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# INFLUENCE OF THE MORPHOLOGY OF SAMPLES IN THE PYROLYSIS OF PVC

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PVC was used as a model substance to study the dependence of thermal measurement data on the preparation and morphological characteristics of samples The PVC treated was a commercially available suspension polymer, Ongrovil S 155, produced by the Borsodi Vegyi Kombinát.

The whole thermal process was followed by TG and DTG measurements in air and argon atmospheres by means of a Du Pont 990 Thermoanalyzer. Evolved-gas analysis was performed with a home-made apparatus. Pyrolysis gas chromatography was accomplished using a Hamilton type pyrolyzer and a Carlo Erba chromatograph furnished with a flame ionization detector.

The investigations showed benzene and other components to be evolved from the initial polymer and an alteration depending on the morphological characteristics of the samples. This was suggested to be due to the different mechanisms of thermal degradation of the PVC.

The thermal analysis of polymers has been widely used for the characterization and structure determination of polymers [1, 2]. It is well known, however, that the kinetics and mechanism of thermal degradation depend on the experimental conditions [3, 4].

In our earlier pyrolytic measurements [5] PVC was used as a model substance in the study of the dependence of the data obtained on the preparation and morphological characteristics of samples to be analyzed. We found that in the course of thermal analysis of thin PVC films the composition of the volatile products of degradation changes qualitatively as well as quantitatively with the variation of the film thickness. The present paper deals with some further investigations concerning the influence of the morphology of PVC samples on the experimental data.

## Experimental

### *Materials*

The starting sample of PVC was a commercially available suspension polymer prepared by the Borsodi Vegyi Kombinát, Ongrovil S 155, having a $K$ value of 55 (Fikentscher's constant) as computed from viscosity measurements.

### *Elemental composition*

This was determined by microcombustion (C: 38.8; H: 4.9; Cl: 53.6 in weight percent). PVC samples to be analyzed were as follows: PVC precipitates and film cast from tetrahydrofuran (THF) solution onto mica plate.

### *Film casting*

PVC solutions of different concentrations were made in THF as solvent. The PVC was applied onto mica plate as substrate by an immersion technique. The thickness of the PVC films thus prepared was 400 – 10.000 Å. The morphological characteristics of films were investigated by light microscope and scanning electronmicroscope [5].

### *Precipitates*

These were made just before use. Commercial PVC powder was dissolved in freshly distilled tetrahydrofuran, and then poured dropwise into a large amount of a given poor solvent. The precipitate was filtered off and carefully washed with distilled water before it was left to dry at 60° in vacuo ($3 \times 10^{-3}$ torr).

### *Solvents*

THF produced by Merck, free from peroxide, analytical grade; water freshly doubly distilled.

### *Inert gases*

Argon of 99.99% purity, $O_2 < 50$ ppm, moisture less than 10 ppm; nitrogen of 99.995%, $O_2$ content $< 30$ ppm, moisture 10 ppm, other impurities: inert gases.

### *Methods*

TG and DTG measurements were made using 5 – 6 mg samples for degradation in air or argon atmospheres with a gas flow of 250 ml/min at a heating rate of 5°/min, using a Du Pont 990 Thermoanalyzer.

### *Evolved-gas analysis (EGA)*

A home-made apparatus was used for EGA measurements (Fig. 1).

EGA measuring conditions were as follows: purging gas ($N_2$) rate: 40 ml/min, heating rate: 10°/min. Weight of sample 0.05 – 0.10 mg.

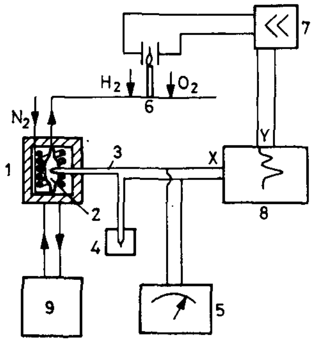

Fig. 1 Apparatus for EGA measurements. 1-furnace; 2-sample space; 3-thermocouple; 4-cold point; 5-voltmeter; 6-FID; 7-amplifier; 8-XY recorder; 9-programmer

PGC was performed with a Hamilton pyrolyzer coupled with a Carlo Erba Fractovap Model D gas chromatograph furnished with FID and glass capillary column (20 m in length, coated with OV 101). $N_2$ carrier gas rate: 1.6 ml/min. Recorder: Honeywell; integrator: Chromolog 2; time of pyrolysis: 30 sec.

## Results and discussion

### *EGA measurements*

Figure 2 demonstrates EGA diagrams of PVC powders and dried films. Two peak maxima appear near 290° and 450°, and a shoulder at 320°.

