THERMAL DEGRADATION OF BUTYL ACRYLATE-METHYL ACRYLATE-ACRYLIC ACID-COPOLYMERS

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The thermal degradation of copolymers based on butyl acrylate-methyl acrylate-acrylic acid used as acrylic pressure-sensitive adhesives, especially for bonding of plasticizer containing materials, has been investigated using thermogravimetry and pyrolysis-gas chromatography at 250°C. It was observed that during the pyrolysis of butyl acrylate-methyl acrylate-acrylic acid copolymers unsaturated monomers as methyl acrylate, methyl methacrylate, butyl acrylate and butyl methacrylate were formed. During the side-chain butyl acrylate-methyl-acrylate-acrylic acid-copolymer degradation the presence of methyl alcohol and butyl alcohol was observed.

Introduction

Acrylic copolymers based on alkyl acrylates and unsaturated carboxyl acids with low glass transition temperature are important specialty polymers using as pressure-sensitive adhesives (PSA) for manufacturing of diverse self-adhesive product as mounting and masking tapes, splicing tapes, packaging tapes, labels, sign and marking films, protective films, medical pads, hydrogels and biomedical electrodes [1–3]. 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.

Thermal degradation of vinylidene chloride/[4-(t-butoxycarbonyloxy)phenyl]methyl acrylate copolymers was described to evaluate the thermal stability of this important material in the packaging industry [4]. Jakab, Meszaros and Omastowa studied the thermal stability of polypyrrole using among other things thermogravimetry and pyrolysis-gas chromatography in inert atmospheres [5]. The thermal mechanical properties and thermal degradation behaviors of with heterocyclic polymers prepared fibers were studied in [6]. Very interesting investigations about thermal analysis of crosslinked polymer coatings based on recent breakthrough in nanoscale thermal probe technology were performed in work of Germinario and Shang [7].

A target of this work was the investigation of thermal degradation of acrylic PSA based on butyl acrylate-methyl acrylate-acrylic acid-copolymer using thermogravimetry (TG) and gas chromatography (GC). Thermal resistance of organic polymers is important in

many scientific and engineering applications. Thermal degradation of polymers has been studied from a scientific perspective to gain insight into molecular structure, and from an engineering perspective to determine how specific materials behave at elevated temperatures. A particular area of interest is the behavior of polymer materials in fire environments [8].

It is very interesting, from the practical technological point of view, to study the effects of thermal degradation of so much important groups of plasticizer resistance acrylic PSAs.

Experimental

The necessary acrylic PSA was synthesized from 65 mass% butyl acrylate (BA), 30 mass% methyl acrylate (MA) and 5 mass% acrylic acid (AA) in ethyl acetate using 0.1 mass% 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 mass%
- 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 mass%

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- viscosity 6.4 Pa s
- concentration of residual monomers <0.3 mass%
- mass average molecular mass $\overline{M}_w$ 535 000 Dalton
- number average molecular mass $\overline{M}_n$ 148 000 Dalton
- polydispersity $P_d = \overline{M}_w / \overline{M}_n$ 3.61

This synthesized acrylic copolymer PSA was characterized by thermal and chromatographic methods. The thermal degradation experiments were performed by pyrolysis-gas chromatography techniques at following parameters: gas chromatograph – Intersmat IGC 131, capillary column – (QC2/BP1) 25 m·0.25 mm (100% dimethyl polysiloxane), carrier gas – He 80 kPa, detector FID –250°C, injector temperature –250°C, oven – temperature program –50°C (0 min) to 230°C at 10°C min^{-1} (32 min), sample –0.3 μL and pyrolysis-gas chromatography techniques. Thermal polymer stability was assessed by thermogravimetry (TG) using TA Instruments Inc. model 2950 TG unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. All sample about ca. 10 mg were contained in a platinum sample pan and the TG cell was swept with nitrogen at 60 mL min^{-1} during degradation process. The temperature was ramped at 5°C min^{-1}.

Results and discussion

The stability of the acrylic PSA containing butyl acrylate (BA), methyl acrylate (MA) and acrylic acid (AA) was investigated by thermogravimetry (Fig. 1). As can readily be seen, the rate of thermal degradation for butyl acrylate-methyl acrylate-acrylic acid-copolymer increases with temperature increasing reaches 50 mass% 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 2 shows the pyrolysis chromatogram of PSA containing butyl-, methyl acrylate and acrylic acid. The pyrolysis
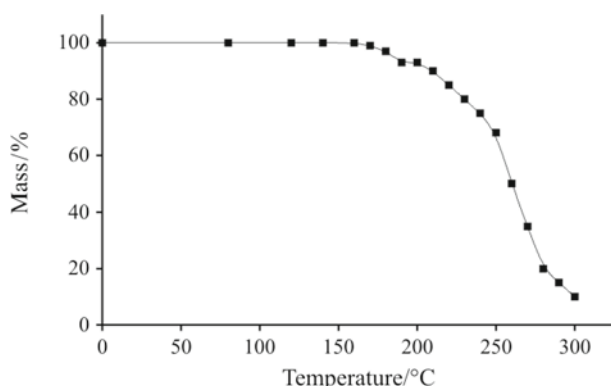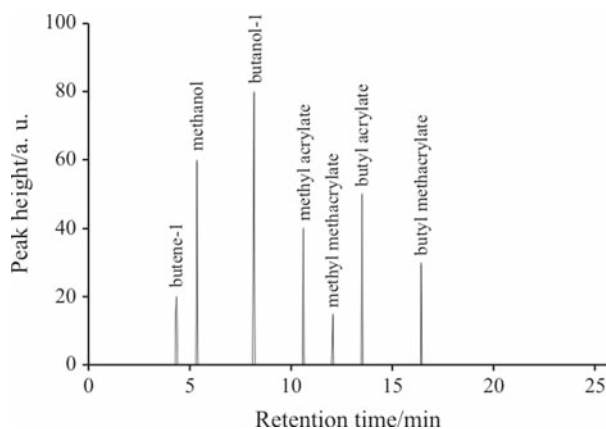
Fig. 2 Pyrolysis chromatogram of PSA containing butyl-, methyl acrylate and acrylic acid

