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EFFECTS OF SOME METHODOLOGICAL FACTORS ON QUANTITATIVE CHARACTERISTICS OF THERMAL STABILITY OF POLYIMIDE MATERIALS

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Thermogravimetry and differential thermal analysis of films and fibres prepared from polypyromellitimidediphenyl oxide were carried out with standard Derivatograph and Du Pont-951 thermoanalyzers. The results were used for the investigation of some methodological factors affecting the processes of thermal degradation of polyimides, and the quantitative characteristics of these processes. It was shown that the pattern of thermal degradation of polyimide and its thermal characteristics depend on the construction of the sample holders, on the weight of the sample and on its packing in the holder. It is concluded that strict standardization of conditions of comparative thermal analysis and a detailed description of the conditions of carrying out the analysis are necessary to obtain comparable results.

Investigation of the thermal stability of polyimide materials is of great importance for the determination of the temperature ranges in which these materials retain their physicochemical characteristics and do not undergo degradation due to reversible chemical processes.

Thermal analysis used in the past decade as the principal method for determination of the thermal stability of thermally stable polymers, made it possible to elucidate some peculiarities of their thermal degradation. At present the most widespread method, thermogravimetry (TG), in particular, in combination with differential thermal analysis (DTA), is often used for characterization of the thermal stability of polymers. For this purpose the following quantitative parameters are used in TG: temperatures of the start of thermal degradation, and of 5, 10, 50 and 100% weight loss, rates of weight loss over a certain temperature range, temperatures of maximum rate of weight loss or maximum effect of heat evolution or absorption according to DTA data, values of activation energy at different stages of degradation etc.

Unfortunately, in spite of great efforts of the International Confederation on Thermal Analysis [1–3] and Garn's recommendations [4], up to the present the researchers working in the field of thermal analysis do not use the same terminology. This defect, together with the lack of detailed information on methodological conditions of sample testing in TG or DTA, make it impossible to compare results obtained by different authors.

The manufacture of serial instruments for thermal analysis provides a great advance in the standardization of methods of thermal analysis and permits com-

parable results to be obtained with strict observation of standard methods of analysis. Nevertheless, at present several leading instrument-making companies (Perkin-Elmer, Stanton, Du Pont, Mettler, Leina, Denki Rigaku and others) manufacture high-quality thermoanalytical instruments with different constructions of both heating elements and sample holders. Although the analysis of identical samples may be performed correctly and accurately, nevertheless these differences lead to different thermal characteristics for these samples. Consequently, when quantitative measurements are made, it is always necessary to carry out several additional analyses with standard samples, and when data obtained with different instruments are compared, correlation between these data should be made. Moreover, even when instruments of the same type are used in the analysis, the indispensable condition ensuring the comparability of the parameters obtained is a detailed description of all methodological experimental conditions. In addition to instrumental and methodological differences affecting the results of thermal analysis, it is also important to know the conditions of synthesis, preparation and preliminary treatment of the sample. The results reported in this work show that it is necessary to satisfy these conditions in order to enhance the significance of thermal analysis.

Experimental

Samples of a polymer of high thermal stability, "Arimide PM", in the form of film or fibres, were chosen for investigations. They were obtained from polypyromellitimidediaminodiphenyl oxide and prepared by a method described previously [5, 6]. Thermal analysis of these samples was carried out with an OD-102 Derivatograph (MOM, Hungary) and a Du Pont 990, TGA-951 thermoanalyzer (Du Pont, USA).

Conditions of analysis with the Derivatograph

Heating rate: 4.5 °/min; rate of air flow through the furnace: 50 cm^3/min; sample weight: 20, 50 and 200 mg; a large standard platinum crucible 9 mm in diameter with a cover, and standard platinum plates were used as sample holders.

Conditions of analysis with the Du Pont 990, TGA-951

Heating rate: 4.5 °/min; rate of air flow through the furnace: 50 cm^3/min; sample weight: 3–4 mg; a standard platinum pan was used as holder; sensitivity of TG: 0.5 mg/inch.

Discussion of results

TG curves, and in particular DTA curves obtained simultaneously with TG curves with a Derivatograph (Fig. 1), clearly show that the construction of the holder and the arrangement of the samples of polyimide film (identical in proper-

ties and weight) affect the thermal degradation of the polymer. A sharp difference in the rate of thermal degradation of samples in a closed crucible (curves 1, 2 and 3) and in an open plate (curves 4 and 5) shows that the use of holders of different constructions leads to a change in the conditions of thermal degradation.

