Thermochimica Acta, 18 (1977) 101–111

SOME APPLICATIONS OF THERMAL ANALYSIS AS A SUPPLEMENT TO OR REPLACEMENT FOR ASTM TESTING STANDARDS*

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ABSTRACT

Modern thermal analysis instrumentation, such as DSC, TMA, and TG, are rapid and accurate and should be given serious consideration as supplements to, or in some cases, as replacements for some of the ASTM testing standards. Thermal analysis instrumentation provides a logical advancement in the search for not only simpler techniques but those which provide an increase in accuracy and speed of determination. Indeed, one of the ASTM Committees, E-37, is solely committed to the application of thermal analysis instrumentation. It is the purpose of this report to suggest some areas of ASTM testing where thermal analysis instrumentation can prove its unique capabilities. It is not meant to imply that these procedures be adopted by ASTM in this suggested form as any procedures accepted by ASTM must be arrived at by the standard ASTM format; that is, by a consensus of the appropriate ASTM Committees. The following examples, then, are again merely suggestions.

1. INTRODUCTION

Modern thermal analysis instrumentation, such as DSC, TMA and TG, are rapid and accurate and should be given serious consideration as supplements to, or in some cases, as replacements for some of the ASTM testing standards. Thermal analysis instrumentation provides a logical advancement in the search for not only simpler techniques but those which provide an increase in accuracy and speed of determination. Indeed, one of the ASTM Committees, E-37, is solely committed to the application of thermal analysis instrumentation. It is the purpose of this report to suggest some areas of ASTM testing where thermal analysis instrumentation can prove its unique capabilities. It is not meant to imply that these procedures be adopted by ASTM in this suggested form as any procedures accepted by ASTM must be arrived at by the standard ASTM format; that is, by a consensus of the appropriate ASTM Committees. The following examples, then, are again merely suggestions.

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*Presented at the 6th North American Thermal Analysis Society Conference, Princeton, N. J., June 20–23, 1976.

2. EXPERIMENTAL

Differential scanning calorimetry was performed with a Perkin-Elmer Model DSC-2. With an instrument of this type, both temperature and energy are obtained simultaneously. Thermomechanical analysis was performed with a Perkin-Elmer Model TMS-1 which continuously monitors a sample's expansion or contraction as a function of temperature. Thermogravimetric analysis was performed with a Perkin-Elmer Model TGS-2, which continuously monitors the weight loss or gain of a sample as a function of temperature. Where required, samples were precisely weighed with a Perkin-Elmer Model AD-2Z Autobalance.

3. DIFFERENTIAL SCANNING CALORIMETRY

The following examples are meant to suggest some areas of ASTM testing where DSC may improve the speed and reliability of the testing. Suggested instrument parameters, such as sample size, scanning rate, and sensitivity, are also discussed.

3A. Melting point of polymers—DSC

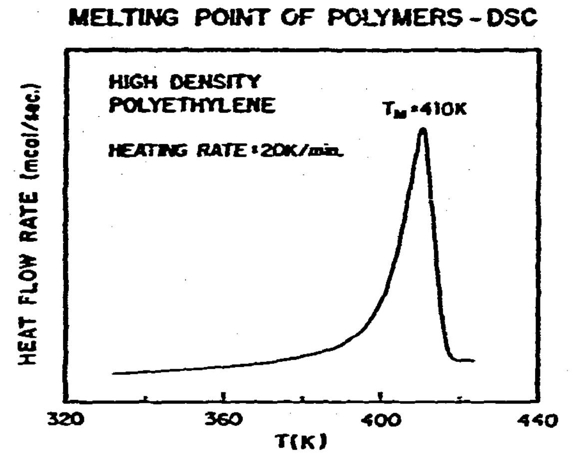
Semi-crystalline thermoplastic polymers, upon the application of heat, undergo a process of fusion, or melting, where the crystalline character of the polymer is destroyed. While polymers melt over a temperature range due to a difference in size and regularity of the individual crystallites, the melting point of a polymer is generally reported as a single temperature where the melting of the polymer is complete. (There are some reported instances where the melting of a polymer occurs above its degradation point; however, the determination of the melting point in this instance is beyond the scope of this discussion.)

The importance of determining the melting point of a polymer is obvious since this temperature represents the minimum temperature for the processing of the polymer by extrusion or injection molding, for example, and also, in most cases, represents the upper use temperature where structural integrity of the polymer is required.