The curves show significant differences in the peak height depending on the thickness of samples, which indicates different degradation processes in the

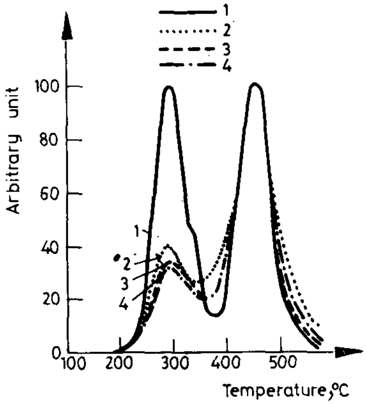

Fig. 2. Effect of thickness of samples on the EGA diagram. 1-PVC powder; 2-film of 10000 Å thickness; 3-film of 900 Å thickness; 4-film of 400 Å thickness

Table 1

Evolved gas analysis of PVC Measured data

| No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| | Sample | Particle size | Thickness | Ratio of height of peaks | Technique of sample preparation |
| 1 | Film | — | 400 Å | 0.33 | Immersion technique |
| 2 | Film | — | 900 Å | 0,35 | Immersion technique |
| 3 | Film | — | 10 000 Å | 0.41 | Immersion technique |
| 4 | Powder | Small | — | 0.38 | Precipitation by ethanol |
| 5 | Powder | Medium | — | 0.54 | Precipitation by acetone |
| 6 | Powder | Large | — | 1.33 | Precipitation by water |
| 7 | Powder | Large | — | 1.35 | Precipitation by water |
| 8 | Powder | Large | 50–250 μm | 1.00 | Commercial product Ongrovil S 155 |

polymers. We found that this dependence can be well characterized by the ratio of the two peaks. The values are given in Table 1.

The FID detector applied in the EGA measurements is not sensitive to the HCl evolved in the thermal degradation of PVC. We followed the total process of degradation by thermogravimetry, where the evolution of hydrocarbons and HCl were detected. Figure 3 depicts the curve for commercial PVC powder in an $O_2$ atmosphere.

Similar curves were found in measurements on precipitates in oxygen. In

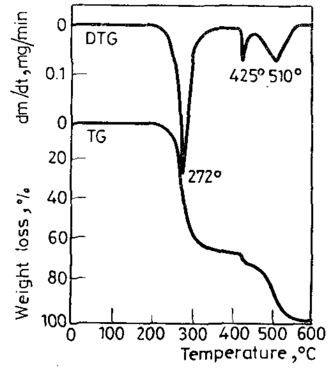

Fig. 3. Thermal decomposition of PVC in $O_2$ atmosphere

contrast to the results obtained in oxygen, different DTG curves are observed in argon, depending on the sample preparation.

The commercial powder and the precipitate obtained by usage of water as poor solvent show similar characters (Fig. 4), while the DTG curves of fine powders precipitated by acetone and by alcohol (Fig. 5) exhibit some alterations compared to the curves of rough particles in Fig. 4.

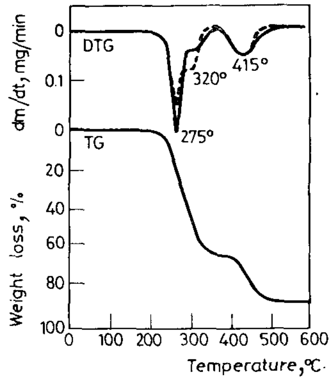

Fig. 4. Thermal decomposition of PVC in argon atmosphere. —— commercial powder; - - - precipitated by water

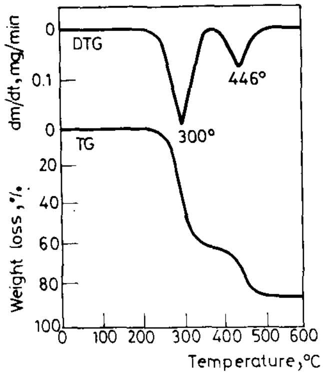

Fig. 5. Thermal decomposition of PVC in argon atmosphere (precipitated by alcohol or acetone)

An interesting similarity is observed in the DTG and EGA curves near 320°. A shoulder appears in this region in the DTG (Fig. 4) and EGA (Fig. 2) curves for samples with relatively large particle diameters.

Obviously, this is due to the mechanism of thermal degradation of PVC, which seems to be significantly dependent on the morphology.

Information on the reaction mechanism was obtained by means of PGC measurements (Fig. 6). On pyrolysis of commercial PVC powder (curve 1) at 447° the maximum of the benzene peak (labelled by "a") is higher by an order of magnitude than the maximum of component "b".

If the thickness is reduced, the size of the benzene peak diminishes with respect to the other components, as can be seen in curve 2 for the pyrolysis of PVC film of 400 Å thickness. It could be concluded that the composition of the volatile products of thermal degradation is affected by the thickness of the samples. Benzene peaks were identified by chromatographic means according to the retention times, and the peak area was observed to be dependent on the thickness.

