Characterization of Thermosetting Resins by Thermal Analysis

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ABSTRACT

Thermoanalytical techniques are valuable tools for the characterization of thermosetting polymers. Examples are given of the application of thermal methods to the identification of filled and unfilled epoxy and amino resins. Various thermoanalytical methods of following the curing of thermosetting polymers are considered. Thermal techniques are essential to the study of degradation reactions; the decomposition of a melamine formaldehyde resin is discussed in detail. It is concluded that the usual methods of thermal analysis alone are insufficient to characterize fully the degradation of amino resins.

Thermosetting resins are intractable materials. They are frequently filled or reinforced with inorganic materials which inhibit normal spectroscopic techniques. While thermal analysis is no panacea, it can prevent headaches in those who are required to identify resins, to find the degree of cure, and to study degradation reactions.

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IDENTIFICATION OF POLYMERS

Epoxy Resins

Initial epoxy resins were based on bisphenol (Shell Epikote 828, Ciba-Geigy CT200) but cycloaliphatic materials (e.g., CY175) and mixtures (X83/260) are now encountered. Figure 1 shows that the differential thermal analysis (DTA) curves of common commercial resins are sufficiently distinctive for them to be distinguished one from another. Thermogravimetry (TG) may also be used to distinguish between these reactions [1].

When fillers are to be identified, the advantages of thermal analysis are most apparent. Hydrated alumina $Al(OH)_3$ is widely used because of the improvement in tracking properties, and calcium carbonate is employed where castings have to be machined. Resins filled with these materials can be readily distinguished by TG (Fig. 2) or by DTA. Other common fillers, such as glass silica and asbestos, can also be identified by thermal analysis [2].

Thermogravimetry is a convenient method for the quality control of epoxy resins. Figure 3a shows Epikote 828 containing 45% of phthalic anhydride, and Fig. 3b, 15%. With excess hardener the initial loss of weight is due to sublimation of uncombined anhydride. The DTG next shows, beginning at 220°C, the breakdown of the ester links with the liberation of carbon dioxide. A small peak at 360°C is not well resolved due to the large amount of material lost in the decarboxylation process. The weight losses beyond 400°C are attributed to oxidation reactions.

In the case of the resin cured with insufficient hardener, there is no free anhydride to sublime and the decomposition begins just below 200°C. This figure gives a better indication of the true decarboxylation temperature.

Amino Resins

Characteristic DTA curves are obtained for melamine and urea formaldehyde resins. These enable one to distinguish between cured and uncured specimens and also to say whether combinations of melamine with urea or phenol are mixtures or genuine copolymers.

A cured melamine formaldehyde (MF) resin contains methylol groups, ether groups, and methylene groups. The proportions of these three groups per triazine ring varies but all three groups may be found in normal cured molding powder.

