Journal of Thermal Analysis, Vol. 28 (1983) 295–302

EPOXY POLYMERS
Use and misuse of non-isothermal DTA and DSC in the study of the curing process

A. Schiraldi and *P. Baldini*

DIPARTIMENTO DI CHIMICA FISICA DELLA UNIVERSITÀ DI PAVIA,
VIALE TARAMELLI 16, 27100 PAVIA, ITALY

The current use of non-isothermal DTA or DSC for the investigation of polymers is based upon assumptions which allow a number of conclusions supported only by data drawn from the DTA or DSC traces of prepolymer samples.

A more adequate procedure involving the analysis of the DTA or DSC traces of several samples previously cured to different polymerization degrees under isothermal conditions is proposed.

A comparison of the results obtained with the two procedures is reported for two composite materials.

Calorimetric investigations on polymers are currently carried out under non-isothermal conditions, viz. through DTA or DSC at a given heating rate.

This kind of approach, although experimentally simple and rapid, must be considered with some caution, as it can result in misleading conclusions when the chemical process investigated occurs with a complex mechanism, as in the polymerization and reticulation of resins.

The present work reports some typical examples of the misuse of non-isothermal DTA and DSC data and suggests how this kind of investigation should be employed to characterize the kinetics of a polymerization process.

A direct comparison of the results obtained with the misleading and the correct approaches is also reported.

General considerations

Typical misuse

Many authors and qualified firms report the kinetic parameters of curing processes, drawn from the evaluation of point derivatives, dQ/dT, along the profile of the exothermic peak recorded in the DTA or DSC scan for the so called prepolymer.

This procedure is based on the following assumptions [1]:

– the heat Q delivered at a given time in the DSC scan is proportional to the curing degree α reached at that time;

– the overall heat delivered, $Q(0)$, viz. the heat amount corresponding to the total area underlying the peak, is actually representative of the complete process, from the initial to the final state.

Accordingly, they put

$$\alpha = 1 - Q(t)/Q(0) \tag{1}$$

Such a procedure is indeed correct [2] when the chemical reaction investigated is a process involving well-defined initial and final states, the reagents and the products, respectively, the chemical natures of which are not affected by the conditions imposed, e.g. $T, P, \mathrm{d}T = 0$, etc.

Polymerization processes, and especially those concerning complex materials such as epoxy resins [3], should not be assumed to obey the above conditions without the support of previous experimental evidence.

As a matter of fact, it is easy to verify [4] that, all the other conditions being fixed, the mechanical and thermomechanical properties of the polymers are generally dependent on the curing temperature, T_{cure} [5]. In other words, it is justified to claim that the polymers, i.e. the final products, obtained from the same prepolymeric material at different T_{cure}'s are fairly different from one another [5].

This implies that:

(i) the polymerization process taking place in the course of a non-isothermal DTA or DSC scan leads to a final product which may be significantly different from that obtained under isothermal conditions;

(ii) in such cases the curing degree evaluated through Eq. (1) should be considered with some caution.

A correct approach

A hypothetical mixture of monomers undergoing a DTA or a DSC scan at a given heating rate would deliver a heat amount Q_0, which is basically different from $Q(0)$, i.e. from that delivered by the prepolymer. There is no doubt that, although not directly attainable through experiment, Q_0 is conceptually more adequate than $Q(0)$ as a reference quantity.

The heat delivered by a partially cured sample in a DTA or DSC scan depends on several parameters, viz. the mass and the shape of the sample, the heating rate and, above all, the degree of polymerization previously attained [5].

The heating rate can indeed affect the actual number of new chemical bonds formed during the scan, as the corresponding kinetics of formation depends both on the specific stereochemical situation and on the actual availability of reactive sites very close to the propagating front of the reaction process.

Finally, the latter variable is affected by the previous extent of the polymerization throughout the sample.

In the case of an isothermal curing process at a given T_{cure}, the only parameters to be controlled are the mass and the shape of the sample and the curing time, t_{cure}.

As T_{cure} is maintained constant, the proportions of stereochemically different bonds formed in the process do not vary with t_{cure} (except perhaps at the very beginning), just as predicted by the Wegscheider law for parallel chemical reactions of the same kinetic order.

Hence, samples of the same mass and shape, cured at the same T_{cure} for different t_{cure}'s, may be referred to as different extents of the same chemical process, i.e. different values of an unambiguous isothermal curing degree, α_i.

During the non-isothermal DTA or DSC scan, each sample will deliver a heat amount Q, which may be correlated to the lapse of time t previously spent at T_{cure} [3], so that $Q = Q(t)$, and a non-isothermal curing degree α should be defined as

$$\alpha = 1 - Q(t)/Q_0 \tag{2}$$

where $Q(t)$ is the quantity described above and $Q_0 \neq Q(0)$ is the heat which would be delivered by the corresponding mixture of monomers (viz. a sample cured for an actually null time).