Figure 1 illustrates a typical DSC determination of the melting point of a polymer, in this case, high density polyethylene. The melting point is taken as the peak temperature where melting is complete, or at least, nearly so. The heating rate chosen for this experiment was 20 K min^{-1}, a moderately fast scanning rate, to reduce the experimental time although there may be some advantage to using a slower heating rate to reduce any potential problems associated with super-heating. For readers interested in considerably more detail on the melting of polymers, please consult the reference by Wunderlich[1].

3B. Glass transition temperature of polymers—DSC

Thermoset polymers and the amorphous regions of thermoplastic polymers, upon the application of heat, undergo a process known as the glass transition where the polymer proceeds from a hard, more or less brittle glassy state to a rubbery or viscous state[2]. The temperature at which this process occurs is known as the glass transition temperature usually abbreviated as T_g. For example, if the polymer is above its glass transition at room temperature (T_g<300 K), it is typically limp and flexible. Similarly, if the polymer is below its glass transition at room temperature (T_g>300 K), it is typically characterized by stiffness, hardness, and dimensional stability and frequently by transparency and high optical quality. Known T_g values then suggest the areas for end use applications of the polymer.



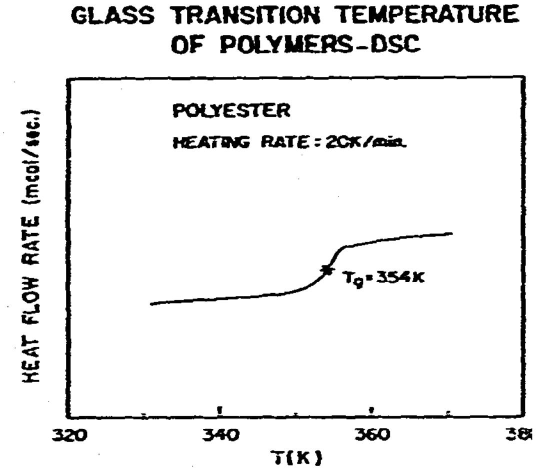


Fig. 1. Melting point of polymers—DSC.

Fig. 2. Glass transition temperature of polymers—DSC.

The glass transition is evidenced by a change in the heat capacity (and also the expansion coefficient) as a polymer material is heated or cooled through this transition region and, as such, is easily measured by DSC. An example of this determination is illustrated in Fig. 2, where the glass transition temperature of poly(ethylene terephthalate), commonly called polyester, was measured. In this example, we have chosen to measure T_g at the $1/2\ \Delta C_p$ point. While this choice is somewhat arbitrary and other authors have suggested alternate techniques such as taking T_g at the extrapolated onset of the transition, we have found the $1/2\ \Delta C_p$ method to be reliable and reproducible. The ultimate disposition of this choice is, of course, the decision of the interested ASTM Committees.

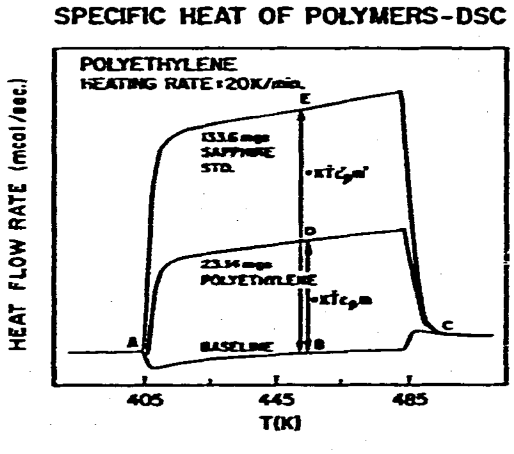
3C. Specific heat of polymers—DSC

A general method for the measurement of specific heat functions by DSC has been previously described by O'Neill[3] and has been extended by others[4,5] to include the measurement of specific heat functions of polymers. As a result, this procedure will be only briefly reviewed.

