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Thermal degradation of solvent-borne water soluble acrylic acid–butyl acrylate copolymers

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Thermal degradation of water soluble copolymers synthesized from acrylic acid and butyl acrylate, used as water soluble self-adhesives, especially for bonding of different kinds of paper, was investigated at 250 °C using pyrolysis-gas chromatography. The thermal degradation process and the kind and amounts of the pyrolysis products provide relevant information about the thermal resistance of water soluble acrylic adhesives. It was observed that during the pyrolysis of acrylic acid–butyl acrylate copolymers main breakdown products as carbon dioxide, butene-1, butanol-1, butyl acrylate and butyl methacrylate were formed.

Key words: *adhesion; pressure-sensitive adhesive; thermal resistance; thermal degradation products*

1. Introduction

Solvent-borne water soluble polymers, used as pressure sensitive adhesives (PSAs), are still something of a speciality. They are applied as one-sided and double-sided tapes or as transfer films for web splicing in the paper industry. A challenging area of water soluble PSA application is their use for water-dispersible labels, medical devices, such as surgical tapes and bioelectrodes [1]. Solvent-based water soluble PSAs can be synthesized using a water-insoluble monomer, such as butyl acrylate (BA), and soluble monomers, such as acrylic acid (AA) or ß-acryloyloxy propionic acid (PAA) [2].

Times of dissolution in water of acrylic copolymers based on unsaturated acrylic acid or ß-acryloyloxy propionic acid and butyl acrylate at various pH values (4, 7 and 11) are shown in Fig. 1 [3]. It is evident from the figure that the increase in pH value improves the water solubility of acrylic PSAs containing hydrophilic acids in the polymer structure. A shorter dissolving time was observed for polymers containing

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acrylic acid. In the manufacture, coating and printing of various paper types, the continuous production methods used in the paper industry require paper reels to be spliced by joining the end of one reel to the beginning of the next. Similarly, paper reels must be spliced back together after blemishes and defects have been cut out. For this purpose either double-sided, single-sided or transfer adhesive tapes are used, depending on the individual application. These tapes containing water soluble acrylic copolymers are characterised by aggressive bonding strength on the paper surface.

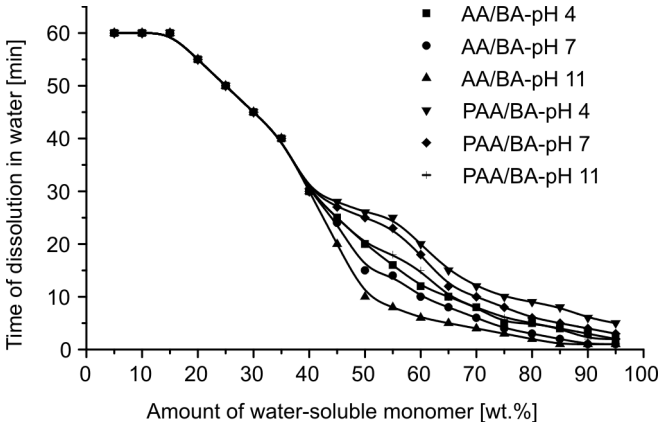

Fig. 1. Times of dissolution in water of PSAs at various pH values and various concentrations of unsaturated acid monomers

Since many processes in the paper industry require high temperatures (180–240 °C), reliable adhesion at these temperatures must be ensured by appropriate thermal shear strength of the splicing tape. In the interest of recycling, the splices which are cut out are not discarded, but are recovered for reprocessing and, therefore, the pressure-sensitive adhesives used in the manufacture of splicing tapes must be completely water soluble under production conditions [4]. A goal of this investigation was the testing of the thermal resistance and the thermal degradation of water soluble acrylic PSAs, based on acrylic acid–butyl acrylate copolymers using thermogravimetry and gas chromatography for the pyrolysis products.