When heated in a closed cell (Fig. 4a), the double endotherms of curing are clearly seen followed by the characteristic exotherm near 360°C. Figure 4b shows the DTA curve of resin cured under normal
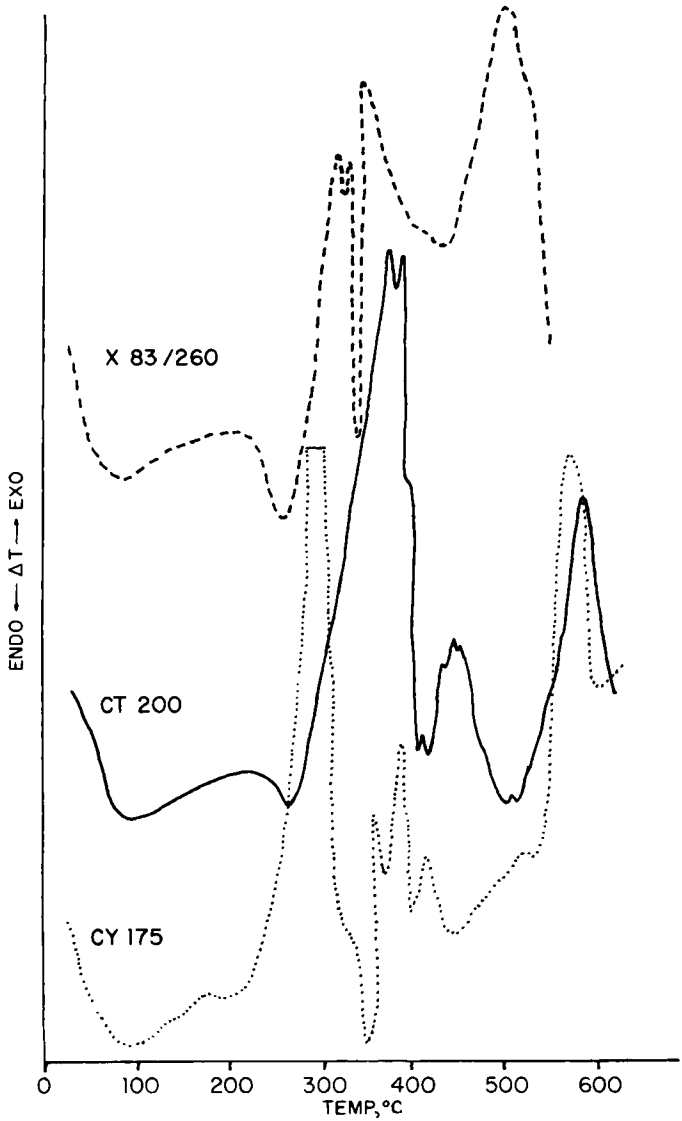
FIG. 1. DTA of uncured epoxy resins; CT200 bisphenol type, CY175 cycloaliphatic type, and X83/260 mixed types.
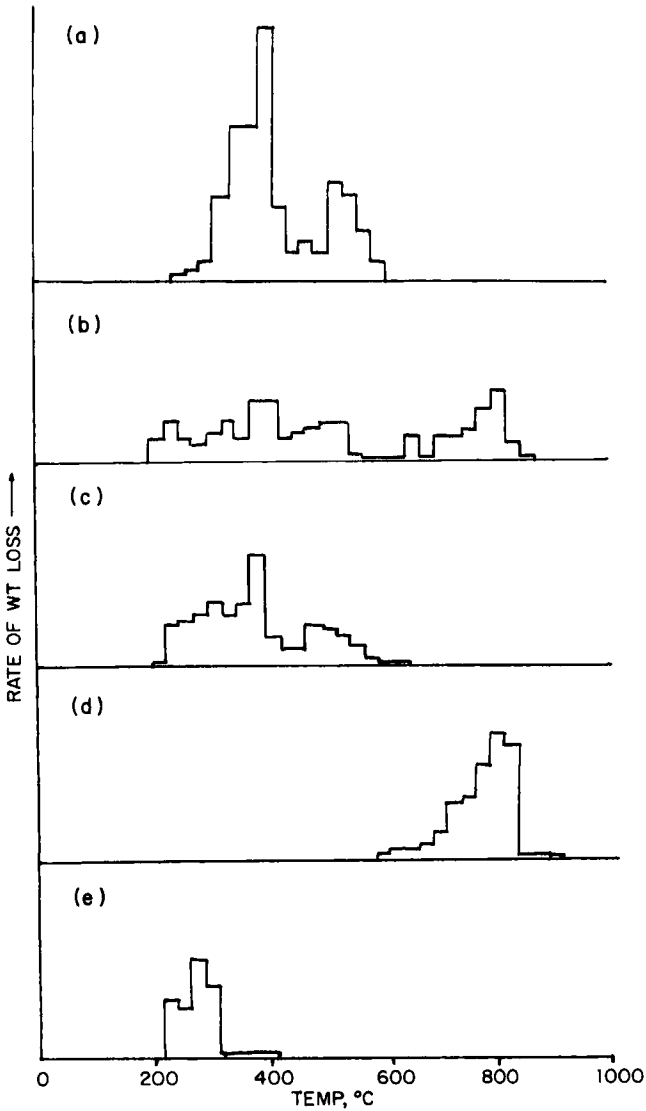
FIG. 2. TG of CT200, (a) Uncured. (b) Cured with HPA and filled with $CaCO_3$. (c) Cured with HPA and filled with $Al(OH)_3$. (d) $CaCO_3$ alone. (e) $Al(OH)_3$ alone.
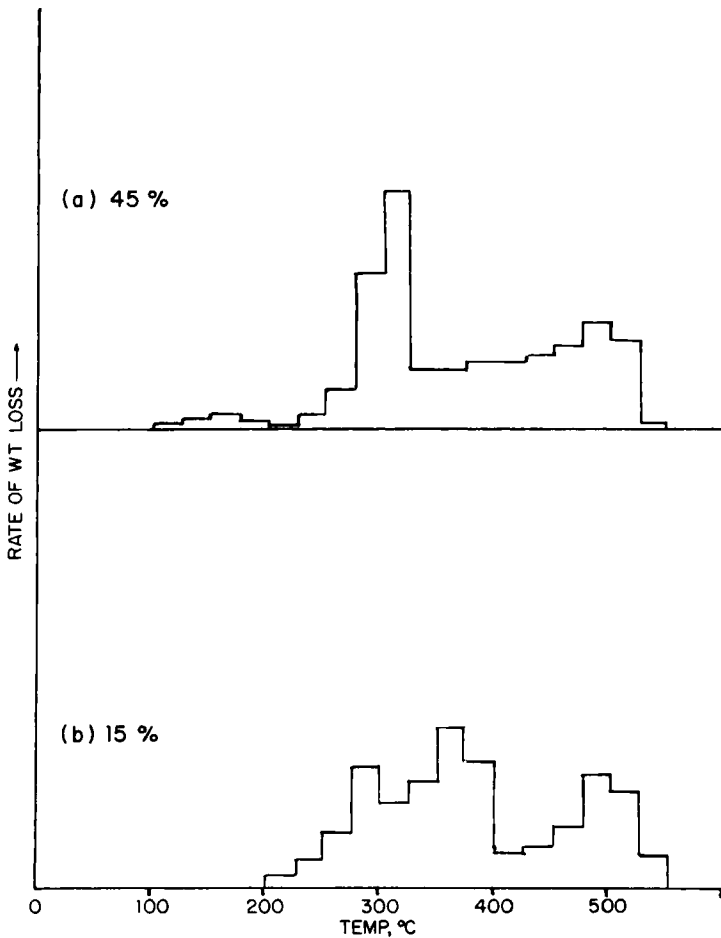
FIG. 3. TG of Epikote 828. (a) With 45% phthalic anhydride. (b) With 15% phthalic anhydride.

