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THERMAL DEGRADATION OF SOME CROSS-LINKED COPOLYMERS OF VINYL ACETATE

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Pyrolysis in combination with gas chromatography and thermogravimetry were used to study the thermal degradation of some cross-linked copolymers of vinyl acetate with divinylbenzene and ethylstyrene. The temperature was varied in the range 200° and 800°. The thermal decomposition products of the analyzed copolymers vary greatly, both with the temperature and with the composition of the samples. The experimental data obtained led to the assumption of a complex degradation mechanism, evidenced by the overlapping processes and the unexpected contents of certain evolved compounds as a function of composition.

Study of the thermal behaviour of copolymers is of importance from both scientific and practical points of view. Such studies lead to prediction of the molecular structure, such as the sequence and arrangement of the repeating units, or monomers and side-groups in the copolymer chain. They also help in selection of the materials with the best properties for specific uses and suggest the way to synthesize copolymers with high thermal stability.

The experimental techniques often used for the thermal degradation of copolymers include pyrolysis in combination with gas chromatography (P–GC), and thermogravimetry (TG).

The P–GC technique has been successfully used for evaluation of the structure and the monomer distribution in the polymer chain, for identification of the decomposition products, and for study of the kinetics and thermal degradation mechanism of a great number of binary copolymers [1]. In the case of vinyl acetate (VAc), such studies extended to the copolymers with methacrylic, acrylic and maleic esters [2], ethylene [3, 4], vinyl chloride [5, 6], butyl acrylate or dibutyl maleate [7] and acrylonitrile [7].

The application of P–GC to the study of copolymers with more than two comonomers is limited, due to the complexity of the thermal degradation mechanism. Moreover, in such cases, as a result of the great number of products evolved during the degradation, there is the possibility of the overlapping or

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superposition of some chromatographic peaks. Nevertheless, there are papers on the P–GC of some ternary and quaternary copolymers [9–11].

The use of TG for the study of copolymers leads to information with regard to the relative thermal stability or to quantitative data [12].

More comprehensive data about the thermal degradation of copolymers are obtained if the results attained with P–GC are correlated with those from TG [3, 13, 14].

The present paper deals with the thermal behaviour of some ternary macroporous copolymers of VAc with ethylstyrene (ES) and divinylbenzene (DVB), respectively.

Experimental

A. Synthesis of copolymers

VAc and DVB (tech-grade) freed from inhibitors were freshly distilled before use. The DVB used for the preparation of copolymers had the following chemical composition, as determined by gas chromatography: 57.34% DVB, 32.27% ethylstyrene, and 10.39% unpolymerizable compounds, i.e. inert chemical compounds. The reaction was initiated with benzoyl peroxide (1.5% *vs.* monomer quantity).

The copolymerization process was performed in aqueous suspension (organic/aqueous phase ratio 1 : 5) at 70° for 24 hr [15]. The copolymers obtained

Table 1 Chemical composition and main characteristics of VAc–ES–DVB copolymers

Sample	Chemical composition, %			Apparent density, g/ml	Cyclohexane coefficient, g/g	Surface area, m^2/g	Remarks
	VAc	ES	DVB				
A	4.59	35.41	60.0	0.4730	1.0651	458.9	white beads prepared in the presence of gasoline (b.p. 110°C–150°C; $f_v = 0.55$*
B	28.44	26.56	45.0	0.4945	0.9621	724.65	white beads prepared in the presence of gasoline (b.p. 110°C–150°C; $f_v = 0.40$)
C	44.40	20.60	35.0	0.7341	1.2453	469.0	white beads prepared in the presence of toluene ($f_v = 0.50$)
D	80.66	7.33	12.0	—	1.1010	—	transparent beads, gel type
E	91.94	3.06	5.0	—	1.0832	—	transparent beads, gel type

$$* f_v = \frac{\text{volumes of monomers}}{\text{volumes of monomers} + \text{diluent volume}}$$

(as gel or porous beads) contained variable percentages of VAc. A few experiments were performed in the presence of toluene or gasoline (b.p. 110–150°) in order to prepare porous networks (Table 1).

The copolymer samples were washed with warm water and then extracted with benzene and methanol in a Soxhlet apparatus. The composition and some other characteristics of the synthesized copolymers are listed in Table 1.

The comonomer content in the ternary copolymers was assumed to be equal to the initial monomer amount [16].

The apparent density was determined pycnometrically at a residual pressure of about 10^{-3} mmHg. The uptake coefficient measurements were performed with the copolymer sample (1.0 g) immersed in cyclohexane for 48 hr. The specific surface area was measured by the BET method, at $-196°$, on a Ströhleim AREA-meter apparatus.

B. Thermal characterization of copolymers. Pyrolysis-gas chromatography

The copolymer sample weighed in a small platinum boat was pyrolyzed by means of a filament-type pyrolysis unit [17] at temperatures between 320° and 780°.