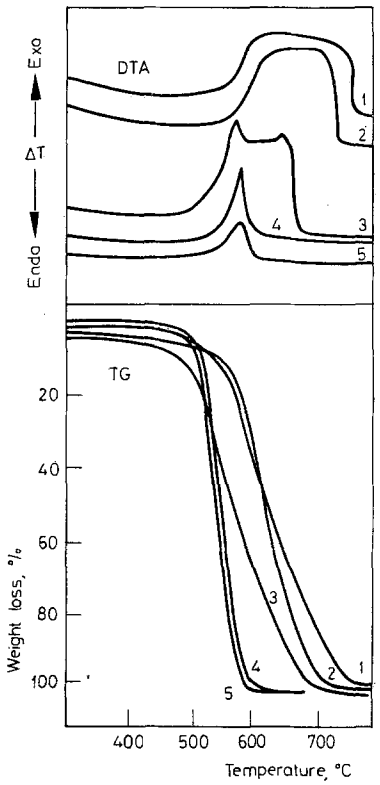

Fig. 1. TG and DTA curves for polyimide film in analysis with a Derivatograph. Curve 1. Film with sample weight of 50 mg in a standard platinum crucible (9 mm in diam.) with a closed lid. The sample is placed in a single layer and is attached to the whole inner surface of the crucible. Curve 2. Same conditions as for curve 1. The sample is folded in four layers and placed in the upper part of the crucible. Curve 3. Same conditions as for curve 1, but the sample is placed on the bottom of the crucible. Curve 4. Standard platinum plate holder consisting of one section. The sample is placed in a single layer. Curve 5. Same conditions as for curve 4, but the sample is placed in four layers. The conditions of thermoanalysis are described in the Experimental part

In contrast to many inorganic compounds, for organic compounds, and particularly for polymers, this leads to a complete change in structure in the course of analysis and, hence, to a pronounced change in characteristics as compared to the initial sample. The above Figure shows that the exothermic effects accom-

panying degradation of the polyimide film in a closed volume last longer and do not show such a sharp "flash" as in samples undergoing degradation under the same conditions but on open surfaces. This difference in the character of thermal degradation is caused by the free access of oxygen from the surrounding medium

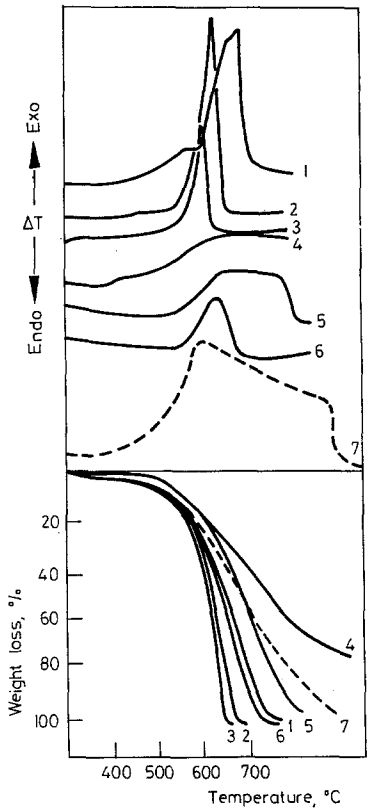

Fig. 2. TG and DTA curves for polyimide films in analysis with a Derivatograph. Curves 1—3. The sample is placed on an open holder in three layers; (1) 200 mg, (2) 50 mg, (3) 20 mg. Curves 4—6. The sample is placed in a closed crucible folded in four layers; (4) 200 mg, (5) 50 mg, (6) 20 mg. Dotted curve: experiment similar to that represented by curve 6 but the crucible has no lid. The conditions of thermoanalysis are described in the Experimental part

to a holder of open type, whereas in a closed volume degradation proceeds under conditions of a self-generating atmosphere. Thus, conditions of thermal analysis alone may help us to understand the behaviour of polyimide films in articles with different degrees of access of oxygen. The method of placing the samples in a holder also affects the character of their thermal degradation. In the same Figure we can see the difference in DTA curves for samples of polyimide film of the same

weight and thickness placed in a crucible as a folded band on the bottom (curve 3), near the upper edge of the crucible (curve 2), and in a single layer upon all the inner surface of the crucible (curve 1). This difference is also noticeable for the open holder on which an identical film was placed in a single layer (curve 4) and as

