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TG-DSC AS A NEW METHOD OF INVESTIGATION OF POLYMERS AND RESINS

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The introduction of the simultaneous TG–DSC method using only one sample permits a new approach to the characterization of polymeric materials. The correlation between the data obtained from the TG and DSC curves is made easier and is no longer affected by the inhomogeneity of the material.

In the case of polyethylene, a first heating under inert gas up to 560 °C allows measurement of the temperature and the heat of melting by DSC and the decomposition of polyethylene simultaneously via the TG and DSC curves. If oxygen is introduced above 560 °C, the oxidation of carbon black is detected by TG and DSC. For the investigation of resins and especially preimpregnated compounds, this TG–DSC method permits accurate measurement of the reticulation of the prepreg sample and the amount of resin on the support. With only one run on the same sample, the TG–DSC method yields many reliable data.

The characterization of polymeric materials has created a very wide range of applications for the thermal analysis methods, especially DSC and TG [1].

The polymer or resin samples have to be investigated on separate instruments, even if the microprocessor-based control allows monitoring of both experiments with the same heating conditions. With the introduction of the TG-DSC method, a new approach to polymeric materials is now possible. The SETARAM TG-DSC 111 [2] provides the TG and DSC curves with only one sample. In such a situation, the heating conditions and the gas control are strictly identical in the two experiments. The correlation between the data obtained from the TG and DSC curves is made easier and is no longer affected by the inhomogeneity of the sample, its porosity or other experimental factors.

TG-DSC investigations of polymers and resins

As concerns the investigation of polymeric samples by the DSC and TG methods, each of them has its specific applications. Decomposition and combustion are the two main applications with a TG system. From the TG diagrams, the contents of polymers or resins, various fillers, etc. are calculated. DSC is mostly used to characterize thermal effects occurring in

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polymeric samples without any mass variation: melting, crystallization, glass transition, cross-linking reactions, etc.

The data arising from the two experiments are correlated. But what is the precision of this correlation when only 10 mg samples of such complex compounds are heated in two different instruments? Polymers and resins are not pure products, but formulations. Many different compounds are combined to improve their characteristics, e.g. plasticizers, fillers, stabilizers, lubricants, antioxidants, fire retardants, blowing agents, etc. Some of these compounds are introduced in very small amounts. When 10 mg of such a sample is tested, what is the reproducibility of the polymer composition for such a mass? Most resins are used on supports (glass fibres, graphite fibres, etc.). What is the reproducibility of the resin impregnation on the support when only 10 mg of sample, including resin and support, is investigated?

These few questions show that in some cases there is a limitation to the possibility of obtaining a good correlation between the TG and DSC results coming from two different samples. The new TG-DSC method makes it possible to detect and measure precisely all types of thermal transformations, with or without mass changes, using only one sample, with a single instruments. Some examples are given to illustrate the potential of such a method.

Polyethylene

Polyethylene has been widely investigated by DSC and TG. Typical DSC applications are melting, determination of the degree of crystallinity, crystallization, and oxidative induction. Via the TG method, degradation, oxidation and filler contents are measured. Through use of the TG-DSC method, most of these applications are possible in a single run, as shown in Figs 1 and 2. A granule of polyethylene is heated from ambient temperature up to 560° under nitrogen, and then under oxygen from 560° up to 650°. Prior to the heating, the system is purged under vacuum, and then filled with nitrogen. During the first part of the test (Fig. 1), the polyethylene is pyrolytically decomposed, as seen in the TG curve. The mass variation (−72.6%) gives the percentage of polymer in the sample.

The value of the DSC curve for this temperature range is the detection of polyethylene melting and the determination of the corresponding heat. As the amount of polymer is precisely known from the TG curve, it is possible to relate the heat of melting to the real polyethylene percentage: $Q =$ 8.1 cal/g of the total mass, or $Q = 11.2$ cal/g of polyethylene.

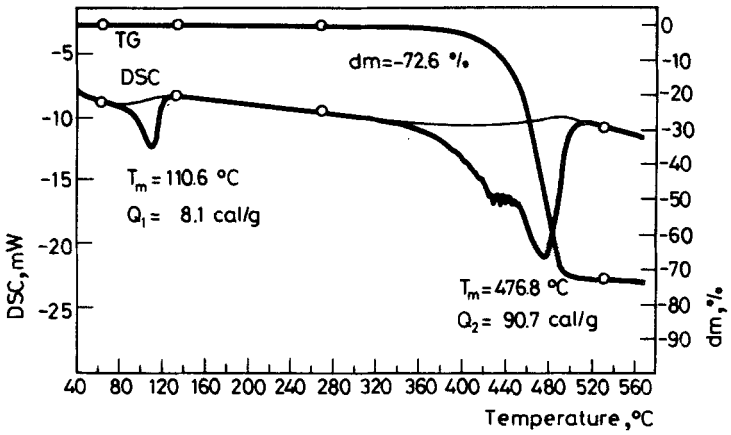

Fig. 1 Polyethylene (nitrogen). Sample mass: 22.100 mg, heating rate 5.0 deg min^{-1}

The percentage crystallinity may be determined from this heat value. The melting temperature (T_m = 110.6°) indicates that the sample is a low-density polyethylene.

