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USING OF THE PYROLYSIS FOR COMPOSITION INVESTIGATIONS OF ACRYLIC PRESSURE-SENSITIVE ADHESIVES

Doctoral thesis

Dissertation under supervision of:
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DSc. PhD

Szczecin 2012

This work is dedicated for my parents.

I would like to thank heartily

my mentor and friend Robert Pełech

for help and precious hints,

professor Zbigniew Czech

for possibility to make this work happen

and all of people who supported me.

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LIST OF ABBREVIATIONS

2-EHA – 2-ethylhexyl acrylate

2-EHMA – 2-ethylhexyl methacrylate

α-MS-MMA – α-methylstyrene-methyl methacrylate

AA – acrylic acid

AIBN – 2,2'-azobisisobutyronitrile

BA – butyl acrylate

b_p – boiling point

CI – chemical ionization

DBTL – dibutyltin dilaurate

DHS – dynamic headspace

DMPA – dimethylolpropionic acid

DSC – differential scanning calorimetry

EA – ethyl acrylate

EB – electron beam

EDA – ethylene diamine

E-MMA – ethylene-methyl methacrylate

EVA – vinyl-acetate-copolymers

FID – flame ionization detector

FTIR – Fourier transform infra red

GC – gas chromatography

HFP – hexafluoropropylene

HTPB – hydroxyl telechelic polybutadiene

IGC – inverse gas chromatography

IPDI – isophorone diisocyanate

IR – infra red

LDI – laser desorption ionization

LVS – low viscosity system

MA – methyl acrylate

MA-S – methyl acrylate-styrene

MB –methylene blue

MEK – methyl ethyl ketone

MMA-2-EHA – methyl methacrylate-2-ethylhexyl acrylate

MS – mass spectrometry

NMR – nuclear magnetic resonance

OFCB – octafluorocyclo butane

PSA – pressure-sensitive adhesives

PPG – polypropylene glycol

PTFE – polytetrafluoroethylene

Py-GC – pyrolytic gas chromatography

TEA – triethyl amine

TFE – tetrafluoro ethylene

T_g – glass transition temperature

TGA – thermo-gravimetric analysis

Tp – pyrolysis temperature

UV – ultra violet

WS-PSA – water-soluble pressure-sensitive adhesive

PART I.   PREFACE

Since their industrially introduction half a century ago, acrylic pressure-sensitive adhesives have been successfully applied in many industrially areas. They are used in mounting tapes, splicing tapes, masking tapes, self-adhesive labels, sign and marking films, protective films and as well as in medical applications, such as plaster, OP-tapes, dermal dosage systems and biomedical electrodes.

In the last sixty years or so, acrylic pressure-sensitive adhesives (PSA) have made tremendous strides from what was virtually a black art to what is now a sophisticated science. So much so that both the few larger manufacturers of pressure-sensitive adhesive articles and their even larger suppliers now use very expensive equipment to study pressure-sensitive adhesive behavior: tack, adhesion and cohesion. The first measures the adhesive's ability to adhere quickly, the second its ability to resist removal by peeling, and the third its ability to hold in position when shearing forces are exerted.

The properties of acrylic pressure-sensitive adhesives, such as tack, peel and shear, synthesized by co-polymerization of acrylate monomers in organic solvent, water or solvent-free phase are to a large degree determined by the kind of acrylate monomers, molecular weight of acrylic copolymer, polymerization method and especially by the type and quantity of the crosslinking agents added to the PSA.

Although the production of acrylic pressure-sensitive adhesives in Europe is characterized by a constantly increasing productivity, and in the year 2011 it had indeed grown to about 165.000 tons, up to now a complex publication concerning thermal degradation of acrylic PSAs has not been published.

A target of my PhD dissertation was the investigations of thermal degradation of own synthesized acrylic PSA with known compositions and using of pyrolysis of acrylic PSA for identification of thermal degradable by-products, analysis of acrylic PSA compositions and using of thermal degradable products from acrylic PSA waste after pyrolysis.

PART II.   THEORETICAL BACKGROUND

1. Pressure-sensitive adhesives (PSA)

Pressure-sensitive adhesives (PSA) are polymeric materials used to bond other materials, mainly on their surfaces through adhesion and cohesion [1]. Adhesion and cohesion are phenomena, which may be described thermodynamically and chemically, but actually they cannot be measured precisely. The most important bonding processes are bonding by adhesion and bonding with pressure-sensitive adhesives. The properties, which are essential in characterizing the nature of PSA comprise: tack, peel adhesion, and shear strength. The first measures the adhesive's ability to adhere quickly, the second its ability to resist removal through peeling, and the third its ability to hold in position when shear forces are applied [2].

1.1.Classification of pressure-sensitive adhesives according to the synthesis

Pressure sensitive adhesives can be applied in form of solvent solutions, water dispersions, or solvent-free systems. Most pressure sensitive adhesive are applied as one-sided, double-sided (double faced tape) or carrier-free (transfer) tapes [3].

Solvent-based adhesives use organic solvent to reduce viscosity for earlier application. Solvent adhesives must be carefully considered prior to their introduction into an assembly operation. They are applied by spraying, dipping, or brushing, but the solvent must be driven off before joint is assembled. Solvent-based adhesives may be cross-linked, usually through the application of curing agent (either incorporated directly into single part systems or added as a second part to the base resin), heat or using crosslinking radiation (ultraviolet-UV or electron beams-EB) [4].

Water-borne adhesives are usually emulsions of thermoplastic resins. Emulsion adhesive ingredients are polymerized in water, applied to the web and dried to create a functional adhesive. This kind of pressure-sensitive adhesives are not water and moisture resistant [5].

Solvent-free pressure-sensitive adhesive systems are additional types of adhesives. Solvent-free in form of hot-melt adhesives, warm-melt adhesives or low viscosity systems

(LVS), are made of thermoplastic rubbers or other kinds of polymers (acrylic, polyurethane, polyesters or ethylene-vinyl acetate copolymers). They are formulated using tackifying resins, oils, plasticizers, and antioxidants to achieve coating on the web at high temperatures. Solvent-free pressure-sensitive adhesives are a relatively new group of self-adhesive technical and medical products. The main aspect is the reduction of environmental impact during production and exploitation to a minimum. Solvent-free PSA systems are crosslinked using UV radiation or EB technology [6-7].

1.2. Classification of pressure-sensitive adhesives according to the kind of polymers

The markets and technology of high performance pressure-sensitive adhesives are still expanding. The growing market is the result of expansion in both current and new application areas. The increased trend to utilize PSA technology, coupled with versatile polymer chemistry, has created a dynamic, expanding and challenging market. The versatility of polymer chemistry is inherently useful in the design of high performance PSAs. A broad raw material base and a versatility of polymerization processes lend themselves to design of base polymers with unique properties. Suitable kinds of polymers with pressure-sensitive properties in use nowadays include acrylics, natural and synthetic rubbers, silicones, polyurethanes, polyesters, polyether and vinyl-acetate-copolymers (EVA) (Figure 1), but volumes and high performance of these are in many cases relatively small compared to the acrylic polymers [8-10].
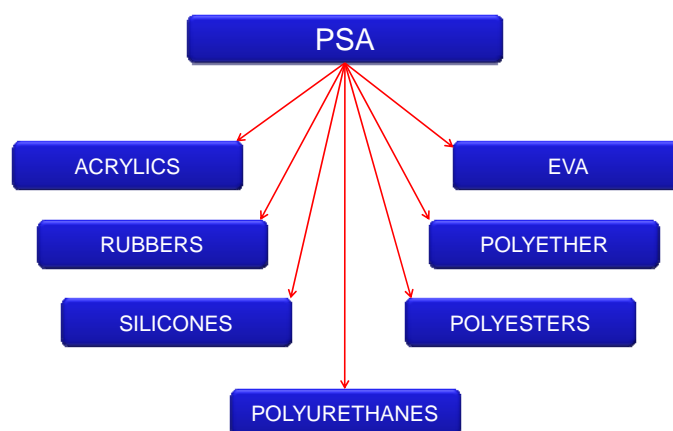
Figure 1 Polymers used for manufacturing of pressure-sensitive adhesives

Acrylic based pressure-sensitive adhesives are made from higher alkyl esters of acrylic acid without need of tackifiers and provide excellent physical properties. Monomer composition and molecular weight of the polymer determine most of the adhesive's properties. Because acrylic PSAs can be free of those additions, they are less irritating to skin and often preferred to medical applications. Nevertheless, many commercial acrylics PSAs are formulated with other components such as tackifiers, plasticizers, antioxidants, pigments, and fillers. Modified acrylic adhesives contain tackifiers that improve initial tack and adhesion levels while decreasing resistance to solvents, migration of plasticizers, and high temperatures. Acrylics PSAs have superior environmental stability, adhesion to high surface energy materials and greater resistance to oxidation when compared with rubber based PSAs. In addition, they are more stable to light and heat [11]. The dominate raw materials used for production PSAs are acrylic esters of C_4-C_{12} alcohols, from which the most commonly use are butyl acrylate and 2-ethylhexyl acrylate. The use of acrylic acid is very important by crosslinking reaction and ameliorating of thermal resistance [12]. Acrylics PSA are applied as solution, water dispersion or in form of 100 % systems, which are hot-melts or LVS (low viscosity systems) also known as room-temperature RT-coatable PSA [13].

Rubber-based pressure-sensitive adhesives are composed of natural or synthetic rubber, various resins, oils, anti-aging agents and antioxidants. Blending rubber with tackifiers produces high quality PSAs, the properties of which are determined by tackifier. Because natural rubber is expensive addition of fillers modify properties and reduce costs as well. Other components, such as antioxidants, included protecting the unsaturated backbone polymer from degradation, pigments, plasticizers, and fillers are also added. Rubber-based adhesives are said to be the most cost-effective PSA systems. However, long-term aging stability is low. Most of solvent-based rubbers PSA are produced as 35 % solution in hexane, similar petroleum fraction, or toluene. The other kind of rubbers PSAs are solvent-free systems, especially hot-melts [14].

Silicone monomers are polymerized to yield silicone polymers that based on gum containing dimethylsiloxy and diphenylsiloxy groups show adhesive and cohesive properties. Since silicones are expensive, their market use is normally limited to special fields of extremely high temperature resistance. Solvent-borne silicone pressure-sensitive adhesives are high performance adhesives in toluene or xylene, which can be utilized over a wide range of

temperatures, from -40 to 300ºC. They bond, especially to both low energy and high energy surfaces [15].

Polyurethane PSAs fulfill many of the industry's most severe requirements in terms performance, environment and easy of practical application. They have been widely used in self-adhesives, sealants and electrical products owing to its low glass transition temperature (T_g) between -40 and -60°C, hydrophobicity, acid-based resistance and excellent dielectric properties. In many industries, the research, development and application on the coating technology area having a lower chemical impact on occupational health and environment is warmly welcomed, especially when it is accompanied with robust application conditions and high standards of performance [16].

Polyester PSA are characterized by excellent adhesion to the wide range of substrates. They can be obtained with aliphatic polyesters with molecular weights ranging from 10·000 to 50·000 g/mol and glass transition temperature T_g between -25 and -47°C. The practical crosslinking process of polyester PSAs is possible by the use of multifunctional isocyanates or by using UV radiation [17].

Another group of PSAs are poly(vinyl alkyl ether) blends. That polymers group are mostly use in medical application, especially poly(vinyl ethyl ether) because of its high moisture vapour permeability, valuable for patient comfort during long-term application to the skin. The production involves blending high and low molecular weight polymers, from which low molecular weight polymer provides spreading on the adherent surface and the high molecular weight polymer determine cohesive strength [18].

Polyether based PSA are very rare group of pressure-sensitive adhesives. They are produced only by BASF and are applied for medical self-adhesives in the wide range of medical materials, such as plaster, self-adhesive wound dressing, OP-tapes and diverse medical and biomedical electrodes [19-20].

1.3.Acrylic solvent-borne pressure-sensitive adhesives (PSA)

Solvent-borne PSA acrylics offer several advantages such as excellent aging characteristics and resistance to elevated temperatures and plasticizers, exceptional optical

clarity due to the polymer compatibility and non-yellowing. They also have the excellent balance of adhesion and cohesion and an high water resistance. Acrylics are harder than rubbers. This can be seen in a less aggressive tack and slower build-up of peel strength. Lower adhesion to non-polar polyolefins is caused by the polar chemistry of acrylics. Acrylic polymer chemistry is expanding through the introduction and utilization of new raw materials, different polymerization techniques, and novel cross-linkers and cross-linking methods [21].

1.4. Synthesis of solvent-borne acrylic PSA

The versatility of acrylic chemistry is inherently useful in the design of high performance pressure-sensitive adhesives. A broad raw material base and a versatility of polymerization processes lend themselves to design of base polymers with unique properties.

The glass transition temperature (T_g) is the main issue for adhesion properties, such as tack and adhesion, of various polymers, allowing the selection of raw materials for PSAs applications. Its value defines the tack of PSAs; a low T_g is a prerequisite for tacky materials. On the other hand the T_g alone does not permit to obtain a real image of the adhesive performance. For permanent adherent acrylic pressure-sensitive adhesives T_g ranges from about –70°C to –25°C [22].

The design parameters utilized to produce high performance solvent-borne adhesives include: monomer selection, selection of solvents, and using of different synthesis characterized by polymerization parameters. Specific design parameters are used to achieve desired surface properties of tack and peel in combination with the bulk property of cohesive strength. The balance of these properties is needed for high performance products [23].

1.4.1. Selection of monomers

For manufacture of acrylic pressure-sensitive adhesives, primarily tackifying common acrylic acid esters are preferred with $C_4 – C_{12}$ carbon atoms in the alkyl moiety together with other co-monomers. The composition of acrylic polymers that are inherently pressure-sensitive is a combination of soft (low T_g), hard (high T_g) and functional monomers. The most important monomers of this class are compiled in Table 1.

Table 1 Important monomers used by synthesis of PSA based on acrylics

Monomer	(Homopolymer) T_g [°C]
tackifying monomers (soft)	
2-ethylhexyl acrylate	-70
isooctyl acrylate	-70
n-butyl acrylate	-54
hardening monomers (hard)	
ethyl acrylate	-24
methyl acrylate	-6
vinyl acetate	+28
isobornyl acrylate	+94
functional groups containing monomers	
2-hydroxyethyl acrylate	-15
2-hydroksypropyl acrylate	-7
acrylic acid	+106
acryl amide	+179

Table 1 contains 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 especially 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. The functional groups containing monomers such as acrylic acid or 2-hydroxyethyl acrylate are incorporated into the balanced monomers for specific adhesion to desired substrates and to provide sites in form of active centers for cross-linking [24-25].

1.4.2. Selection of organic solvents

The media applied for radical synthesis of acrylic single organic solvents or their mixtures whose molecules buffer the heavily exothermic polymerization reaction. The selection of suitable solvents is distinctly limited due to following requirements: the solvent has to be: inexpensive, reclaimable, absolutely inert and has to have the proper boiling point between 50°C and 120°C, a relatively low transfer constant and a good solvency for acrylics.

The last mentioned points on the check list for solvents influence the molecular weight being crucial for the entire properties of pressure-sensitive adhesives which should be as high as possible. The higher the boiling point of the solvent the more the properties decrease. Per se very low molecular weights bring about solvents with a high transfer constant, such as petrol with special boiling point. This deficiency can be compensated to a great extent by a versed conduction of the synthesis process. Such endeavors make sense since aliphatic mixtures particularly meet the first three items of the above catalogue of requirements best [26].

In pressure-sensitive acrylic adhesive solvents available on the market, only a small group of solvents may be found, which is not surprising: ethyl acetate, special boiling point petrol (bp = 60 to 95°C), acetone, n-hexane, methyl ethyl ketone (MEK) and toluene. Ethyl acetate or solvent mixtures on ethyl acetate basis only permit the formulation of acrylic pressure-sensitive adhesives with an outstanding performance level [27].

1.4.3. Synthesis parameter

Typically, the polymerization is done batch wise by adding monomer to organic solvents in the presence of a soluble peroxide or azo initiator. As the polymerization is a chemical reaction, its course is dictated by concentrations of initiator, monomers, and by rates of input and loss of heat. These factors are controllable on the large scale and are reproducible, but they are very difficult to predict on the basis of a small scale laboratory work. It is for these reasons that the scale up of a polymer is not a fast process. It must be done on the basis of successive steps of increasing size up to full size and often calls for more laboratory work between each step to ensure that the desired product is produced in commercial quantities [28].

Generally, the process ability of solvent-borne PSA depends on their viscosity and polymer content. Coating devices are designed for a given viscosity; whereas the coating weight and the drying speed depend on the solids content. In general, the solids content and viscosity should be measured for formulated compositions. This method of synthesis is suitable for the preparation of high performance solvent-borne pressure-sensitive adhesives with high molecular weights of about 500.000 to 900.000 Dalton. Pressure-sensitive adhesive based on acrylics with higher molecular weight are not only difficult to prepare by this

method, but also have viscosities too high for easy handling. The really high performance adhesives are only all pressure-sensitive adhesive solvent-borne acrylics [29].

1.5. Role of acrylic PSA in the self-adhesive materials technology

In the giant field of adhesives the pressure-sensitive adhesives make up but a low percentage and the acrylic pressure-sensitive adhesives with about 200.000 tons per annum in Europe in 2011 year are almost a quantity negligible within this group.

The numerous advantages of solvent-borne acrylic PSA have led to their wide use in the manufacture of self-adhesive products (Fig. 2). Solvent-borne acrylic pressure-sensitive adhesives represent more than 45% of the total PSA produced. The adhesives-chemist can attain the required property image of the acrylic adhesive by means of a wide range of possibilities. Be it by exerting a direct influence on the composition of the acrylic polymer or, later on, by the kind of cross-linking or by varying additives. The cross-linking agents are usually added for ameliorated cohesion [30].

47 % solvent-borne   15 % hotmelt

38 % water-based
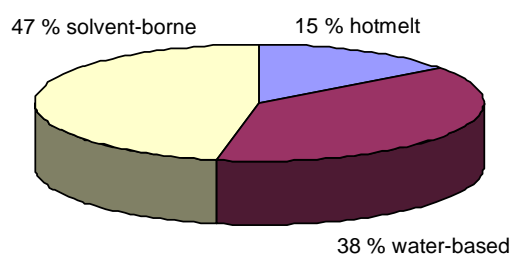
Figure 2 Market share in Europe of different types of pressure-sensitive adhesives

1.6. Qualitative analysis of acrylic PSA compositions

Acrylic copolymers based on alkyl acrylates and unsaturated carboxyl acids with low glass transition temperature are important specialty polymers using as pressure-sensitive adhesives for manufacturing of diverse self-adhesive product. Acrylic PSA used for the production of these self-adhesive articles are thermal resistant to about 160-180°C. They are not evaluated according the thermal stability and thermal degradation by the use of pyrolysis. The analysis of diverse kind of acrylic polymers has been reported, based on infra red (IR) [31-34] and gas chromatography [35]. Nelson et al. [33] found that there is little similarity between the monomer and polymer IR spectra.

The IR method is not exactly enough for identification of acrylate monomers. With IR analysis we can find only functional groups, such ester group, CH_3-, CH_2- and CH-groups, but it not allows the exactly identification of acrylic PSA structure etc.

That is why the other analysis technique is necessary to exactly analyze the composition of acrylic PSA [36-37]. This technique is gas chromatography.

Gas chromatography (GC) is a universal separation technique for breakdown products by thermal degradation of acrylic PSAs [38]. 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 perform this concept. GC techniques are cost effective and encompass a wide range of analytical problems. Assay and trace level analyses are achieved with minimal sample preparation. A wide variety of special detectors are available for quantification and specific identification of various classes of compounds. Gas chromatography, coupled with controlled temperature pyrolysis technique, provides a rapid method for the identification of acrylic polymers and allows pyrolysis/GC and pyrolysis/GC/MS identification of thermal decomposition products of polymeric materials, acrylic pressure-sensitive adhesives too [39-40].

Polymer characterization using thermal analysis, chromatography and spectroscopy are currently some of the most dynamic fields in applied research. Synthetic polymer chemists rely on the detailed analysis of their systems in order to prepare high-performance material in an efficient, knowledgeable manner. The diversity of GC application in research, quality control and process areas has been matched by continuing requirements demanded by polymer usage throughout the chemical industry [41].

As far as organic analysis of polymeric systems (natural and synthetic) is concerned, there are many analytical methods such as analytical pyrolysis/dynamic headspace combined with packed and capillary column GC and spectral detection methods for analysis polymer structures and degradation mechanisms. Inverse GC complements these studies of composition with unique capabilities to probe surfaces and sub-surfaces for detailed study of physiochemical phenomena [41].

As noted above, GC is just one of several polymer characterization tools. Mass spectrometry (MS) either following GC separation of pyrolysis fragments or receiving the fragments directly from the pyrolyzer, is an important developing tool. The interdisciplinary fields of gel permeation, liquid chromatography, thermal analysis (differential scanning calorimetry – DSC, thermogravimetric analysis – TGA) nuclear magnetic resonance (NMR),

infrared (IR)/Raman have also made possible highly detailed microstructural and compositional analysis. Limitations in sample form and amount, coupled with the nature of information needed, direct the researcher to the most appropriate tools [42].

A major segment of GC applications to polymer analysis has developed in the field of analytical pyrolysis. This is in addition to the problem solving studies of additives, monomer occlusions and the "traditional" roles played by GC instrumentation. In early work, the marked dependence of polymer degradation on experimental conditions resulted in discrepancies between pyrolysis data from varied laboratories. Diverse equipment and conditions were partly responsible for the apparent differences. Early work by several researchers demonstrated that only "pyrograms" (chromatograms) resulting from the experiments with controlled exposure temperatures and defined rise times were useful in providing reproducible information for polymer microstructure. Quantitative comparison with known references requires such controlled conditions in order to provide reliable and informative data. Commercially available pyrolyzer systems have now made this limitation a minimal problem, in conjunction with advances in GC, Fourier transform IR (FTIR), mass spectrometry (MS) [43].

Additionally, precise thermal conditions are needed to determine occluded solvents, residual monomers, and additives in polymer and their composites. Headspace analysis is a technique whereby sampling vapors is conducted in a chamber containing a heated solid polymer matrix for purity or composition studies. In a static headspace experiment, the temperature/pressure conditions of the sample vessel are critical to accurate quantitative analysis. Equilibrated vapor samples (above a known weight of the solid polymer) are removed under such controlled temperature and pressure conditions and injected into the GC for separation.

Dynamic headspace (DHS) extends the method and uses concentrator technology to achieve far more sensitive detection limits. In a common dynamic headspace method, an inert gas (helium) sweeps over the sample while heat is applied to drive the volatiles into the vapor state and to concentrate them onto a sorbent trap. Thermal desorption of the trap the releases the volatiles into an analytical separation/identification system, such as a GC, MS or FTIR. The DHS/GC approach can be applied to solids, films, powders, semisolids and liquids in a direct manner with minimal sample preparations. Ancillary equipment for concentration and enrichment of trace volatiles is now commercially available and provides for careful interfacing to the GC with appropriate attention to manipulations for precise quantization and identification [44].

For both pyrolysis GC and traditional GC schemes used in polymer analysis, select chromatographic columns and complex valving arrangements make possible details in degradation, trace contaminants and identification effluents. In addition to pyrolysis GC and headspace investigations, an important area of advance in polymer characterization has taken place with inverse GC (IGC). Rather than conduct the common GC experiment with injection (syringe, DHS, pyrolysis) of unknown vapors for separation and identification, IGC utilizes known solutes (molecular probes) that are introduced into the chromatographic column which is filled with the unknown substrate to be studied. Information about the substrate is obtained concerning its surface activity, solubility parameters, diffusion phenomena, and thermal transition behavior (for example glass transition-temperature) from recording chromatographic parameters of the molecular probes interacting with the substrate in the column. The current need to explore polymer surface phenomena is met in cases where polymer to be studied is loaded into the chromatographic column as either a solid particulate, a thin-film coated upon a support, coated upon column wall or in fiber form [45].

The IR (infrared) method is a very good and dependable tool in analysis of many organic compounds, which are usually pure and they give strong signals creating sort of "fingerprint pattern". However when we deal with analysis of pyrolyzate, which is usually a mixture of many compounds, it is almost impossible to analyze the products of pyrolysis, because of superimpose of signals from different substances in the mixture.

2. Pyrolysis

Pyrolysis has been utilized by humans probably since prehistoric times. The common experience of smelling smoke often gives us useful information about the burning and/or degrading materials. Even now the differentiation of textile materials by oxidation pyrolysis (burning) combined with smelling the smoke is utilized as an important practical technique. Analytical pyrolysis finds its application in versatile areas such as:
- polymer chemistry,
- process control of polymeric materials,
- biochemistry,
- organic geochemistry,
- soil chemistry,
- microbiology,

- numerical taxonomy,

- pathology,

- clinical science,

- forensic science,

- food science,

- wood science,

- toxicology,

- environmental chemistry,

- energy conservation,

- extraterrestrial studies [46].

Pyrolysis has been used extensively over the last 20–30 years as an analytical technique in which large molecules are degraded into smaller volatiles species using only thermal energy. The ultimate objective of analytical pyrolysis is to use the chromatographic information of pyrolysis products to determine the composition or structure of the original sample. The complexity of polymeric materials can vary extensively and they can be very challenging to analyze. Pyrolysis, combined with modern analytical methods, such as gas chromatography and/or mass spectrometry (Py–GC/MS) has become a quick, convenient and powerful tool for characterizing polymers from non-volatile, complex heterogeneous samples. Degradation results from free radical reactions initiated by bond breaking within the molecules; the bond that is more easily broken will be favored. Thermal and environmental conditions, such as temperature and additional reactants, can affect both the extent and route of degradation of a polymeric material and the nature (physical and chemical) and quantity of molecular species generated by pyrolysis. Molecular degradation of a sample will occur as soon as the temperature is high enough to initiate bond breaking, but at this point will not necessarily yield much useful product. With much higher temperatures, other bonds will break simultaneously, creating very small and non-specific free radicals. Generally, the higher the temperature, the smaller the radicals and molecules produced. The optimum pyrolysis temperature, which will be different for every polymer, is the point at which degradation produces a wide array of chemically useful products [47].

In the literature it can be found that pyrolysis means controlled splitting of the sample into small molecules with heat in oxygen free circumstances. The quantities of compounds during pyrolysis depend on the temperature program used. The temperatures used in general

are between 400 - 900°C. Formed compounds are separated and analyzed by the arrangement of GC/MS. There are three stages in pyrolysis: initiation, propagation and termination. The fast rising of the temperature of the sample into pyrolytic temperature and the fast removing of the products with inert gas (helium) from the heated part of the equipment are important as to avoid secondary reactions and to obtain optimal degradation. The TG-curve helps to find the right temperature of pyrolysis [48].

Analytical pyrolysis is considered to be a small-scale thermal degradation method that is very useful for the chemical characterization of materials from their pyrolysis products. This technique usually involves an integrated pyrolysis-analysis system that is carefully controlled to give reproducible results and that uses small (nanogram to microgram range) amounts of samples [49].

For GC to be applicable, the molecules of interest need at least some degree of volatility, a requirement polymers clearly do not meet. Still, GC can be used to study polymeric material if suitable sample preparation is applied. Pyrolysis is a thermal pre-treatment method widely used in the study of (bio)macromolecules with GC. In a pyrolysis treatment the nonvolatile material is subjected to a rapid, destructive thermal treatment to yield smaller, much more volatile fragments which fall within the application boundaries of GC. Once formed, the compounds are rapidly flushed out of the heated zone to avoid secondary reactions. The degradation products are hence characteristic for the polymer and can be used to determine specific compositional or structural parameters of the original material.