molding pressure; there are, of course, no curing endotherms, and it is also noticeable that the characteristic exotherm is sharper (instead of a split peak there is only a shoulder) and at a higher temperature. Curve c shows a curve of cured resin under pressure; here the endotherm following the characteristic exotherm is suppressed, indicating that this trough is caused by volatilization of decomposition products.

When MF resins are molded, excess formaldehyde escapes when

FIG. 4. DTA of melamine formaldehyde resin. (a) Uncured MF resin in pressure DTA cell. (b) MF resin cured by compression molding in conventional DTA. (c) Molded resin in pressure DTA cell.

the mold is "breathed," but when cured in a closed DTA cell this HCHO
may react further with the melamine. Commercial conditions there-
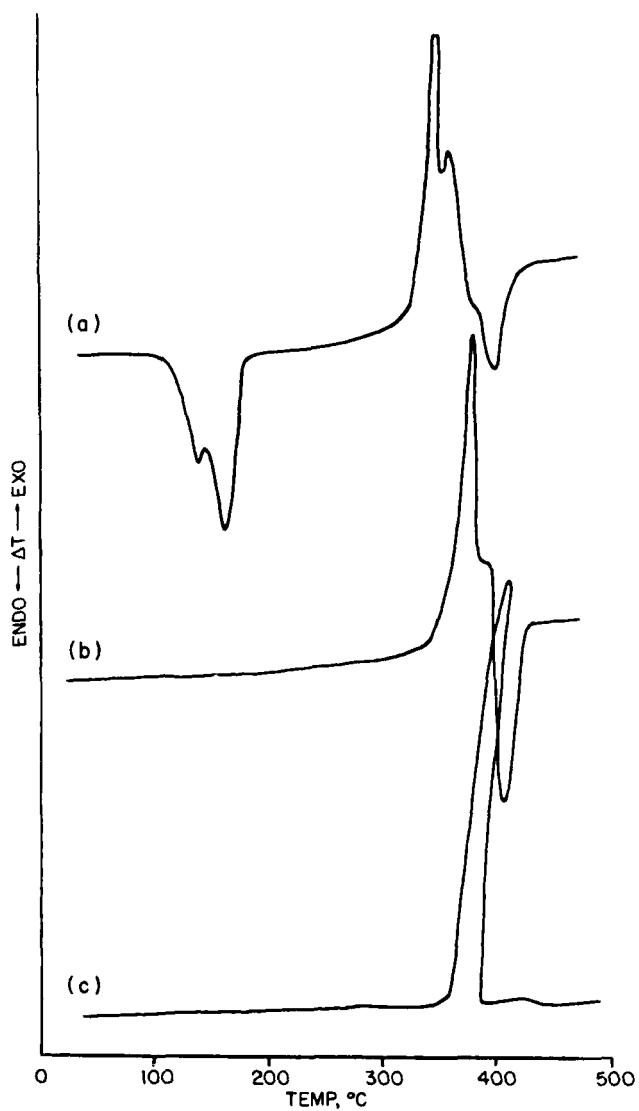fore favor a resin with methylene bridges as the linking units while the
DTA cured resins have more methylol and ether groups. These latter
are less stable than methylene bridges and are presumed to be
responsible for the lower temperature of the characteristic exotherm.