According to the literature mass-spectrometric thermoanalysis data [6] the maximum rate of HCl formation in the thermodegradation corresponds to the temperature maximum of benzene evolution.

We should like to underline that this maximum is followed at about 320°, which is nearly the point of the shoulder in the curves of our DTG and EGA measurements presented here.

On the other hand, the data presented in Table 1 show that there is a range of thickness below a maximum limit in which the peak ratios are very similar to each other. Consequently, this is the range in which the measured data are comparable. This is therefore the suitable range of thermal analysis.

All these phenomena suggest a reaction mechanism governed by the residence time of the volatile fragments in the polymer layer. The concentration of hydrogen chloride seems to be a fundamental factor in this case; it may be controlled by the diffusion path and therefore by the thickness or diameter of samples to be analyzed. Further details on the thermal degradation will be reported later.

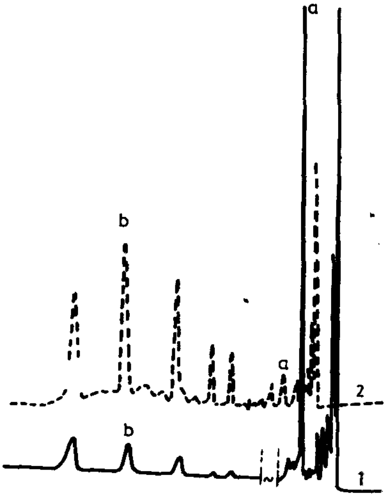

Fig. 6. PGC curves of PVC at 447°. 1-commercial PVC powder; 2-PVC film of 400 Å

## References

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Résumé — Afin d'étudier la relation entre les données obtenues et la préparation et les caractéristiques morphologiques des échantillons le PVC a été utilisé comme substance modèle pour les mesures thermiques effectuées par les auteurs. Le PVC traité était un polymère commercial en suspension, Ongrovil S 155, fabriqué par Borsodi Vegyi Kombinát.

Le processus thermique complet a été suivi par TG et TGD en atmosphère d'air et d'argon, à l'aide du thermoanalyseur Du Pont 990. L'analyse des gaz dégagés s'est effectuée dans un appareil construit par les auteurs. La chromatographie en phase gazeuse des produits résultant de la pyrolyse s'est effectuée en utilisant un pyrolyseur type Hamilton et un chromatographe Carlo Erba avec un détecteur d'ionisation de flamme.

Les études ont mis en évidence le dégagement de benzène et d'autres composés du polymère initial ainsi qu'une altération qui dépend des caractériques morphologiques des échantillons; ces phénomènes sont attribués au mécanisme de la dégradation thermique du PVC.

Zusammenfassung — Um die Abhängigkeit der erhaltenen Angaben von der Vorbereitung und den morphologischen Charakteristika der Proben zu untersuchen wurde PVC als Modellsubstanz bei thermischen Messungen eingesetzt. Das behandelte PVC war ein handelsübliches Suspensionspolymer Ongrovil S 155, hergestellt von der Firma Borsodi Vegyi Kombinát.

Der ganze thermische Vorgang wurde mittels TG und DTG-Messungen in Luft und in Argon-Atmospäre unter Einsatz des Du Pont 990 Thermoanalyser verfolgt. Die Analyse des entwickelten Gases wurde in einem Eigenbau-Gerät durchgeführt.

Die Pyrolysen-Gaschromatographie wurde mittels eines Hamilton Pyrolysegeräts und eines Carlo Erba Chromatographen mit Flammenionisationsdetektor durchgeführt.

Die Prüfungen zeigten die Entwicklung von Benzol und anderer Verbindungen aus dem Ausgangspolymer und eine von den morphologischen Eigenschaften der Proben abhängige Änderung, welche dem unterschiedlichen Mechanismus der thermischen Zersetzung von PVC zugeschrieben wurde.

Резюме — Для изучения зависимости полученных при термических измерениях образцов от способа получения и их морфологических характеристик, был использован ПВХ в качестве модельного соединения. В качестве обработанного ПВХ использовали промышленный суспензионный полимер Онгровил С 155, производимый Боршодским химическим комбинатом. Термический процесс был исследован с помощью ТГ, ДТГ и ДТА в атмосфере воздуха и аргона посредством термоанализатора Дюпон 990. Анализ выделенного газа проводили на аппаратуре собственного производства. Пиролизная газовая хроматография была проведена с пиролизером Хамильтона и Карло Эрба хроматографом, снабженным пламенно-ионизационным детектором. Исследования показали присутствие бензола и других компонент, выделяющихся из исходного полимера, и изменения, зависящие от морфологических характеристик образцов, которые, как было предположено, обусцовлены различным механизмом термического распада ПВХ.