By other authors pyrolysis is the process of converting large molecules into smaller fragments by thermal energy in the absence of oxygen. Which products are actually formed during pyrolysis depends on the molecular structure and the bond-dissociation energies of the polymeric materials. Hence, the degradation products contain information about the composition and the molecular architecture of the original macromolecules. Three mechanisms responsible for the breakdown of the polymeric material can be distinguished: side-group scission, monomer reversion (or depolymerization) and random scission. Side-group scission refers to the release of side-groups from the backbone of the polymer. Monomer reversion is in fact a reversed polymerization process: the pyrolysis fragments are the original monomers of the polymer. Random scission finally refers to the breaking of the backbone of the polymer at random and varying positions. Also other mechanisms can take place, such as for example crosslinking. In general these mechanisms are undesired. The original pyrolysis products formed should not be allowed to react with each other. This would

result in the formation of the so-called secondary reaction products which complicate the interpretation of the pyrograms [50].

2.1.   Methods and parameter of pyrolysis

Analytical methods including pyrolysis are closely connected with instruments used in analysis. Recent progress in methods development has been largely a result of improvements in analytical instrumentation. This is especially true for chromatographs and detectors. For the last 60 years a huge progress in pyrolysis based methods is noticed. Among the related techniques and methodologies are the development of various specific pyrolyzers, highly efficient and specific separation and identification techniques for the complex pyrolysis products and a combination of chemical reactions (derivatization) with thermal degradation. The developments in supporting new technologies and materials such as electronics, data processing techniques by computers, laser and optical fiber techniques and high performance materials also played a very important role. In 1948, the first reports on the off-line pyrolysis-MS (Py-MS) of polymers were published by Madorsky and Straus and Wall. In 1953, Bradt et al. described on-line Py-MS for which pyrolysis of polymer samples was affected within the instrument. Thus, for example, valuable structural information about the samples became obtainable; pyrolyzates were observed up to the pentamer (520 Dalton) from polystyrene. The pyrolysis-infrared (Py-IR) technique was also reported by Barnes et al. in 1948 and then by Harms in 1953. This technique was mostly used for rapid identification of polymeric materials, rather than for chemical structure determination.

Two years after the introduction of GC by James and Martin in 1952, Davison et al. reported the first work on off-line Py-GC of polymers. These workers demonstrated that Py-GC is quite effective for the characterization of polymeric materials. In 1959, on-line Py-GC systems and their applications to polymer analysis were reported independently by three research groups: Lehrle and Robb, Radell and Strutz, and Martin. These achievements triggered a boom of Py-GC studies. The advent of highly sensitive flame ionization detector (FID) in 1958 strongly accelerated he development of Py-GC.

The high resolution capillary columns introduced by Golay in 1958 had a strong impact on Py-GC. However, general appreciation of their effectiveness was held back until the advent of the chemically inert fused-silica capillary columns in 1979; the earlier metal capillary columns were not suitable for the separation of polar and/or higher boiling point

compounds. The new generation capillary columns, which stemmed from the modern fused-silica optical fiber technique, greatly accelerated the resurgence of Py-GC as a reproducible analytical technique for various polymeric materials.

Various types of pyrolyzers for attaining specific and reproducible pyrolysis have been developed and improved. Now, various heated filament-, furnace- and Curie-point type pyrolyzers exist for both Py-MS and Py-GC. Among these, the Curie-point method, in which a ferromagnetic sample holder is placed in a high-frequency induction coil, attracted the attention of many researchers in the field of analytical pyrolysis. This device, proposed by Giacabbo and Simon, allowed to rapid, reproducible and precise heating of the samples to well defined Curie-point temperatures.

In 1966, Simon and co-workers reported the first directly coupled Py-GC/MS system using a Curie-point pyrolyzer, a metal capillary column GC, and a rapid scanning MS. In 1968, Schuddemage and Hummel introduced field ionization (FI)-MS to simplify the mass spectra resulting from Py-MS. This technique dramatically improved the effectiveness of direct Py-MS, as the observed mass spectra obtained by EI-MS are generally very complex owing to the overlapping of fragment ion peaks formed from the ionization process. In 1973, Meuzelaar et al. reported a new directly coupled Curie-point Py-MS system in which a quadrupole mass spectrometer was used.

To summarize, some of the important instrumental developments in analytical pyrolysis have been: various highly specific pyrolyzers, chemically inert high-resolution capillary columns for GC, highly specific detection systems for GC, rapid scanning highly sensitive GC/MS, various soft ionization techniques for MS such as chemical ionization (CI), FI, and laser desorption ionization (LDI), newly developed MS/MS systems, and data handling techniques and chemometrics aided by computers.

Modern analytical pyrolysis is now the most extensively practiced using Py-MS and Py-GC (or Py-GC/MS), where the characterization of the original sample is carried out through on-line separative analysis of the resulting complex pyrolyzates [46].

One of the main criterions in pyrolysis's methods division is type of pyrolyzer that is used. There are known various types of pyrolyzers, from which the most are used: furnace pyrolyzer, pyrolyzer with resistance heating or induction heating or laser pyrolyzer. All those solutions provide repeatable conditions for quick degradation of investigated sample (during tens of milliseconds) in temperature range 400 – 1000ºC.

Furnace pyrolyzers are assembled directly onto gas chromatograph's feeder. They are usually made of metal or quartz tube wrapped with heating conduit, properly isolated and

sealed. Liquid samples and solid samples solved in appropriate solvent could be inserted into furnace heated to desirable temperature using standard microsyringe. Samples in solid state form could be inserted using syringes with special construction, which function as "syringe in syringe". Another solution, which enables inserting solid samples, is a special construction of the pyrolyzer with isolated cold chamber. Sample is inserted into this cold chamber on a special crucible and is lowered into hot zone where pyrolysis is conducted. To ensure thermal stability furnace pyrolyzers must have size, which is linked with relatively high space, which sample must surmount before getting into chromatographic column. It could be a significant defect, especially in case of furnaces with metal tubes, where catalytic reactions could proceed. An advantage of furnace pyrolyzers is simple construction connected with this a relatively low price and ease in maintenance. As distinct from furnace pyrolyzers, in pyrolyzers with heating fiber sample is placed on a cold heating element, which is next very fast heated to suitable temperature.

In inductive pyrolyzers the temperature of degradation is established using Curie point, that is the temperature above which a ferromagnetic material becomes paramagnet. The inductive pyrolyzer and the mode of assemble onto gas chromatograph's feeder is presented below (Figure 3).
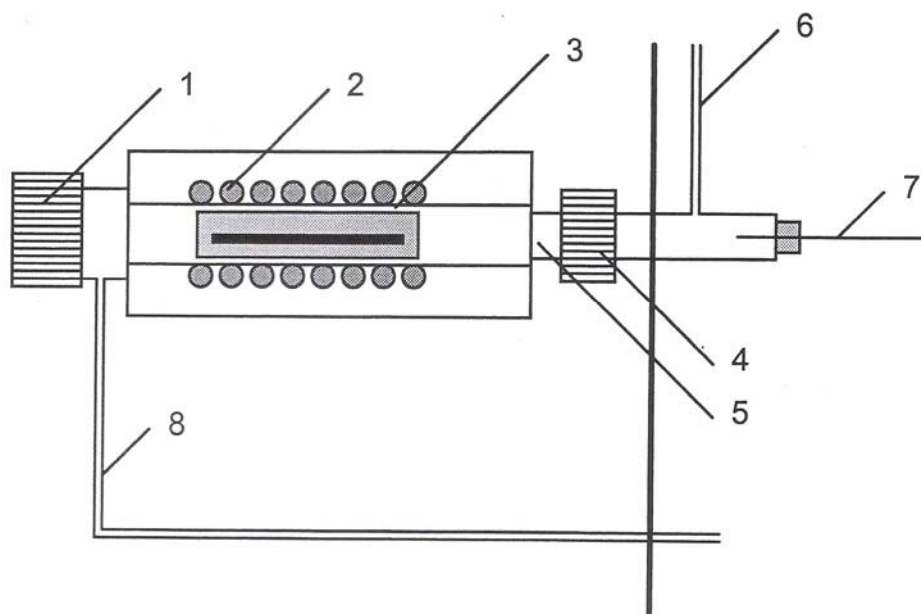
Figure 3 Scheme of inductive pyrolyzer mounted on gas chromatograph's feeder:

1 – sample feeder, 2 – induction coil, 3 – heating element made of ferromagnetic material,

4 – gas chromatograph's feeder, 5 – connector, 6 – splitter's outlet, 7 – capillary column,

8 – carrier gas inlet

Electric current induced by coil heats ferromagnetic material to Curie point temperature in which it loses ferromagnetic properties and stops from further heating. The Curie point temperature is different for different ferromagnetic materials and their alloys ex. g. for iron is 770ºC and for the alloy composed of 40 % nickel and 60 % cobalt – 900ºC.

The pyrolysis temperature could be established only through selection of suitable material. The main advantage of this solution is certainty that sample will be heated to specific and well known temperature in fast (tens of milliseconds) and repeatable way, without necessity of temperature calibration. In order to ensure fast heating to desirable temperature, both heating element and sample must have small mass. The best way to put the sample of investigated substance (with mass grade about few micrograms) on heating element is to immerse the element in sample's solution and next the evaporation of solvent, which allows us to obtain coating of very thin layer. The samples which cannot be solved must be applied by other methods ex. g. after precise size reduction it is possible to immerse heating element in suspension of sample or after melting sample and next the sample congeal on the heating element. It is possible to use heating elements with special shape ex. g. flattened or with hollow trays. Because of the fact that heating is through induction and the heating elements are not connected in any way with the current generator the dosage of samples could be easily automated. The main disadvantage of pyrolyzers, which use Curie point, is fact that utilizing specific ferromagnetic it is possible to attain only one pyrolysis temperature. In order to conduct pyrolysis of sample in different temperatures it is necessary to use heating elements made of different materials. Investigations in temperature between Curie points of ferromagnetic using this technique are impossible. This method also cannot be applied in investigations, which require slow, gradual heating of the sample or longer time of pyrolysis.

In resistively heated pyrolyzers heating elements mostly made of iron, platinum and chromo-nickel are used. Heating follows as a result of controlled passage of current through this element. Depending on type of investigated samples and method of sample introduction the heating elements with different shapes are used – fibers, coils, and bands. The sample could be put in similar way as inductive pyrolyzers by coating with thin layer out of solution or suspension. In some solutions sample introduction is done using small boats or tubes into heating coil. For the sake of necessity of direct connection of heating element with

temperature controller it is difficult to automate the sample dosage process. Precise temperature control is the biggest problem in that kind of systems, because resistance (not only of heating element but also connection conduits) and residue after sample decomposition have effect on it. It is necessary to conduct temperature calibration frequently. The main advantage of resistively heated pyrolyzers is possibility to choose any pyrolysis temperature and different speed of sample heating. However possibility of catalytic influence of metallic surface of heating element on the degradation process (similar as in inductive pyrolyzers) exists.

In laser pyrolyzers, in order to decompose sample placed in mounted tube on the chromatograph's column inlet, a laser beam is used. Main limitation of this method is fact that only polymers which absorb light of laser beam could undergo pyrolysis. Solution of this problem could be addition of carbon black to sample, but it has significant effect on look of the program. In comparison with pyrograms it is essential to use identical concentrations of carbon black in investigated samples. It is necessary to stress the fact, that obtained pyrograms using the laser pyrolysis method have look less complicated than when using other. The decomposition pyrolyzers in flowing tubular furnace is often used as investigation method in thermal degradation of plastics. The apparatus is composed of ceramic or quartz tube placed in furnace with regulated temperature (Figure 4).
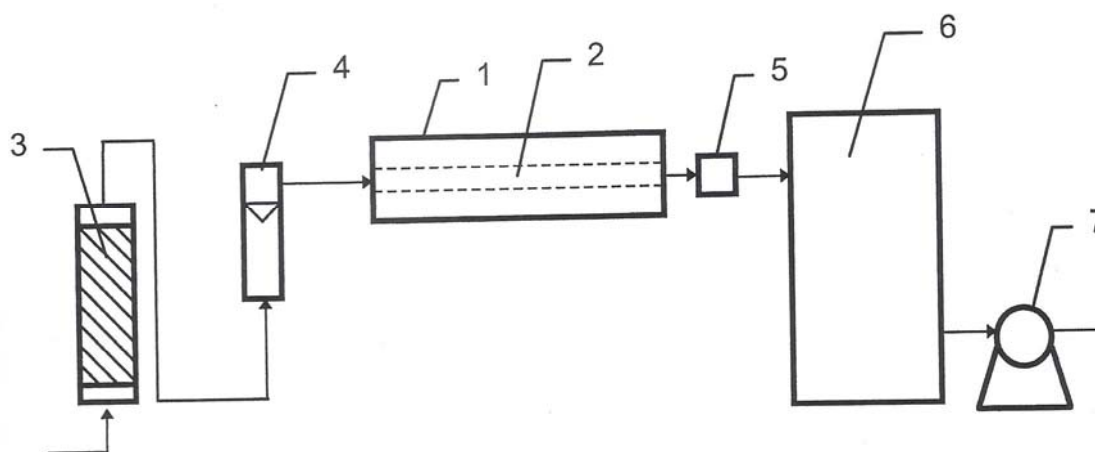
Figure 4 Scheme of apparatus in thermal degradation investigations of plastics using flowing tubular furnace

Polymer samples of weight from tens of milligrams to few grams are introduced to tube in small ceramic or quartz boats. Through furnace atmospheric air, inert gases (nitrogen, helium, argon) or gas mixtures with any composition are passed. The investigations could be conducted in isothermal conditions (introducing the sample into furnace with stabilized in suitable temperature) or using progressive sample heating to obtain desirable temperature.

Degradation products could be collected with different methods in dependence of later used analysis method. Hermetic vacuous tanks, washers, liquid nitrogen freezing out traps, tubes filled with active carbon, glass wool or other adsorbent, filters made of unwoven glass cloth to stop non-volatile compounds. Separated products are analyzed using gas chromatography method, liquid chromatography and spectrophotometry. A very comfortable of unknown substances identification method is gas chromatography method with mass detector with possibility to use extensive computer library of spectra.

Investigation of thermal decomposition of plastics using flowing tubular furnace method has many advantages, most of all possibility to chose arbitrary degradation temperature, arbitrary time of heating and arbitrary degradation atmosphere. Heating could be conducted by isothermal or programmed temperature. For the sake of lack of sample contact with metallic elements, there is no problem with catalytic influence of metal on the degradation process. Introducing the sample is very simple independently from its form, it does not require dissolution and any other treatment. This method is very useful in hazard assessment of toxic products which are formed during plastics combustion, for the sake of possibility of conducting research in air atmosphere and with longer time than using coupled pyrolytic methods, which allows creating conditions close to reality.

A modification of discussed method is utilizing furnace heated to specified temperature, shifted along sample placed in quartz tube, which allows obtaining conditions close to spreading out the fire. Polish standard applied to investigations of toxic products emission during degradation and combustion of materials recommends to use moving furnace, shifted along quartz tube with length of 1 meter in counter-flow to air which flows with velocity of 100 dm^3/h. Investigated sample is introduced to quartz flow cell and degradation process is conducted during 30 minutes, when furnace is shifted with velocity of 20 mm/min. The investigations are conducted in temperatures 450, 550 and 750ºC, where rightly emission of carbon oxide and dioxide (gas chromatography method), hydrogen cyanide, hydrogen

chloride, nitrogen dioxide and sulfur dioxide (colorimetric method) are determined. On the basis of results the so-called toxicometric index is calculated, which serves to classify materials.

Presented above methods are the most used in thermal degradation investigations of polymeric materials, however methods used for this purpose are many more. Often samples in analysis of toxic content of degradation products are drawn from installation and devices used in material combustibility investigations. For attention deserves complex method of investigation in material combustibility threat determination resulted from using flammable materials in construction and equipment of rooms. In this method the material sample with dimensions of 140x420mm is treated by thermal radiation in presence of safety pilot. During investigation time head of flame transition is observed through consecutive zones of sample, course of temperature changes and combustion gases optic permeability is recorded and combustion gases samples are drawn to analyze their chemical composition.

Many researchers claimed that in order to full toxic hazard assessment during fire, it is necessary to conduct research at full scale in conditions similar to real. The research were conducted most often in system: room – corridor, placing investigated material on walls and ceiling of the room. By opening and closing a hole between room and corridor the air exchange was regulated. The fire was caused by ignition a pile of wood placed in the centre of the room and during research permanent temperature measurement, concentration of carbon oxide and dioxide and optical density of smoke was conducted.

Often utilization of different investigation techniques of thermal decomposition of plastics leads to obtain different products. It may be caused by using different speed of heating, degradation time, sample size and composition of atmosphere where degradation proceeds. Selection of specific method is conditional upon purpose of research. Some methods are more useful to investigate thermal degradation mechanism, other to determine influence of degradation conditions on products composition, and other to investigate toxic substances which may be hazardous in human safety during plastic processing and during fire.

Although the acrylic pressure-sensitive adhesives are very interesting and important group under other adhesives, up to now a complex publication concerning thermal behavior, thermal degradation and using of pyrolysis of acrylic PSA for identification of acrylic PSA, acrylic- and methacrylic copolymers has not been published in last years.

2.2.   Pyrolysis as a method of waste utilization.

Pyrolysis is a well known method of polymer waste utilization such as polytetrafluoroethylene (PTFE). The wastes are produced during mechanical working (cutting, chips). The amount of waste produced during mechanical working of product often amounts for a several to tens of percent in relation to the mass of polymer used. From the producers of PTFE point of view it is the best to limit the amount of waste forming during production and to recover monomer by utilizing for example pyrolysis.

PTFE cannot be processed by methods typical for thermoplastics due to their high viscosity in the molten state. The almost linear structure of PTFE renders it susceptible to depolymerization to the initial monomer - tetrafluoroethylene (TFE). The linear structure of PTFE causes all C-C bonds to be equally vulnerable. Thermal decomposition of the polymer begins with homolysis of the C-C bond at any point on the fluorocarbon chain forming two free radicals. The chain radicals undergo further fragmentation yet the location of chain fragmentation is no longer random as bonds energies are not equal anymore. The weakest C-C bond (184 kJ/mer CF_2) is located next to the radical end of the perfluorocarbon chain and this bond splits forming a difluoromethylene diradical and a radical chain which next decomposes to :CF_2. The formed diradicals immediately undergo dimerization to tetrafluoroethylene as the $CF_2= CF_2$ form is thermodynamically more stable. TFE could (in different temperatures) undergo dimerization and further polymerization (oligomerization), which is better presented in Figure 5.
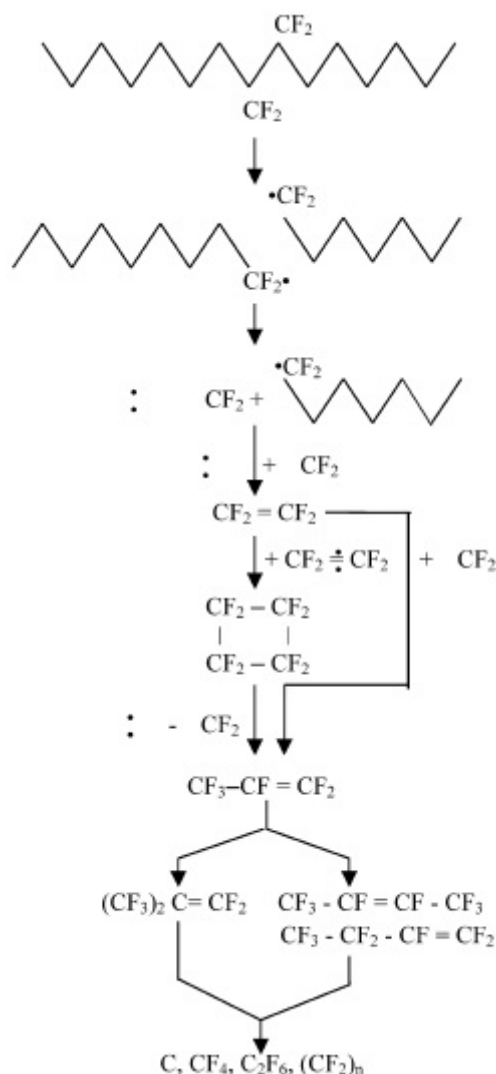
Figure 5 General scheme and mechanism of PTFE depolymerization

The depolymerization of PTFE was the subject of investigations of many authors. Meissner et al. [51] were conducting research toward obtaining TFE, HFP, OFCB and mixture of 1- and 2-OFB during pyrolysis of PTFE. The materials (Tarflen - an homopolymer PTFE produced by Nitrogen Plant Tarnów from Poland) in investigations were waste gaskets and chips from mechanical working. Pyrolysis was carried out in a two-stage nickel reactor presented below in Figure 6.
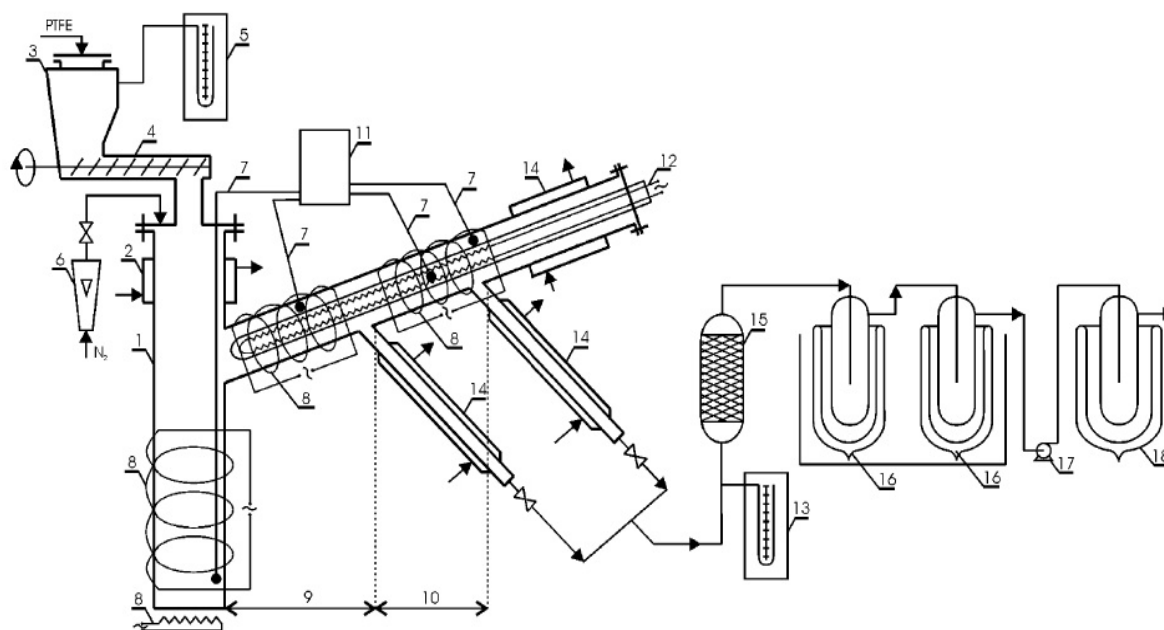
Figure 6 Scheme of experimental installation for pyrolysis of waste polytetrafluoroethylene
1 – vertical reactor, 2 – water condenser, 3 – PTFE feeder, 4 – feeding screw, 5 – manometer,
6 – rotameter, 7 – thermocouple, 8 – heating coil, 9 – horizontal reactor (first section),
10 – horizontal reactor (second section), 11 – temperature recorder, 12 – heating coil,
13 – manometer, 14 – water condenser, 15 – dust separator, 16 – freezer, 17 – vacuum pump,
18 – freezer

The reactor was specifically designed to decompose PTFE taking into consideration the properties of the raw material. In vertical reactor PTFE underwent degradation in temperature below 400ºC and then vapors (products of pyrolysis) were heated in horizontal reactor to the temperature 600-800ºC and the desirable perfluorocarbon compounds were obtained. The pyrolysis products were analyzed by gas chromatography on CHROM-5 apparatus equipped with FID detector. TFE was obtained from PTFE pyrolysis at 620ºC and 100 mmHg. The temperature in vertical reactor was constant (520ºC) and after research it was determined that in the horizontal reactor the beneficial range temperature for obtaining TFE was 650-800ºC, pressure 100-760 mmHg and nitrogen flow rate 0-200 dm^3/h. As the temperature and pressure were lowered the TFE yield was increased. Tetrafluoroethylene besides hexafluoropropylene is one of the major products of PTFE pyrolysis. The concentration of TFE both in the first and the second section of the reactor is mainly affected by the temperature and pressure. The influence of temperature, both in the first and the second section of the reactor is not equal over interval from 600 to 800ºC. The influence of the flow rate of nitrogen and residence time of products in the reaction zone is less pronounced.

A decrease of temperature below 600ºC causes an increase of the TFE content above 50mol%, and as a consequence the spontaneous polymerization of TFE takes place. The PTFE dust sediment formed at the reactor outlet causes the installation to become choked. A rapid increase of pressure in the reactor was found. This makes the process operation impossible below 600ºC. In order to prevent the TFE polymerization the residence time of the reaction products along the way to the reactor cold trap should be short. This can be achieved using higher vacuum or larger flow of inert gas. The achievement of vacuum of few mmHg is difficult in an apparatus of such construction. However a significant dilution by nitrogen impedes the condensation of the pyrolysis products. The highest concentration of TFE was achieved under the following conditions: temperature 600ºC, pressure 100 mmHg, PTFE feeding 1000 g/h and nitrogen flow 200 dm^3/h. Under these conditions when the products is collected from the first or second section of the reactor the TFE concentration of 40 wt.% can be achieved. The preliminary studies of PTFE pyrolysis using a small installation, where a vacuum of 1 mmHg was achieved and at a temperature 550ºC, TFE with the yield of 98 wt.% was obtained.

Kaminsky et al. [52] has reported that pyrolysis of PTFE is one of the few cases where it is possible to recover monomer as the predominant product (pyrolysis temperature 555ºC; yield of TFE 76 wt. %).

Other authors using a Curie-point pyrolyzer proved that TFE is the only product (100 mole %) of pyrolysis at relatively low temperature range 500-590ºC (with little conversion about 0.1-0,2 wt. %) [53].

Platonov [54] found that reduced pressure (1 Torr) during pyrolysis (600ºC) increases the yield of TFE to 98%, while at atmospheric pressure octafluorocyclo butane is obtained.

2.3.   Influence of pyrolysis parameter on pyrolyzate composition

Significant influences on the pyrolysis process have parameters such as:
- temperature,
- time of pyrolysis,
- temperature program,

The same raw material could give different products of pyrolysis in pyrolyzate depending on the parameters mentioned above. In order to use pyrolysis as an effective analysis method in comparative research it is essential to use exactly the same parameters during analysis (reproducibility). Many articles proved this theory in practice.

In the 1980 Wolf et al. [55] have stressed in their report the significant role of reproducibility in pyrolysis analyses. They have also described the influence of temperature. It is a well known that reaction rates and mechanism is change with temperature. In Py-GC the equilibrium pyrolysis temperature (Tp) of the heat source is extremely important in determining the final product distribution and most of the workers attempt to control this particular parameter carefully. Temperature influences the mechanism by either affecting initiation step or controlling subsequent reactions. The initiation reactions involved in the pyrolysis of most organic materials involve the generation of free radicals by the cleavage of a single bond or by the unimolecular elimination of sample molecule such as H_2O or CO. Both of these processes are highly temperature dependent. The subsequent reactions of these species via abstraction or combination reactions or by diffusion are also markedly sensitive to temperature. Lehman and Brauer showed that the yield of monomeric methyl methacrylate from the pyrolysis of poly(methyl methacrylate) is highly temperature dependent, decreasing from nearly 100% for pyrolysis temperatures less than 600ºC to approximately 20% at pyrolysis temperatures greater than 850ºC. From 700 to 800ºC, the monomer yield decreased from 80 to 35%, corresponding to 0.5% per degree.

Ettre and Varadi [56] have investigated the effect of temperature on thermal degradation of nitrocellulose, poly(vinyl alcohol) and poly(n-butyl methacrylate).