2. Experimental

Water soluble acrylic PSAs under investigation were synthesized in acetone using acrylic acid (AA) and butyl acrylate (BA) in the presence of 0.1 wt. % radical starter AIBN at 56 °C. All components were purchased from BASF Germany in Ludwigshafen. The polymerization process was conducted with a 1 h dosage time and a 5 h post reaction. The synthesized water soluble acrylic PSAs having ca. 50 wt. % polymer content, dependent on the initial composition, are characterized through viscosity at 20 °C measured with a Rheomat RM 189 from Rheometric Scientific (spindle No. 3)

(Table 1). Thermal acrylic polymer stability was assessed by thermogravimetry (TGA) using a TA Instruments Inc. model 2950 TGA unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. All samples, ca. 10 mg, were placed in a platinum sample pan and the TGA cell was swept with nitrogen at 60 cm^3/min during the degradation process. The temperature was ramped at 5 °C/min.

Table 1. Viscosity of the synthesized PSA

PSA	Acrylic acid [wt. %]	Butyl acrylate [wt. %]	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 with the following parameters: Unicam 610, 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 from 50 °C (0 min) to 230 °C at 10 °C/min (32 min), sample 0.3 µl and pyrolysis gas chromatography/mass spectrometry techniques.

3. Results and discussion

The thermal resistance testing of the water soluble acrylic PSA synthesized from acrylic acid and butyl acrylate using the thermogravimetry method is shown in Fig. 2.

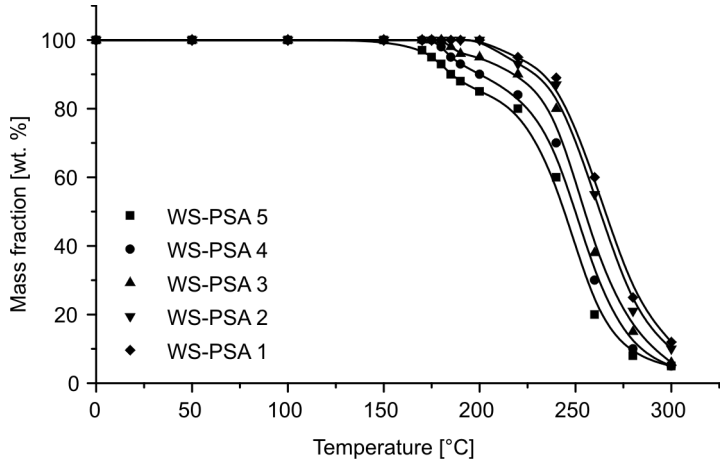

Fig. 2. Thermal degradation of water soluble copolymers from acrylic acid and butyl acrylate

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* improvement to the thermal resistance. All the evaluated water soluble polymers were stable up to about 160 °C. Water soluble copolymers WS–PSAs 1–2 with 95 and 97 wt. % of acrylic acid (Table 1) are thermally stable to about 210 °C. At higher temperatures, their thermal decomposition begins, and depends on the concentration of acrylic acid in the copolymers. The gaseous and liquid thermal decomposition products of water soluble copolymer PSA 2 are listed in Table 2.

Table 2. Thermal degradation products of water soluble acrylic PSA containing 95 wt. % of acrylic acid and 5 wt. % of butyl acrylate as a function of pyrolysis time

Products of pyrolysis	Products of termal degradation 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
Liquid 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 gases	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