TG has proved as useful for the characterization of filled amino
resins [2] as it has for the epoxies. Evolved gas analysis (EGD) is a
useful complement to DTA for identifying melamine compounds.
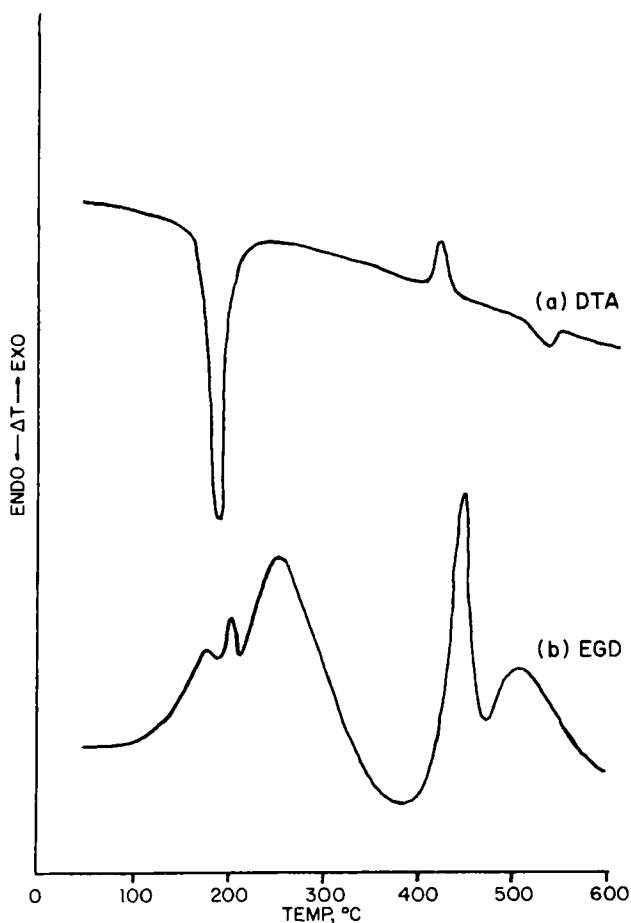Figure 5a is a DTA trace of hexamethylol melamine resin, and Fig. 5b

FIG. 5. (a) DTA of hexamethylol melamine resin. (b) EGD of
hexamethylol melamine resin.

is the EGD record showing the loss of water and formaldehyde com-
mencing at 100°C and followed by further evolution of gas concomitant
with the curing reaction. The characteristic peak of the melamine
appears just after the DTA peak, and around 460°C gas is evolved from
a subsequent reaction. When compared with the conventional DTA
(Fig. 5a), the extra resolving power of EGD is evident. EGD on cured
melamine resins show peaks corresponding to the reactions observed
by May [3] and thus provide a further means of identifying and studying
these materials. When using a gas density detector the 460°-melamine
peak is seen to have two components, one lighter and one heavier than
argon.

CURING REACTIONS

The curing of thermosetting resins was one of the first applications
of DTA [4], and it has been extensively applied to the study of the
kinetics of the reaction.

One source of error, however, arises from heat transfer from the
specimen to the reference cell. Figure 6 shows the area of exothermic
peak obtained with various sizes of specimen in a Du Pont 900 Thermal
Analyzer operated in the DSC mode. The ratio is only constant for
certain sample sizes, and departures from linearity increase as the
sample size increases. This factor does not seem to have been taken
into account in some reported work on curing of resins with DTA and
DSC. It can easily be avoided in specially designed apparatus [5].