Luce et al. [57] have also described the effect of pyrolysis temperature on their research in analyses of polyester resins using Py-GC. They analyzed their material in 427, 649, 871 and 1093ºC temperatures. There was not very much evidence of breakdown at the lowest temperature. As the temperatures increases above this level, further breakdown takes place with increase in light products. Maximum molecular fragmentation, indicated by the number of component peaks was at 649ºC. At the highest temperature decomposition is nearly complete, resulting probably in hydrogen (could not be detected because of FID detector) and elemental carbon.

Saiz-Jimenez [49] in his research was searching for optimal pyrolysis temperature for humic substances. From literature of other authors he concluded that the 500ºC is the optimum pyrolysis temperature for conventional pyrolysis as well as pyrolysis/methylation of humic substances.

Boateng et al. [58] also reported the temperature effect on the noncondesable gas yield. There was a strong temperature effect on the yields of all hydrocarbons and H_2 with yields increasing rapidly between 500 and 700ºC (even 2 times fold) and from 700 to 900ºC (about the same amount) pyrolysis temperature.

Ishida et al. [59] have studied the effect of pyrolysis temperature on intensities of characteristic peaks in program of polyacetal copolymer.

Li et al. [60] have investigated the change in degradation products at different temperatures. The concentration of products did not change from 500 to 550ºC. The concentrations of alcohol and acrylate monomer decrease linearly with pyrolysis temperature from 500 to 700ºC and the concentration of olefin is directly proportional to the pyrolysis temperature. The degradation coefficient of degradation products decreases linearly with the pyrolysis temperature from 550 to 700ºC.

Time of pyrolysis is strongly connected with temperature program. It is well recognized that pyrolysis temperature greatly affects the product distribution. What is not so well known and what may be equally important in Py-GC, is the effect of the heating rate of the pyrolyzer. Temperature rise-time (t_r) is defined as the time required for the pyrolyzer to reach a temperature of $(1-1/e)T_p$. Although rise times of 10 ms have been reported for T_p's as high as 600ºC it is important to note that the rise time is markedly affected by the geometry of the filament, amount of sample and design of the power supply. For most experiments it is desirable to uniformly heat the sample to its pyrolysis temperature as rapidly as possible. Special power supplies utilizing capacitive boosted discharge have been used to increase the heating rate of filament pyrolyzers. The temperature rise-time of Curie-point pyrolyzers is markedly affected by the output of the rf power supply. Thus, the advantage of reproducible pyrolysis temperatures inherent in Curie-point pyrolyzers can be lost if low-powered units are used. These systems may require hundreds of milliseconds to reach the desired pyrolysis temperature [55].

In the 1960's there were some studies about influence of time and temperature during pyrolysis. Some of the authors have studied pyrolysis products of unmodified corn starch. They have noticed that no appreciable amount of volatile products have formed within 10 minutes for pyrolytic temperature below 350ºC. Between 380ºC and 450ºC the gas chromatograms exhibit well defined patterns with only slight changes at different temperatures within this range. The products show further decomposition, as indicated by the changing intensities of the peaks, when the temperature reaches above 500ºC. At 400ºC the pattern peaks remains almost unchanged between 8 and 15 minutes for test made at one-minute increments. The optimum conditions chosen by the author was pyrolytic temperatures 400ºC and a time of 10 minutes [61].

Farre-Rius and Guichon [62] estimated that in most of the pyrolyzers used in Py-GC studies, the actual pyrolysis temperature of the sample remains unknown and depends on the

sample heating rate. From known thermodynamic method data they estimated the half-time for decomposition of polystyrene, poly(tetrafluoro ethylene) and poly(ethyleneglycol adipate) at several different temperatures. At 400ºC, 97% of a polystyrene sample decomposes in less than 100 ms and even a relatively stable material such as polytetraethylene is 97% decomposed in 130 ms at 600ºC. Many experiments which report pyrolysis temperature as high 800 or 900ºC are heating only surface and the bulk of the sample is considerably cooler (the "roast effect"). Thus, it is difficult to accurately reproduce the true pyrolysis temperatures in different laboratories unless the temperature conditions are carefully controlled.

The effects of both parameters pyrolysis duration (time) – Table IV and pyrolysis temperature – Table V are also presented in work of Jackson and Walker [63]. They have described that variations of duration or hold time (from 2.0 to 12.5 sec) at a fixed Curie temperature reflected no change in the nature of components formed, however changes in product distributions were observed. Additionally temperature rise time (from 0.1 to 1.5 sec) is not a critical factor in Curie point pyrolysis in a styrene-isoprene copolymer, either with regard to the products formed or the relative distributions. However the variations in Curie temperature (from 474 to 985ºC) at fixed pyrolysis duration produced drastic changes in the principal products from the Curie pyrolysis of the copolymer and phenyl ether compound.

2.4. Pyrolysis as a method of identification of acrylic polymers

Py-GC has been used extensively to determine the microstructure of acrylic polymers. Often it is the method of choice when a particular structural determination is required. Some of the authors recommended, in preference to IR or chemical methods, Py-GC as a means to determine the composition of methyl methacrylate-2-ethylhexyl acrylate (MMA-2-EHA) copolymers. Polystyrene was used as an internal standard and the quantization was accomplished by comparing the 2-ethylhexyl acrylate/styrene peak high ratio with ratios obtained from known PS/MMA-2-EHA blends. Copolymers of MMA and 2-EHA, rather than blends of homopolymers were used as standards, since only the copolymers yields a significant 2-EHA peak in the pyrogram. The homopolymer poly-2-ethylhexyl acrylate does not decompose to monomer. In general low molecular weight products are formed in preference to monomer when acrylate homopolymers are pyrolyzed. But, when isolated acrylate unit is situated between runs of methacrylate monomers, a substantial yield of acrylate monomer can be obtained.

Willis [64] has cited an example where the use of Py-GC was invaluable to the final structural determination of an acrylic copolymer. The particular copolymer under investigation was composed of methyl methacrylate, lesser amounts of ethyl acrylate and much smaller quantities of methyl acrylate and butyl methacrylate. An infrared spectrum of the copolymer indicated that the material was primarily an MMA-EA copolymer, but the IR data could not exclude the possibility that other comonomers might be present. Further investigation of the copolymer by ^{13}C NMR showed that methyl, ethyl and butyl esters were present. However, the ^{13}C NMR spectrum could not be used to determine if the esters were distinctly due to acrylate or methacrylate groups or both. The pyrolysis products, identified by MS, were MMA, EA, and BMA. A combination of all of the above information led to the final structural determination.

In less complex situations Py-GC methods are sufficient to determine the composition of methacrylate copolymers, particularly when used in conjunction with ancillary techniques. Ahlstrom and Liebman demonstrated that the composition of butyl methacrylate-isobutyl methacrylate copolymers can be determined using Py-GC/FTIR. Vapor-phase IR spectra of methacrylate monomers are distinctive and high sensitivity can be achieved using modern FTIR equipment. The samples were pyrolyzed at 550ºC and the spectrum of each peak was collected and stored on disk as it emerged from the chromatograph. Identified from the IR spectra were butyl methacrylate, isobutyl methacrylate, butanol, methacrylic acid and isobutylene. The quantitative data available from GC, coupled with the quantitative information supplied by the FTIR, provided the necessary structural information [65].

Tsuge et al. [66] used Py-GC to characterize the sequence distribution in methyl acrylate-styrene (MA-S copolymers polymerized to high conversion). This work occurred during the development of the boundary effect theory. Homopolymers of MA and S as well as various MA-S copolymers were pyrolyzed at 510ºC and the products were identified by MS. The homopolymers yielded monomer, dimers and trimers as did the copolymers, but the copolymers formed characteristic hybrid dimers and trimers, which could be used to determine dimer formation, probability constants.

The degradation behavior of α-methylstyrene-methyl methacrylate (α-MS-MMA) copolymers is in complete contrast to that of MA-S copolymers. Almost no hybrid dimers or trimers are formed. Hummel has showed that the yield of monomers from α-MS-MMA copolymers approaches 100%. In fact, the major hybrid dimer formed in the PFIMS spectrum of a copolymer containing 42% MMA had an intensity of only 3% of the base peak. In such

a situation it is relatively easy to relate monomer yield to polymer composition but other vital information such as sequence length distribution of monomer units is lost.

Much of the pyrolysis work on acrylic polymers has been conducted in order to establish degradation mechanisms. Naturally, a thorough understanding of such mechanisms lead to a more profitable interpretation of the program and lends an air of predictability or at least not complete astonishment the product distribution obtained. For example Tsuge et al. suggested that formation of cyclic product obtained from the pyrolysis of MA-S copolymers could support the degradation mechanisms proposed for MA-copolymers by Cameron et al. and Grassie et al [67].

In other work [68] Tsuge and coworkers used a combination of flash stepwise Py-GC so they were able to detect subtle differences in the structures of two similar ethylene-methyl methacrylate (E-MMA) copolymers. Two series of random E-MMA copolymers A- series and B- series were synthesized by a high-pressure radical polymerization method. The comonomers were more homogeneously mixed during the polymerization of the A-series than during the copolymerization of the B- series. The result was that two copolymer series had very similar compositions, but minor structural variations. Weight loss data obtained by thermogravimetric analysis indicated that the onset of weight loss for the B- series copolymers consistently occurred at lower temperatures than for A- series copolymers. This difference in weight loss could be explained, in part by the fact that the B- series copolymers contained more low molecular weight fractions with higher MMA content. However weight-loss data on the copolymers following extraction of the low molecular weight fractions showed that the B- series copolymers were still less stable than A- series copolymers having nearly equivalent MMA concentrations.

Flash pyrolysis experiments were conducted at 690ºC and the products were separated on three types of column. Separation of the high molecular olefins, up to C_{35}, suggested the presence of fairly long ethylene sequences in both A- and B- series copolymers. However, the intensities of the peaks due to branched alkenes and diene compounds were significantly greater in pyrograms of the B- copolymer. Since the formation of branched alkenes and diene compounds in pyrograms of PE are related to chain branching. These data suggested that the B- copolymer was more highly branched than the A- copolymer [69].

Studying the yields of intermediate molecular weight fragments provided a quantitative analysis of the copolymers and indicated that both copolymer chains consisted of randomly distributed short MMA sequences surrounded by ethylene units.

Information obtained from an analysis of light hydrocarbon fraction agreed with the conclusions drawn from the study of high molecular weight fraction. A comparison of the butadiene/1-butene peak area ratio showed that the B- series copolymers gave significantly larger amounts of butadiene than did A- series copolymers. The greater relative yield of butadiene supported the idea that the B- series copolymers were more highly branched.

The stepwise pyrolysis technique employed by Tsuge in this case was to carry out a series of successive degradations on a single sample at a constant temperature of 400ºC. A series of pyrograms obtained by this stepwise technique confirmed that the yield of MMA from the B- series copolymers were considerably higher than from the A- series copolymers, particularly on the first few pulses. These results were consistent with the interpretation that distribution of MMA units in the B- series copolymers was more localized than in the A- series copolymers and that this uneven distribution contributed to the thermal instability of the B- series copolymers [38].

As far as pyrolysis gas chromatography of coating materials is concerned a review paper of Haken [70] is a sort of guide to pyrolysis results of different polymers and copolymers used as coating materials. There are nearly 500 works (including of course papers applied to acrylates).

PART III.   MOTIVATION OF THESIS

The purpose of this work was to develop method, which allows to determine the chemical composition of acrylic pressure-sensitive adhesives of unknown composition. In the first stage of the research solvent-based pressure-sensitive adhesives of known composition were synthesized. In the next stage the obtained material was pyrolyzed.

The products of pyrolysis process were identified using gas chromatography method and confirmed by other thermal analysis methods such as: thermogravimetry (TG).

Based on the results the influence of the temperature on the pyrolyzate composition was determined, which was the basis in further developing of pyrolysis process as a qualitative method of analyzing of thermal degradation products of acrylic PSA .

Developing optimal pyrolysis conditions for acrylic pressure-sensitive adhesives allowed to quantitative analysis. The elaborating of dependence between quantitative and qualitative results of pyrolysis allows significant analysis of pressure-sensitive adhesives composition.

The results from off-line method were compared with the results from on-line method, where pyrolytic gas chromatography (Py-GC) was used, in order to evaluate the possibilities of utilization of pyrolysis coupled with gas chromatography for the purpose of acrylic pressure-sensitive adhesive composition determination.

PART IV.   EXPERIMENTAL

3. Raw materials

All starting materials such as acrylate monomers, solvents, radical starter AIBN, were technical pure and were used in technological process without further purification.

The description of all start materials for the synthesis of solvent-based acrylic pressure-sensitive adhesives are presented in the Table 2

Table 2 Raw materials for the synthesis of investigated solvent-based acrylic PSA

Kind of raw material	Abbreviation	Chemical formula	Supplier
2-ethylhexyl acrylate	2-EHA	$CH_2{=}CH{-}\overset{\overset{O}{\|\|}}{C}{-}O{-}CH_2{-}\overset{\overset{C_2H_5}{\|}}{CH}{-}C_4H_9$	BASF (Germany)
butyl acrylate	BA	$CH_2{=}CH{-}\overset{\overset{O}{\|\|}}{C}{-}O{-}(CH_2)_3{-}CH_3$	BASF (Germany)
ethyl acrylate	EA	$CH_2{=}CH{-}\overset{\overset{O}{\|\|}}{C}{-}O{-}C_2H_5$	BASF (Germany)
methyl acrylate	MA	$CH_2{=}CH{-}\overset{\overset{O}{\|\|}}{C}{-}O{-}CH_3$	BASF (Germany)
2-propylheptyl acrylate	2-PHA	$CH_2{=}CH{-}\overset{\overset{O}{\|\|}}{C}{-}O{-}CH_2{-}\overset{\overset{C_3H_7}{\|}}{CH}{-}C_5H_{11}$	BASF (Germany)
acrylic acid	AA	$CH_2{=}CH{-}\overset{\overset{O}{\|\|}}{C}{-}O{-}H$	BASF (Germany)
2-ethylhexyl methacrylate	2-EHMA	$CH_2{=}\overset{\overset{CH_3}{\|}}{C}{-}\overset{\overset{O}{\|\|}}{C}{-}O{-}CH_2{-}\overset{\overset{C_2H_5}{\|}}{CH}{-}C_4H_9$	BASF (Germany)
butyl methacrylate	BMA	$CH_2{=}\overset{\overset{CH_3}{\|}}{C}{-}\overset{\overset{O}{\|\|}}{C}{-}O{-}C_4H_9$	BASF (Germany)
ethyl methacrylate	EMA	$CH_2{=}\overset{\overset{CH_3}{\|}}{C}{-}\overset{\overset{O}{\|\|}}{C}{-}O{-}C_2H_5$	BASF (Germany)
methyl methacrylate	MMA	$CH_2{=}\overset{\overset{CH_3}{\|}}{C}{-}\overset{\overset{O}{\|\|}}{C}{-}O{-}CH_3$	BASF (Germany)
methanol		CH_3OH	BASF (Germany)

ethanol		C_2H_5OH	BASF (Germany)
butene-1		$CH_3-CH_2-CH=CH_2$	BASF (Germany)
butanol-1		C_4H_9OH	BASF (Germany)
2-ethylhexene-1		$C_4H_9-\overset{\displaystyle \|}{\underset{\displaystyle C_2H_5}{C}}=CH_2$	Aldrich (Nederland)
2-ethylhexanol-1		$C_4H_9-\underset{\displaystyle C_2H_5}{CH}-CH_2OH$	Aldrich (Nederland)
ethyl acetate		$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-O-C_2H_5$	Shell (Holland)
acetone		$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$	Shell (Holland)
2,2'-azo-bis-diisobutyronitrile	AIBN	$CH_3-\underset{\displaystyle CN}{\overset{\displaystyle CH_3}{C}}-N=N-\underset{\displaystyle CN}{\overset{\displaystyle CH_3}{C}}-CH_3$	Wako Chemie (Germany)

4. Test methods (Instrumentation)

4.1. Viscosity of synthesized acrylic PSA

The viscosity of the investigated solvent-borne acrylics pressure-sensitive adhesives was determined with a Rheomat RM 189 from Rheometric Scientific, with spindle No 3 at 23°C.

4.2. Polymer content of synthesized acrylic PSA

The amount of solid materials was found according to DIN EN 12092.

4.3. Free monomers concentration of synthesized acrylic PSA

The residual of monomers were measured with gas chromatograph CP−3800 from Varian (see Figure 7). It was applied chromatographic column J&W DB−1 with the length of 30 mm and diameter of 0.25 mm. The 0.1 µl of gaseous phase sample for analysis from above

PSA were injected into chromatographic column with syringe Hamilton 7001 with the volume from 0.01 to 1.0 μl.

Figure 7 Gas chromatograph CP-3800 from Varian

4.4. Molecular weight of synthesized acrylic PSA

The molecular weight studies were performed in tetrahydrofurane with a liquid chromatograph LaChrom system: RI Detector L-7490 and LaChrom UV Detector L-7400 from Merck-Hitachi, equipped with a PLgel 10^6Å column from Hewlett-Packard.

It was evaluated the weight average molecular weight M_W, the number average molecular weight M_n and the polydispersity $P_d = M_W/M_n$.

4.5. Thermal stability of synthesized acrylic PSA using thermogravimetry (TGA)

Thermal acrylic 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. All samples about ca. 10 mg were 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.

4.6. Pyrolysis conditions by thermal degradation of synthesized acrylic PSA

Py-GC investigations were performed with the use of ThermoScientific GC8000^{Top} chromatograph with capillary RESTEX RTX-5 30 m x 0,53 mm, 1,5 µm film (5% diphenyl/95% dimethyl polysiloxane). Helium (80 kPa) as carrier gas was used. Pyrolysis conditions: detector FID - 250°C, feeder temperature - 250°C, oven temperature program – from 40°C (5 min) to 295°C with increment 15°C/min (10 min), sample volume – 0,1 μl.

5. Pyrolysis as thermal degradation analysis method of acrylic PSA compositions

Gas chromatography, coupled with controlled temperature pyrolysis technique, provides a rapid method for identification of acrylic and methacrylic polymers. Small samples of these polymers are pyrolyzed and thermal degradation by-products are fed directly into a gas chromatograph by using of a gas sampling valve. Chromatographing the complete pyrolyzate allows for the separation and identification of higher boiling thermal degradation products of investigated synthesized acrylic PSA.

5.1. Influence of molecular weight of acrylics copolymers on the course of the pyrolysis and type of forming products of the thermal degradation of copolymers from 2-ethylhexyl acrylate and acrylic acid

Gas chromatography (GC) is a universal separation technique useful for analysis of complex mixtures resulting from thermal degradation of acrylic PSAs, and can be used for both identification and quantification. Various ancillary GC techniques, such as headspace/GC, pyrolysis/GC and other multidisciplinary techniques are also applicable in this area. GC is cost effective and can be used to address a wide range of analytical problems. Assay and trace level analyses are possible with minimal sample preparation, and a wide variety of special detectors are available for quantification and specific identification of various classes of compounds. Coupled with controlled temperature pyrolysis, GC provides a rapid method for the identification of acrylic polymers [71-72].

In the early stage of the research there were conducted investigations on thermal stability of copolymers based on 2-ethylhexyl acrylate and acrylic acid in order to determine

the possibility of influence of the molecular weight of acrylics on the course of the pyrolysis and type of forming products of thermal degradation. To achieve this goal some of PSAs copolymers were synthesized as follows.

Water-based PSAs were synthesized from 2-ethylhexyl acrylate (90-97 wt.%) and acrylic acid (3-10 wt.%) with the use of free radical polymerization in presence of polymerization medium ethyl acetate (boiling point 77°C) using 0.1 wt.% AIBN (2,2'-azobisisobutyronitrile) as radical thermal polymerization initiator. The polymerization was performed with following conditions:

- addition of monomers blended with AIBN in ethyl acetate before polymerization was 50 wt.%,
- dosage time of the rest of the mixture monomers: 1.5 h,
- post-reaction time (reduce of residue monomer concentration): 6 h
- polymer concentration: 50 wt.%

Prepared PSAs were characterized with the following properties, such as: free residue monomers, viscosity, weight average molecular weight (M_W), number average molecular weight (M_n) and polydispersity (P_d) (Table 3).

Table 3 Molecular weights and polydispersity of acrylic PSA synthesized from 2-ethylhexyl acrylate (2-EHA) and acrylic acid (AA)

Concentration		Viscosity	M_W	M_n	$P_d=M_W/M_n$
2-EHA [wt.%]	AA [wt.%]	[Pa·s]			
97	3	4.6	546 000	210 000	2.60
95	5	6.1	582 000	220 000	2.65
93	7	7.5	633 000	232 000	2.73
90	10	9.1	711 000	258 000	2.76

The amount of solid materials was about 50 wt.%. The measurement concentration of free residue monomers concentration was 0.26 wt.% (less than 0.3 wt.%-the limit of free residue monomers typically for acrylic PSA for medical application). It affected only free residue monomers from 2-ethylhexyl acrylate (2-EHA) were observed. In comparison with 2-EHA the acrylic acid is very high reactively and is never presented as residue monomer in acrylic PSA compositions.

Corresponding to high reactivity of acrylic acid the viscosity of synthesized solvent-based acrylic PSA increases by the increasing of the acrylic acid concentration.

The resulted molecular weight values reveals that acrylic acid presence influences positive the high molecular weights increasing of investigated acrylic PSA and a little bit improve the acrylic copolymers polydispersity.

Investigations on the thermal degradation of copolymers based on 2-ethylhexyl acrylate and acrylic acid were performed using a pyrolysis gas chromatography with the use of Intersmat IGC 131 chromatograph with capillary column (QC2/BP1) 25 m x 0,25 mm (100% dimethyl polysiloxane). Helium (80 kPa) as carrier gas was used. Pyrolysis conditions: detector FID - 250°C, feeder temperature - 250°C, oven temperature program – from 50°C to 230°C with increment 10°C/min (32 min), sample volume – 0,3 μl.

The products of the pyrolysis were swept into chromatograph column with nitrogen. The composition of the polymeric composition was determined by comparison of chromatogram of the sample with the chromatograms of known monomers and pyrolyzates of known polymers.

The analysis of gaseous products was conducted using a isochoric manometer coupled with infra-red spectroscopy as was described in [73].

The main gaseous product of thermal degradation of copolymers based on 2-ethylhexyl acrylate and acrylic acid (2-EHA/AA) was carbon dioxide and the rest of liquid thermal degradation products were 2-ethylhexen-1, an olefin corresponding to side group of ester 2-ethylhexyl acrylate in synthesized polymers, except when only carbon dioxide is formed.

The amount of carbon dioxide and other non-condensable products, formed during pyrolysis of copolymers of 2-EHA/AA is presented in Figure 8. The amounts are little compared to other products of the thermal degradation. For more detailed investigations a PSA consisting 93 % weight of 2-EHA and 7 % weight of AA were chosen. Acrylic PSA containing about 7 wt.% acrylic acid polymerized in the polymer structure are used for manufacturing of the wide range of mounting tapes.

Concentration of forming 2-ethylhexen-1 seems to vary as the number of β-hydrogen atoms in the alkyl group [74]. In every of the polymers molar ratio of olefin to carbon dioxide is of the order of unity over substantial part of the reaction. Content of the products of degradation is presented in Table 3.
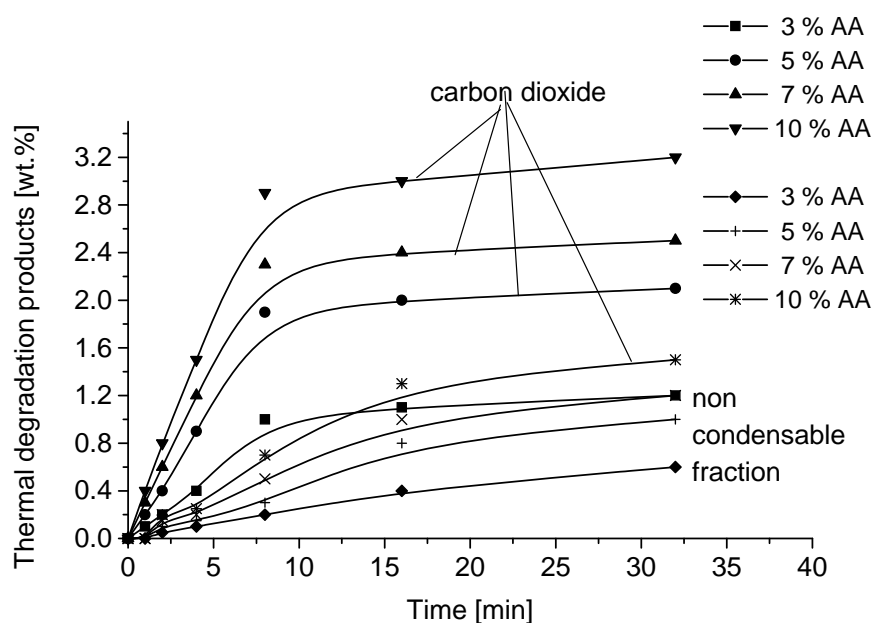
Figure 8 Forming of gaseous products during pyrolysis of PSA based on 2-EHA/AA

The liquid products of degradation of PSA based on 93 wt.% 2-EHA and 7 wt.% AA were analyzed using gas chromatography. Figure 9 presents liquid products of thermal degradation such as: olefin 2-ethylhexen-1 and alcohol 2-ethylhexanol (mean amounts) also 2-EHA and corresponding 2-ethylhexyl methacrylate (2-EHMA), which in this case is connected with main chain decomposition. Results of this investigation in dependence of time of the pyrolysis are presented in Table 4.
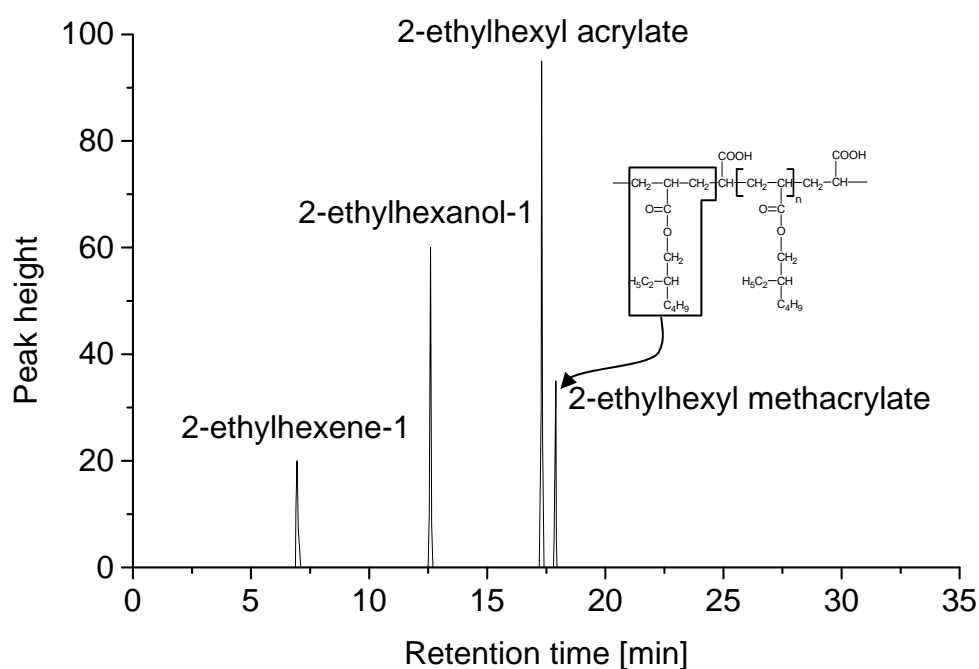
Figure 9 Forming of liquid products of degradation of copolymer based on 2-EHA/AA

(structure of 2-EHA-AA-copolymer is presented on Fig. 9)

Table 4 Forming of gaseous products of thermal degradation of PSA synthesized from 93% weight 2-EHA and 7% weight AA after variety time of pyrolysis