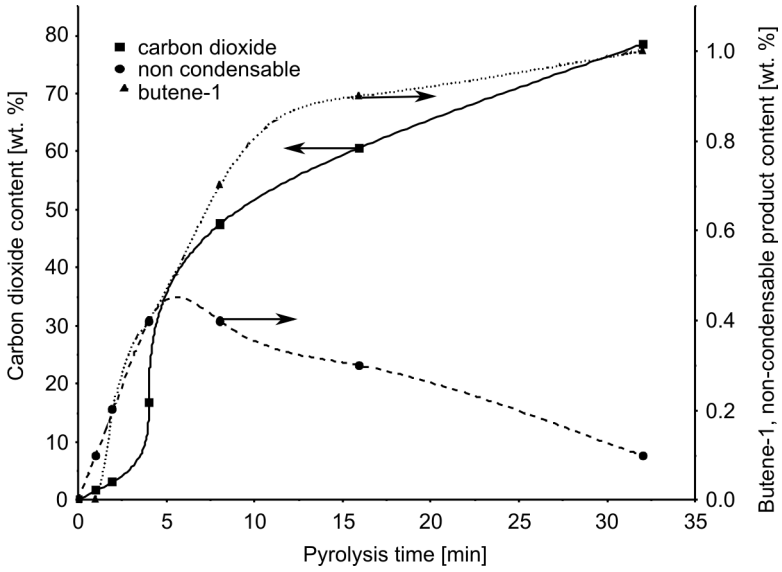

Fig. 3. Formation of carbon dioxide, butene-1 and non condensable products during pyrolysis of water-based acrylic PSA based on copolymer obtained from acrylic acid and butyl acrylate

The main decomposition gasses (Table 2) were carbon dioxide, butene-1 and non condensable products. An olefin, butene-1, corresponded to the butyl ester side groups in the synthesized copolymers. The olefin, being less volatile, in this case appears among the liquid products. The formation process of gaseous pyrolysis products is shown in Fig. 3. The amounts of carbon dioxide, ranging between 1.6 and 78.5 wt. % after 32 min pyrolysis time, were not comparable with the amounts of butene-1 (0.1–0.4 wt. %) and the amounts of non condensable pyrolysis products (between 0.2 and 1.0 wt. %) produced during the pyrolysis of acrylic acid–butyl acrylate-copolymer.

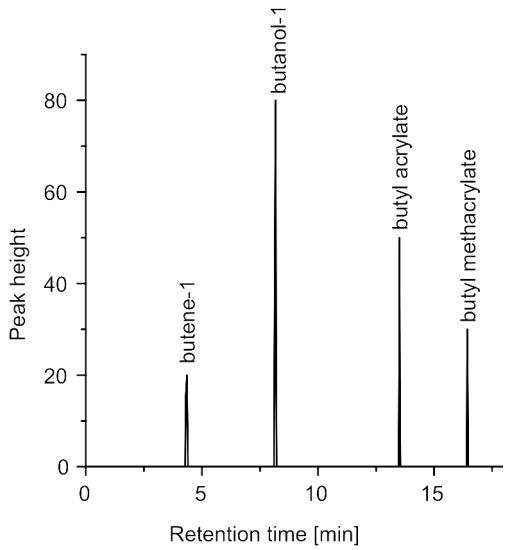

Fig. 4. Pyrolysis chromatogram of water soluble copolymer synthesized from acrylic acid and butyl acrylate

Figure 4 shows the pyrolysis chromatogram of water soluble acrylic acid–butyl acrylate-copolymer PSA 2. It contains four principal peaks. The first one corresponds to butene-1 and the second to butanol-1 from butyl acrylate. The presence of these peaks in the pyrolysis chromatogram at higher pyroylsis temperatures is possibly due to the thermal degradation of acrylate groups in the side chain. The other peaks correspond to butyl acrylate and to butyl methacrylate from the thermal decomposition of the 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 are the first order reactions, the latter being much slower than the former one. It was also found that water and carbon dioxide were the only volatile pyrolysis products in the range between 170 and 240 °C [5].

4. Conclusions

Water soluble acrylic copolymers synthesized with concentrated acrylic acid (ca. 95 wt. %) are characterized by their excellent thermal resistance at high temperatures between 180 and 24 0°C and can be used for the manufacture of splicing tapes for the paper industry and water dispersible labels. The composition of their breakdown products at high temperatures, determined by the pyrolysis method, includes butene-1, butanol-1, butyl acrylate and butyl methacrylate. One may reasonably presume that butane-1 and butanol-1 are formed in quite distinct ester decomposition processes. Butene-1 formation almost inevitably involves the formation of carboxyl groups or carboxyl radicals whose decomposition could yield carbon dioxide. A comparable pyrolysis reaction of the tested water soluble acrylic copolymer would produce butyl acrylate and butyl methacrylate. Butyl acrylate is formed in rather greater amounts than butyl methacrylate and probably arises by depropagation from an acrylate terminated polymer radicals, although this is known to be only a very minor reaction in acrylics.

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