Special Review

PROSPECTS OF THERMAL ANALYSIS IN POLYMER RESEARCH

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A survey and an analysis of the publications concerned in thermal analysis (TA) published in four renowned journals during the years 1965—1974 were performed. The published data were evaluated from three points of view: TA methods used for polymers, properties and phenomena studied by TA methods, types of polymers investigated by TA methods. From the statistical data were derived the future trends for the application of particular TA methods in polymer science.

The methods of thermal analysis have gradually found very wide application in research into the structures and properties of polymers. The first sporadic contributions on the differential thermal analysis (DTA) of polymers date from about 1945, on their isothermal thermogravimetry from about 1949, and on their dynamic thermogravimetry from about 1959. Differential scanning calorimetry (DSC) and quantitative DTA were applied to polymers immediately after their discovery [1]. There has been an extraordinary increase in the applications of the three main TA techniques (DTA, DSC, TG) in the physics and chemistry of macromolecules in the past ten years. This is due to several specific circumstances: The design of precise and sensitive automatic equipment eliminated the disadvantages of polymers as objects for TA (low thermal conductivity, low phase transition heats, thermal gradients in measuring cell). TA apparatuses suitable for polymer research are offered at present by several tens of producers and these apparatuses have become virtually standard equipment in laboratories studying the properties of polymers from different aspects.

The enormous interest in high-temperature-resistant polymers evoked the need for their evaluation and stimulated the design of new types of thermoanalytical equipment, especially thermobalances. This simultaneity of the needs for methods of evaluating the properties of new polymers and for the development of thermoanalytical equipment was the deciding moment for the spreading of TA methods in the polymer field.

In order to assess the present state of the application of TA methods in polymer research, we considered it appropriate to analyse in some detail the range of publications concerning the TA of polymers in the past ten years, i.e. the time of mass adoption of TA methods in polymer research. This analysis of published material forms the substance of the present work. In our opinion, such an analysis not only

provides a quantitative view of the present state of the TA of polymers, but also supplies information on development trends and prospects of particular TA techniques and their future applications.

Method of analysis

The publications on the TA of polymers are scattered over a very wide range of journals. However, a preliminary survey showed that the great majority of the contributions have been published in one or other of the following four journals:

1. Journal of Polymer Science (including the editions Chemistry, Physics, Letters);
2. Journal of Applied Polymer Science;
3. Polymer;
4. Vysokomolekularnyje Sojedinenija (including the series A and B).

The frequency of occurrence of relevant works in other journals was essentially lower (on average, for every contributions in the above-mentioned journals there was one publication in a further ten journals specializing in the physics, chemistry and technology of polymers). We therefore considered these four journals as an adequately representative selection for the purposes of the analysis.

The technique of analysis was rather laborious, but very simple. It was clear that neither the subject indexes of particular volumes of the journals, nor the titles of the papers are a satisfactory basis for the analysis. It was necessary to inspect page after page the published material selected for analysis and to check whether the "Experimental" sections, Tables or Figures include data indicating the application of TA methods. Each such registered source was characterized by four descriptors: bibliographic data, the TA methods used, the phenomena studied by the TA methods, and the types of polymers investigated. It would certainly be interesting to inspect the whole time interval, from the beginning of the application of TA methods to polymers to the present. However, it was necessary to limit the inspection to the volumes for 1965, 1970 and 1974. A further simplification introduced was the recording of the three main TA methods only (DTA, DSC, TG). The term DSC used in this work includes both classical DSC and quantitative DTA. The literature data often do not allow one to identify which of these two methods was actually used.

The applications of TA to polymers were classified in seven groups:

1. Melting and crystallization of polymers.
2. T_g temperature of polymers.
3. Heat capacity of polymers.
4. Thermal stability and degradation of polymers.

5. Analysis and identification of polymers.
6. Cross-linking of polymers.
7. Other applications.

As regards the material used, the publications were very heterogeneous. We therefore formed nine groups including the most frequently investigated polymers, a tenth group covering all the other types with a frequency of occurrence lower than 3% of the considered set. In these classifications, publications dealing with several TA methods or applications were registered as many times as the number of independent classifying elements they included.