The separation and analysis of the thermal decomposition products were carried out with a Siemens L–400 gas chromatograph provided with a flame ionization detector, under the following operational parameters: the chromatographic column (stainless steel, 2×3 mm i.d.) was packed with Chromosorb W (60–80 mesh) coated with 15% free fatty acid phase (FFAP); the column temperature was programmed from 60° to 180° at a rate of 7 degree/min, and it was then isothermally operated at 180°; argon was used as carrier at a flow rate of 26 ml/min.

The sensitivity of the flame ionization detector was not determined for all the components, but as the pyrolysis of the studied copolymers led only to the aromatic hydrocarbons and as the response of the detector is a function of the number of carbon atoms contained by each component, the relative weight sensitivity of the components could be regarded as approximately unity. In this way, we could accomplish a semiquantitative determination of the pyrolysis products of VAc–ES–DVB copolymers of variable compositions.

As the sample size and pyrolysis time are important parameters influencing the reproducibility of the results obtained by P–GC, the working conditions for these two experimental parameters were first established.

Earlier experiments [10, 13] showed that copolymer sample weights up to 0.8 mg do not influence the mode of pyrolysis of VAc–ES–DVB copolymers. Accordingly, we used 0.5 mg samples throughout the measurements. The pyrolysis time was 30s for temperatures up to 450°, and 15s for temperatures higher than 500°.

C. Thermogravimetry

The TG curves were recorded on a MOM derivatograph (Paulik–Paulik–Erdey type), using powdered copolymer samples with a granulation of 0.1–0.5 mm in mixtures with freshly calcined Al_2O_3 (20% sample) at 1100°. The experimental conditions were as follows: sample weight 50 mg; heating rate 12.4 deg/min.

Results and discussion

The thermal decomposition of VAc–ES–DVB copolymers takes place by a complex degradation mechanism. This assumption can be drawn from the TG curves of the copolymers (Fig. 1), which show that the weight losses of the copolymer samples with variable composition are a function of the decomposition temperature. For comparison, Fig. 1 also shows TG curves of poly(vinyl acetate) (PVAc) and poly(ethylstyrene-divinylbenzene) (PES-DVB), respectively.

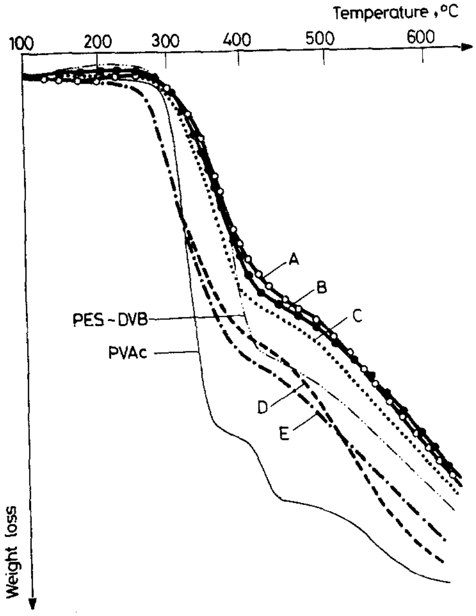

Fig. 1 TG curves for the decomposition in air of the VAc–ES–DVB crosslinked copolymers, PVAc and PES–DVB polymers

As revealed by Fig. 1, the decomposition of VAc–ES–DVB copolymers starts at temperatures above 200° and ends before 600°. The shape of the TG curves for samples D and E, where the VAc content prevails (> 80%), suggests the existence of a degradation mechanism close to that for PVAc, but more complex, without clear separation of the decomposition processes.

A more complex degradation mechanism is observed for samples A, B and to a lesser extent C, which have an increased content of DVB. The shapes of the TG curves for these samples are similar to those for PES–DVB, showing the superposition of the processes and the presence of the thermostable structure on the chain. This points to the existence of a high cross-linking degree in such copolymers.

The complexity of the thermal decomposition of VAc–ES–DVB copolymers results in the large number of products evolved at high temperatures. For example,

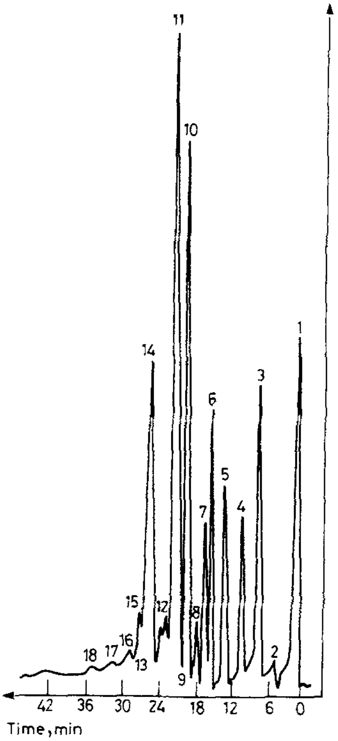

Fig. 2 Pyrogram of copolymer *E* at 640°C. Peaks: 1. C_1—C_4 volatile hydrocarbons; 3. benzene; 4. toluene; 5. xylenes; 6. ethylbenzene; 7. styrene; 10. ethylstyrene; 11. acetic acid; 14. m-, p-DVB; 17. naphtalene; 2, 8, 9, 12, 13, 15, 16 and 18 unidentifieds

Fig. 2 shows the pyrogram of a copolymer pyrolyzed at the decomposition temperature of 640°.