Products of pyrolysis			Products of thermal degradation of PSA [wt.%]					
			1 min	2 min	4 min	8 min	16 min	32 min
Residue (soluble)			84.0	78.1	69.4	57.2	41.1	15.8
	Chain fragments	2-EHA	13.0	16.0	18.5	20.3	26.0	43.0
		2-EHMA	2.7	4.4	6.1	7.0	10.0	14.1
	Liquids	2-ethylhexanol-1	0.0	0.9	3.6	9.1	14.3	17.3
Volatile compo-nents		2-ethylhexen-1	0.0	0.0	1.2	4.1	5.7	6.6
	Condensable gases	Carbon dioxide	0.2	0.4	0.9	1.9	2.0	2.1
	Non-condensable gases		0.0	0.1	0.2	0.3	0.8	1.0

In each of synthesized polymers a 2-EHMA forming was confirmed (Figure 9), as a result of decomposition of main chain (this substance was not present during synthesis of

solvent-borne PSA). Retention time values of 2-ethylhexen-1, 2-ethylhexanol, 2-EHA and 2-EHMA is presented in Figure 9 and concentrations of these products in Figure 10.
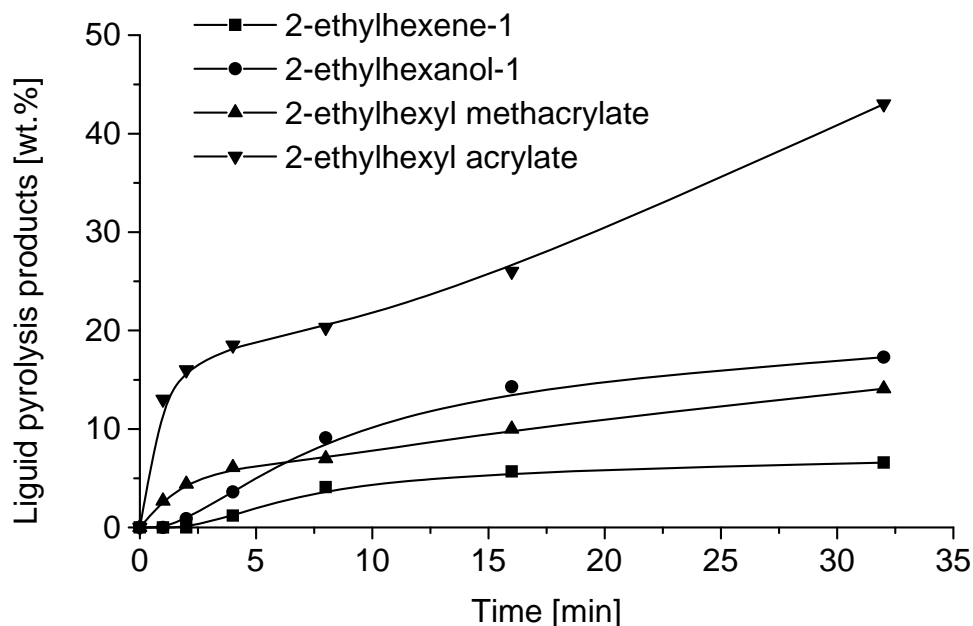
Figure 10 Radical responsible for thermal decomposition of poly(2-ethylhexyl acrylates)

Grassie and Bain [75] suggested, that because of little monomer is formed; the mechanism of thermal reactions that appear in case of 2-ethylhexyl acrylate and similar polymers, a free-radical course is not involved. In fact small molecules of ester do not normally undergo decomposition under 400°C. In polymer environment and especially when radical is stabilized by the resonance or the inductive effects can be formed, there is a overwhelming proof for proceeding of free-radical mechanism under 300°C. Indeed in temperatures above 280°C decomposition mechanism without involving free-radicals is rare. Initial step during acrylates degradation is probably decomposition in some unspecified point of the polymer molecule. Cameron and Kane [76] found, that initially formed free-radicals would remove tertiary hydrogen atoms from the polymer backbone giving relatively stable radical (Figure 11) and all the major decomposition reactions in acrylics are initiated by this radical.
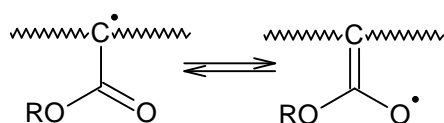

Figure 11 Radical responsible for thermal decomposition of acrylics

The evidence confirming this theory for other acrylics are thermograms and comparability their characteristic products of decomposition. A difficulty was to explain how these products could be formed in one step unless all of reactions would have one precursor. During thermal degradation of PSA based on 2-EHA and AA carbon dioxide and olefin are formed in molar ratio close to unity (at least in early stages of the reaction). Therefore it seems that reaction proceeds according to type I (Figure 12) or type II (Figure 13).
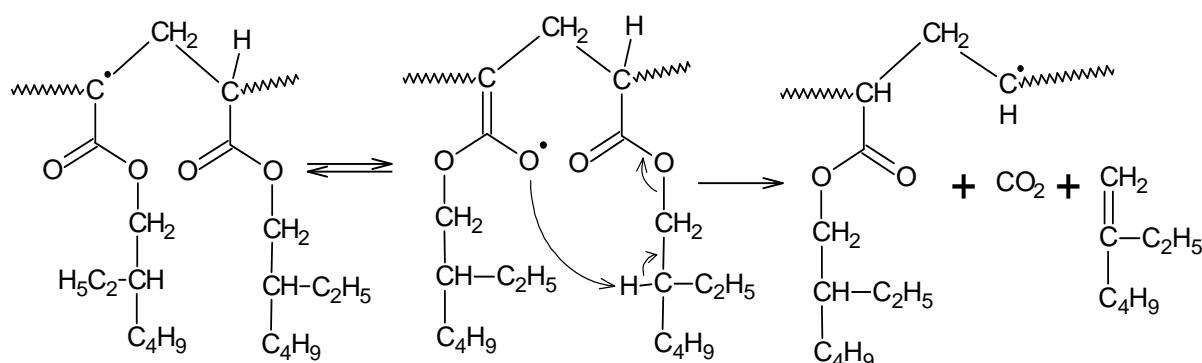
Figure 12 Reaction of thermal degradation of PSA based on 2-EHA and AA with CO_2 and olefin forming
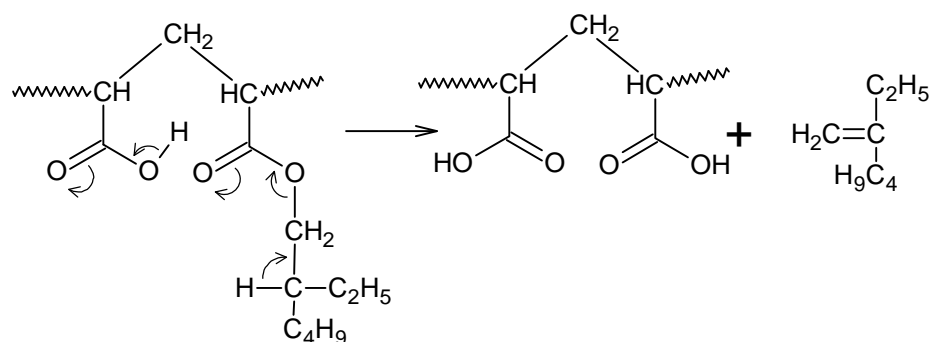
Figure 13 Reaction of thermal degradation of PSA based on 2-EHA and AA with olefin forming

The amounts of volatile condensable and non-condensable gases were always small (less than 3.1 wt.%). Probably carbon dioxide was the main non-condensable product. There is no proof for autocatalytic production of olefin, therefore competition of reaction type I and reaction type II, proposed in order to explain autocatalytic decomposition of 2-ethylhexyl acrylate is acknowledge as insignificant. However reaction type I is shown as catalyzed by the radical on a neighboring monomer unit, which does not exclude why every available radical could not be initiator. The reaction type I is in close relation between forming an olefin and number of β-hydrogen atoms in the alkyl group. In that case ester

2-ethylhexyl is connected with monomers of acrylate and methacrylate, which they are relatively low volatility in PSA based on 2-EHA and AA. The fraction forming from this part of chain is usually yellow color and the intensity of the color increases with the time of degradation.

The investigations on PSA based on 2-EHA and AA were successfully conducted. The results showed, that main gaseous product of pyrolysis was carbon dioxide and 2-ethylhexen-1. Table 3 showed that 2-ethylhexanol-1, 2-EHA and 2-EHMA were the main liquid products of pyrolysis during thermal degradation of synthesized PSA. The forming mechanism of all previously mentioned compounds could be explain with characteristic properties of typical acrylate PSA, which easily undergo pyrolytic decomposition to carbon dioxide and derivatives of 2-ethylhexyl corresponding to the main component of the ester of acrylic PSA.

The residual copolymer synthesized from 2-EHA and AA becomes more intensely colored with progression of degradation. The color is probably a result of mainly coupled doubled carbon-carbon bonds but it is also possible carbonyl groups. Double carbon-carbon bonds are forming in polymer during reaction shown in Figure 14 or as a result electron transfer reaction.

During formation of first double bond tend to weaken of adjacent carbon-hydrogen bonds is observed. This way the electron will be liberated from sequence of adjacent acrylate units resulting in carbon-carbon conjugation in the polymer backbone.
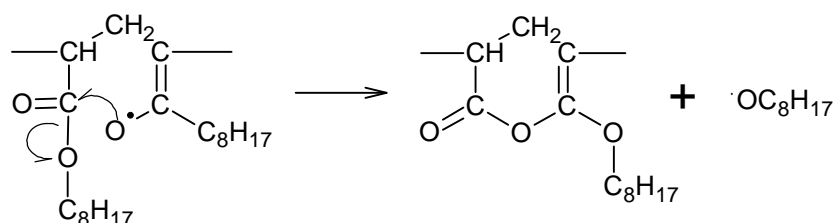
Figure 14 Reaction of thermal degradation of PSA with alcohol and double bonds forming

The conducted research on thermal stability of PSAs based on 2-ethylhexyl acrylate (90-97% weight) and acrylic acid (3-10% weight), which were varying with such properties as weight average molecular weight (M_W), number average molecular weight (M_n) and polydispersity (P_d), indicated that these properties had minor influence on thermal stability of synthesized copolymers and the mechanisms, which lead to formation of gaseous and liquid products of the pyrolysis, were the same for all of the investigated samples.

In the next steps of doctoral works it will be concentrated on acrylic PSA characterized by diverse composition using typical commercially available acrylic monomers.

5.2. Acrylic pressure-sensitive adhesives based on butyl acrylate and acrylic acid

Experiments were conducted using solvent-based acrylic PSAs containing butyl acrylate (BA) and acrylic acid (AA). The PSAs were synthesized from 90−97 wt.% butyl acrylate and 3−10 wt.% acrylic acid using ethyl acetate as the organic solvent at the boiling point temperature of about 77°C. AIBN (0.1 wt.%) was used as the thermal initiator to start radical polymerization.

The polymerization was conducted under the following conditions: (i) monomers were blended with AIBN in ethyl acetate (50 wt.%) before polymerization (reactor charge), (ii) the dosage time of residual monomers with residual AIBN was 1 h, and (iii) the post-reaction time was 5 h.

The synthesized PSA with 50 wt.% polymer content and 0.25 wt.% residue butyl acrylate were characterized according to viscosity, weight average molecular weight (M_W), number average molecular weight (M_n), and polydispersity (P_d) (Table 5). Their hypothetical structure is presented in Figure 15.

Table 5 Molecular weight of PSA containing different amounts of carboxylic groups

Concentration of AA [wt.%]	BA [wt.%]	Viscosity [Pa·s]	$\overline{M}_w$ [Dalton]	$\overline{M}_n$ [Dalton]	$P_d = \dfrac{\overline{M}_w}{\overline{M}_n}$
3	97	8.5	803 000	310 000	2.59
5	95	9.2	850 000	322 000	2.64
7	93	9.9	893 000	331 000	2.70
10	90	11.3	1 050 000	387 000	2.71

The thermal degradation experiments were performed by pyrolysis−GC with the following parameters: Intersmat IGC 131GC with a QC2/BP1 capillary column (25 m × 0.25 mm, 100% dimethyl polysiloxane), N_2 as carrier gas (80 kPa, detector FID 250 ^{o}C), injector temperature 250 ^{o}C, oven temperature program 50 ^{o}C at 0 min to 230 ^{o}C at a rate of 10 ^{o}C/min (full run time 32 min), sample volume 0.3 μl, and pyrolysis−GC/mass spectrometry techniques.

The pyrolysis apparatus was assembled and connected to the gas sampler valve in place of the constant volume tube. Plugs were placed in the regular sample inlet and in the vent openings of the gas sampler valve. Products resulting from pyrolysis were swept into the gas chromatography column with N_2. Identification and composition of the polymers was determined by comparisons of the sample chromatograms with chromatograms of known monomers and pyrolyzates of known polymers.
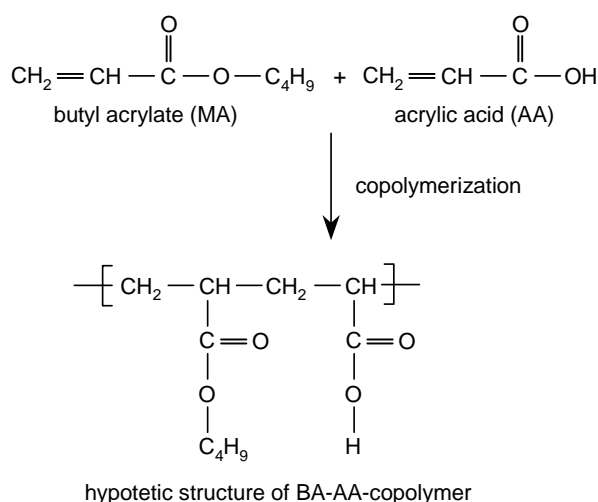
Figure 15 Hypothetic structure of BA-AA-copolymer

The major gaseous products (Figure 16) were carbon dioxide, 1-butene corresponding to the butyl ester group in the copolymer. The olefin, being less volatile, in this case appeared among the liquid products.

The amounts of carbon dioxide (about 30 wt.%) and 1-butene (about 12 wt.%) produced during the pyrolysis of the butyl acrylate/acrylic acid copolymers were very similar. We also evaluated pyrolysis of the acrylic PSA containing 95 wt.% butyl acrylate and 5 wt.% acrylic acid.
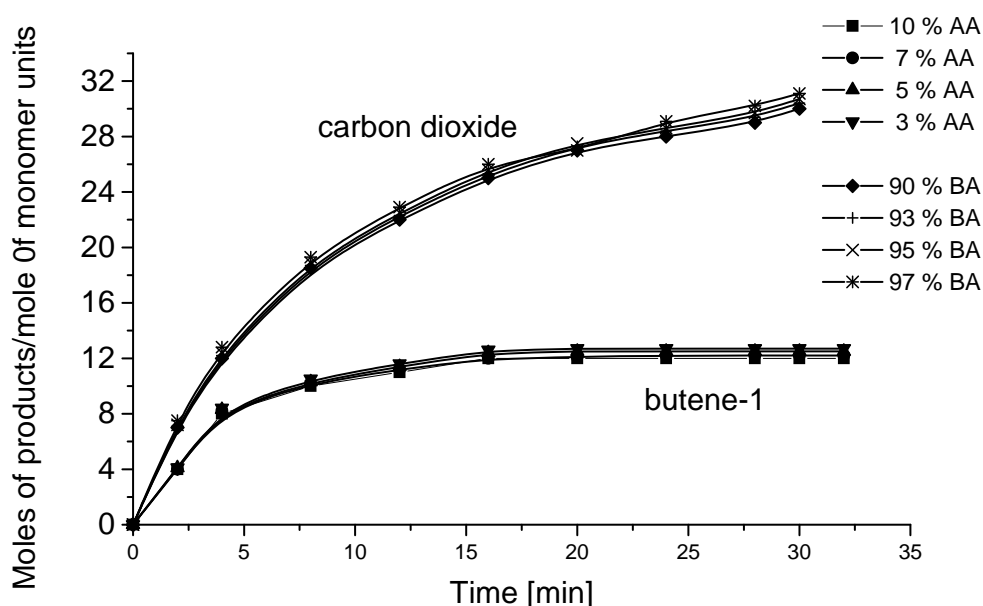
Figure 16 Production of carbon dioxide and 1-butene during degradation of acrylic PSA based on copolymer butyl acrylate (BA) and acrylic acid (AA)

The amount of olefin (1-butene) produced seemed to vary with the number of β-hydrogen atoms in the alkyl group. For each polymer the molar ratio of olefin to carbon dioxide was of the order of 1:1 over an appreciable part of the reaction. Table 5 illustrates the mass balance of the reaction in terms of the proportions of monomer units involved.

The gaseous and liquid products from the acrylic PSA formed from butyl acrylate and acrylic acid were analyzed by GC (Figure 17). The alcohol butanol-1 was the major liquid pyrolysis product, with smaller amounts of the monomer butyl acrylate and the corresponding methacrylate, butyl methacrylate (Table 6).
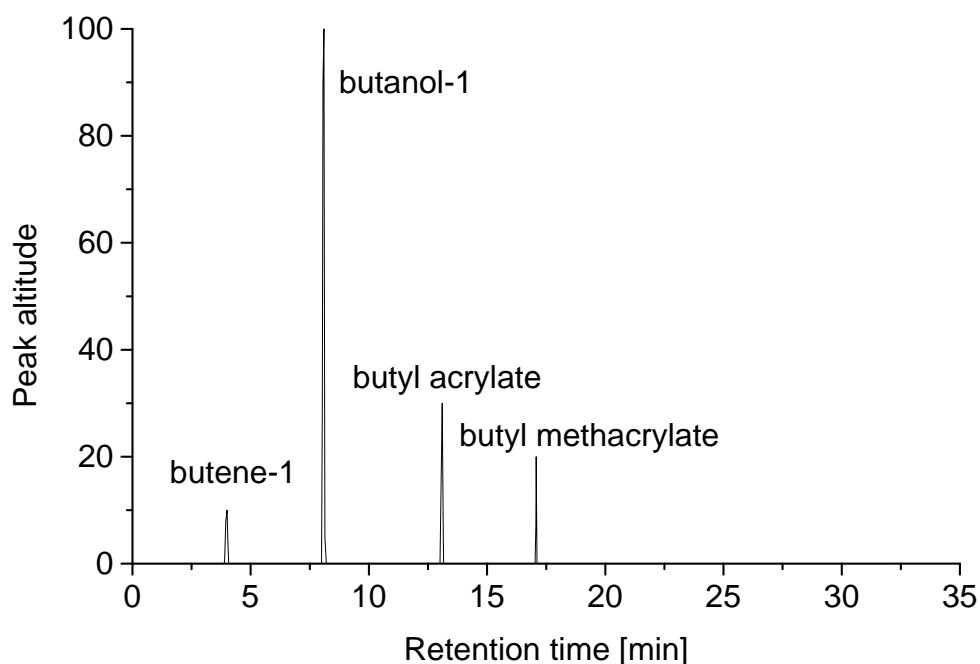
Figure 17 GC of the gaseous and liquids degradation products of evaluated acrylic PSA

For each polymer, it was confirmed that the corresponding methacrylate was a genuine degradation product and not simply present with the monomer used to synthesize the PSA. The evolution of 1-butanol, butyl acrylate and butyl methacrylate is illustrated in Figure 18 in terms of the proportion of monomer units involved.

Table 6 Balance table for thermal degradation of PSA containing 95 wt.% BA and 5 wt.% AA for various lengths of time

Pyrolysis products	Thermal degradation products of PSA [wt.%]					
	1 min	4 min	8 min	16 min	24 min	32 min
Residue	90.0	74.0	67.2	55.8	35.2	33.9
Insoluble	5.0	5.0	13.1	29.6	33.6	33.9
Soluble	85.0	69.0	54.1	26.2	1.6	absent
Chain fragments	7.7	11.1	11.5	16.3	17.1	21.7
Total liquids	0.4	10.3	9.8	19.8	28.7	29.6
Butanol-1	0.2	2.6	9.0	17.6	19.6	20.7
Butyl acrylate	absent	0.08	0.1	0.16	0.20	0.20
Butyl methacrylate	absent	0.03	0.04	0.05	0.05	0.05
Remaining liquids	0.2	7.3	0.7	2.0	8.9	8.6
Condensable gases	1.8	5.1	9.4	14.8	15.4	15.5
Carbon dioxide	0.5	2.0	4.2	8.3	9.1	9.6
1-butene	1.3	3.1	5.2	6.5	6.3	5.9

|						
Non condensable	0.1	0.2	0.5	1.1	1.1	1.2
Total volatiles	10.0	26.7	31.2	52.0	62.3	68.0
Total products	100.0	100.7	98.4	107.8	97.5	101.9
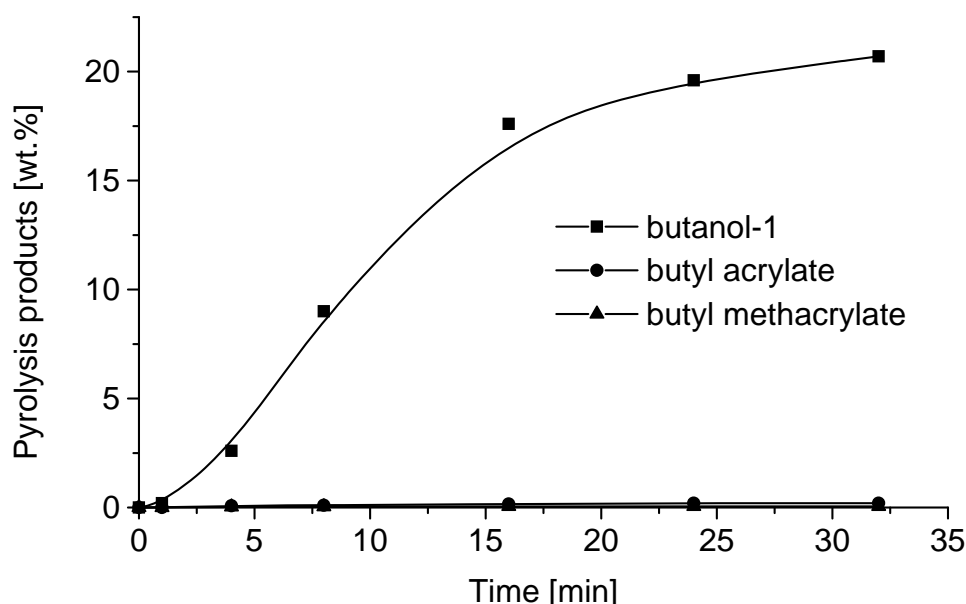
Figure 18 Production of relevant liquid products during degradation of acrylic PSA based on copolymer butyl acrylate (BA) and acrylic acid (AA).

Madorsky [77] suggested that because little monomer is formed, the mechanism of the thermal reactions of poly(butyl acrylate) or butyl acrylate/acrylic acid copolymer does not involve free radicals. Indeed, small ester molecules do not normally undergo bond scission to form free radicals at temperatures below 400°C. However, in a polymer environment, and particularly when a radical stabilized by resonance or inductive effects can be formed, there is overwhelming evidence that a free radical mechanism may operate below 300°C. Indeed, at temperatures above 280°C degradation processes not involving radicals are rare.

The initial step in the degradation of the primary acrylics is therefore likely to be scission at some unspecified point in the polymer molecule. Cameron and Kane [78] suggested that these initially formed radicals would remove tertiary hydrogen atoms from the polymer backbone to give a relatively stable radical (Figure 19), and that all the major decomposition reactions in poly(alkyl acrylate) are initiated by this radical.

Evidence that this hypothesis may reasonably be extended to other poly(primary alkyl acrylates) is provided by their similar thermograms and patterns of reaction products. It

is difficult to explain how such a variety of products could be formed in a one-step process unless all the reactions have a common precursor.
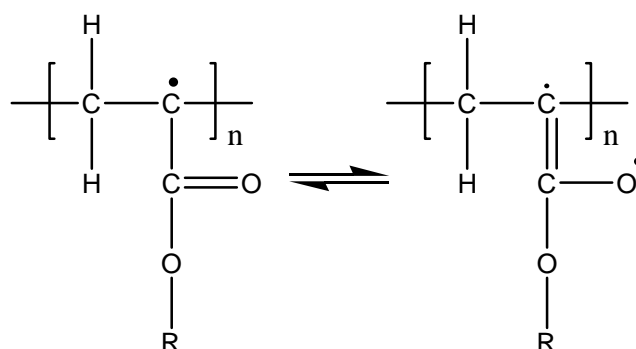

Figure 19 Radical responsible for thermal decomposition of poly(alkyl acrylates)

During the thermal degradation of butyl acrylate/acrylic acid-based acrylic PSA, the molar ratio of carbon dioxide to olefin evolved was close to unity, at least in the early stages of the reaction. It therefore seems probable that a reaction of type I (Figure 20) or type II (Figure 21) is involved. There was no evidence of autocatalytic production of olefin, so competition between type I and II reactions, proposed to account for the autocatalytic decomposition of poly(butyl acrylate), is assumed to be negligible.
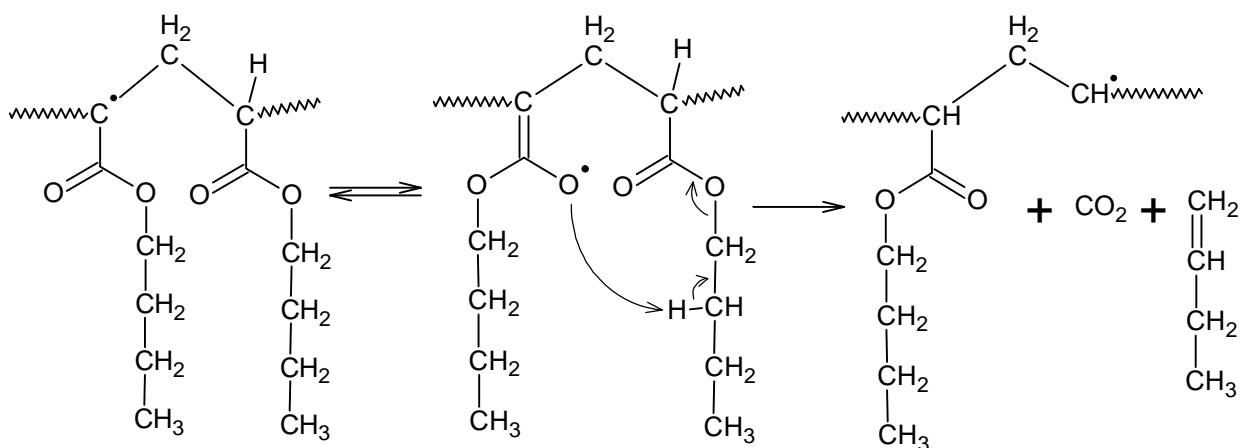
Figure 20 Thermal decomposition reaction of acrylic PSA formed CO_2 and olefin
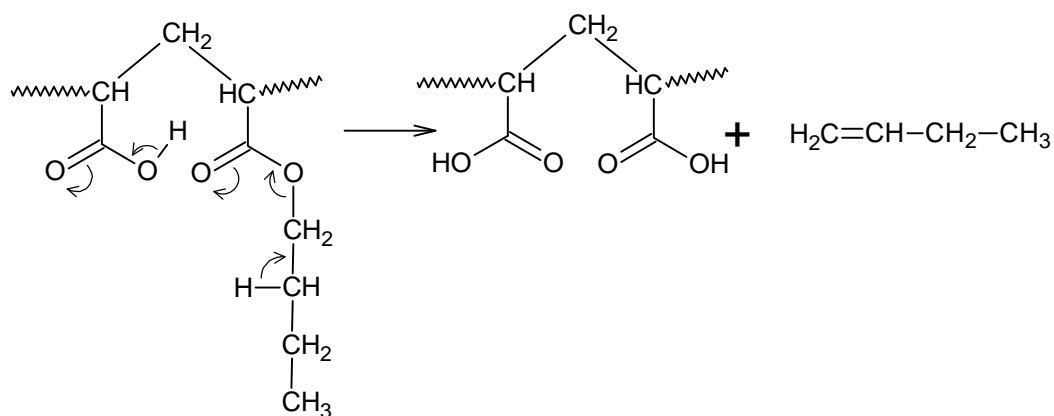
Figure 21 Thermal decomposition reaction of acrylic PSA formed olefin.