A more detailed discussion about the parameters entering Eq. (2) is reported elsewhere [6]. Here it will be sufficient to emphasize that, although $Q(t)$ and Q_0 entering Eq. (2) are non-isothermal quantities, the curing degree α defined in the equation will correspond to α_i.

This statement may easily be demonstrated [6].

Thus, the curing degree evaluated through Eq. (2) may be treated as the reaction degree of the isothermal unambiguous chemical process, viz.

$$\mathrm{d}\alpha/\mathrm{d}t = K_n(1-\alpha)^n \tag{3}$$

where n and K_n play the role of a reaction order and of a kinetic constant, respectively.

Due to the fact that $Q(t)$ and Q_0 correspond to the overall amounts of heat delivered by the portion of the sample not yet cured during the previous isothermal annealing, it is mandatory to employ Eq. (3) only in the integral form, which can be solved numerically through iterative calculation [3].

Typically, in the case of epoxy resins, one finds $n = 1$ or $n = 2$, $K_n = 10^{-2} - 10^{-1}$ min^{-1} and $Q_0 = 80 - 250$ J g^{-1} [3, 4, 6].

It is obvious that the parameters Q_0, n and K_n adjusted to fit the experimental $Q(t)$ *vs.* the isothermal curing time t refer only to the curing creation at the T_{cure} fixed for the investigation.

The same material isothermally cured at another T_{cure} would undergo a different curing mechanism, leading to a different final polymer, as suggested also by the variation observed for Q_0 and even for n [4].

It is therefore nonsense to evaluate an activation energy from K_n values obtained for different T_{cure}'s and from K_n values attained through the analysis of the point derivatives along the profile of the polymerization peak of the prepolymer.

Some examples

To exemplify the validity of this approach and the unreliability of the misleading procedure presented before it, it is expedient to make a comparison of the results obtained.

Epoxy composites NARMCO 5216 and CIBA 920 have been investigated with a Mettler 3000 TA system, which analyses the point derivative along the peak profile, and with a Du Pont Thermoanalyser 900, which has been employed to investigate a series of partially cured samples of these composites ($T_{cure} = 373$ K).

Table 1 summarizes the principal data: the close agreement between the $Q(0)$ values (both relating to the prepolymer) supports the reliability of the comparison as for the use of two different calorimeters.

	NARMCO 5216		CIBA 920	
	I	II	I	II
$Q(0)$, J g^{-1}	375.31	381.84	342.66	334.40
Reaction order	1.63	1	1.54	1
Kinetic constant, min^{-1} at 300 K	$2.7 \cdot 10^{-5}$	$3.6 \cdot 10^{-2}$	$1.5 \cdot 10^{-5}$	$4.9 \cdot 10^{-2}$
Activation energy, kJ mol^{-1}	157.24	–	172.55	–

Table 1 Comparison of results obtained through different approaches. The data of the first procedure (I) are drawn from the analysis of the peak profile of the prepolymer in the DSC trace obtained with a Mettler TA 3000 system; the second set (II) comes from the DTA investigation (carried out with a Du Pont Thermoanalyser 900) of several samples previously cured to different polymerization degrees under the same isothermal conditions ($T_{cure} = 373$ K). In both cases a heating rate of 10 degree min^{-1} was employed, with Al_2O_3 as reference material.

A preliminary consideration has to be made: according to the former procedure, which deals only with data collected in the T range where the exothermic peak is recorded, no significant polymerization would occur at lower temperatures. This is contradicted by the experimental evidence provided by the samples partially or totally cured at 373 K, which have been employed for the latter analysis of the process.

Accordingly, no reliability may be attributed to the K_n values obtained through the former procedure, or to the corresponding activation energy and reaction order.

In this respect, another comment should be added: correct K_n values are of crucial importance to plan the technical schedule for the industrial manufacturing of any kind of article from composite materials, or to predict the time required to achieve a good adherence with a given adhesive.

Finally, an investigation limited to the prepolymer may not give any information about the actual behaviour of partially or completely cured materials.

In the particular case of composites, no decomposition effect is predictable with such an approach.