Methods of thermal analysis

The results of the survey of the three years' issues of the selected journals according to particular thermoanalytical methods are summarized in Table 1. In addition to the absolute number of publications concerning the TA of polymers, the Table indicates the application of the particular TA method as a percentage of the total number of publications in the corresponding year, and its increase (I) calculated on the basis of the value for 1965.

Table 1

	1965			1970			1974		
TA method	Number	%	I	Number	%	I	Number	%	I
DTA	44	59	1	61	33	1.39	50	24	1.14
DSC	3	4	1	41	22	13.7	79	37	6.3
TG	28	37	1	84	45	3.00	82	39	2.93
Total number	75	100	1	186	100	2.48	211	100	2.81

Let us first consider the total number of publications. Even in 1965 the number of works dealing with the TA of polymers was appreciable (75). During ten years this number tripled. The increase in the field of the thermogravimetry of polymers corresponds to the average. The number of publications concerned with DTA can be considered as steady in the relevant time interval. The most pronounced increase during the past ten years was observed in DSC. This is easy to understand, because the years around 1965 represent the start of this modern thermoanalytical method. However, from a comparison of the data for 1970 and 1974 it is clear that while the number of contributions on DTA and TG were constant, the number on DSC doubled. These conclusions may be illustrated by the percentage data for the particular TA techniques: In 1965 DTA was used in 59% of the publications

and DSC in only 4%. In 1970 the proportion for DTA fell to 33% (a slight increase in absolute terms), while the proportion for DSC increased to 22%. In 1974 there was again marked drop in DTA applications and a significant increase in both the proportion (37%) and the absolute number of publications on the DSC of polymers. As regards TG, the proportion of contributions on this TA method did not vary essentially during 1965–74. As already mentioned, the increase corresponds to the average. On the basis of this analysis, with regard to the increases in the absolute numbers of publications and the frequencies of application of the particular TA methods, the following conclusions were reached: The general increasing trend in the number of publications on the TA of polymers is continuing. The broadening of the applications of TG corresponds quantitatively to this general trend. The DSC techniques are replacing DTA, even in measurements where its quantitative characteristics are not exploited.

Applications of thermal analysis

In the next stage of the analysis of the published material on the TA of polymers we determined what properties, processes and phenomena in polymers were investigated by the main TA methods. The results of this stage of the analysis are presented in Table 2. The numerical data in the Table represent the numbers of publications relating to the appropriate column. For instance, in 1974 108 papers were published in which TA methods were applied for evaluation of the termal stabilities and degradations of polymers. In 76 cases TG methods, in 24 cases DTA methods, and in 8 cases DSC methods were used.

It is immediately clear from the Table that the applications of TA to polymers can be classified practically without exception into the six groups mentioned in the introduction. The "other applications" will therefore not be considered further. There is also a significant differentiation in the six main groups. If we consider the listed data, two types of TA applications predominate: the evaluation of the thermal stabilities of polymers, and the study of phase transitions. The other applications appeared in relatively few cases. The data also confirm that the two main regions of application of TA exhibit the greatest increase in the number of publications in the past ten years in comparison with the other regions of application. Applications of TG in general are concentrated on evaluation of the thermal stabilities of polymers, and its use in other regions is rather sporadic, DTA and DSC are especially useful for the investigation of phase transitions in polymers. For these purposes, classical DTA is being replaced stepwise by DSC techniques. There are surprisingly relatively few TA applications in the study of the cross-linking of polymers, though in this field DSC has especially wide potential possibilities. In contrast, it is interesting that there are numerous applications for determination of the glass-transition temperatures of polymers, although a number of other methods could be used for this purpose [2].