Although reaction type I is represented as being catalyzed by a radical on a neighboring monomer unit, it is likely that any available radical could be the initiator. Further evidence for reaction type I is that there appears to be a direct relationship between the production of olefin and the number of β-hydrogen atoms on the alkyl group.

This study investigated the thermal degradation of acrylic PSAs containing various amounts of butyl acrylate and acrylic acid. Copolymers of butyl acrylate and acrylic acid were examined to establish whether ester interchange could occur under the experimental pyrolysis conditions. The results showed that carbon dioxide and 1-butene were the main gaseous pyrolysis products of the acrylic PSAs studied, and the main thermal degradation products were 1-butanol, butyl acrylate and butyl methacrylate. The mechanism of formation of these compounds can be explained by the characteristic properties of acrylic PSAs, which easily undergo pyrolytic decomposition to carbon dioxide and the butyl derivatives, and correspond to the main acrylic ester component of the PSAs.

5.3.   Acrylic pressure-sensitive adhesives based on butyl acrylate and acrylic acid with high amount of acrylic acid for manufacturing of water-soluble acrylic PSA

Solvent-borne water soluble polymers, especially based on acrylics are still something of a specialty and not commercially available on the market. They are applied as one-sided, double-sided and carrier-free tapes for web splicing in the paper industry. Challenging fields for this kind of acrylics PSA are water-dispersible or water-soluble labels, surgical tapes and biomedical electrodes.

Water soluble PSA solvent-based (WS-PSA) were synthesized from compositions of butyl acrylate (3-15% weight) and acrylic acid (85-97 wt.%) with the use of free radical polymerization in presence of acetone (boiling point 56°C) using 0.1 wt.% 2,2'-azobisisobutyronitrile (AIBN) as thermal radical polymerization initiator. The polymerization was performed with following conditions. The components were dosed for 1 hour and then the post-reaction was conducted for 5 hours. Water soluble PSAs were obtained with 50 wt.% content of the polymer, which were characterized using viscosity tested in 20°C. The results are presented in Table 7.

Table 7 Viscosities of obtained PSAs

PSA	Acrylic acid [% weight]	Butyl acrylate [% weight]	Viscosity [Pa·s]
WS-PSA 1	97	3	29.6
WS-PSA 2	95	5	20.3
WS-PSA 3	93	7	12.7
WS-PSA 4	90	10	7.6
WS-PSA 5	85	15	4.4

The thermal degradation experiments were performed by pyrolysis-gas chromatography and pyrolysis-gas chromatography/mass spectrometry techniques at following parameters:

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 resistance testing of the water-soluble acrylic PSA synthesized from acrylic acid and butyl acrylate using thermogravimetry method was shown in Figure 22.
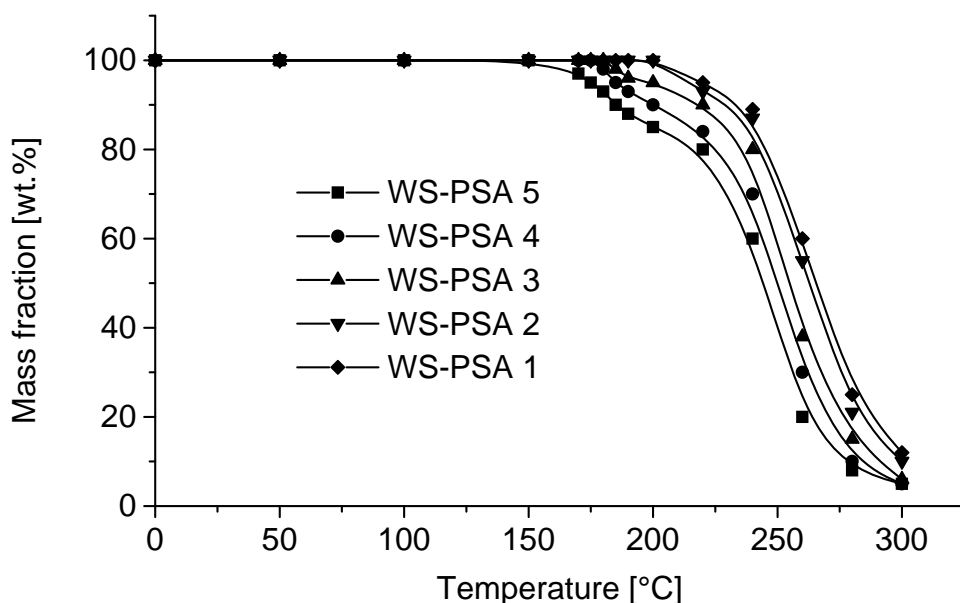

Figure 22 Thermal degradation of water-soluble copolymers synthesized from acrylic acid and butyl acrylate

As can be seen in Figure 22, the rate of thermal degradation of water-soluble acrylic copolymers containing acrylic acid and butyl acrylate depends on their composition. More acrylic acid into polymeric backbone means de facto ameliorating of thermal resistance. All evaluated water-soluble polymers were stable to about 160°C. Water-soluble copolymers WS-PSA 1-2 with adequately 95 and 97 wt.% acrylic acid (Tab. 7) are thermal stable to about 210°C. At higher temperatures begins, according to acrylic acid concentration in copolymers, their thermal decomposition. The gaseous and liquid thermal decomposition products of water-soluble copolymer WS-PSA 2 containing 95 wt.% acrylic acid and 5 wt.% butyl acrylate is presented in Table 8.

Table 8 Thermal degradation products of water-soluble acrylic PSA containing 95 wt.%
acrylic acid and 5 wt.% butyl acrylate as function of pyrolysis time

Pyrolysis products	Thermal degradation products of WS-PSA 2 [wt.%]					
	1 min	2 min	4 min	8 min	16 min	32 min
Residue (soluble)	86.0	80.0	70.3	41.9	34.9	18.0
Liquids products	12.2	16.3	12.0	9.5	3.1	2.3
butyl acrylate	10.4	13.2	7.1	5.4	2.5	1.9
butyl methacrylate	1.6	2.2	3.1	3.0	0.4	0.3
butanol-1	0.2	0.9	1.8	1.1	0.2	0.1
Condensable gases	1.7	3.4	17.2	47.8	61.0	78.6
carbon dioxide	1.6	3.2	16.6	47.4	60.7	78.5
butene-1	0.1	0.2	0.4	0.4	0.3	0.1
Non condensable	0.0	0.2	0.4	0.7	0.9	1.0
Total volatiles	13.9	19.9	29.6	58.0	65.0	81.9
Total products	99.9	99.9	99.9	99.9	99.9	99.9

The main decomposition gaseous (Table 8) were carbon dioxide, butene-1 and non condensable products. Olefin butene-1 corresponding to the butyl ester side groups in the synthesized copolymers. The olefin, being less volatile, in this case appears among the liquid products. Forming process of gaseous pyrolysis products was shown in Figure 23.
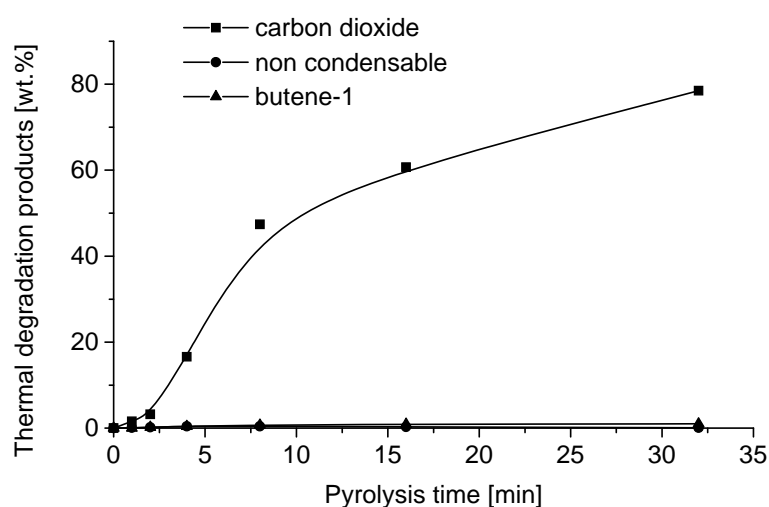
Figure 23 Forming of carbon dioxide, butene-1 and non condensable fraction during
pyrolysis of water-based acrylic PSA based acrylic acid and butyl acrylate

The amounts of carbon dioxide between 1.6 and 78.5 wt.% after 32 min pyrolysis time were not comparable with butene-1 (0.1-0.4 wt.%) amounts and amounts of non condensable pyrolysis products (between 0.2 and 1.0 wt.%) produced during the pyrolysis of acrylic acid-butyl acrylate-copolymer.

Figure 24 illustrates the pyrolysis chromatogram of water-soluble acrylic acid-butyl acrylate-copolymer WS-PSA 2.
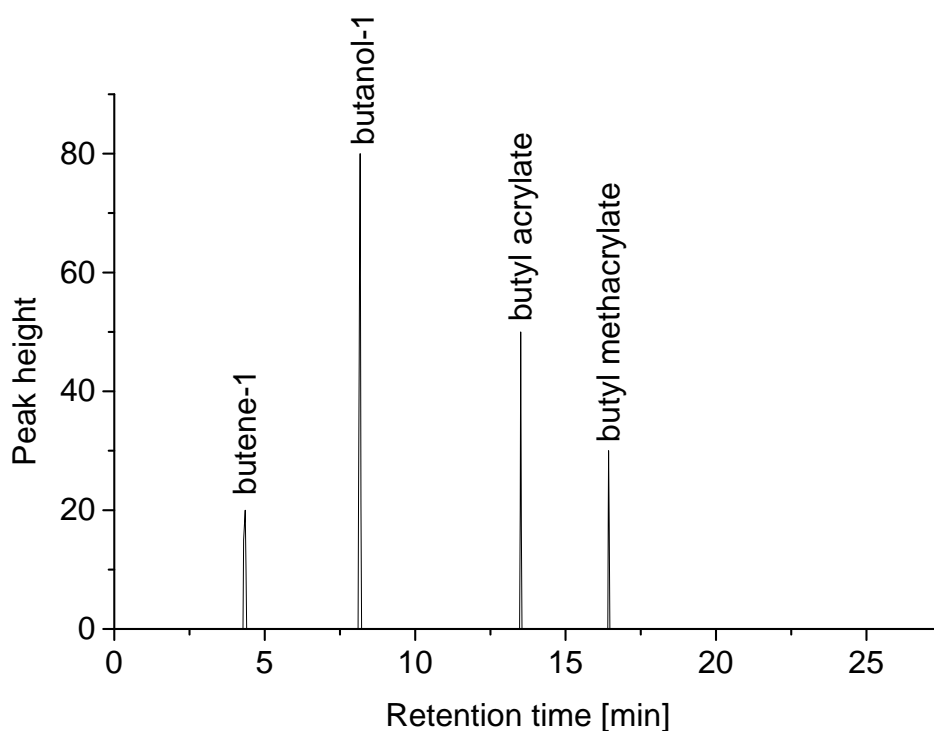
Figure 24 Pyrolysis chromatogram of water-soluble copolymer WS-PSA 2 synthesized from acrylic acid and butyl acrylate

The pyrolysis chromatogram of investigated acrylic copolymer WS-PSA 2 (Figure 22) contains four principal peaks. The first is butene-1 and the second is butanol-1 from butyl acrylate. The presence of butene-1 and of butanol-1 peaks in the pyrolysis chromatogram at higher pyrolysis temperatures is possibly due to thermal degradation of acrylate groups in the side chain. The next peaks belong to butyl acrylate and butyl methacrylate from the thermal decomposition of main chain acrylic copolymer.

The elimination of water in the presence of carboxylic groups from acrylic acid is necessary for anhydride formation. The probability of anhydride formation is also minimized by the space concentration of carboxylic groups along the copolymer backbone. It was observed that the dehydratation and decarboxylation reactions are first order reactions, the latter being much slower than the former and found that water and carbon dioxide were the only volatile pyrolysis products in the range between 170 and 240°C [79].

The water-soluble acrylic copolymers synthesized with very high acrylic acid concentration of about 95 wt.% are characterized by excellent thermal resistance at high temperatures between 180 and 240°C and can be used for manufacturing of splicing tapes for paper industry and water dispersible labels. The composition of their breakdown products at high temperatures using a pyrolysis process includes butene-1, butanol-1, butyl acrylate and butyl methacrylate. The characteristics of the production of butene-1 and butanol-1 corresponding to used acrylate monomers for synthesis are quite different but even similar, so that one may reasonably presume that are formed in quite distinct ester decomposition process. Butene-1 formation almost inevitably implies the formation of carboxyl groups or carboxyl radicals whose decomposition could yield carbon dioxide. A comparable pyrolysis reaction of tested water-soluble acrylic copolymer would give butyl acrylate and butyl methacrylate. Butyl acrylate is formed in rather greater amount than butyl methacrylate and probably arises by depropagation from an acrylate terminated polymer radical although this is known to be only a very minor reaction in acrylics.

5.4.   Acrylic pressure-sensitive based on ethyl acrylate and acrylic acid

Ethyl acrylate is a very important monomer used for production of pressure-sensitive adhesives in medical applications. Acrylic PSA based on ethyl acrylate are used for manufacturing of wide range of medical products, such as typical plaster, transdermal therapeutic systems (TTS-plaster), self-adhesive wound dressing and biomedical electrodes.

The synthesis of solvent-based copolymers consist 95 wt.% ethyl acrylate and 5 wt.% acrylic acid are conducted at boiling point of polymerization medium ethyl acetate in presence of 0.1 wt.% thermal radical starter AIBN under the following conditions:

The polymerization process was carried out under the following conditions:

- dosage time of monomers mixture containing AIBN: 1 h
- time of post-reaction: 5 h
- polymer content: 50wt.%

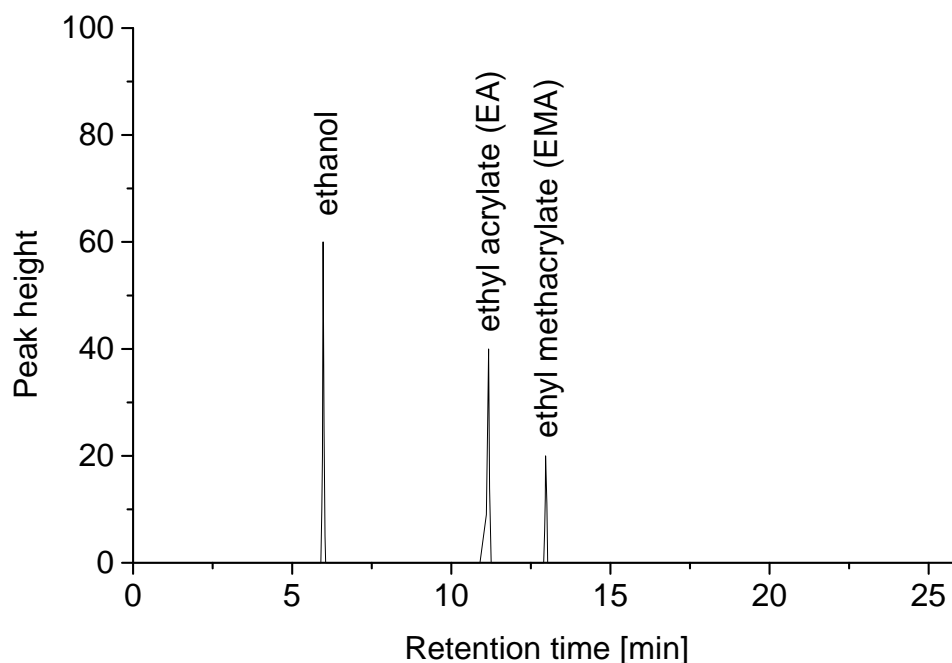The synthesized solvent-borne acrylic copolymer (Figure 25) was characterized by viscosity of 6.0 Pa·s.

hypotetic structure of EA-AA-copolymer
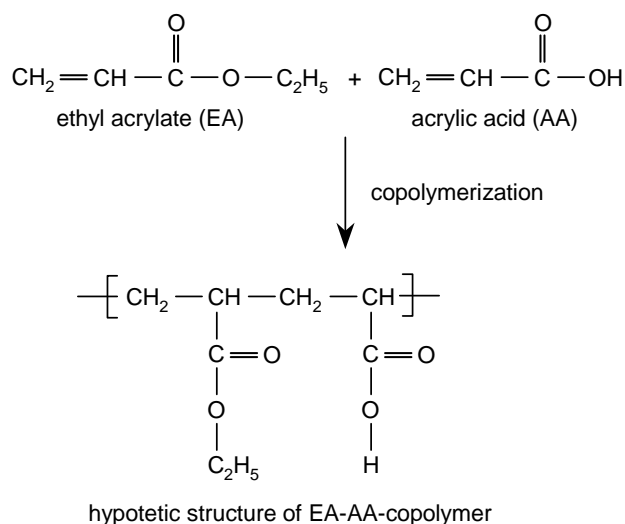
Figure 25 Hypothetic structure of ethyl acrylate-acrylic acid-copolymer

After coating of synthesized solvent-based acrylic PSA on silicon paper and after 10 min drying at 105°C the resulted PSA film was pyrolyzed at following conditions:

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 pyrolysis apparatus was taken apart at the reduction union and a 5 mg acrylic polymer was placed in the bottom of the loop. Thy pyrolysis apparatus was reassembled and connected to the gas sampler valve in place of the constant volume tube. Plugs were placed in the regular sample inlet and in the vent openings of the gas sampler valve. Helium was used to flush the air from the apparatus and the system was closed. The loop of the apparatus was heated at 500°C for 30 second. Products resulting from the pyrolysis were swept into the gas chromatographic column with helium.

The identification and composition of the tested acrylic copolymers were determinated by comparison of the chromatogram of the sample with chromatograms of known pyrolysis products of synthesized acrylic copolymer with known composition (Figure 26).

Figure 26 Chromatogram of the pyrolyzates of acrylic copolymer ethyl acrylate-acrylic acid

The pyrogram of the ethyl acrylate-acrylic acid-copolymer showed ethanol, ethyl acrylate and ethyl methacrylate as the thermal degradation products. The forming of thermal degradation products are presented in Figure 27.
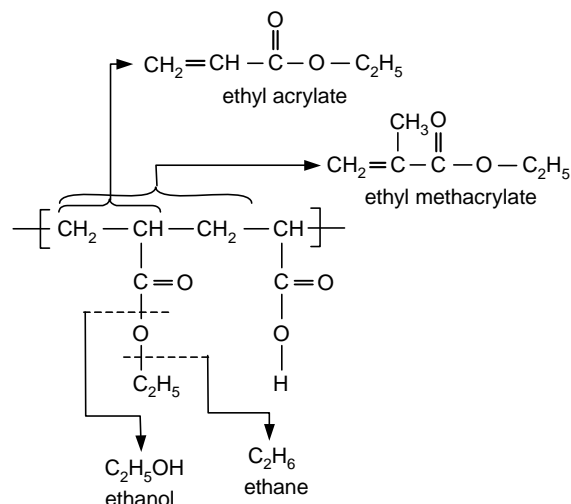
Figure 27 Formation of ethanol, ethyl acrylate and ethyl methacrylate during pyrolysis of ethyl acrylate-acrylic acid-copolymer

5.5.   Acrylic pressure-sensitive based on methyl acrylate and acrylic acid

Methyl acrylate plays very significant role in the PSA industry by manufacturing of adhesives characterizing by excellent plasticizers resistance. Its incorporating into polymer structure during polymerization process improves shear strength (cohesion), viscosity and other mechanical properties of polymeric film, such as strength by elongation.

The synthesis of solvent-based copolymers consist 95 wt.% methyl acrylate and 5 wt.% acrylic acid are conducted at boiling point of polymerization medium ethyl acetate in presence of 0.1 wt.% thermal radical starter AIBN under the following conditions:

The polymerization process was carried out under the following conditions:
- dosage time of residual monomers with residual AIBN: 1 h
- time of post-reaction: 5 h
- polymer content: 50wt.%

The synthesized solvent-borne acrylic copolymer was characterized by the viscosity 7.3 Pa·s.

hypotetic structure of MA-AA-copolymer
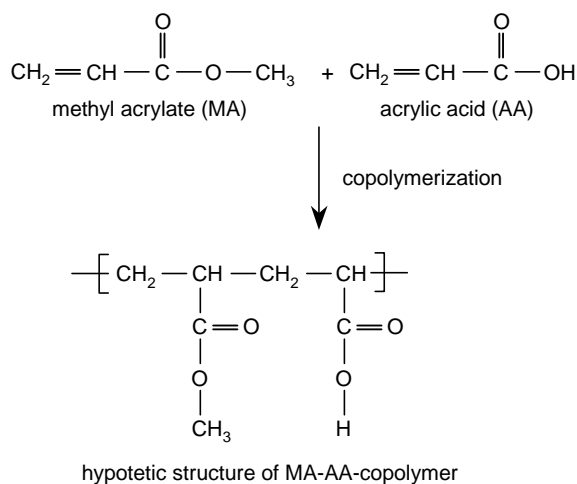
Figure 28 Hypothetic structure of methyl acrylate-acrylic acid-copolymer

After coating of synthesized solvent-based acrylic PSA on silicon paper and after 10 min drying at 105°C the resulted PSA film was pyrolyzed at following conditions:

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 pyrolysis apparatus was taken apart at the reduction union and a 5 mg acrylic polymer was placed in the bottom of the loop. The pyrolysis apparatus was reassembled and connected to the gas sampler valve in place of the constant volume tube. Plugs were placed in the regular sample inlet and in the vent openings of the gas sampler valve. Helium was used to flush the air from the apparatus and the system was closed. The loop of the apparatus was heated at 500°C for 30 second. Products resulting from the pyrolysis were swept into the gas chromatographic column with helium.

The identification and composition of the tested acrylic copolymers were determinate by comparison of the chromatogram of the sample with chromatograms of known pyrolysis products of synthesized acrylic copolymer with known composition (Figure 29).

Figure 29 Chromatogram of the pyrolyzates of acrylic copolymer methyl acrylate-acrylic acid

The pyrolysis chromatogram of examined acrylic copolymer based on methyl acrylate and acrylic acid (Figure 29) 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 acrylic polymer chain.

The forming mechanism products of thermal degradation of copolymer synthesized from methyl acrylate and acrylic acid are presented in Figure 30.

$CH_2=CH-C(=O)-O-CH_3$

methyl acrylate

$CH_2=C(CH_3)-C(=O)-O-CH_3$

methyl methacrylate

$-[CH_2-CH-CH_2-CH]-$

CH_3OH methanol

CH_4 methane
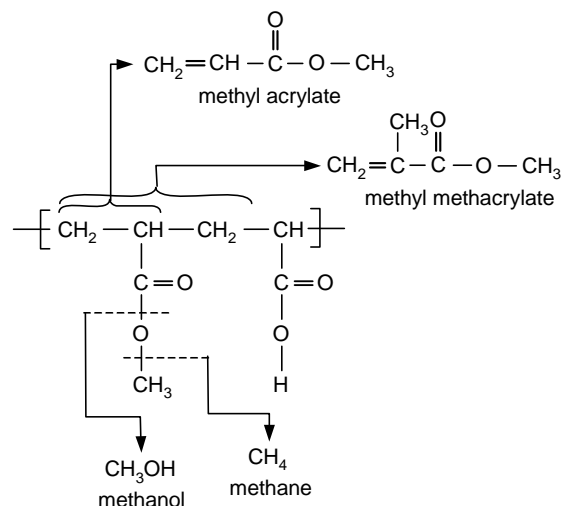
Figure 30 Formation of methanol, methyl acrylate and methyl methacrylate during pyrolysis of ethyl acrylate-acrylic acid-copolymer

5.6.   Acrylic pressure-sensitive based on butyl acrylate, methyl acrylate and acrylic acid

Typical acrylic PSAs are synthesized from tackifying alkyl acrylates (butyl or 2-ethylhexyl acrylate), hardening acrylates (methyl or ethyl acrylates) and functional groups containing unsaturated monomers (acrylic acid). The highest peel adhesion values for acrylic PSA containing butyl acrylate has been observed. Even butyl acrylate is used for synthesis of acrylic PSA with excellent performances. The best plasticizer resistance has been achieved using acrylic PSA containing methyl acrylate. The functional groups containing monomers such as acrylic acid are incorporated into the balanced monomers for specific adhesion to desired substrates and to provide sites in form of active centers for crosslinking [80].