The DSC curve also provides interesting information on the heat evolved during polyethylene pyrolysis. Some noise peaks are seen on the pyrolysis effect, probably due to emergence of gas from inside the sample. The heat of pyrolysis (90.7 cal/g of the total mass) is equal to 124.9 cal/g of polyethylene.

In the second part (Fig. 2) of the experiment, oxygen is introduced into the system to combust the carbon black contained in the remaining sample.

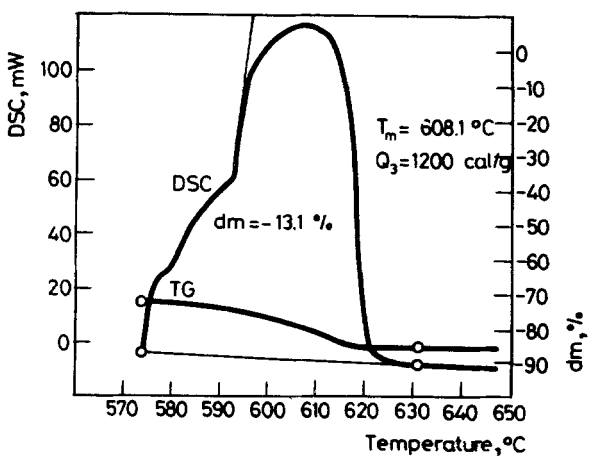

Fig. 2 Polyethylene(oxygen). Sample mass: 22.100 mg, heating rate 2.0 deg min^{-1}

The TG curve gives the percentage of carbon black (13.1%). Integration of the large exothermic peak in the DSC curve provides the heat of combustion (1200 cal/g of the total mass). After the combustion of the carbon black, some inert filler remains (14.3%). Thus, from a single experiment, it has been possible to learn the composition of a polyethylene sample (TG curve), to characterize the type and the crystallinity of the polyethylene (DSC curve), and to measure the amount of evolved during the degradation and the combustion process.

Epoxy resin

DSC has also been widely used to characterize the curing of epoxy resin, epoxy powder, epoxy prepreg, etc. The detection of the glass transition gives an indication of the state of curing of the epoxy sample. With the TG method, the degradation of epoxy compounds is investigated. It allows, for example, measurement of the glass content is the case of epoxy printed circuit boards is to cut reproducible samples.

Figures 3 and 4 show a TG-DSC run for a sample of epoxy printed circuit board. The sample is heated from ambient temperature up to 560° under nitrogen, and then under oxygen from 560° up to 700°. Prior to the heating, the system is purged under vacuum, and then filled with nitrogen. During the first part of the test (Fig 3), the epoxy resin is decomposed, as seen in the TG curve. The DTG peak shows that the rate of degradation is high. A slower degradation is detected from 350° up to 560°. In the DSC curve, the corresponding peak of decomposition of the organic matter (maximum temperature at 306.2°) is followed by another broad exothermic effect, probably corresponding to another degradation in the sample.

Corresponding to the exothermic effect (16.3 cal/g of the total mass), the organic content is 27.2%. Before the decomposition, it is possible to detect the glass transition (T_g = 114.2°) in the DSC curve; this gives information on the state of curing of the epoxy sample.

In the second part of the experiment (Fig. 4), the carboneous residue is burnt when oxygen is introduced into the system. The TG curve gives the content of this residue (10.9%), and the DSC curve provides the amount of heat evolved in the combustion (809 cal/g of the total mass).

At the end of the experiment (700°), the amount of glass fibres can be measured (56.8%). By means of such a test, it is really possible to relate the state of curing of the epoxy resin, its organic content and its glass fibre content.