The pyrolysis products were identified by using the relative retention times of various reference compounds and taking into consideration the literature results concerning the thermal decomposition products of VAc [5, 6] or ES–DVB copolymers [18–20].

For the studied copolymers, we paid special attention to the variation in content of the main products evolved during the degradation process (acetic acid, ES and DVB) with both temperature and composition.

As can be seen in Table 2, which shows the influence of temperature upon the decomposition of copolymer B, the content of the products obtained depends strongly on the temperature.

Table 2 Percentage content of the decomposition products of copolymer sample B in function of temperature

Decomposition products	Temperature, °C				
	320°	410°	525°	640°	780°
	Content, %				
C_1—C_4 volatile hydrocarbons		4.0	9.7	21.8	21.7
Benzene	Trace	0.9	2.2	13.4	17.7
Toluene	3.3	1.9	2.9	4.4	3.4
Xylenes		4.3	4.2	1.8	2.3
Ethylbenzene		6.1	2.9	1.3	1.2
Styrene		1.9	4.1	5.9	4.8
Ethylstyrene	4.9	11.5	13.0	7.6	6.9
Acetic acid	66.2	26.7	19.5	10.0	8.1
m-, p-DVB	24.2	27.0	28.9	12.5	10.7
Naphtalene	6.6	0.8	0.8	3.8	10.0
Unidentified	1.2	14.7	12.5	17.4	13.1

The decomposition of VAc–ES–DVB copolymers at temperatures higher than 300° leads to the formation of acetic acid (the main decomposition product) together with other products, e.g. DVB, ES, toluene and naphthalene.

It has been found that, with the increase of the pyrolysis temperature, there is a pronounced decrease in the acetic acid content. The decrease in other products with the increase of temperature was also observed for DVB, ES and styrene, respectively. In turn, the contents of both C_1—C_4 volatile hydrocarbons and benzene simultaneously increase with the temperature. This particular behaviour might be explained by the presence of the appropriate decomposition processes, some cracking reactions of hydrocarbons, decarboxylation of acetic acid, etc., which could take place at high temperature.

The contents of the decomposition products of VAc–ES–DVB copolymers vary considerably with the sample composition, too (Table 3).

In contrast with expectations, with the increase in the VAc content in the copolymers there was a decrease in the acetic acid content. In turn, the variation of the other decomposition products developed normally, e.g. with the decrease in the contents of ES and DVB in the copolymers, the pyrolysis process led to a decreased yields of ES, DVB and styrene, respectively. It was also observed that, with the decrease of the contents of ES and DVB in the copolymers, there was an increase in the contents of benzene and gases with high volatility during the pyrolytic process.

Table 3 Composition of the pyrolysis products of VAc–ES–DVB copolymers at 525°C

Decomposition products	Copolymer sample				
	A	B	C	D	E
	Content, %				
C_1—C_4 volatile hydrocarbons	8.6	9.7	12.6	16.9	18.9
Benzene	1.2	2.8	3.6	8.7	9.3
Toluene	3.5	2.9	3.1	4.9	5.3
Xylenes	3.3	4.2	4.9	6.7	4.8
Ethylbenzene	2.6	2.9	3.8	4.8	5.2
Styrene	7.4	5.1	5.8	4.7	4.6
Ethylstyrene	14.6	13.0	12.4	8.6	7.8
Acetic acid	22.2	20.5	18.6	16.4	15.4
m-, p-DVB	28.9	26.9	22.4	17.2	15.7
Naphtalene	0.9	0.8	2.2	2.1	1.4
Unidentified	6.8	11.2	8.8	9.7	11.6

The experimental data obtained with P–GC on the VAc–ES–DVB gel and macroporous type copolymers suggest a very complex degradation mechanism, with the impossibility of a clear separation of the decomposition process, and unexpected variations in the contents of certain products as a function of the sample composition.

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Zusammenfassung — Pyrolyse in Kombination mit Gaschromatographie und Thermogravimetrie wurde zu Untersuchung des thermischen Abbaus einiger vernetzter Kopolymere von Vinylacetat mit Divinylbenzol und Äthylstyrol herangezogen. Die Temperatur wurde im Bereich von 200–800° variiert. Die thermischen Zersetzungsprodukte sind sehr unterschiedlich, abhängig von der Temperatur und der Zusammensetzung der Probe. Aus den experimentellen Daten wird auf einen komplexen Zersetzungsmechanismus geschlossen, der durch die Überlappung der Prozesse und durch das auftreten bestimmter unerwarteter Verbindungen in Abhängigkeit von der Zusammensetzung bestätigt wird.

Резюме — Комбинированный метод пиролиза с газовой хроматографией и термогравиметрией был использован для изучения термического распада некоторых сетчатых сополимеров винилацетата с дивинилбензолом и этилстиролом. Температура распада менялась в интервале 200–800°. Продукты термического распада изменялись как от температуры, так и от состава образцов. Полученные экспериментальные данные показали сложный механизм распада, сопровождающийся перекрывающимися процессами и неожидаемым содержанием определенных летучих соединений в зависимости от состава образцов.