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Thermal degradation of acrylic pressure-sensitive adhesives based on copolymers of 2-ethylhexyl acrylate and acrylic acid

Summary — The thermal degradation of acrylic pressure-sensitive adhesives (PSAs) based on copolymers of 2-ethylhexyl acrylate and acrylic acid has been conducted at about 230 °C using pyrolysis-gas chromatography. The types and amounts of the pyrolysis products give important information about of thermal degradation of acrylic pressure-sensitive adhesives and the mechanism of their thermal degradation. It was observed that during the thermal degradation of 2-ethylhexyl acrylate and acrylic acid copolymers such main decomposition products as corresponding alken (2-ethylhexen-1), corresponding alcohol (2-ethylhexanol-1) and unsaturated monomers such as 2-ethylhexyl acrylate and 2-ethylhexyl methacrylate were formed.

Key words: acrylic pressure-sensitive adhesives, solution polymerization, pyrolysis, thermal degradation, 2-ethylhexyl acrylate/acrylic acid copolymer.

DEGRADACJA TERMICZNA AKRYLANOWYCH KLEJÓW SAMOPRZYLEPNYCH NA BAZIE KOPOLIMERÓW ZBUDOWANYCH Z AKRYLANU 2-ETYLOHEKSYLU ORAZ KWASU AKRYLOWEGO

Streszczenie — Przeprowadzono badania nad termiczną degradacją akrylanowych klejów samoprzylepnych na bazie kopolimerów zbudowanych z akrylanu 2-etyloheksylu oraz kwasu akrylowego. Pirolizę próbek kleju prowadzono w temperaturze 230 °C z zastosowaniem chromatografii gazowej do identyfikacji produktów degradacji. W trakcie termicznej degradacji kopolimeru zbudowanego z akrylanu 2-etyloheksylu oraz kwasu akrylowego powstają głównie produkty typu alken, alkohol oraz nienasycone monomery, takie jak: 2-etyloheksen-1, 2-etyloheksanol-1, akrylan 2-etyloheksylu oraz metakrylan 2-etyloheksylu.

Słowa kluczowe: akrylanowe materiały samoprzylepne, polimeryzacja rozpuszczalnikowa, piroliza, degradacja termiczna, kopolimer: akrylan 2-etyloheksylu-kwas akrylowy.

Since their introduction half a century ago, pressure-sensitive adhesives (PSAs) have been successfully applied in many fields. They are used in self-adhesive tapes, labels and protective films as well as in dermal dosage systems for pharmaceutical applications, in biomedical electrodes, the assembly of automotive parts, toys, electronic circuits and keyboards. In the last fifty years or so, acrylic PSA products have made tremendous strides from what was virtually a black art to what is now a sophisticated science. The few larger manufacturers of PSA articles and their even larger suppliers use now very expensive equipment to study PSA behavior: a tack, adhesion and cohesion [1]. Acrylic PSAs offer several advantages such as excellent ageing characteristics and resistance to elevated temperatures and plasticizers, exceptional optical clarity due to the polymer compatibility and non-yellowing. They also have the fine balance of adhesion and cohesion and an excellent water resistance. Typical acrylic PSAs are synthesized using about 5 wt. % of acrylic acid and 95 wt. % of alkyl acrylates, such as butyl, hexyl, 2-ethylhexyl, isooctyl or decyl acrylate. The copolymers synthesized from 2-ethylhexyl acrylate and acrylic acid are used for manufacturing of acrylic PSAs with excellent adhesive properties to soft carriers as polyethylene foam [2]. The analysis of diverse kinds of acrylic polymers has been reported, based on gas chromatography [3].

Gas chromatography (GC) is an universal separation technique for the products of thermal degradation of acrylic PSAs [4]. GC is commonly used to analyze the 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 possible with minimal sample preparation. A wide variety of special detectors are available for quantification and specific

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identification of various classes of compounds. GC, coupled with controlled temperature pyrolysis technique, provides a rapid method for the identification of acrylic polymers and allows pyrolysis/GC and pyrolysis/GC/mass spectroscopy identification of thermal decomposition products of polymeric materials [5, 6].

EXPERIMENTAL

Materials

All starting materials such as 2-ethylhexyl acrylate (2-EHA), acrylic acid (AA), ethyl acetate and 2,2′-azo-bis-diisobutyronitrile (AIBN) available from BASF (Germany) were technical grade.