chromatogram of evaluated acrylic PSA (Fig. 2) contains eight principal peaks with different retention times (rt). The first is butene-1 (rt: 4 min 20 s) from butyl acrylate and the second is methanol (rt: 5 min 23 s) from methyl acrylate. The next peaks belong to butanol-1 (rt: 8 min 12 s), methyl acrylate (rt: 10 min 40 s), methyl methacrylate (rt: 12 min 8 s), butyl acrylate (rt: 13 min 30 s) and butyl methacrylate (rt: 16 min 28 s). An oily residue remained after the pyrolysis of BA-MA-AA-copolymer. This residue material no decolorized bromine water rapidly and gave a iodine number, while not reproducible, indicated a low degree of unsaturation. The residue became noticeably smaller at pyrolysis at higher temperatures. The pyrolysis behavior of BA-MA-AA-copolymer (Fig. 3) agrees well with the own works, conducted at Lohmann (Germany) twenty years ago. 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 Fig. 4. The presence of a butane-1 peak
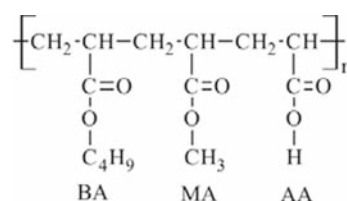
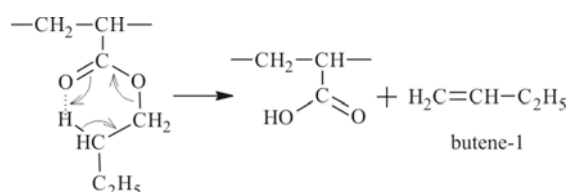Fig. 3 Acrylic PSA copolymer based on butyl acrylate, methyl acrylate and acrylic acid

Fig. 1 Thermal degradation of butyl acrylate-methyl acrylate-acrylic acid-copolymer

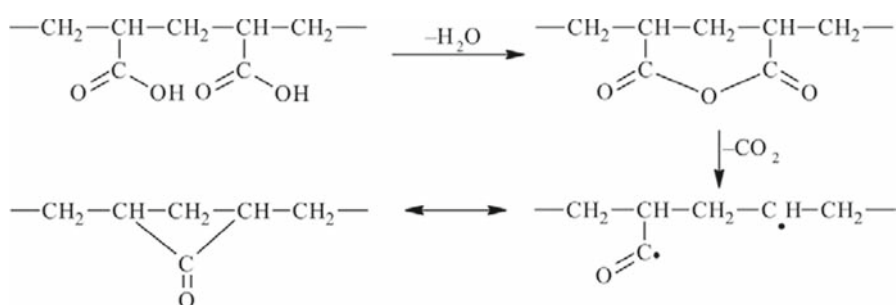Fig. 4 Formation of alkene butane-1 by pyrolysis of PSA containing butyl acrylate

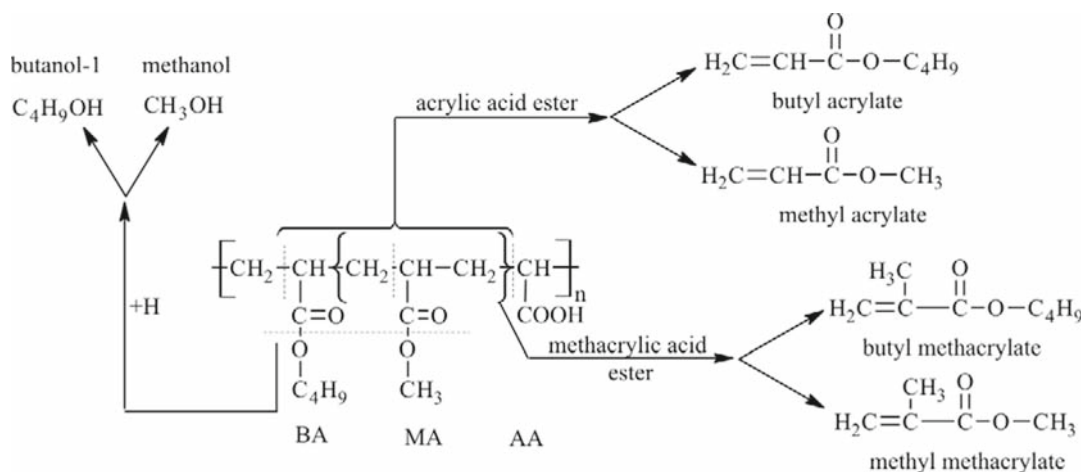**Fig. 5** Thermal degradation of polymer containing carboxyl groups

Fig. 6 Forming of alcohols, acrylic and methacrylic monomers during the thermal degradation of selected acrylic PSA

in the pyrolysis chromatogram 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 [9]. 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 [10] (Fig. 5), is further supported by the absence of water from the chromatogram at the used column. 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. The dehydration 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 dehydration and decarboxylation reactions. Forming mechanism of methanol and butanol-1 in terms of the proportion of monomer units involved is

illustrated in Fig. 6. 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.

Conclusions

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 gas phase formed alkoxyl radicals have a stability similar than a methyl radical [11]. Thus it may be ex-

pected 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.

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