The necessary acrylic PSA was synthesized from 65 wt.% butyl acrylate (BA), 30 wt.% methyl acrylate (MA) and 5 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 blend of monomers with AIBN into ethyl acetate
  before the polymerization (amount of reactor charge):   50 wt.%
- dosage time of residual monomers with residual AIBN: 2 h
- time of post-reaction: 5 h

The synthesized solvent-borne acrylic pressure-sensitive adhesive was characterized by the following main parameters:

- amount of solid materials (solid content)   50 wt.%
- viscosity   6.4 Pa·s
- concentration of residual monomers   < 0.3 wt.%
- weight average molecular weight $\overline{M}_w$ 535 000 Dalton
- number average molecular weight $\overline{M}_n$ 148 000 Dalton
- polydispersity $P_d = \overline{M}_w/\overline{M}_n$ 3.61

The thermal degradation experiments were performed by pyrolysis-gas chromatography and pyrolysis-gas chromatography/mass spectrometry techniques at following parameters:

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 stability of the acrylic PSA containing butyl acrylate, methyl acrylate and acrylic acid was investigated by thermogravimetry (Figure 31).
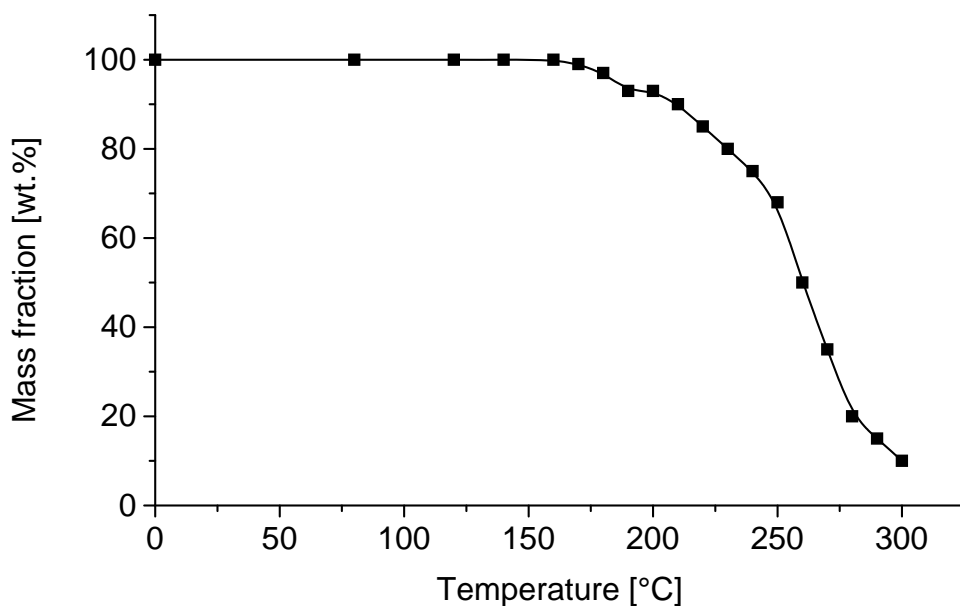
Figure 31 Thermal degradation of butyl acrylate-methyl acrylate-acrylic acid-copolymer

As can readily be seen, the rate of thermal degradation for butyl acrylate-methyl acrylate-acrylic acid-copolymer increases with temperature increasing reaches 50 wt.% at about 260°C. This evaluated acrylic PSA was thermal stable to about 160°C. As thermal degradation were formed gaseous, liquid and insoluble pyrolysis products. Figure 32 shows the pyrolysis chromatogram of BA-MA-AA-copolymer.
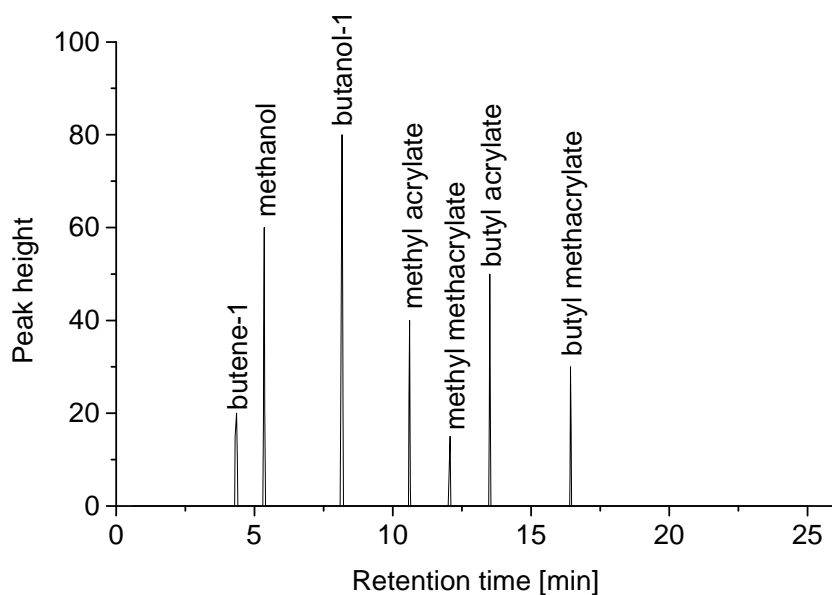
Figure 32 Pyrolysis chromatogram of PSA containing butyl-, methyl acrylate and acrylic acid

The pyrolysis chromatogram of evaluated acrylic PSA (Fig. 32) contains eight 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. An oily residue remained after the pyrolysis of BA-MA-AA-copolymer. This residue material no decolorized bromine water rapidly and gave an iodine number, while not reproducible, indicated a low degree of unsaturation. The residue became noticeably smaller at pyrolysis at higher temperatures. The decrease residue was associated with an increase in the methane peak on the pyrolysis chromatograms. Although no serious effort was made to determine the exact nature of the residue, chemical tests indicate a polyunsaturated chain residue from the acrylic polymer backbone (Figure 33).
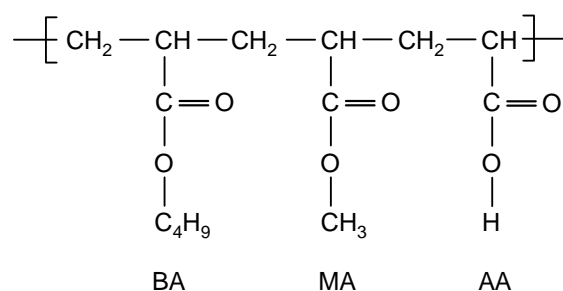
Figure 33 Acrylic PSA copolymer based on butyl acrylate, methyl acrylate and acrylic acid

The decomposition of simple side chain esters almost certainly occurs by way of a six-membered ring transition state, which for poly(alkyl acrylate) in the case of butyl acrylate component is represented in Figure 34.
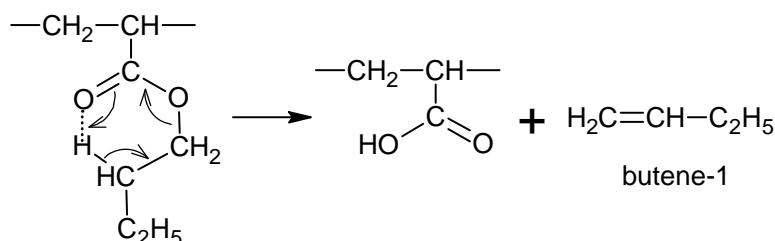
Figure 34 Formation of alkene butane-1 by pyrolysis of PSA containing butyl acrylate

The presence of a butane-1 peak in the pyrolysis chromatogram at higher pyrolysis temperatures is possibly due to thermal decomposition of acrylate groups in the side chain.

The pyrolysis behavior of acrylic is in good agreement with own 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 [81] (Figure 35), is further supported by the absence of water from the chromatogram at the used column.
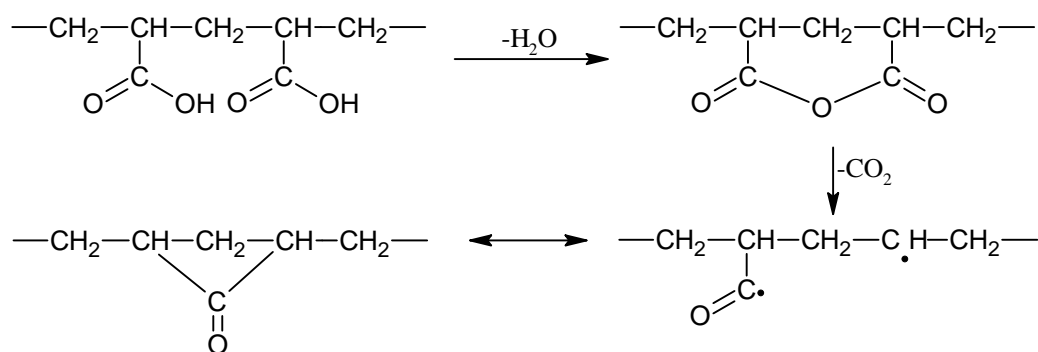
Figure 35 Thermal degradation of polymer containing carboxyl groups

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 dehydratation and decarboxylation are first order reactions, the latter being much slower than the former and found that water and carbon dioxide were the only volatile pyrolysis products in the range between 170 and 240°C. It is very important the competition between dehydratation and decarboxylation reactions.

Forming mechanism of methanol and butanol-1 in terms of the proportion of monomer units involved is illustrated in Figure 36.
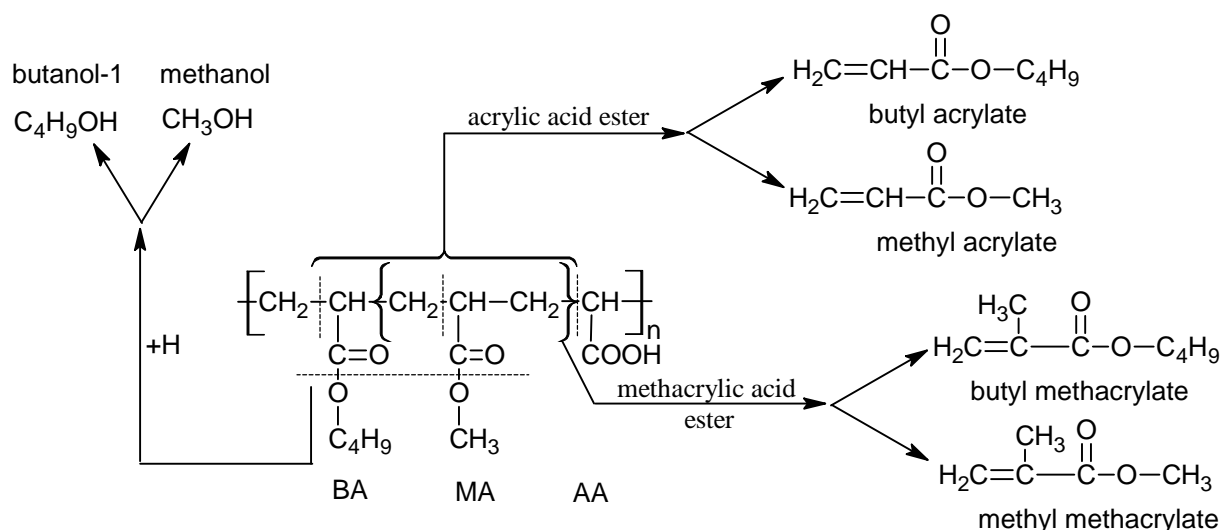
Figure 36 Forming of alcohols, acrylic and methacrylic monomers during the thermal degradation of selected acrylic PSA

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

The composition of the breakdown products of acrylic copolymers investigated was given at high temperatures, using a pyrolysis process. The characteristics of the production of olefins and alcohols corresponding to used acrylate monomers are quite different but even similar, so that one may reasonably presume that are formed in quite 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 in the gas phase formed alkoxyl radicals have a stability similar than 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.

The residual polymer becomes progressively more intensely colored as degradation proceeds. A comparable pyrolysis reaction of investigated copolymer would give methyl

acrylate and methacrylate and butyl acrylate and methacrylate. From evaluated BA-MA-AA copolymer, acrylates are formed in rather greater amount than methacrylates and probably arises by depropagation from an acrylate terminated polymer radical although this is known to be only a very minor reaction in acrylics.

5.7. Acrylic pressure-sensitive adhesive based on methyl, ethyl, butyl, 2-ethylhexyl acrylate and acrylic acid

For evaluation purposes the solvent-based acrylic PSA, which contains all of the investigated commercially important acrylates, such as methyl-, ethyl-, butyl- and 2-ethylhexyl acrylate in its structure, was synthesized using the same method as previous the radical polymerization with 0.1 wt.% AIBN as thermal radical initiator.

The synthesizes acrylic PSA was synthesized in ethyl acetate from monomers compositions containing: 40 wt.% butyl acrylate (BA), 35 wt.% 2-ethylhexyl acrylate (2-EHA), 10 wt.% ethyl acrylate (EA), 10 wt.% methyl acrylate (MA) and 5 wt.% acrylic acid (AA). The synthesized acrylic PSA is characterized by 50 wt.% polymer content, 0,26 wt.% residue monomers (0.02 wt.% MA, 0.04 wt.% EA, 0.08 wt.% BA and 0.12 wt.% 2-EHA) and viscosity of 5.7 Pa·s.

The most satisfactory conditions for pyrolysis of investigated acrylic polymers were a temperature of about 500°C for 30 seconds in a helium atmosphere. The expected pyrolysis products of evaluated acrylic copolymers were introduced using gas chromatograph Unicam 610 under following conditions:

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 pyrolysis apparatus was taken apart at the reduction union and a 5 mg acrylic polymer was placed in the bottom of the loop. The pyrolysis apparatus was reassembled and connected to the gas sampler valve in place of the constant volume tube. Plugs were placed in the regular sample inlet and in the vent openings of the gas sampler valve. Helium was used to flush the air from the apparatus and the system was closed. The loop of the apparatus was heated at 500°C for 30 second. Products resulting from the pyrolysis were swept into the gas chromatographic column with helium.

The identification and composition of the tested acrylic copolymers were determinate by comparison of the chromatogram of the sample with chromatograms of known pyrolysis products of synthesized acrylic copolymer with known composition (Figure 37).

Figure 37 Chromatogram of the pyrolyzates of investigated acrylic copolymer containing commercial alkyl acrylates and acrylic acid

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

individual polymers. The analyzed acrylic copolymer was identified as being composed of methyl acrylate, ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate.

Mechanism of formation of the above mentioned and established liquid breakdown products can be explain on the basis of the characteristic property and thermal resistance of typical acrylic copolymers (Figure 38).
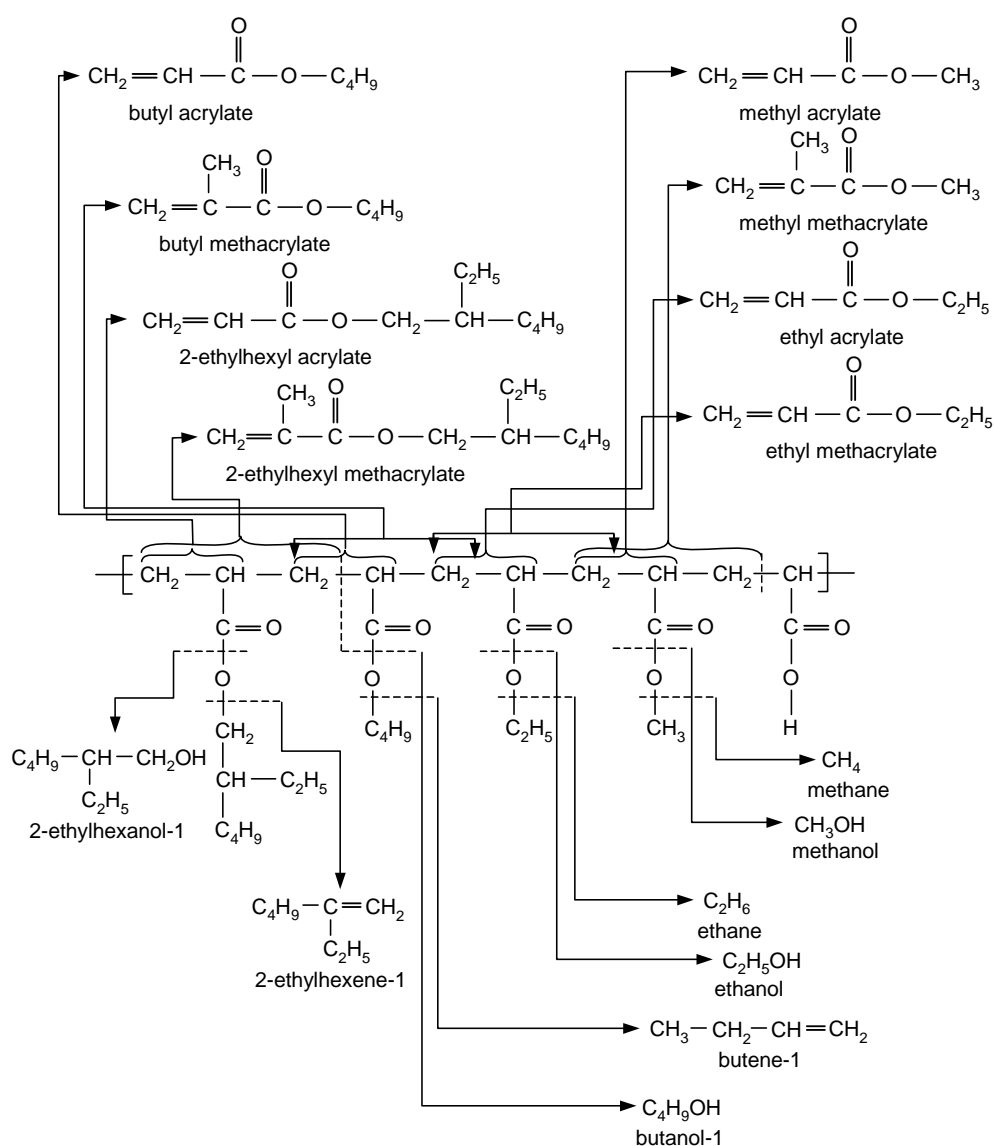
Figure 38 Formation of thermal degradation products during the pyrolysis of acrylic PSA based on typical commercially available acrylic monomers (2-EHA, BA, EA, MA)

Gas chromatography, coupled with a controlled temperature pyrolysis technique, provides a rapid method for the identification of acrylate and methacrylate copolymers. Small samples of the investigated copolymers are pyrolyzed and the pyrolyzate is fed directly into a gas chromatograph by the use of a gas sampling value. Chromatographing the complete pyrolyzate allows for the separation and identification of higher boiling substances, monomers and the same esters of acrylic and methacrylic acid.

Gas chromatography method can also be used for the semiquantitative determination of acrylate and methacrylate monomers in different mixture 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.

5.8.   Acrylic pressure-sensitive adhesives based on 2-propylheptyl acrylate and acrylic acid

5.9.   Determination of acrylic acid concentration in acrylic copolymers using pyrolysis and gas chromatography

Acrylic polymers or copolymers synthesized using acrylic acid have many excellent properties, especially exterior durability. Solvent-borne acrylic copolymers containing carboxylic groups from acrylic acid were used for automotive top coast. Their high solvent levels make possible brilliant metallic colors since they permit orientation of aluminum flake pigment in the films parallel to the surface. Acrylics polymers containing more than 40 wt.% acrylic acid are used directly or after special modification for water-soluble compositions. Poly(acrylic acid) prepared by chain-growth polymerization is known as a very efficient super absorber [86].

The pyrolysis of poly(acrylic acid) (PAA) and copolymers containing acrylic acid segments has been studied by several scientist over a number of years. In an early study, was recognized that water and carbon dioxide were major volatile pyrolysis products, with the initial degradation ensuing ca. 160°C [87]. Other scientist studied the degradation kinetics of PAA and concluded that anhydride bonding occurs mostly via an intramolecular route [88].

They observed, using a TGA technique, that dehydratation and decarboxylation are first order reactions, the latter being much slower than the former. The forming of anhydride structure increases glass transition temperature (T_g) of PAA. Fyfe and McKinnon found by investigations of PAA degradation that water and carbon dioxide were the only volatile breakdown products at pyrolysis temperature between 160 and 240°C [89]. McNeill and Sadeghi performed an extensive study of PAA degradation using thermal volatilization analysis and thermogravimetry. Appreciable decomposition was observed only above 175°C and dehydratation, decarboxylation and chain scission as three stages of thermal degradation were described. This was the first report naming acrylic acid monomer as a volatile degradation product, albeit only a "trace" amount was detected [90]. Barlow, Lehrle and Robb found water by thermal degradation of poly(vinyl alcohol), however at high temperatures at about 500°C [91].

Acrylic polymer characterization using thermal analysis and chromatography (GC) are currently some of the most dynamic fields in applied research. A major segment of GC applications to acrylic polymer analysis has developed even in the area of analytical pyrolysis for characterization of thermal resistance and composition of synthesized acrylic polymers, usually in form of gaseous and liquid products [92].

From the practical and technological point of view it was be important the connection to evaluate the influence of carboxyl groups content into polymer chain on the composition of resulted breakdown pyrolysis products. Especially through measuring of water amount the possibility of acrylic acid concentration determinate in acrylic copolymers containing carboxylic groups was investigated.

By the thermal degradation of acrylic polymers containing carboxylic groups from acrylic acid arises among other things water as by-product and an anhydride formation into polymer backbone [93] (Figure 45).
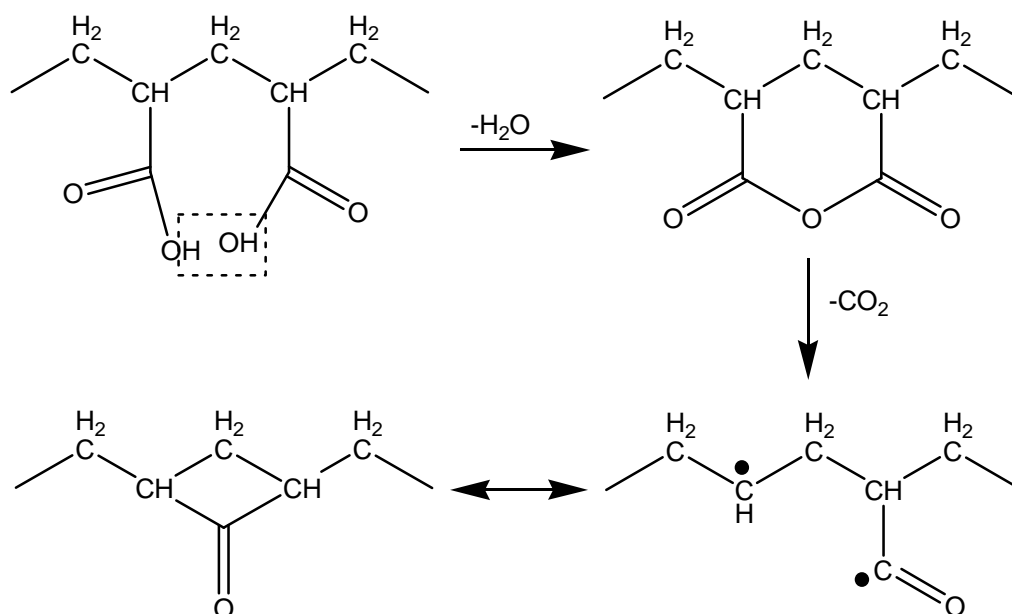
Figure 45 Anhydride formation by thermal degradation of acrylic polymers containing carboxylic groups with elimination of water

The gas chromatography, coupled with a controlled temperature pyrolysis technique, provides interesting method for the measurement of acrylic acid concentration into acrylic copolymers. Incorporation of acrylic acid during the polymerization into an acrylic polymer chain does not problems with the controlling of resulted compositions. Water from acrylic acid by forming of anhydride structures at higher temperatures can be as pyrolysis product completely determinate using of a Karl Fisher titration and correlated with acrylic acid concentration in synthesized acrylic copolymers. This method allows the adoption of this new procedure combined with water Karl Fisher titration for exactly determinate of acrylic acid concentration in unknown carboxylated polymers.

5.10.   Thermal degradation of poly(alkyl methacrylates)

The special group of acrylic resins, namely poly(alkyl methacrylates) are attractive and important specialty polymers. They are very interesting for adhesive applications, characterized by excellent compatibility with acrylic and methacrylic polymers and with wide range of other polymers. They can be used especially for modification of aqueous acrylic and methacrylic dispersions. These polymers display several unique properties, such as extremely good weather and aging resistance, non yellowing properties, low permeability of oxygen, and

good plasticizers resistance. Their major advantages are photostability and resistance to hydrolysis [94].

The thermal behavior of acrylics and also acrylic copolymers has been the target of some reports [95-97]. Investigation of thermal behavior and thermal decomposition of poly(alkyl methacrylates) are relevant to the study of deterioration of materials properties during high-temperature processing. For this purpose, the thermal properties and decomposition of poly(alkyl methacrylates) have been investigated by pyrolysis–gas chromatography (PGC) techniques. PGC has been used extensively to determine the chemical structure resistance as a function of temperature increasing, especially by thermal degradation. Thermal decomposition of methacrylic polymers is relevant to deterioration of polymers properties during high-temperature processing [98]. The use of pyrolysis-based analytical techniques and pyrolytic methods to recover chemical feedstock from polymer waste are also of interest.

The polymerization trials of 95 wt.% methyl acrylate, ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate as copolymers with 5 wt.% acrylic acid were conducted as solvent-borne polymers in organic solvent ethyl acetate at 77°C in nitrogen atmosphere in the presence of 0.1 wt.% 2,2'-azo-bis-diisobutyronitrile (AIBN) according to polymerized monomer as a thermal initiator to start radical polymerization with 1 h dosage time of monomer by 3 h post-reaction and with 50 wt.% polymer content. The synthesized methacrylic copolymers were characterized by viscosity, weight average molecular weight ($\overline{M}_w$), number average molecular weight ($\overline{M}_n$), and polydispersity (P_d) (Table 11).

Table 11 Molecular weight and viscosity of synthesized methacrylic copolymers

Copolymer	Viscosity [Pa·s]	$\overline{M}_w$ [Dalton]	$\overline{M}_n$ [Dalton]	$P_d = \dfrac{\overline{M}_w}{\overline{M}_n}$
methyl methacrylate/acrylic acid	8.8	875 600	280 600	3.12
ethyl methacrylate/acrylic acid	8.0	798 000	212 800	3.75
butyl methacrylate/acrylic acid	7.4	723 800	168 000	4.31
2-ethylhexyl methacrylate/acrylic acid	6.5	643 700	141 500	4.55

As results of polymerization of selected alkyl methacrylates, such as methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA) and 2-ethylhexyl methacrylate (2-EHMA) with acrylic acid were received copolymers characterized by low concentration of residue free monomers < 0.3 wt.%, exactly in the case of MMA (0.09 wt.%), EMA (0.12 wt.%), BMA (0.19 wt.%) and for 2-EHMA (0.23 wt.%), and polymer content of 49.8 wt.%.

The synthesized solvent-borne poly(alkyl methacrylates) were dried 10 min at 110°C in drying canal and after drying as polymer films pyrolyzed. The formed pyrolysis-products were investigated using gas chromatography.

The quantitative and qualitative analyses were conducted by using of the following gas chromatography methods:

The determination of liquid products were conducted with an external standard method and following analytical conditions: gas chromatograph ThermoScientific GC8000^{Top}, capillary column–RESTEK RTX-5 30m ^{x} 0.53mm, 1.5µm film, carrier gas–He 5cm^3/min, detector temperature (FID)–300°C, injector temperature–280°C (split 1:2), oven–temperature program–45°C (4min) to 320°C at 10°C/min.

The determination of gaseous products were conducted with an external standard method and following analytical conditions: gas chromatograph ThermoScientific TraceUltra micropacked column–ShinCarbon ST 100/120, 1m, 0.95mm, carrier gas–He 8cm^3/min, detector temperature (TCD)–200°C, injector temperature–100°C, oven–temperature program–45°C (10min) to 250°C at 10°C/min.

The breakdown products from poly(alkyl methacrylates) between 300°C and 800°C are summarized in Tables 12-15, which also shows the concentration of the breakdown products but now in a different temperature range. At lower temperatures, the polymers degrade nearly completely to the monomers alkyl methacrylates, alcohols and gases (carbon dioxide, carbon monoxide, methane and later ethane) appear only in small quantities. At higher temperatures, the alkyl methacrylates concentration decreases slowly, while the gas component content simultaneously increases.

Table 12 Composition of breakdown products from investigated poly(methyl methacylate)

Pyrolysis	Pyrolysis temperature

products	[°C]					
	300	400	500	600	700	800
	Weight per cent of original methacrylic polymer					
Carbon dioxide	-	0.7	1.0	3.3	20.3	21.4
Carbon monoxide	-	0.7	1.0	3.6	19.6	20.1
Methane	-	0.3	1.6	3.3	15.9	16.7
Ethane	-	-	0.3	0.6	0.9	1.5
Methyl methacrylate	99.7	96.6	92.1	80.3	20.8	11.8
Methanol	-	-	0.4	0.6	2.1	3.4
Ethanol	-	0.7	1.0	2.1	6.2	6.1
Propanol	-	0.6	1.1	2.3	5.9	5.8

Table 13 Composition of breakdown products from investigated poly(ethyl methacylate)

Pyrolysis products	Pyrolysis temperature [°C]					
	300	400	500	600	700	800
	Weight per cent of original methacrylic polymer					
Carbon dioxide	0.4	0.8	1.4	6.0	22.6	23.1
Carbon monoxide	0.6	1.2	1.6	5.4	22.2	22.0
Methane	-	0.7	2.2	4.0	16.2	17.2
Ethane	-	-	0.3	0.6	0.8	1.6
Ethyl methacrylate	98.3	94.1	86.0	71.2	13.6	8.6
Methanol	-	-	0.3	0.8	2.6	3.3
Ethanol	0.3	1.5	2.2	4.0	6.0	6.0
Propanol	-	1.3	2.0	4.0	5.8	6.0

Table 14 Composition of breakdown products from investigated poly(butyl methacylate)

Pyrolysis products	Pyrolysis temperature [°C]					
	300	400	500	600	700	800
	Weight per cent of original methacrylic polymer					
Carbon dioxide	0.5	1.2	4.0	7.8	23.5	24.5
Carbon monoxide	0.7	1.8	4.3	6.9	22.5	22.5
Methane	-	0.8	3.0	5.8	20.5	20.5
Ethane	-	-	0.5	0.8	1.0	2.0
Butyl methacrylate	97.5	92.0	80.9	63.8	7.7	-
Methanol	-	-	0.5	1.0	3.0	3.5
Ethanol	0.5	1.8	3.0	5.0	7.0	8.0
Propanol	0.4	1.8	2.8	5.0	6.0	6.5

Between 600°C and 700°C, however, the alkyl methacrylates amount drops sharply from about between 60 % (2-ethylhexyl methacrylate) and 80 % (methyl methacrylate) to about accordingly 5-20 %. At the same time the concentration of gases increases very sharply (Figs. 46-49). The content of alcohols shows a nearly continuous increase up to 600°C; above 800°C; however, they completely disappear. Probable, the pyrolysis products above 900°C are composed only of gases.