In many cases, however, what is required is not a knowledge of the
full curing process, but an indication of the degree of cure. As the
residual exotherm is small, modified DTA is preferred to traditional
apparatus for this application. One modification is to use a larger
sample; a second is to reduce the rate of loss of heat from the sample
[5] in order to increase the autocatalytic effect; third, one may replace
thermocouples with thermistors [6]. In most instances isothermal
operation is preferred to normal DTA.

When dealing with resins that show a glass transition (T_g), such as
the bisphenol epoxies, another method of determining the degree of cure
is to follow the T_g. This provides a sensitive index of degree of cure
that can be correlated with standard heat distortion temperatures.

Figure 7a shows the values found for T_g of CT200 cured with phthalic
anhydride at 160° after gelation at 120°C for 24 hr. The curing is sub-
stantially complete after 16 hr at 160°. These results give good correla-
tion with other thermal and classical techniques.

This method is restricted to polymers with rigid chains and is of
much less utility with the normal filled resin of commerce. These both
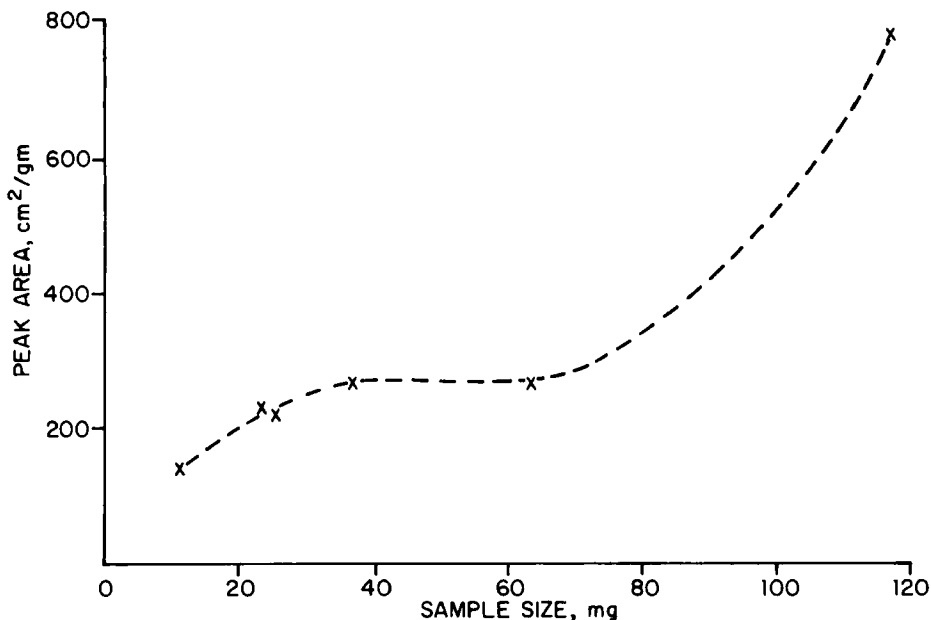raise T_g and reduce the sensitivity of the technique.

FIG. 6. Area of exothermic peak obtained in curing various
sizes of epoxy resin.

As before, however, it is possible to make specialized apparatus
with higher sensitivity than that of standard DTA equipment; e.g., T_g
may be determined in heat flow apparatus [7].

DEGRADATION REACTIONS

As a practical tool TG is very valuable [8], but it has dis-
advantages for measurement of absolute kinetic values [9]. Figure 7b
shows how T_g measurements may be used to monitor the degradation
of epoxy resins.