Table 2

Applications of TA methods to polymers

TA method / Application	Year	DTA	DSC	TG	Total
Melting and crystallisation	1965	24	2	—	26
	1970	25	27	—	52
	1974	17	47	—	64
T_g	1965	4	0	—	4
	1970	10	7	—	17
	1974	1	12	—	13
C_p	1965	—	0	—	0
	1970	—	3	—	3
	1974	—	7	—	7
Thermal stability and degradation	1965	6	0	25	31
	1970	20	1	78	99
	1974	24	8	76	108
Analysis and identification	1965	2	0	1	3
	1970	0	1	0	1
	1974	0	0	2	2
Cross-linking	1965	6	1	1	8
	1970	0	2	0	2
	1974	5	4	0	9
Other applications	1965	2	0	1	3
	1970	6	0	6	12
	1974	3	1	4	8

Polymers investigated by TA methods

As regards which types of polymers were the objects of TA, our analysis was intentionally restricted to the 1974 volumes of the selected journals. Consideration relating to time would indicate which new types of polymers were reported rather than the changes in the polymer range investigated by TA methods.

Table 3 lists the polymers in the sequence of diminishing frequency of occurrence in the publications concerning properties of concrete polymeric objects. Polymers mentioned in less than 3% of the publications are included in the overall group "other polymers". It can be seen that this group comprises a quarter of the considered set. This is explainable by the fact that, especially in papers from the field of the synthesis of high-temperature-resistant polymers, it has become

Table 3

Polymers as objects of TA methods

	Number	%
Polyolefins	35	27
Polyimides	17	13
Polyesters	12	9
Polyamides	10	8
Polyaromatics	7	6
Polyquinoxalines	4	3
Polyurethanes	4	3
Polymers with N and S heterocycles	4	3
Polyvinylchloride	4	3
Other polymers	32	25
Total number	129	

almost a rule to document the properties of a new polymer by evaluation of its thermal stability by means of thermogravimetry.

The polymers most frequently (27%) studied by TA are the polyolefines, and more than 90% of these papers deal with polyethylene. In the studies on this polymer, the problems of the influence of the thermal history on the morphologic structure and on the properties dependent on this structure predominate. The interest in this polymer is understandable considering the importance of this mass-producted material. It has been assumed that this polymer is a suitable model for a detailed study of the phase transitions and crystallization kinetics of polymers and that the information thus obtained could be applied to other polymers. Recent works in the field of the TA polymers indicate that this semicrystalline polymer is a more complex system than originally supposed [3].

The other polymers named in the Table belong to the category of high-temperature-resistant polymers (except PVC). The absolute lack of unambiguous criteria for evaluation of the thermal stabilities of these polymers led to thermogravimetry being applied as practically a standard for this purpose. In a number of monographs concerned with the synthesis and properties of thermally polymers, thermogravimetry is practically the sole method for evaluation of their stabilities (for example [4–6]).

One interesting result of the analysis of the published literature is the fact that, although a number of TG methods have been elaborated for evaluation of the thermal stability, at present the most used procedure is the relative evaluation via conventionally chosen characteristics of the TG curves. The most frequently used criteria are: the temperature of the beginning of mass loss, the temperature of a definite mass loss (5–50%), or inversely the mass loss corresponding to a certain temperature level (100–400°). This conclusion is confirmed, for instance, in the recent work of Sazanov and Koton [7].

Prospects of application of TA methods on polymers

In addition to the statistical results given above, the analysis of the published literature enabled us to estimate the future trends and forecast the prospects of further spreading of TA in research into the structures and properties of polymers. As regards the possibilities of the particular TA techniques, the most promising appears to be quantitative differential thermal analysis, the DSC technique. This has become an important tool for the investigation of a wide range of properties, phenomena and processes in polymers. There is perhaps only one field in which it has not fulfilled expectations: the measurement of the heat capacities of polymers. It was earlier assumed that (in spite of its lower precision) DSC could be used instead of measurements with adiabatic calorimeters, and would enable the rapid accumulation of the great mass of data necessary for the interpretation of the relations between the structures and the heat capacities of polymers [8]. The survey of the published literature has not confirmed these expectations.

As already mentioned thermogravimetry has the dominating position in the evaluation of the thermal stabilities of polymers, and its further spreading in this field can be expected. On the other hand, it seems that the most recent period has given no new stimulus for the study of degradation kinetics, although this was not long ago one of the most used applications of TG [9] and although non-isothermal kinetics has in general attained significant sucesses.