Synthesis of PSA

The solvent-borne pressure-sensitive adhesives were synthesized from 90 to 97 wt. % of EHA and 3 to 10 wt. % of AA in ethyl acetate at its boiling point about 77 °C using 0.1 wt. % of AIBN as an initiator to start radical polymerization. The polymerization was conducted under the following conditions:

— addition of monomers blended with AIBN into ethyl acetate before the polymerization (reactor charge) was 50 wt. %,

— dosage time of residual monomers with residual AIBN was equal to 1.5 h,

— time of post-reaction was 6 h.

Characterization of PSA samples

The synthesized PSA were described by following important properties as viscosity, weight average molecular weight ($\overline{M}_w$), number average molecular weight ($\overline{M}_n$) and polydispersity (P_d) (Table 1).

T a b l e 1. Molecular weights and polydispersity of acrylic PSAs synthesized from 2-EHA and AA

Concentration of		Viscosity Pa · s	$\overline{M}_w$	$\overline{M}_n$	P_d = $\overline{M}_w / \overline{M}_n$
2-EHA wt. %	AA wt. %				
97	3	4.6	546 000	210 000	2.60
95	5	6.1	582 000	320 000	2.65
93	7	7.5	633 000	232 000	2.73
90	10	9,1	711 000	258 000	2.76

The viscosity of solvent-borre acrylic PSAs was determined using a Rheomat RM 189 (Rheometric Scientific) with spindle No. 3 at 23 °C. The molecular weight studies were performed in tetrahydrofurane using liquid chromatograph LaChrom system: RI Detector Li-7490 and LaChrom UV Detector L-7400 from Merck-Hitachi, equipped with a PLgel 10^6 Å column from Hewlett-Packard.

Degradation process

The thermal degradation experiments were performed by pyrolysis-gas chromatography using gas chromatograph Intersmat IGC 131 with capillary column (QC2/BP1) 25 m × 0.25 mm (100 % dimethyl polysiloxane). Helium (80 kPa) was used as a carrier gas. The following conditions were set for tests: detector FID — 250 °C, injector temperature — 250 °C, temperature program for oven — from 50 °C (0 min) to 230 °C at a rate 10 °C /min (32 min), sample volume — 0.3 µl.

The pyrolysis apparatus was reassembled and connected to the gas sampler valve. Plugs were placed in the regular sample inlet and in the vent openings of the gas sampler valve. Products resulting from the pyrolysis were swept into the gas chromatographic column with nitrogen. The identification and composition of the polymer were determined by comparison of the chromatogram of the sample with chromatograms of known monomers and pyrolyzates of known polymers.

Analysis of gaseous products was carried out by the combined application of a constant volume manometer and infrared spectroscopy as it was described in detail in [7].

RESULTS AND DISCUSSION

Gaseous products

The major decomposition gaseous products were carbon dioxide and 2-ethylhexene-1, olefin corresponding to 2-ethylhexyl ester side group in the synthesized copolymers, except for the case of the 2-ethylhexyl ester, when carbon dioxide alone appeared in the fraction. The olefin, being less volatile, in this case appears among the liquid products.

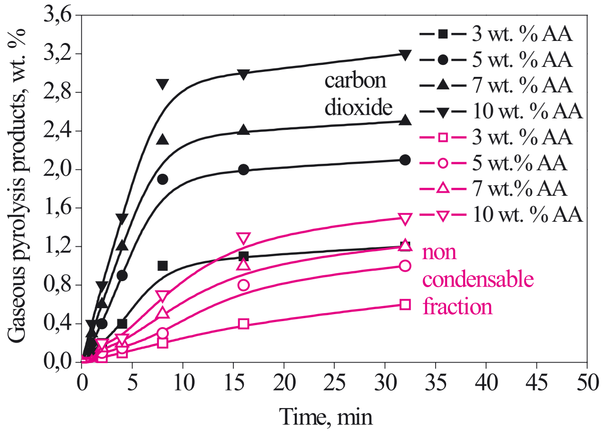


Fig. 1. Formation of gaseous products during the pyrolysis of acrylic PSA based on 2-EHA/AA copolymer

T a b l e 2. Formation of thermal degradation products of acrylic PSA synthesized from 93 wt. % of 2-EHA and 7 wt. % of AA after the various pyrolysis times

Pyrolysis products			Thermal degradation products 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
Total volatiles	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
		2-ethylhexene-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

As it was shown in Figure 1 the amounts of carbon dioxide between 1.2 wt. % (for sample with 3 wt. % of AA) and 2.5 wt. % (for sample with 10 wt. % of AA) and of other noncondensable pyrolysis products (between 0.6 and 1.5 wt. %) produced during the pyrolysis of 2-EHA/AA copolymers are very little in comparison to the other pyrolysis products. For further investigations we have decided to evaluate the acrylic PSA containing 93 wt. % of 2-EHA and 7 wt. % of AA.