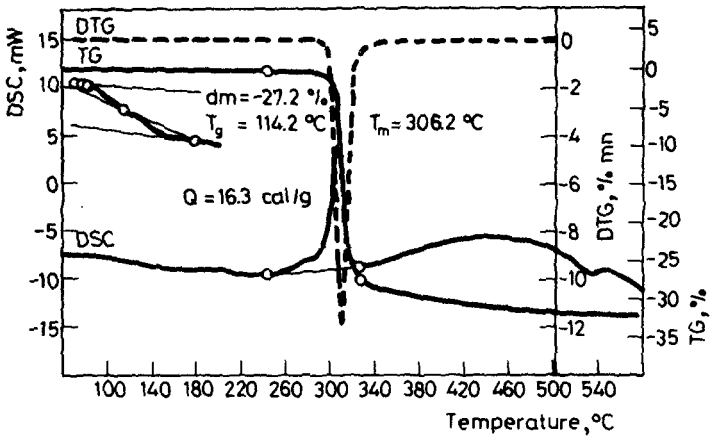

Fig. 3 Epoxy printed circuit board (nitrogen). Sample mass: 39.400 mg, heating rate: 5.0 deg min^{-1}

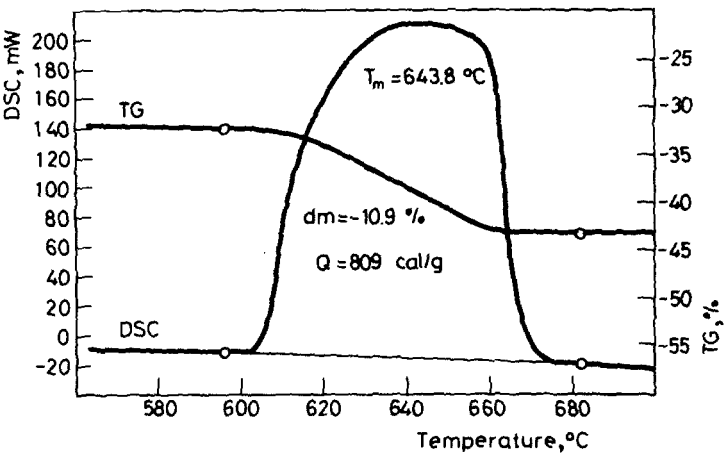

Fig. 4 Epoxy printed circuit board (oxygen) Sample mass: 39.400 mg, heating rate: 5.0 deg min^{-1}

The same test can be performed on uncured samples, in order to correlate the heat of curing to the real resin content. Through use of the same sample for all the TG and DSC determinations, the problem of the inhomogeneity of the sample is solved.

Conclusion

The TG-DSC method provides a new mode of investigation in the field of polymeric materials. It combines the TG and DSC determinations on one and the same sample; this permits a better correlation of the experimental data.

References

1 E. A. Turi, The thermal Characterization of Polymeric Materials, Academic Press, 1981.

2 P. Le Parlouër, Proc. 14th NATAS Conf., San Francisco (USA) Sept. 1985.

Zusammenfassung – Mit der Einführung der simultanen TG-DSC-Methode wird unter Verwendung nur einer Probe eine neue Verfahrensweise zur Untersuchung von Polymeren möglich. Die Korrelation der TG-und DSC-Kurven wird vereinfacht und bleibt unbeeinflusst von der Inhomogenität des Materials.

Beim Polyethylen erlaubt ein anfängliches Heizen unter Inertgas bis 560 °C eine Messung der Schmelztemperatur und -wärme mittels DSC sowie die Untersuchung der Zersetzung des Polymeren gleichzeitig mittels TG und DSC-Kurven. Wird oberhalb 560 °C in Sauerstoff gearbeitet, dann kann die Oxidation von Russ ebenfalls durch TG und DSC verfolgt werden.

Bei der Untersuchung von Harzen und imprägnierten Verbundwerkstoffen bietet die TG-DSC eine Möglichkeit, die Vernetzung des Vorprodukts genau zu messen und den Harzgehalt zu bestimmen. Mit nur einem TG-DSC-Versuch an einer Probe können zahlreiche Ergebnisse zuverlässig erhalten werden.

РЕЗЮМЕ — Применение совмещенного метода ТГ и ДСК представило возможность нового подхода для характеристики полимерных материалов. Корреляция между данными ТГ и ДСК устанавливается более легко и больше не затрагивается негомогенностью полимерного материала. Так, в случае полиэтилена, его начальный нагрев в инертной атмосфере до температуры 560°, позволил определить методом ДСК температуру и теплоту плавления, а разложение его — совмещенным методом ТГ и ДСК. В случае напуска кислорода при температуре выше 560°, такой совмещенный метод позволил определить окисление углеродистого остатка. При исследовании смол и, особенно, предварительно импрегнированных соединений, совмещенный метод ТГ и ДСК предоставляет способ точного определения сетчатого строения импрегнированного образца и количество смолы на подложке. Проведенное совмещенным методом ТГ и ДСК только одно измерение с одним и тем же образцом, позволяет получать значительно большее число приемлемых данных.