Classical DTA has at present been practically completely replaced by QDTA and DSC, and it seems that there is no specific field for its application in future. For the same reason the simultaneous techniques (DTA combined with TG) have not exhibited a marked growth. Some commercial equipment allows performance of simultaneous measurements on the same sample, but in most applications on polymers either DTA or TG must be preferred in the planning of the experimental conditions. In contrast, the ranges of special thermoanalytical techniques (DTG, EGA, TMA and some others) have expanded. Nevertheless, in general all these techniques lag far behind the applications of TG and DSC. The same is valid for coupled simultaneous techniques, e.g. combinations of TA with some other method of structural analysis (mass-spectrometry, gas chromatography).

With regard to new applications of TA methods, essential changes cannot be expected. During the past ten years the possibilities of the TA of polymers were thoroughly proved. From time to time new applications appear in the literature, for instance the estimation of the molecular weight of polytetrafluoroethylene by means of DSC [10], on the basis of the relation between the molecular weight and the heat of crystallisation. Such cases, however, are an exception rather than a rule. Doubtless, one can expect a further quantitative extension of the main fields of application of DSC in the study of phase transitions, and of TG in the evaluation of the thermal stabilities and degradations of polymers.

References

1. I. GÖMÖRY, Proceedings of the Conference Macrotest. Pardubice 1971, Main Lectures, p. 139.
2. W. A. LEE, G. J. KNIGHT, The Glass Transition Temperature of Polymers. Polymer Handbook Interscience Publishers, New York, 1966, III-61—III-91.
3. W. WRASIDLO, Thermal Analysis of Polymers, Advances in Polymer Science, 13 (1974).
4. A. H. FRAZER, High Temperature Resistant Polymers, Interscience Publishers, New York, 1968.
5. R. T. CONLEY, Thermal Stability of Polymers, Marcel Dekker, Inc., New York, 1970.
6. V. V. KORŠAK, Khimitseskoe stroenie i temperaturnye charakteristiki polimerov, Nauka, Moskva, 1970.
7. M. M. KOTON and J. V. SAZANOV, J. Thermal Anal., 7 (1975) 165.
8. B. WUNDERLICH, Advan. Polymer Sci., 7 (1970) 151.
9. L. REICH and D. W. LEVI, Dynamic Thermogravimetric Analysis in Polymer Degredation, Macromolecular Reviews, 1, Interscience Publishers, New York, 1967, p. 173—275.
10. B. C. LOFT, Applications of Thermal Analysis to Polymers, J. Polymer Sci., Symposium No. 49 (1975) 127.

RÉSUMÉ — Mise au point et analyse des publications ayant trai à l'analyse thermique des polymères et publiées entre 1965 et 1974 dans quatre périodiques connus. Les données publiées sont évaluées sous trois aspects: méthodes d'analyse thermique utilisées pour les polymères, propriétés et phénomènes étudiés par ces méthodes, types de polymères étudiés. Les directions futures d'application des méthodes d'analyse thermique particulières dans le domaine des polymères sont déduites des données statistiques.

ZUSAMMENFASSUNG — Es wird eine Übersicht und Analyse der in vier bekannten Zeitschriften in den Jahren 1965—1974 erschienen Veröffentlichungen über die Thermoanalyse (TA) von Polymeren gegeben. Die veröffentlichten Angaben wurden nach drei Gesichtspunkten beurteilt: für Polymere angewandte TA-Methoden, mittels TA-Methoden untersuchte Eigenschaften und Erscheinungen, mittels TA-Methoden untersuchte Typen von Polymeren. Aus den statistischen Daten wurden die künftigen Richtlinien für den Einsatz bestimmter TA-Methoden in der Polymerwissenschaft abgeleitet.

Резюме — Представлен обзор и анализ публикаций, касающихся ТА полимеров, опубликованных в четырех известных журналах в период времени 1965—1974 годы. Опубликованные данные были разделены, исходя из трех точек зрения: методы ТА, используемые для полимеров, свойства и явления, изугенные методами ТА, типы полимеров, исследованные методами ТА. Из статистических данных были выведены будущие тенденции применения специфических методов ТА в науке о полимерах.