The concentration of 2-ethylhexene-1 produced seems to vary as the number of β-hydrogen atoms in the alkyl group [8]. For each polymer the molar ratio of olefin and carbon dioxide is of the order of unity over an appreciable part of the reaction. In Table 2 the contents of products of the degradation reaction are given.

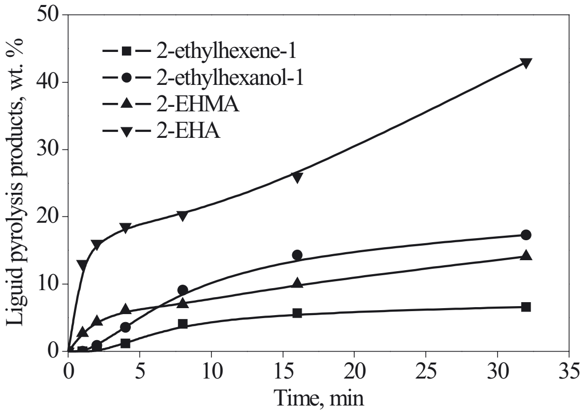


Fig. 3. Formation of relevant liquid products during degradation of acrylic PSA based on 2-EHA/AA copolymer

Liquid products

The liquid products of degradation of acrylic PSA based on 93 wt. % of 2-EHA and 7 wt. % of AA were analyzed by gas chromatography. As it is shown in Figure 2 from the liquid thermal degradation products, olefin 2-ethylhexene-1 and alcohol 2-ethylhexanol-1 are the products in average amounts and the monomers 2-EHA and the corresponding 2-ethylhexyl methacrylate (2-EHMA) are in this case the relevant pyrolysis products from main chain fragments composition. The results of products contents investigations depend on degradation time for example samples listed in Table 2.

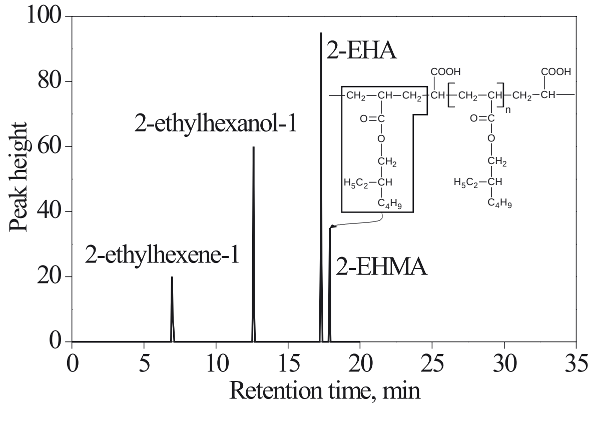


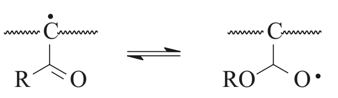
Fig. 2. Gas chromatogram of the liquid degradation products of examinated acrylic PSA

It was confirmed for each polymer that the corresponding 2-EHMA (Fig. 2) is a genuine degradation product and was not present in the monomer used to synthesis of solvent-borne acrylic PSA. The values of time evolution of 2-ethylhexene-1, 2-ethylhexanol-1, 2-EHA and 2-EHMA are illustrated in Fig. 3.

Grassie and Bain [9] has suggested that, because little monomer is formed, the mechanism of the thermal reactions which occur in poly(2-ethylhexyl acrylate) or similar polymers do not involve free radicals. Indeed, small ester molecules do not normally undergo bond scission to give free radicals at temperatures below 400 °C. In a polymer environment, however, and particularly when a radical stabilized by resonance or inductive effects can be formed, there is overwhelming evidence that free radical mechanism may operate below 300 °C. Indeed, at temperatures above 280 °C a degradation mechanism not involving radicals is rare.

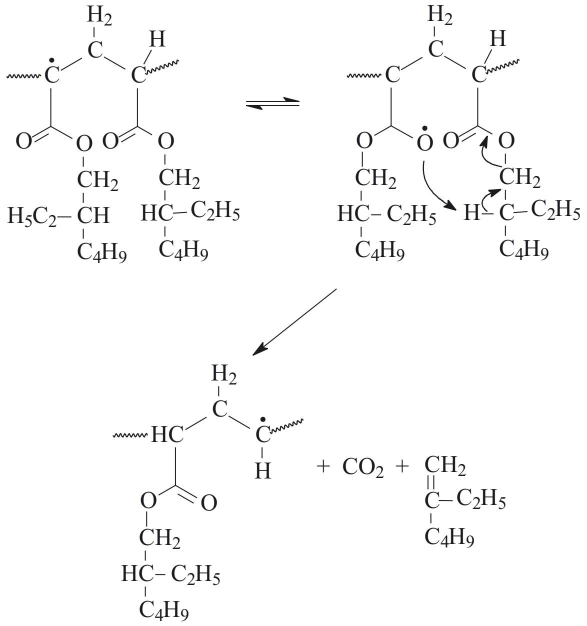
The initial step in the degradation of the primary acrylics is therefore likely to be scission at some unspecified point in the polymer molecule. Cameron and Kane

[10] suggest that these initially formed radicals would remove tertiary hydrogen atoms from the polymer backbone to give the relatively stable radical and that all the major decomposition reactions in poly(alkyl acrylate) are initiated by this radical.