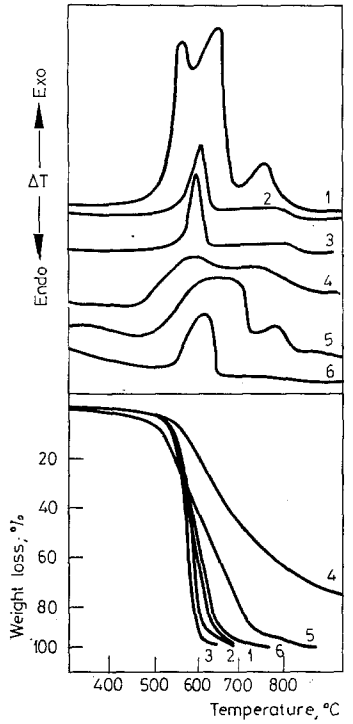

Fig. 3. TG and DTA curves for polyimide fibre obtained under experimental conditions similar to those in Fig. 2, with the same designation of curves

a pack of several layers (curve 5). When the thermal degradation of polyimide film was investigated on an open holder of the Du Pont-951 thermoanalyzer, similar data were obtained. The effect of the amount of the sample on the shapes of the DTA and TG curves is well known. This effect makes it possible to obtain more accurate quantitative results, to determine slight effects with large samples and to achieve a maximum resolution and a closer contact with the surrounding medium with small samples [4, 7, 8]. This is also true for many inorganic and some stable organic compounds. Nevertheless, for polymer materials a change in the sample quantity may lead to effects which do not adequately correlate with changes in quantitative and qualitative factors recorded by the TG and DTA curves. Changes in the volume and the mass of the polymer sample under investigation may lead in particular to the appearance and development of new processes

over the temperature range of the thermal degradation. In this case, as in the case of a change in the construction of the holder, a great change takes place in the characteristics of the product. Hence, when selecting the quantity or the volume of the polymer under analysis, one should remember the practical significance of the experimental conditions. Figure 2 is an example of a pronounced effect of the amount of the polymer sample on the picture of the thermal analysis. It can be seen that both in an open holder (curves 1 – 3) and in a closed holder (curves 4 – 6) an increase in the weight of a sample of polyimide fibre leads not only to an increase in the area of the exothermic effects of the thermal degradation, but also to the

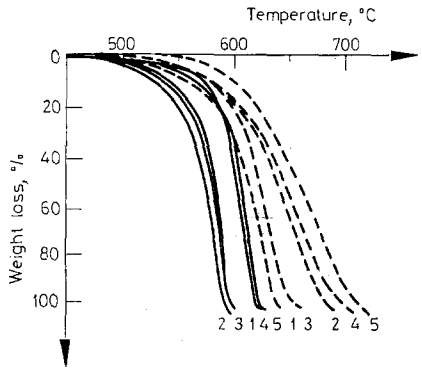

Fig. 4. TG curves for polyimide films prepared according to different conditions described in references [9—11]. Curves 1 [9], 2 [10], 3 [11], 4 [11]: film stored for 1 year under ordinary conditions at room temperature; curve 5 [11]: film stored for 2 years under ordinary conditions at room temperature. Thermal analysis was carried out with a Du Pont 951 thermoanalyzer; the conditions are described in the experimental part. Dotted lines: experiments carried out in helium

appearance of new peaks at high temperatures and to a marked decrease in the rate of thermal degradation. These data indicate that an increase in the mass of the sample leads to a shift in the equilibrium of the two main competing reactions in the polyimide: degradation and cross-linking towards the latter. In connection with this change in the degradation mechanism, the parameters governing the thermal stability of the polymer also change. In some cases, when the thermal characteristics of polymer articles manufactured from the same initial polymer are compared, not only the technology of manufacture and in particular the thermal degradation should be known, but also the shapes of the articles. Even polyimide fibres and films prepared from one solution of polyamido acid differ in the type of thermal effects accompanying their thermal degradation (Fig. 3). In a comparative analysis of the thermal stabilities of polyimide materials it is necessary to take into account the technological conditions of the preparation of the articles, as we ll as the duration and conditions of their storage. This is clearly seen in the

curve in Fig. 4, characterizing polypyromellitimidediphenyl oxide films prepared by different methods and stored under different conditions for different periods of time [9–13].

