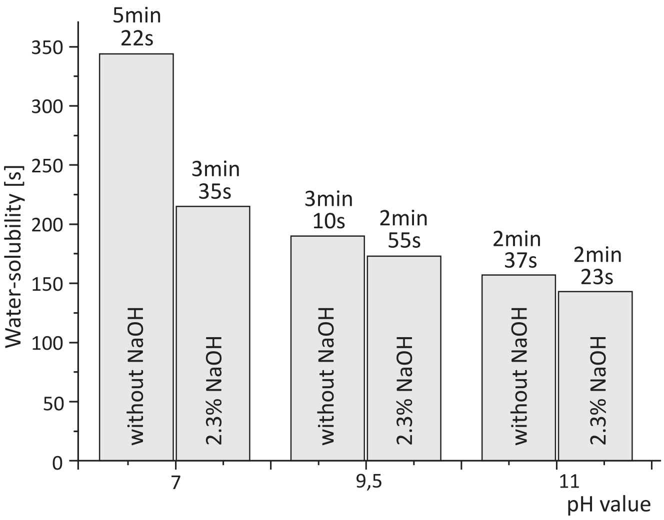

Figure 8. Influence of the NaOH amount on the water-solubility at diverse pH values

stance 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 9).

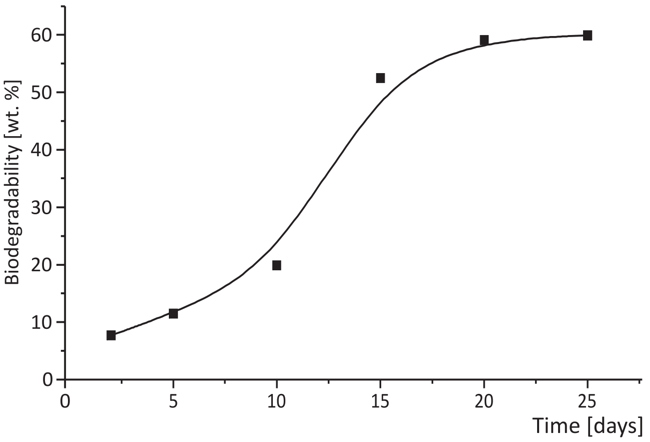

Figure 9. Biodegradability of water-soluble labels

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 the potassium dichromate method, which can be taken as a measure of the complete mineralization of the organic substance contained in the product.

5. SUMMARY

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.

REFERENCES

[1] R. Klein, D. Braun, "Nachwachsend und abbaubar", Farbe & Lack, 2 (2004) 76-86.
[2] C. V. Stevens, A. Meriggi, K. Booten, Biomacromolecules, 2 (2001) 1-16.
[3] M. Bolkenbaas, WO 01/00771 A (2001).
[4] V. Warzelhan, G. Schornick, F. Braun, EP 0 802 941 B (1996).
[5] H. Loclair, Dissertation: "Synthese und Anwendung von lösemittelhaltigen wasserlöslichen Haftklebstoffen auf Polyacrylatbasis", Szczecin University of Technology, Szczecin (2007).
[6] E. Madejska E., Z. Czech, "Metody badawcze redyspergowalnych w wodzie materaiałów samoprzylepnych stosowanych do łączenia papieru", Aparatura Badawcza i dydaktyczna 4 (2010) 25-29.
[7] Czech Z., „Vernetzung von Haftklebstoffen auf Polyacrylatbasis", Ed., Szczecin University of Technology, Szczecin (1999).
[8] Technical Data "Etoxylated Amines", Akzo Chemie, Holland (2001).
[9] Czech Z., "Wasserlösliche Haftklebemassen auf Polyacrylatbasis und ihre Anwendung" ,Swiss Bonding`95, Rapperswill, Switzerland (1995) 131-148.