Table 15 Composition of breakdown products from investigated poly(2-ethylhexyl methacrylate)

Pyrolysis products	Pyrolysis temperature [°C]					
	300	400	500	600	700	800
	Weight per cent of original methacrylic polymer					
Carbon dioxide	1.5	2.1	6.2	8.6	24.7	25.6
Carbon monoxide	1.7	2.4	6.5	8.2	23.0	23.1
Methane	0.4	1.2	4.3	7.1	20.3	20.5
Ethane	-	0.3	0.8	0.9	1.5	2.2
2-Ethylhexyl methacrylate	94.7	88.7	70.4	58.7	5.2	-
Methanol	-	-	0.8	1.7	3.7	4.1
Ethanol	1.1	2.8	3.7	5.3	6.4	8.5

Propanol	0.5	1.9	3.1	5.2	5.9	6.9

To illustrate this effect, in Figures 46-49 the amount of gases, monomer alkyl methacrylate and alcohols is plotted as a function of temperature.
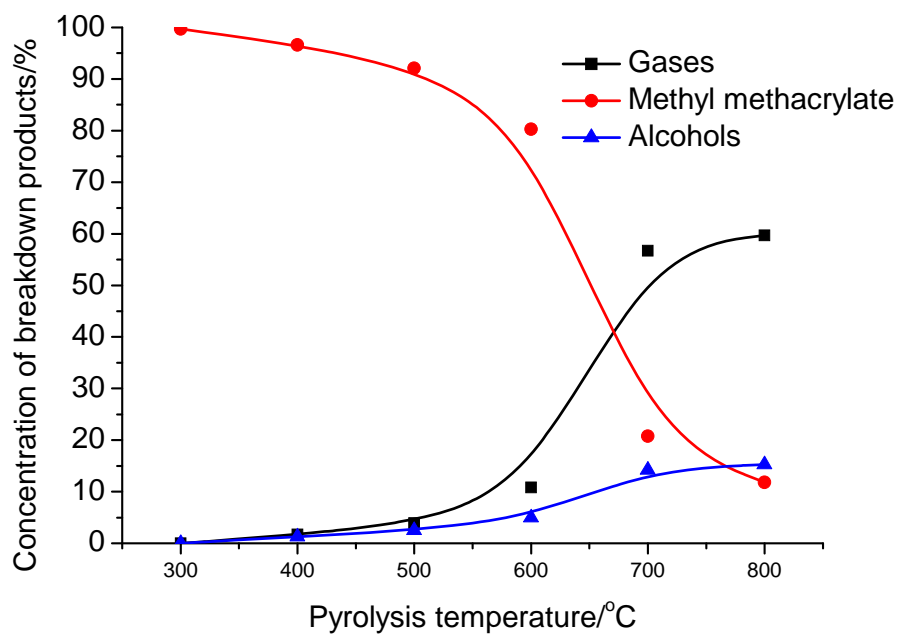
Figure 46 Breakdown products during the pyrolysis of poly(methyl methacrylate)
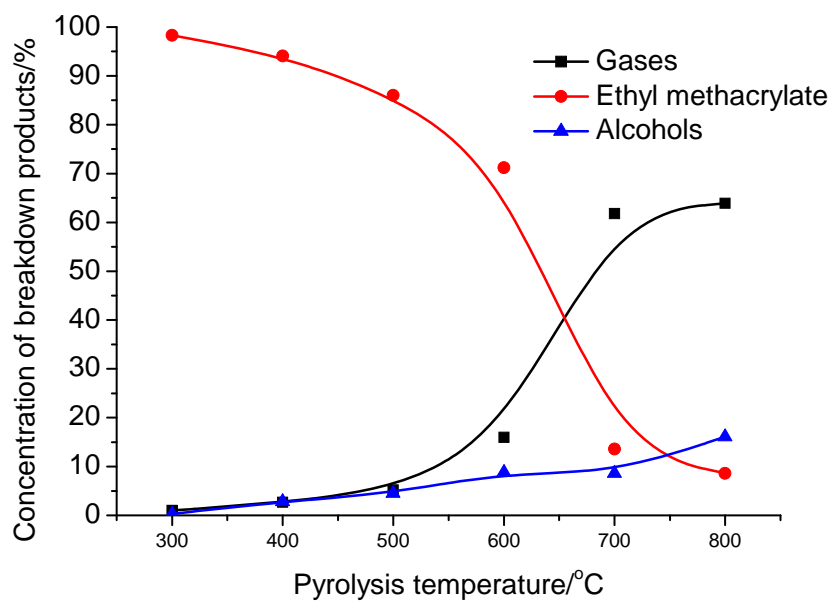
Figure 47 Breakdown products during the pyrolysis of poly(ethyl methacrylate)
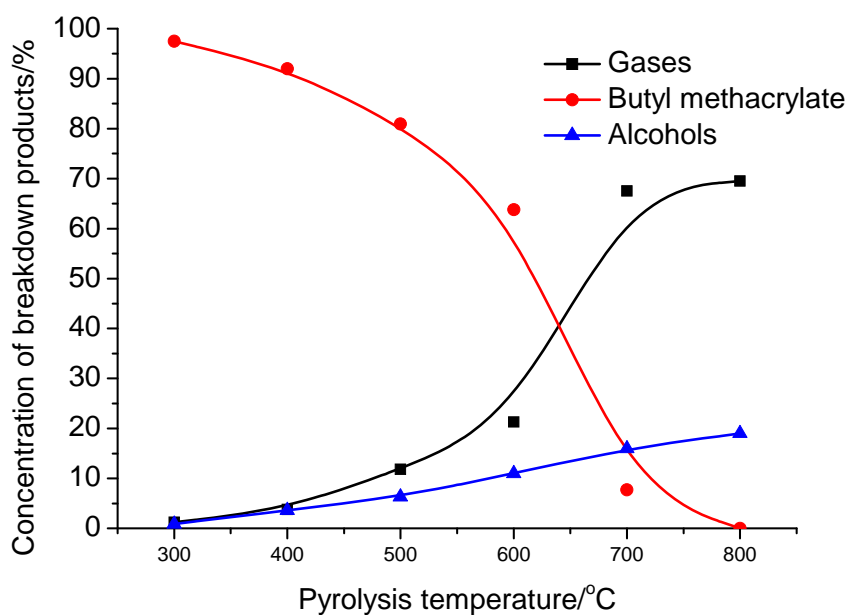
Figure 48 Breakdown products during the pyrolysis of poly(butyl methacrylate)
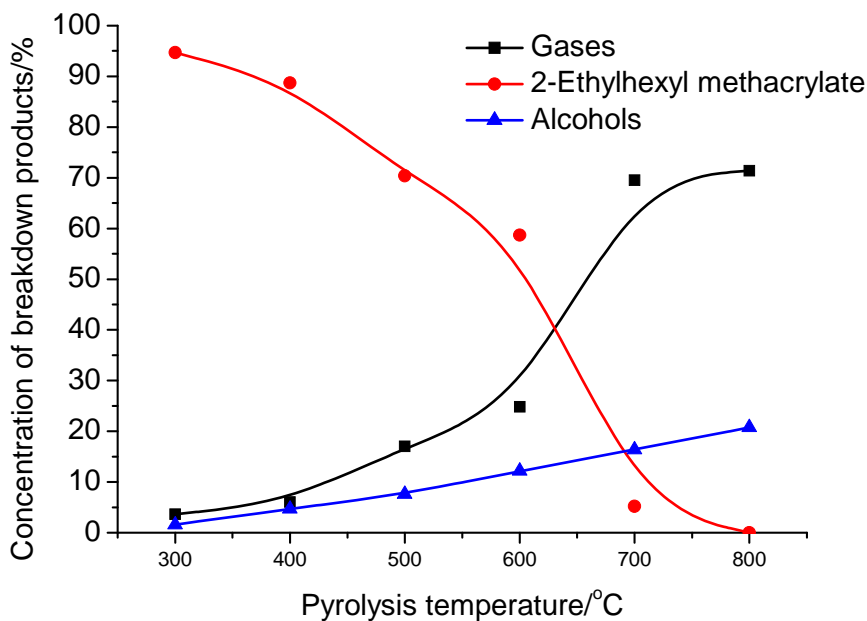
Figure 49 Breakdown products during the pyrolysis of poly(2-ethylhexyl methacrylate)

In discussing the process thermal degradation of poly(alkyl methacrylates), it should be emphasized that it is a complex multistage process. It consists of a series of consecutive and simultaneous reactions of initiation, depolymerization, scission of the side- and the chain of macromolecules, chain termination, recombination etc. The process of diffusion of

degradation products throughout the sample also plays an important role. The most important of these factors are the degradations conditions, which include temperature, heating rate, the atmosphere in which the process occurs.

Figures 50-52 show the influence of pyrolysis temperature on major thermal breakdown products, such as gases (Figure 50), monomers alkyl methacrylates (Figure 51) and alcohols (Figure 52) during the thermal degradation of poly(alkyl methacrylates) based on monomers with different length of alkyl rest.
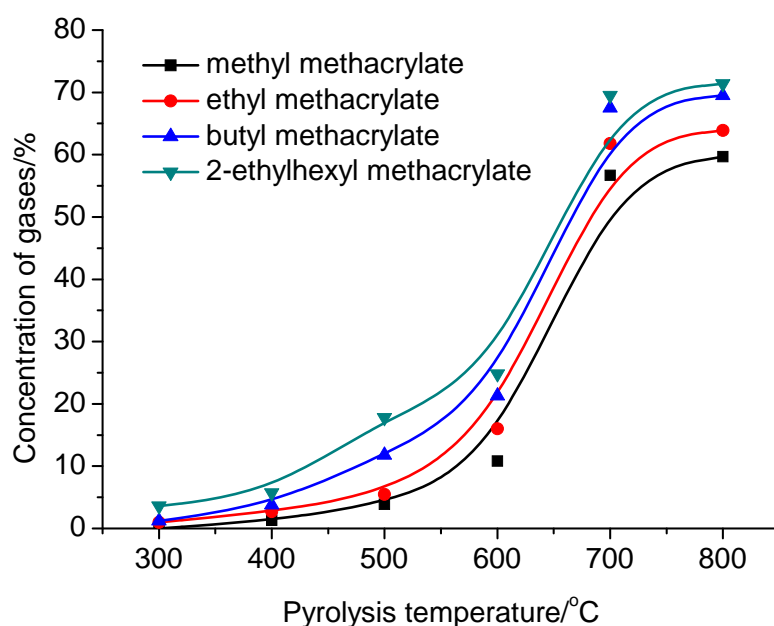
Figure 50 Influence of pyrolysis temperature on gases products yield during degradation of poly(alkyl methacrylates)
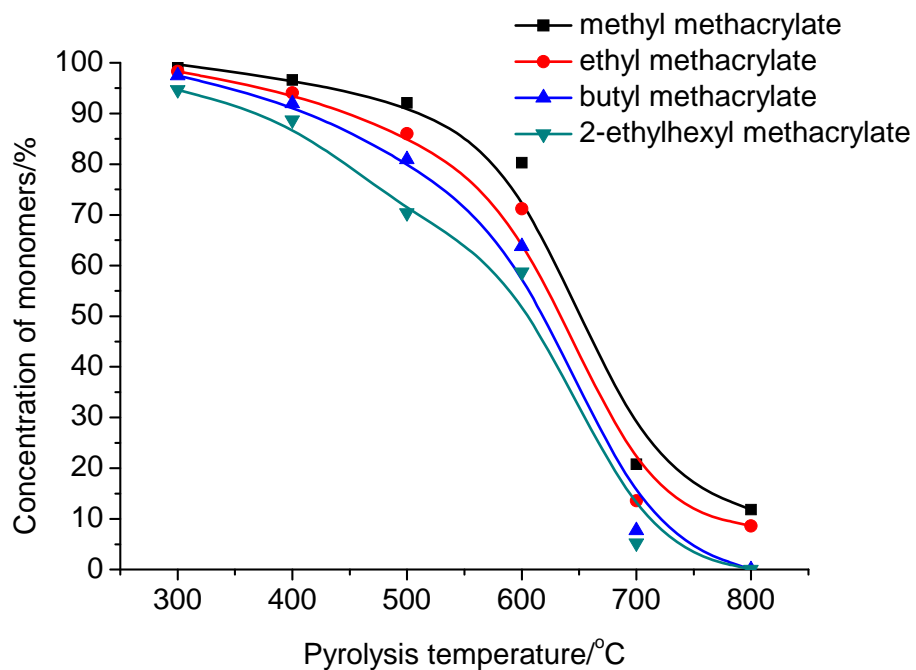
Figure 51 Influence of pyrolysis temperature on monomers yield during degradation of poly(alkyl methacrylates)
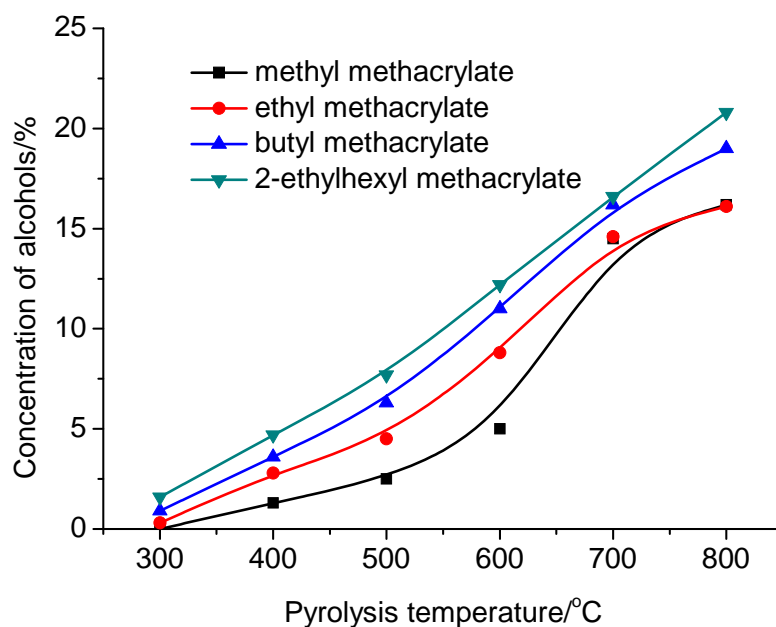
Figure 52 Influence of pyrolysis temperature on alcohols yield during degradation of poly(alkyl methacrylates)

The major breakdown products from thermal degradation of poly(alkyl methacrylates) are gases containing carbon dioxide, carbon monoxide, methane and ethane, alkyl acrylates as accordingly monomers and alcohols mixture containing methanol, ethanol and propanol (Tables 12-15). It has been not observed the formation of typical breakdown products typically for poly(alkyl acrylates), such as alkenes, accordingly alcohols and acrylates. As regards the influence of temperature on the product distribution, high pyrolysis temperatures lead to increased amounts of typically products coming from thermal cracking reaction, such as carbon dioxide, carbon monoxide, methane, ethane, methanol, ethanol and propanol. The gases and alcohol yields increase with an increase of the pyrolysis temperature because the decarboxylation of the polymer chain accelerates at high temperatures.

The evolution of the major breakdown product during the thermal degradation of poly(alkyl methacrylates), namely the accordingly monomers alkyl methacrylates is illustrated in Figure 53.
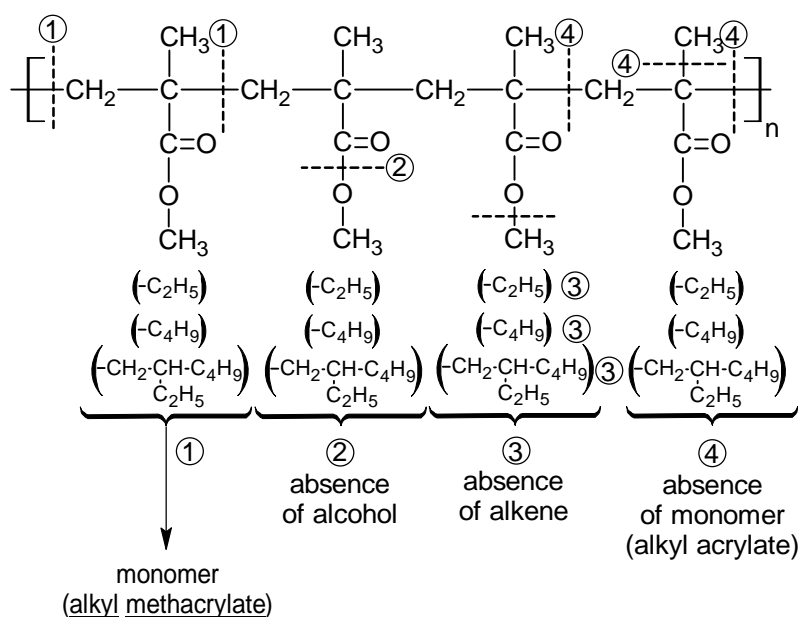
Figure 53 Thermal degradation mechanism of poly(alkyl methacrylates)

The principal degradation products of poly(alkyl methacrylates) are accordingly monomers used in polymerization process, and in the temperature range of interest the amount of the monomer formed (only methacrylates) according to process ① is very dependent upon the pyrolysis temperature. The concentration of monomers was measured at different pyrolysis temperatures between 300°C and 800°C. Figure 53, which is the result of the present investigations, clearly shows that this concentration corresponds directly with kind

of degraded polymers and pyrolysis temperature. From the quantitative results, it is possible to observe the effect of monomer yields, depending on the number of carbon atom in the alkyl side chain. The concentrations of monomers for short alkyl side chain (methyl, ethyl) were higher than for monomers from long side chain (butyl, 2-ethylhexyl). The longer alkyl side chain in the poly(alkyl methacrylates) the less monomers were formed during the pyrolysis. This mechanism of thermal degradation presented in Figure 8 supports the absence of alkenes, accordingly alcohols and monomers alkyl acrylates, what excludes the pyrolysis mechanisms ②, ③ and ④. During cracking reactions, especially at higher temperatures, are formed gases products and mixture of low molecular alcohols.

These present investigations give the all-round picture of thermal degradation of poly(alkyl methacrylates) in the wide range of high temperatures and suggest simple degradation mechanism providing a satisfactory explanation for the formation of major breakdown products, namely accordingly alkyl methacrylates, such as metyl methacrylate, ethyl methacrylate, butyl methacrylate and 2-ethylhexyl methacrylate. Poly(alkyl methacrylates) undergo thermal degradation at high temperatures includes main chain scission. The concurrent reactions by the investigated conditions do not give rise to the formation of accordingly alkenes, acrylates or alcohols. The increase of pyrolysis temperature leads to higher yields of products coming from main and side chains at cracking temperatures, such as carbon dioxide, carbon monoxide, methane, ethane or low molecular alcohols. Poly(alkyl methacrylates) produce during thermal degradation monomer methacrylates as the predominant breakdown product in all tested pyrolysis conditions.

5.11. Catalogue preparing of products possible to form during pyrolysis

In order to begin with the investigations on the pyrolysis' products of the synthesized model pressure-sensitive adhesives the catalogue of products possible to form during pyrolysis was prepared, based on the previous investigations in the field of pyrolysis in West Pomeranian University of Technology in Szczecin. The catalogue containing retention time from usually available and important monomers for PSA technology was prepared for farther investigation on the area of thermal degradation of self-adhesive materials. It was made using gas chromatography method by injecting expected substance to the same apparatus and temperature program as further research on the pyrolysis' products. The most important for

this work monomers and thermal degradation by-products, and their retention times are listed in Table 16.

Table 16 Possible thermal degradation products and their retention times

Thermal degradation product	Retention time
Carbon oxide	1 min 30 s
Methane	2 min 12 s
Isopropanol	2 min 20 s
Butene-1	3 min 42 s
Carbon dioxide	4 min
Methanol	5 min 40 s
Ethanol	6 min
2-Ethylhexene-1	6 min 50 s
Ethane	7 min
Butanol-1	8 min 10 s
Methyl acrylate	10 min 20 s
Ethyl acrylate	11 min 12 s
Methyl methacrylate	12 min 12 s
Ethyl methacrylate	12 min 54 s
2-Ethylhexanol-1	13 min 20 s
Butyl acrylate	13 min 41 s
Butyl methacrylate	15 min 40 s
2-Ethylhexyl acrylate	17 min
2-Ethylhexyl methacrylate	17 min 33 s

5.12. Investigations of pyrolysis process (temperature, type of column) on the quality and quantity (composition) of products of thermal degradation of acrylic polymers

Investigations on the thermal degradation of poly(alkyl acrylates) were performed using a pyrolysis gas chromatography with the use of Intersmat IGC 131 chromatograph with capillary column (QC2/BP1) 25 m x 0,25 mm (100% dimethyl polysiloxane). Helium (80 kPa) as carrier gas was used. Pyrolysis conditions: detector FID

- 250°C, feeder temperature - 250°C, oven temperature program – from 50°C to 230°C with increment 10°C/min (32 min), sample volume – 0,3 µl.

The products of the pyrolysis were swept into chromatograph column with nitrogen. The composition of the polymeric composition was determined by comparison of chromatogram of the sample with the chromatograms of known monomers and pyrolyzates of known polymers.

The analysis of gaseous products was conducted using a isochoric manometer coupled with infra-red spectroscopy as was described in [99].

Additionally an on-line pyrolysis of selected PSA (95% weight of 2-ethylhexylacrylate and 5% weight acrylic acid) was conducted at temperature 350°C directly in ThermoElectron Trace GC Ultra chromatograph (Figure 54) with the special tip of own design as pyrolyzer (Figure 55) and the pyrolyzates were detected by FID.
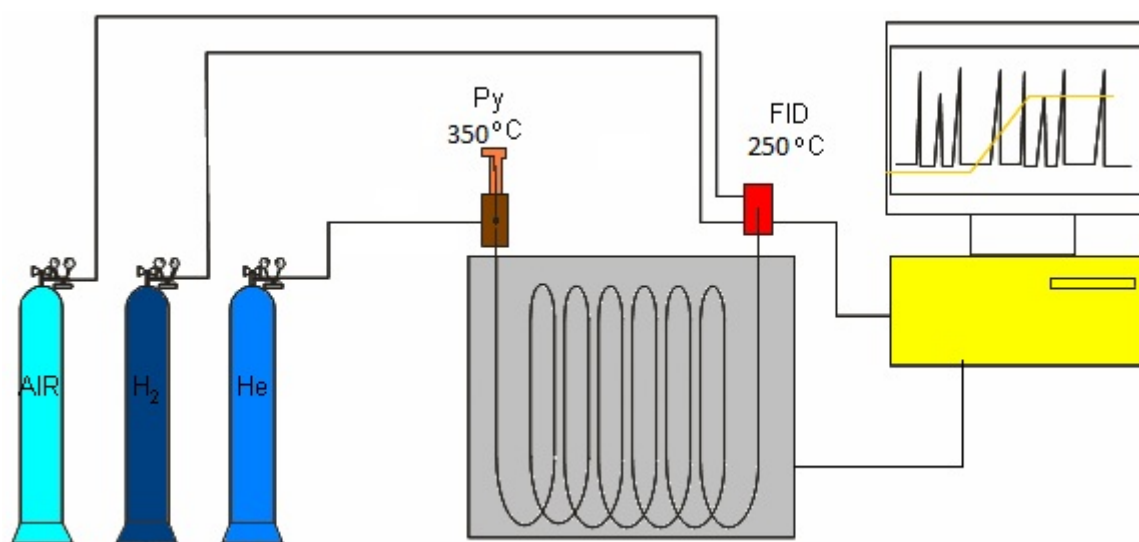
Figure 54 Apparatus for on-line pyrolysis

1. Screw with clamping spring
2. Gasket
3. Clamping ring
4. Gasket's support
5. Insert's cover
6. Insert's graphitoidal packing
7. Quartzinsert
8. Nut with packing supporting glass rod with sample
9. Glass rod
10. Sample insertion line
11. Radiator
12. Sample
13. Glass wool
14. Calmping nut
15. Column's packing
16. Column
17. Nut
18. Heating elements
A – Carrier's gas inlet
B – Blow through line
C – Split stream line

Figure 55 Detailed scheme of the pyrolyzer

For the composition of PSA based on butyl acrylate (95% weight) and acrylic acid (5% weight) another on-line pyrolysis was conducted at temperature 250°C directly in ThermoElectron Trace GC Ultra chromatograph (Figure 54) with the special tip of own design as pyrolyzer (Figure 55) and the pyrolyzates were detected by FID.

For the investigations on thermal stability pyrolysis gas chromatography and pyrolysis gas chromatography coupled with mass spectrometry was also used with following conditions: Unicam 610, capillary column – (QC2/BP1) 25 m x 0,25 mm (100 % dimethyl polysiloxane), carrier gas – He 80 kPa, detector FID – 250°C, feeder temperature – 250°C, oven – program temperature – 50°C (0 min) to 230°C with increment 10°C/min (32 min), sample – 0,3 µl.

For the composition of acrylic PSA (synthesized as it was described in chapter 5.7), which contains all of the investigated acrylates (methyl, ethyl, butyl and 2-ethylhexyl) in its structure on-line pyrolysis was conducted with following conditions: Unicam 610 chromatograph, capillary column – (QC2/BP1) 25 m x 0,25 mm (100 % dimethyl polysiloxane), carrier gas – He 80 kPa, detector FID – 250°C, feeder temperature – 400°C, oven –program temperature – 50°C (0 min) to 230°C with increment 10°C/min (32 min), sample – 0,3 µl. Time of pyrolysis (heating the sample) was 30 seconds.

The pyrolysis processes of poly(alkyl methacrylates described in 5.10) were conducted in a quartz flask with 5 g samples and were heated to demanded temperature in electric furnace. The flask was connected with condenser, where liquid products of pyrolysis were

educed. These products were collected in a tank under condenser. The tank was equipped with a bottom outlet valve which enabled sampling of the condensate. The outlet of the condenser was closed with a hydraulic valve, which enabled collecting gas samples. On the top of the column a membrane was placed in order to sampling gaseous products of pyrolysis.

The products of the pyrolysis were analyzed by gas chromatography method. Liquid products of the pyrolysis were determined by internal standard method. As a internal standard 1-bromonaphtalene was used. Determination of these products were conducted on a gas chromatograph ThermoScientific GC8000^{Top} with following conditions: capillary column – RESTEX RTX-5 30 m, 0,53 mm, 1,5 µm film, carrier gas – helium (50 kPa), detector – FID, oven - temperature program: 45ºC (4 min) increment 10ºC/min to 320ºC.

Gaseous products were analyzed with the use of gas chromatography method using external standard method. Determination of these products were conducted on a gas chromatograph ThermoScientific TraceUltra with following conditions: capillary column – RESTEX RT-Q-BOND 30 m, 0,53 mm, 1,5 µm film, carrier gas – helium (50 cm^3/min), detector – FID, oven - temperature program: 50ºC (5 min) increment 10ºC/min to 280ºC.

6. Possibilities of using pyrolysis as a method of utilization of waste acrylic pressure-sensitive adhesives.

Acrylic adhesives, especially acrylic pressure-sensitive adhesives (PSAs), are used mainly to produce many materials with self-adhesive properties in room temperature and higher temperatures. These materials are produced in form of double-, single-sided as well as carrier-free pressure-sensitive adhesive tapes (films) used to bond variety of materials with themselves. There are many other applications of acrylic adhesives such as: labels, adhesive tapes, sticking plasters, electrodes and bioelectrodes, hydrogels and wide gamut of adhesives products activated thermally. Acrylic adhesives exhibit very good thermal resistance in temperature range about 140-160°C. Prolonged heating of acrylic PSAs over 160-180°C leads to first signs of thermal degradation. Above 180°C they occur slow thermal decomposition, which undergo violent acceleration after exceeding 220-240°C. In temperatures above 440°C acrylic adhesives undergo pyrolysis very easily giving specific gaseous, liquid and solid products of thermal degradation [99].