The degradation of melamine formaldehyde resins has had
comparatively little study and the results obtained are conflicting.
This is in part because MF resins are used in surface coatings as well
as in compression molding. The composition of the resins used are
different in each instance, as are the curing conditions and the criteria
of degradation. The use of different analytical techniques (DTA,
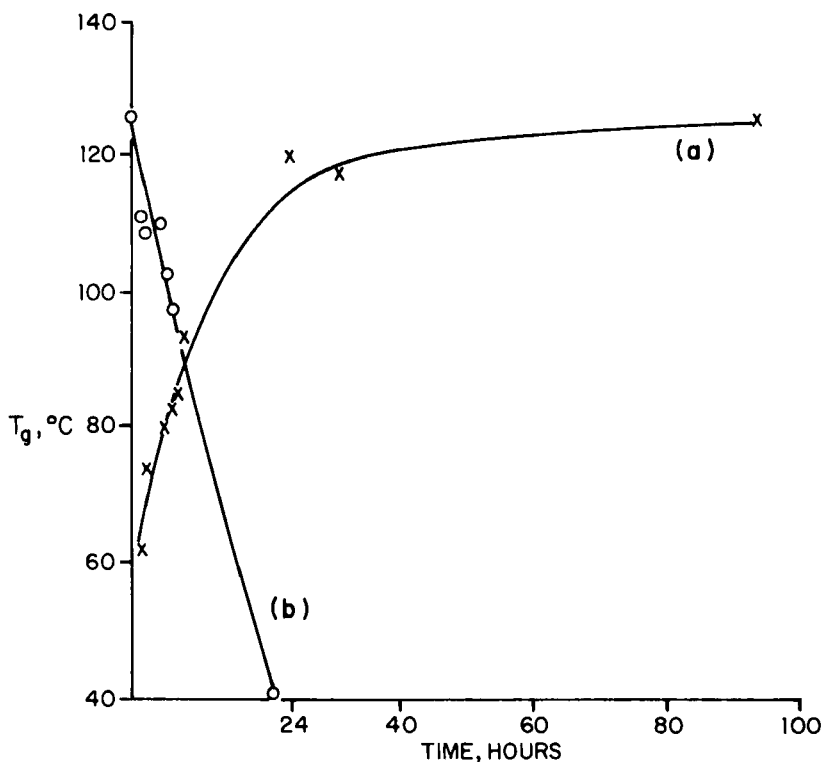pressure DTA, IR, and TG) also give different results [10].

FIG. 7. T_g of CT200 and phthalic anhydride. (a) After curing at 160° (×). (b) After heating at 220° (○).

In studies of compression molded compounds using TG [11], a rapid reaction was observed above 250°C which was attributed to breakdown of the triazine ring. It is more probable that this was an oxidation reaction (it was greatly dependent on the particle size of the material investigated). Melamine begins to sublime above 260°C [11] and thus an oxidation of the methylene bridges followed by sublimation of melamine is the most likely cause of the disappearance of the triazine absorption from the IR spectra.

In the absence of oxygen the triazine ring is stable above 500°C [3, 10], and thus another explanation has to be found for this characteristic exotherm.

This exotherm is not found in phenolic resins and therefore by analogy with the reaction in melamine [3] the following mechanism is postulated:

$$RNHCH_2HNR \rightarrow RNHR + [CH_2NH]$$

If the $[CH_2NH]$ were to dimerize to azomethane, this would decompose exothermically at $400°C$ and the possible reactions are legion. The methyl radicals could dimerize to ethane or, if even a trace of oxygen is present, to polyolefins. If air is introduced above $360°C$ a very sharp, large $(+50°C)$ exotherm is produced that is much too rapid for a normal combustion. Reaction is also possible with the NH_3 [3] present to give amines which have been detected by EGD.

All that can be said for certain is that the reactions are too complex to be fully clarified by thermal analysis alone.

EXPERIMENTAL

The MF resins (F/M ratio 2.5 to 1) were cured at $160°C$ for 10 min and ground to B.SS. 200-300 mesh.

A Stanton thermal balance HT-SM and a Mark IIB electrical thermobalance (C. I. Electronics, Salisbury, Wiltshire) were used. Conventional differential thermal analysis (DTA) was performed on the equipment manufactured by A. R. Bolton of Edinburgh based on a design of R. C. Mackenzie and on the Du Pont 900 using the DSC mode. The pressure cell [10] and EGD apparatus [12] have been described elsewhere.

CONCLUSIONS

Thermoanalytical methods are useful in the characterization of thermosetting compounds, but no single technique suffices to all the complex reactions involved. DTA enables one to identify thermosets and to distinguish between filled and unfilled resins, between resins cured in open or closed cells, and between mixtures and copolymers. EGD is a useful complement to DTA for characterization and curing studies. TG is a conventional method of characterizing commercial amino and epoxy resins. Thermal methods alone cannot resolve the complex degradation reactions of thermosets.

Some of the problems in the study of thermosetting resins are found in many thermal investigations, e.g., problems of diffusion and the effects of particle size, but others such as the sublimation of melamine and the possible reactions between volatile condensation products and the main resin are peculiar to this field of study.

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