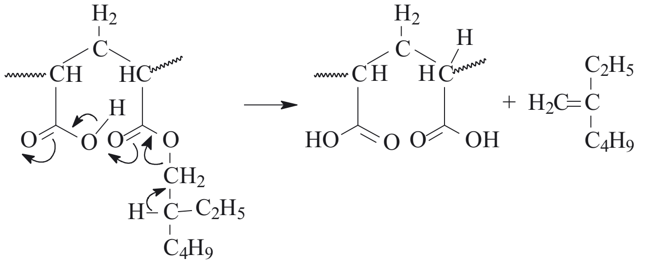


(1)

An evidence that this theory may reasonably be extended to other poly(primary alkyl acrylates) is provided by their closely similar responsible thermograms and the general comparability of their patterns of reaction products. It would be difficult to explain how such a variety of products could be formed in a one-stage process, unless all the reactions have a common precursor. During the thermal degradation of acrylic PSA, based on copolymer of 2-EHA and AA, carbon dioxide and olefin are evolved from these acrylic polymers in a molar ratio close to unity, at least in the early stages of the reaction.



Scheme A. Thermal decomposition reaction of acrylic PSA obtained from 2-EHA and AA with formation of CO_2 and olefin



Scheme B. Thermal decomposition reaction of acrylic PSA obtained from 2-EHA and AA with formation of olefin

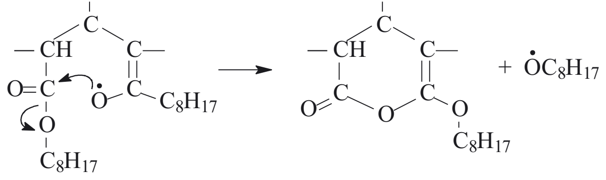
It therefore seems probable that a reaction of the type I (Scheme A) or type II (Scheme B) is proceeded.

The amounts of volatile gases condensable and non condensable were always very small, lover than 3.1 wt. %. Probably the carbon dioxide is the principal non condensable product.

There is no evidence for autocatalytic production of olefin so the competition of the reaction of type I and reaction of type II, which was proposed to account for the autocatalytic decomposition of poly(2-ethylhexyl acrylate), is assumed to be negligible. Although reaction of type I is represented as being catalyzed by a radical at a neighboring monomer unit, there is no reason why any available radical should not be the initiator. Further evidence for the reaction of type I is the fact that there appears to be a direct relation between the production of olefin and the number of β-hydrogen atoms in the alkyl group. In the case of the acrylic PSA based on copolymer of 2-EHA and AA the 2-ethylhexyl ester it also included into the acrylate and methacrylate monomers which are of relatively low volatility. The fraction of this chain fragment is usually yellow in color, the intensity of color increases with time of degradation.

CONCLUSIONS

The investigations have been conducted satisfactorily using acrylic PSAs based on copolymers synthesized from 2-EHA and AA. The results of this study show that carbon dioxide was the main gaseous pyrolysis product and 2-ethylhexene-1, 2-ethylhexanol-1, 2-EHA and 2-EHMA (Tab. 2) are the major liquid products of synthesized acrylic PSA pyrolysis. Mechanism of formation of all the compounds mentioned above can be explained on the basis of the characteristic property of typical acrylic PSA which easily undergos the pyrolytic decomposition to carbon dioxide and 2-ethylhexyl derivatives corresponding to the main component acrylic ester of PSA. The residual polymer from copolymer synthesized from 2-EHA and AA becomes progressively more intensely colored as degradation proceeds. The color is probably the result of conjugation involving principally carbon-carbon double bonds, but possibly also carbonyl groups. Carbon-carbon double bonds will be formed in the polymer during the reaction described by equation (2) or as a result of transfer reaction.



(2)

Once the first double bond is formed it will tend to weaken adjacent carbon-hydrogen bonds. Thus hydrogen will be liberated from the sequences of adjacent acrylate units resulting in carbon-carbon conjugation in the polymer backbone.

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