The pyrolysis of polymers is used recently in utilization of waste and to recover precious organic raw materials. These substances, especially liquid products of thermal degradation of polymers, are separate using distillation and utilize again in processes of

polymer technology and other organic technologies. The investigations on the use of pyrolysis for the identification of the composition of acrylic pressure-sensitive adhesives lead to develop a system for waste management of polymer waste formed during production, coating or application acrylic adhesives. The system bases on utilizing controlled pyrolysis method, which is thermal degradation of waste acrylic adhesives in elevated temperatures in order to obtain and recover liquid products such as: primary alcohols, acrylates, methacrylates and olefins. The separation of these products is possible using distillation and freezing out light gaseous products. Recovered organic products can be successfully reprocessed in polymer technology.

The method for disposal the waste acrylic adhesives consists in thermal decomposition in pyrolysis furnace and in the next stage separation of pyrolysis products. The pyrolysis of the adhesive is conducted in the furnace heated with electric current or in furnace heated with combustion gases of a temperature about 250-500°C [29]. For increase intensification of the process the solid and rotary furnace were applied.

The scheme of the system for pyrolysis integrated with fractionation of the products in solid furnace is shown in Figure 56.

Figure 56 System for pyrolysis integrated fractionation of the products of the pyrolysis:

1 – pyrolysis furnace, 2 – liquid products tanker, 3 – condenser, 4 – liquid products distillation-rectiyfing column, 5 – reflux tanker, 6 – condenser, 7 – gaseous products cold trap, 8 – carbon dioxide absorber, 9 – vacuum pump, 10 – fraction collector, 11 – electrical heater feeder and temperature regulator, 12 – oxide cylinder, 13 – gaseous heater, 14 – exhaust gases outlet, 15 – distillation residue forcing through pump.

The scheme of the system for pyrolysis integrated with fractionation of the products in rotary furnace is shown in Figure 57.
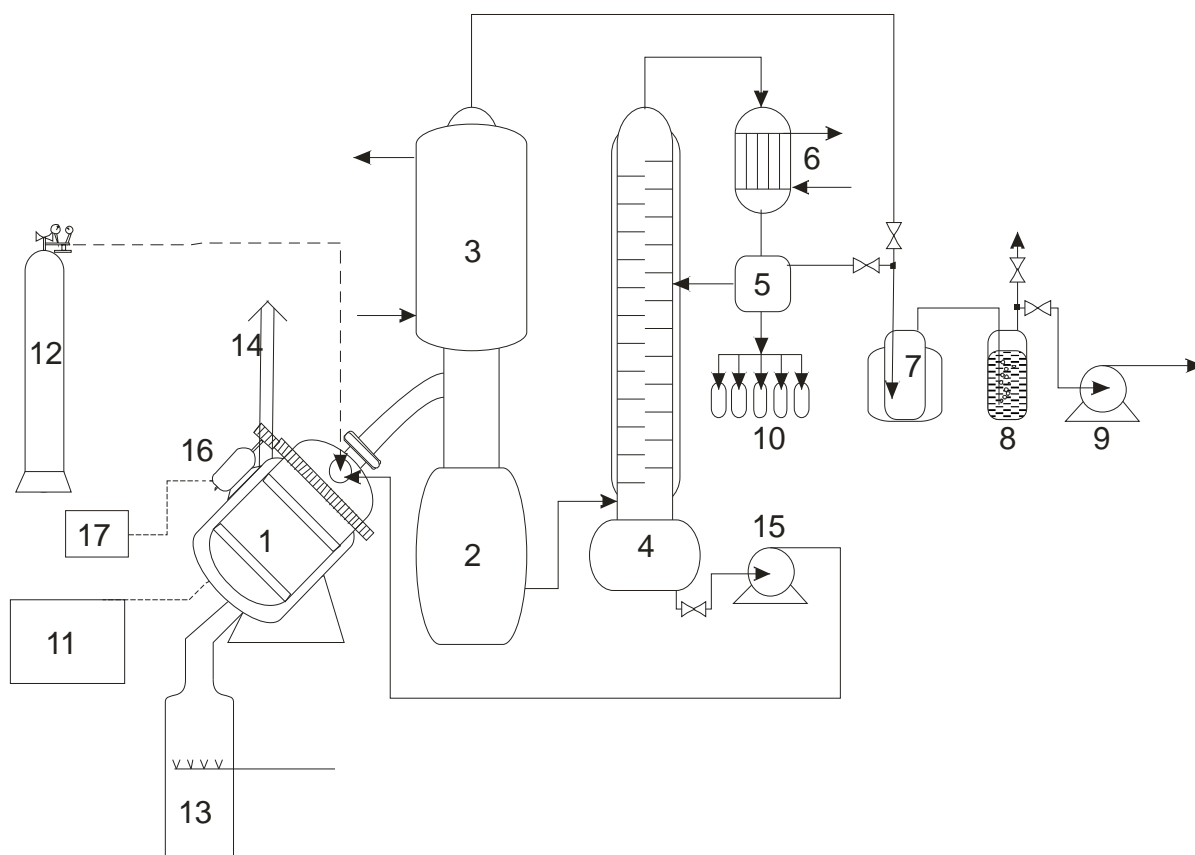
Figure 57 System for pyrolysis integrated fractionation of the products of the pyrolysis:
1 – pyrolysis furnace, 2 – liquid products tanker, 3 – condenser, 4 – liquid products distillation-rectifying column, 5 – reflux tanker, 6 – condenser, 7 – gaseous products cold trap, 8 – carbon dioxide absorber, 9 – vacuum pump, 10 – fraction collector, 11 – electrical heater feeder and temperature regulator, 12 – oxide cylinder, 13 – gaseous heater, 14 – exhaust gases outlet, 15 – distillation residue forcing through pump, 16 – motor, 17 – control and supply of the power feed

The pyrolysis process is conducted periodically. Collected waste of acrylic adhesives are placed in pyrolysis furnace 1. The pyrolysis furnace is heated using electric current feeded from regulator 11. To lower the price of the process heating with combustion gases, derived from combusting of natural gas or products of pyrolysis, could be used. The temperature of the combustion gases should be in range 450 – 650°C. After loading the furnace and starting heating the content of the furnace is heated to temperature 350 – 450°C. At this temperature the content of the furnace give in to pyrolytic decomposition. The acrylic adhesives give in to thermal degradation mainly in the course of main chain depolymerization and side chain thermal degradation in the course of alcohols forming the acrylate and olefins formed as a result of alcohols dehydration. The pyrolysis products in the form of gases are sent to condenser 3 and there are condensed. Liquefied pyrolyzate is collected in tanker 2 placed under the condenser. In the case of pyrolysis adhesives based on acrylates of small molecular alcohols such as ethanol, butanol during pyrolysis gaseous products in form of olefins such as ethylene and butane are formed. These products, after passing through the condenser 3, are freezed out in a cold trap 7. A portion of olefins dissolve in higher boiling products of the pyrolysis. They can be removed directly from the condensate tanker 2 with stripping under diminished pressure with the use of vacuum pump 9. Carbon dioxide, which is formed during pyrolysis, is captured in the absorber placed before vacuum pump. As a absorber a packed column (for example with Raschig rings) is applied sprinkled with aqueous solution of NaOH or KOH with the concentration about 1 – 30 %, depending on the adhesive, or scrubber filled with these solutions. After finishing the pyrolysis (no more drops of the condensate in condenser 3) the collected condensate is sent to distillation-rectifying column 4. In this column the fractionation of the pyrolyzate components is proceeding. The components of the pyrolyzate are collected in the fraction collector 10. Additionally using the vacuum pump the residual light olefins are stripped and freezed out. Distillation residue in the form of dark viscous liquid consisted of mainly higher molecular products of the pyrolysis can be recirculated to pyrolysis furnace and use with the next furnace feed.

The acrylic pressure-sensitive adhesives used in the research were based on butyl acrylate with average weight molecular mass 500 000 D (example 1 and 3) and 250 000 D (example 2 and 4). The research was conducted in the system for pyrolysis integrated with fractionation of the products in solid furnace as well as in rotary furnace. The acrylic PSAs were loaded in the furnace. The temperature of the furnace was set to 450°C. The process was conducted in solid furnace (example 1 and 2) and rotary furnace (example 3 and 4). The results of the pyrolysis are presented in Table 17 and Table 18.

Table 17 The amounts of the pyrolysis products in solid furnace

Example	Furnace feed [g]	Condensate [g]	Residual [g]	Absorbed CO_2 [g]
1	160	140	14	3
2	160	142	9	3

Table 18 Conditions of the pyrolysis of acrylic PSA

Example	Time needed to obtain temperature of the pyrolysis (400°C) [min]	Time of the pyrolysis [min]
1	15	90
2	15	90
3	8	60
4	9	60

After fractional distillation the products of the pyrolysis were analyzed using gas chromatography. After fractional distillation the amounts of the obtained products from solid furnace are as follows:

Example 1: 58 g butyl acrylate, 34 g butanol, 22 g butyl methacrylate, 12 g butane and 8 g of water.

Example 2: 31 g butyl acrylate, 79 g butanol, 12 g butyl methacrylate, 7 g butane and 8 g of water.

After fractional distillation the amounts of the obtained products from rotary furnace were similar as in the examples 1 and 2. After the pyrolysis the furnace was flushed with oxygen at 500°C to burn out the carbonizate, which could be used as a raw material in the production of active carbon.

The disposal of acrylic pressure-sensitive adhesives based on butyl acrylate using pyrolysis could be successfully conducted utilizing system for waste management which was presented. The liquid products of the pyrolysis give in to fractionation on distillation-rectifying column with good enough yields towards advisable products. With the use of rotary furnace the time needed to obtain the temperature of the pyrolysis (400°C) is shorten from 15 minutes to about 10 minutes and the overall time of the pyrolysis from 90 minutes to 60 minutes. The results were satisfactory and promising enough, that the system for waste management of acrylic adhesives, can be utilize in a larger scale in the future.

Unfortunately during every pyrolysis a solid residue (on the level of 2-15% weight of the charge) in the form of carbonizate is formed. The carbonizate could be a raw material for acquisition the adsorbents in the form of active carbon. The research on the sorption properties of the carbonizates, obtained during pyrolysis, of the waste adhesive based on butyl acrylate was held.

The pyrolysis was conducted in the final temperature of $450^{o}C$. During pyrolysis the pyrolytic gases were condensed in condenser and the liquid fraction was collected. The residue after pyrolysis was carbonizate. The fraction of the carbonizate to the charge was 8.5 wt.%. The apparatus for off-line pyrolysis is presented in Figure 39.

The carbonizate was tested for the disposal efficiency of the methylene blue from the water solution. In order to do this to $300cm^3$ of methylene blue solution with the initial concentration $10mg/dm^3$ a 100mg analytical sample of the carbonizate was added. After 4h of intense stirring no change in the concentration of MB (methylene blue) solution was observed. In order to give the sorption properties the carbonizate was activated through calcination with $MgCO_3$.

The whole idea of the research on the sorption properties of obtained carbonizates after off-line pyrolysis (step by step) is presented in Figure 58.
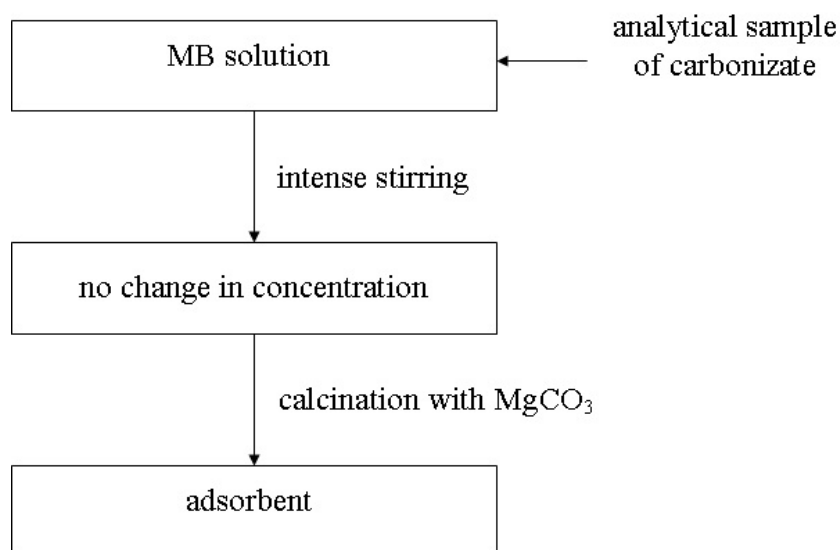
Figure 58 The research procedure on the sorption properties of obtained carbonizates after off-line pyrolysis

In table below (Table 19) the results obtained from the research on the activated carbonizate is presented.

Table 19 Partition coefficient carbonizates

Activator	Temperature	*K*
-	-	0
-	700	382
MgCO₃ (10%)	750	4337

Distribution coefficient *K* is defined as:

$$K = \frac{C_S}{C} \tag{1}$$

Where:

C_S – concentration in the solid phase

$$C_S = \frac{C_0 - C}{m} \cdot m_r \tag{2}$$

C_0, C – the initial and final concentration in the liquid phase [mg/kg], m, m_r – mass of carbonizate and solution [kg]

The raw carbonizate formed during pyrolysis of the PSA does not exhibit sorption properties. An easy method of activation allows obtaining cheap adsorbent, which could be used in water renewal technologies.

The research on the adsorption rate of MB on the carbonizate was also held. The investigations on carbonizate activated with magnesium carbonate were conducted using mixer equipped with mechanical stirrer. It was determined that above 150rpm the rate of sorption of MB from water solution increment does not occur. It indicates that in these conditions the rate of adsorption is limited by in-grain diffusion. In order to distant from the critical point the research in 300rpm was conducted. The obtained kinetic plots on the several carbonizates are presented below. In order to describe kinetic plots a model of pseudofirst-order reaction was used [100]:

$$\frac{dC}{dt} = k(C - C_{eq}) \qquad (1)$$

This equation in integral form is expressed:

$$C = (C_0 - C_{eq}) \cdot exp(-k \cdot t) + C_{eq} \qquad (2)$$

Which could be convert to linear form:

$$ln\left(\frac{C - C_{eq}}{C_0 - C_{eq}}\right) = -k \cdot t \qquad (3)$$

Where:

C, C_{eq}, C_0 – current, equilibrium and initial concentration, k – rate constant, t – time.

Figure 59 describes comparison kinetic plot of adsorption of MB on commercial active carbon (DTO GRYFSKAND) and activated carbonizate.
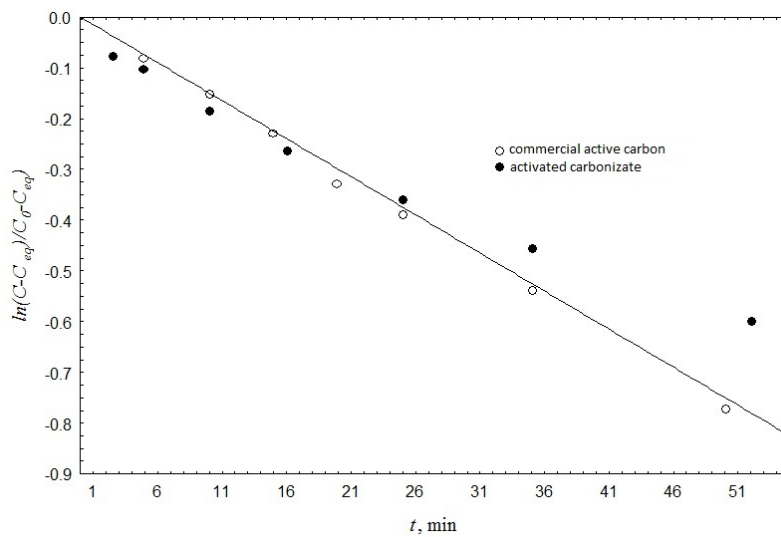
Figure 59 Kinetic plots of absorption of MB on commercial active carbon and activated carbonizate

It was found that activated carbonizate with magnesium carbonate formed during pyrolysis of PSA exhibits close sorption parameters to commercial active carbon.

7. Finding of experiments and discussion

1. The initial step in the degradation of PSA is scission at some unspecified point in the polymer molecule. These initially formed radicals would remove tertiary hydrogen atoms from polymer backbone to give relatively stable radical.

2. The presence of acrylic acid in pyrolyzate was not detected, because of dehydratation and decarboxylation in the next stage.

3. As a result of main chain degradation the methacrylate of alcohol used in synthesis of acrylate is formed.

4. As a result of side chain degradation the alcohol forming used acrylate is formed.

5. Unsaturated product olefin could be formed as a result of side chain degradation.

6. The forming mechanism (in case of copolymers based on 2-ethlhexyl acrylate and acrylic acid) of compounds such as: carbon dioxide, 2-ethylhexene-1, 2-ethylhexanol-1, 2-EHA and 2-EHMA, could be explain with characteristic properties of typical acrylics PSA.

7. During thermal degradation of PSA based on 2-EHA and AA carbon dioxide and olefin are formed in molar ratio close to unity (at least in early stages of the reaction).

8. The residual copolymer synthesized from 2-EHA and AA becomes more intensely colored with progression of degradation. The color is probably a result of mainly coupled doubled carbon-carbon bonds but it is also possible carbonyl groups.

9. Molecular weight has minor influence on thermal stability of synthesized copolymers and the mechanisms, which lead to formation of gaseous and liquid products of the pyrolysis.

10. In case of copolymers based on acrylic acid and butyl acrylate (higher concentration of acrylic acid) butyl acrylate is forming in higher amounts than butyl methacrylate, as a result of depolymerization of polymer terminated with acrylic groups, however this reaction occurs relatively rare in acrylates.

11. The pyrolysis of the ethyl acrylate-acrylic acid-copolymer showed that thermal degradation products are ethanol, ethyl acrylate and ethyl methacrylate.

12. The products of thermal decomposition of MA-AA copolymer are methanol, methyl acrylate and methyl methacrylate corresponding to acrylic acid methyl ester incorporated into acrylic polymer chain.

13. In case of copolymer BA-MA-AA both dehydratation and decarboxylation are first order reactions, the latter being much slower than the former

14. The analyzed acrylic copolymer MA-EA-BA-AA was correctly identified as being composed of methyl acrylate, ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate using Py-GC method.

15. The pyrolysis of copolymer based on 2-propylheptyl acrylate and acrylic acid at lower temperatures proved, that the polymer degrades nearly completely to the by-products, such as olefin 2-propylheptene-1, alcohol 2-propylheptanol-1, monomers 2-propylheptyl acrylate, and 2-propyleheptyl methacrylate and gases appear only is small quantities.

16. Thermal degradation of acrylic polymers containing carboxylic groups from acrylic acid indicates that water is a by-product and an anhydride formation into polymer backbone is possible.

17. The major breakdown products from thermal degradation of poly(alkyl methacrylates) are gases containing carbon dioxide, carbon monoxide, methane and ethane, alkyl acrylates as accordingly monomers and alcohols mixture containing methanol, ethanol and propanol. It has been not observed the formation of typical breakdown products typically for poly(alkyl acrylates), such as alkenes, accordingly alcohols and acrylates.

18. The disposal of acrylic pressure-sensitive adhesives based on butyl acrylate using pyrolysis could be successfully conducted utilizing system for waste management presented in this work.

19. The liquid products of the pyrolysis give in to fractionation on distillation-rectifying column with good enough yields towards advisable products.

20. The raw carbonizate formed during pyrolysis of the PSA does not exhibit sorption properties. An easy method of activation allows to obtain cheap adsorbent, which could be used in water renewal technologies.

21. Activated carbonizate with magnesium carbonate formed during pyrolysis of PSA exhibits close sorption parameters to commercial active carbon.

PART IV.   GENERAL CONCLUSIONS AND OUTLOOK

Acrylic pressure-sensitive adhesives (PSAs) are widely (worldwide production 800 000 tons/year in 2011) used as mounting tapes, splicing tapes, masking tapes, self-adhesive labels, sign and marking films, protective films and as well as in medical applications, such as plaster, OP-tapes, dermal dosage systems and biomedical electrodes. It is essential to know their composition in order to improve their properties such as: tack, peel adhesion, and shear strength as a function of monomers composition. The controlled thermal degradation of acrylic PSA combine with pyrolysis gas chromatography allows to identification of unknowns PSA composition and to avoid of a wide range of unjust complaints.

It has been proven on many acrylic copolymers with self-adhesive performance as well as poly(alkyl methacrylates) that pyrolysis gas chromatography is a method, which can be easily, rapidly and inexpensively used to characterize the polymer formulation.

During the production of acrylic pressure-sensitive adhesives and other kind of acrylic polymers, during coating, modification and converting, and after their application some amount of waste is produced. This can arise in the form of cuttings after mechanical working or as a residue from the spreading process. A part of waste results from failures and unpredictable accidents. One of the methods for disposing of polymeric wastes could be pyrolysis. The research lead to develop a system, which could be applied in order to recover some of the monomers used in synthesis of PSA. The presented apparatus was tested in laboratory environment, however the results were enough satisfactory and promising that it could be utilize in a larger scale in the future.

Additionally in order to manage the residual solid waste after pyrolysis it was also found, that this residual waste in form of carbonizate, could be a raw material for acquisition cheap adsorbents in the form of active carbon. The carbonizate (formed during pyrolysis of PSA) activated with magnesium carbonate exhibited close sorption parameters to commercial active carbon.

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51. KBN grant nr N N209 017438

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SUMMARY

The purpose of my PhD dissertation was to develop method, which allows determining the chemical monomers composition of acrylic pressure-sensitive adhesives.

Nowadays acrylic pressure-sensitive adhesives (PSAs) are used in many fields of life in variety of products as mounting tapes, self-adhesive labels, protective films, sign and marking films, and as well as in medical applications, such as plaster, OP-tapes, dermal dosage systems and biomedical electrodes. The applications of PSAs result from their characteristic properties, which are strongly connected with composition of the copolymer. In order to investigate the composition of PSA a pyrolysis gas chromatography was used.

In the first stage of the research solvent-based pressure-sensitive adhesives of known composition were synthesized. The synthesized copolymers were composed of: 2-ethylhexyl acrylate and acrylic acid, butyl acrylate and acrylic acid, butyl acrylate and acrylic acid (with high amount of acrylic acid for manufacturing of water-soluble acrylic PSA), ethyl acrylate and acrylic acid, methyl acrylate and acrylic acid, butyl acrylate, methyl acrylate and acrylic acid, methyl, ethyl, butyl, 2-ethylhexyl acrylate and acrylic acid.

In the next stage the obtained materials were pyrolyzed. The products of pyrolysis process were identified using gas chromatography method. The identification of pyrolysis products for all of investigated materials indicated, that in characteristic range of thermal decomposition of PSA's, mainly acrylate monomers used in polymerization, and their corresponding methacrylates were formed, however series of other products (alcohols, olefin and gaseous products) were also formed.

The results from these investigations were the basis in further developing of pyrolysis process as a qualitative method of analyzing of thermal degradation products of acrylic PSA.

The optimal pyrolysis conditions for acrylic pressure-sensitive adhesives allowed to quantitative analysis. The elaborating of dependence between quantitative and qualitative pyrolyzate allows significant analysis of pressure-sensitive adhesives composition.

The results from off-line method were compared with the results from on-line method, where pyrolytic gas chromatography (Py-GC) was used, in order to evaluate the possibilities of utilization of pyrolysis coupled with gas chromatography for the purpose of acrylic pressure-sensitive adhesive composition determination.

The research on the PSA's pyrolysis also lead to develop a system, which could be applied in order to recover some of the monomers used in synthesis of PSA. The presented

apparatus was tested in laboratory environment, however the results were enough satisfactory and promising that it could be utilize in a larger scale in the future.

Additionally, bearing in mind the principles of "green chemistry", it was possible to manage the residual solid waste (so called carbonizate) after pyrolysis using it as a raw material for acquisition inexpensive adsorbents in the form of active carbon. The carbonizate (formed during pyrolysis of PSA) activated with magnesium carbonate exhibited close sorption parameters, similar to commercial active carbon.

STRESZCZENIE

Celem mojej rozprawy doktorskiej było opracowanie metody, umożliwiającej określenie rodzaju monomerów wchodzacych w skład poliakrylanowych klejów samoprzylepnych (PSA). Obecnie poliakrylanowe kleje i materiały samoprzylepne są stosowane w wielu dziedzinach życia jako taśmy montażowe, etykiety samoprzylepne, folie ochronne, folie dekoracyjne jak również w zastosowaniach medycznych jako plastry, taśmy operacyjne, układy dozowania skórnego oraz elektrody biomedyczne. Zastosowanie poliakrylanowych klejów samoprzylepnych wynika z ich charakterystycznych właściwości, które są ściśle związane ze składem kopolimeru. W celu zbadania składu poliakrylanowych klejów samoprzylepnych zastosowano pirolityczną chromatografię gazową.

W pierwszym etapie badań zsyntezowano rozpuszczalnikowe kleje samoprzylepne o znanym składzie. Otrzymane kopolimery były zbudowane z: akrylanu 2-etyloheksylu i kwasu akrylowego, akrylanu butylu i kwasu akrylowego, akrylanu butylu i kwasu akrylowego (z wysoką zawartością kwasu akrylowego do produkcji rozpuszczalnych w wodzie poliakrylanowych klejów samoprzylepnych), akrylanu etylu i kwasu akrylowego, akrylanu metylu i kwasu akrylowego, akrylanu butylu, metylu i kwasu akrylowego, akrylanu metylu, etylu, butylu, 2-etyloheksylu i kwasu akrylowego.

W kolejnym etapie zsyntetyzowane kleje samoprzylepne poddano pirolizie. Produkty procesu pirolizy zidentyfikowano za pomocą metody chromatografii gazowej. Identyfikacja produktów pirolizy wszystkich badanych materiałów wykazała, że w charakterystycznym zakresie temperatur rozkładu poliakrylanowych klejów samoprzylepnych, tworzą się głównie monomery akrylanowe (użyte do polimeryzacji kleju) oraz ich odpowiedniki metakrylanowe, przy czym powstaje również szereg innych produktów takich jak alkohole, olefiny oraz inne produkty gazowe, mniej istotne w procesie identyfikacji.

Wyniki z tych badań były podstawą dalszego opracowania i optymalizacji procesu pirolizy jako metody analizy produktów rozkładu poliakrylanowych klejów samoprzylepnych.

Optymalne warunki pirolizy dla poliakrylanowych klejów samoprzylepnych pozwalają generalnie na analizę jakościową. Opracowanie zależności pomiędzy wynikami ilościowymi i jakościowymi pirolizy pozwalają na znaczącą analizę składu poliakrylanowych klejów samoprzylepnych.

Wyniki z metody off-line porównano z wynikami z metody on-line, gdzie zastosowano pirolityczną chromatografię gazową (Py-GC) w celu możliwości zastosowania pirolizy

sprzężonej z chromatografią gazową w celu określenia składu poliakrylanowych klejów samoprzylepnych.

Badania nad pirolizą poliakrylanowych klejów samoprzylepnych doprowadziły również do opracowania układu, który można zastosować w celu odzysku niektórych monomerów użytych do syntezy PSA. Przedstawiona aparatura została zbadana w warunkach laboratoryjnych, jednakże otrzymane wyniki były na tyle zadowalające i obiecujące, że można ją zastosować w przyszłości na większą skalę.

Dodatkowo, mając na uwadze zasady "zielonej chemii", udało się zagospodarować stałe odpady popirolityczne (tzw. karbonizat) stosując je jako surowiec do pozyskania akceptowalnych cenowo adsorbentów w postaci węgla aktywnego. Karbonizat (powstały podczas pirolizy PSA) aktywowany węglanem magnezu wykazywał parametry sorpcyjne charakterystyczne dla komercyjnych węgli aktywnych.