Thus, our experiments showed that in order to obtain comparable characteristics in the investigation of the thermal stabilities of polymer materials detailed information should be available concerning the conditions of preparation of samples, their characteristics and detailed conditions of experiments carried out with appropriate thermoanalytical instruments.

References

1. R. C. MACKENZIE, J. Macromol. Sci., Ser. A, 4 (1970) 1015.
2. R. C. MACKENZIE, J. Thermal Anal., 4 (1972) 343.
3. R. C. MACKENZIE, J. Thermal Anal., 8 (1975)
4. P. D. GARN, Thermoanalytical methods of investigation A. P. N. Y.—L. 1965.
5. M. M. KOTON and YU. N. SAZANOV, J. Thermal Anal., 7 (1975) 165.
6. L. N. KORZHAVIN, Thesis, Leningrad, 1971.
7. L. G. BERG, Vvedenije v termografiyu (Introduction to thermography), Nauka, Moscow, 1969.
8. Thermal Analysis, ed. Schwenker, P. D. Garn, Academic Press, New York—London, 1969, Vol. 1., p. 243.
9. YU. N. SAZANOV, G. N. FEDOROVA and L. M. SHCHERBAKOVA, J. Appl. Polymer Sci., 19 (1975) 2335.
10. G. V. BAGROV, Thesis, Leningrad, 1975.
11. YU. N. SAZANOV, L. V. KRASILNIKOVA and L. M. SHCHERBAKOVA, Europ. Polymer. J., 11 (1975) 801.

RÉSUMÉ — Etude de pellicules et de fibres préparées à partir de l'oxyde de polypyromellit imidediphényle, par thermogravimétrie et par analyse thermique différentielle à l'aide d'un Derivatograph et d'un analyseur Du Pont 951. On a suivi l'influence de quelques facteurs méthodologiques sur le processus de la dégradation thermique des polyimides et sur les caractéristiques quantitatives qui s'y rapportent. On montre que le schéma de dégradation thermique du polyimide et les caractéristiques thermiques dépendent de la construction des supports d'échantillon, de la masse de l'échantillon et de la manière dont celui-ci est disposé dans le creuset. On en conclut que l'obtention de résultats comparables est soumise à l'emploi d'un mode opératoire méthodique et à la description détaillée des conditions expérimentales de l'analyse thermique.

ZUSAMMENFASSUNG — Thermogravimetrie und Differentialthermoanalyse von aus Polypyromellitimid-diphenyloxid hergestellten Filmen und Fasern wurden in den Thermoanalysatoren "Derivatograph" und "Du Pont 951" durchgeführt. Die Ergebnisse wurden zur Untersuchung einiger, den thermischen Zersetzungsprozeß von Polyimiden beeinflussender methodologischer Faktoren und quantitativer Charakteristika dieser Vorgänge eingesetzt. Es wurde gezeigt, daß das "Muster" der thermischen Zersetzung des Polyimids und seine thermischen Charakteristika von der Konstruktion des Probenhalters, vom Gewicht der Probe und seiner Einfüllung in den Probenhalter abhängen. Daraus wird abgeleitet, daß eine strenge Standardisierung der Bedingungen der vergleichenden Thermoanalyse und eine eingehende Beschreibung der Analysenbedingungen zwecks Erhalten vergleichbarer Resultate unbedingt erforderlich sind.

Резюме — С помощью стандартных термоанализаторов таких как дериватограф и прибор «Дюпон-951», были проведены термогравиметрический и дифференциальный термический анализ пленок и волокон, полученных их полипиромеллитимидо-дифенилоксида. Эти результаты были использованы для исследования некоторых методологических факторов, затрагивающих процессы термического разрушения полиимидов и количественных характеристик этих процессов. Показано, что характер термической деградации полиимида и его термические характеристики, зависят от конструкции держателей образца, веса образца и его набивки в держателе. Сделано заключение, что для получения сравнимых результатов, требуется строгая стандартизация условий сравнительного термического анализа и детальное описание условий его выполнения.