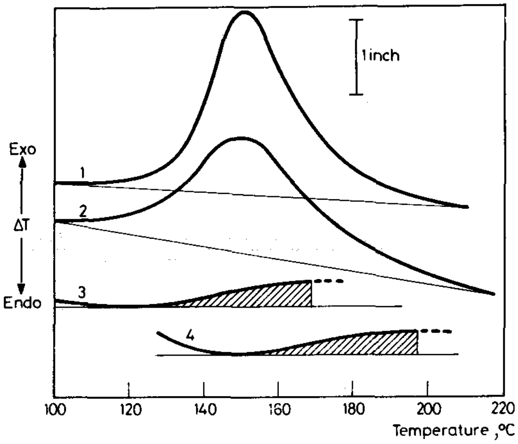

Fig. 1 DTA traces of prepolymer (1) and samples (2), (3), (4) partially cured at 373 K for 5, 45 and 60 minutes, respectively. The sensitivity is 0.5 degree inch^{-1} in all cases (the units are those reported upon the Du Pont instrumentation). Traces (3) and (1) show that a decomposition process takes place: dashed areas underlying them have been assumed to account for approximately half the heat amount which would be delivered in the case of no decomposition

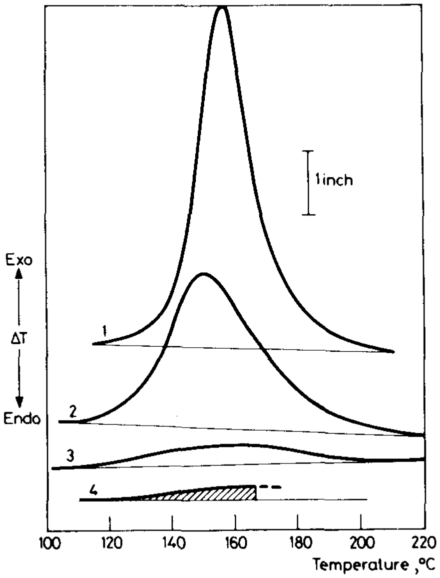

Fig. 2 DTA traces: lettering and comments as for Fig. 1

Figures 1 and 2 show DTA traces of some partially cured samples of NARMCO 5216 and CIBA 920: it is evident that a decomposition process takes place in samples cured for a longer time.

This implies that the corresponding $Q(t)$ values can be attained only in a semi-quantitative way, e.g. by assuming that the area underlying the first part of the peak, viz. that to the left side of the peak maximum, corresponds to half the heat amount which would be delivered in the case of no decomposition.

This approximation also implies that the K_n values reported in Table 1 have a qualitative reliability. The corresponding reaction orders, however, should not be seriously affected, due to the kind of iterative procedure employed for their computation [3, 6].

Conclusions

Non-isothermal curing corresponds to a chemical process which can be dramatically different from the isothermal one and can be seriously affected by the previous thermal history of the material.

Furthermore, if the information about a given material is supported only by data concerning the prepolymer, it cannot be reliable for any technical application. Accordingly, the non-isothermal DTA or DSC investigation of polymers requires

(i) experiments not limited only to the prepolymer;

(ii) a clear correlation between the non-isothermal process occurring during the scan and the isothermal curing;

(iii) no use of point derivatives along the peak profile.

* * *

Work supported by "Progetto Finalizzato Chimica Fine e Secondaria" del CNR, grant N. 82.01137.95.

References

1 G. Widman, Thermal Analysis Proc., Akadémiai Kiadó, Heyden and Son, Budapest, 3 (1974) 359.
2 J. Šestak and J. Kratochvil, J. Therm. Anal., 5 (1973) 193.
3 A. Schiraldi, V. Wagner, G. Samanni and P. Rossi, J. Therm. Anal., 21 (1981) 299.
4 P. Rossi, G. Samanni, V. Wagner and A. Schiraldi, 3rd National Conference A.I.C.A.T. (Associazione Italiana di Calorimetria e Analisi Termica), 1981.
5 R. A. Fava, Polymer, 9 (1968) 137.
6 A. Schiraldi and P. Rossi, Thermal Analysis, B. Miller Ed., J. Wiley & Sons Publ., 1982, vol. II, p. 1151.

Zusammenfassung — Die z.Z. übliche Verwendung der nicht-isothermen DTA oder DSC zur Untersuchung von Polymeren beruht auf Annahmen, die eine Anzahl von Schlussfolgerungen erlauben, die nur durch aus DTA- und DSC-Verläufen von Präpolymerproben erhaltenen Daten gestützt werden. Eine angemessene Prozedur wird vorgeschlagen, die die Analyse von DTA- oder DSC-Verläufen mehrerer, unter isothermen Bedingungen bis zu verschiedenen Graden polymerisierter Proben in sich einschliesst. Die beiden Methoden werden anhand der für zwei Materialkompositionen erhaltenen Ergebnisse verglichen.

Резюме — Обычное использование неизотермической ДТА или ДСК для исследования полимеров основывается на предположениях, допускающих ряд заключений, сделанных на основе ДТА и ДСК исследований мономерных компонент. Предложен более однозначный метод, включающий анализ ДТА- и ДСК-кривых нескольких образцов, предварительно подвергнутых вулканизации в изотермических условиях до различной степени полимеризации. Для двухкомпонентных соединений проведено сопоставление результатов, полученных этими двумя методами.