The ordinate displacement of the differential scanning calorimeter is proportional to $mC_p\dot{T}$ where m is the mass of the sample in grams, C_p is the specific heat, and $\dot{T}$ is the scanning rate in degrees per second. The ordinate displacement due to the heat capacity of the sample during a temperature scanning increment is measured with respect to a baseline displayed before and after this temperature increment is obtained under isothermal conditions. Figure 3 illustrates the presentation as seen on the recorder chart. The figure shows superimposed scans of ABC, a blank run with an empty sample pan in both sample and reference chambers, AEC, a sapphire disc standard, and ADC, a polyethylene sample. Amplitudes are measured from the blank baseline to the sample or standard level at the temperature or temperatures of interest. Using this standard technique, specific heats may be expected to be measured to an accuracy of a few percent[6]. For readers interested in considerably more detail on the heat capacity of polymers, please consult the excellent review on this subject by Wunderlich and Baur[7].

3D: Oxidative stability of polymers—DSC

The oxidative destruction of polymers can have serious economic consequences by rapidly reducing their life expectancy. As a result, polymers are commonly blended with anti-oxidant stabilizers to prevent or at least inhibit the deterioration of properties which accompanies oxidative degradation. Since anti-oxidants are expected to be effective for perhaps decades, methods for testing their efficiency must, of necessity, involve some accelerated test.



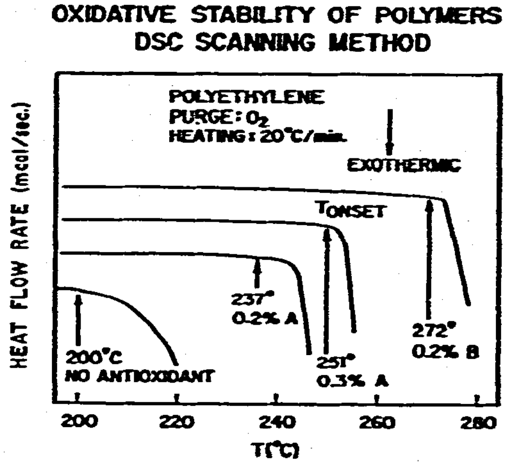


Fig. 3. Specific heat of polymers—DSC.

Fig. 4. Oxidative stability of polymers—DSC scanning method.

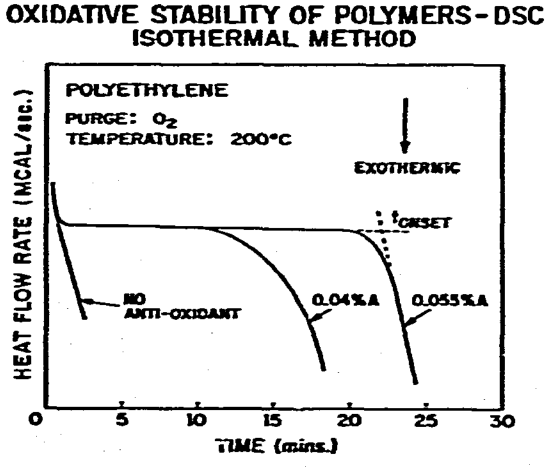
Direct instrumental methods for anti-oxidant testing depend upon the fact that the anti-oxidant prevents the propagation of the oxidation reactions but is itself consumed in the process. When the available anti-oxidant is exhausted, the oxidation reactions at that point are able to proceed. Since the oxidation reactions are highly exothermic, the onset of the process can be detected with excellent sensitivity by any reasonably well-designed temperature or heat-sensing device in thermal contact with the sample. DSC ideally fits such a description and should prove invaluable for accelerated life testing.

There are potentially two methods to obtain information related to the oxidative stability of a polymer by DSC.

The first of these might be called the "continuously-scanning" method. The continuously-scanning method, typical results are illustrated in Fig. 4, involves programming the sample at some selected rate in an oxidizing atmosphere up to and slightly beyond the temperature at which oxidation is observed to begin. This temperature is frequently referred to as the onset temperature for oxidation. The higher this temperature, the more stable the polymer or the more effective the anti-oxidant, or the greater the concentration of the anti-oxidant. The advantage of this method is in the speed of the experimental determination since very stable samples take only a slightly longer time than unstable samples. The disadvantage of the continuously scanning method is that the "stability" scale versus initial oxidative temperature is not linear. In fact, as one would expect, considering the exponential temperature dependence of reaction rates, the sensitivity of this method decreases approximately exponentially toward higher temperatures.

The second method may be called the "isothermal method". Rather than scanning continuously to the onset temperature of oxidation, we may alternately scan rapidly to some preset temperature and measure the time to oxidation at that temperature.

Typical results for the isothermal method are illustrated in Fig. 5. As in the previous figure, the particular polymer chosen was polyethylene with different levels of anti-oxidant.



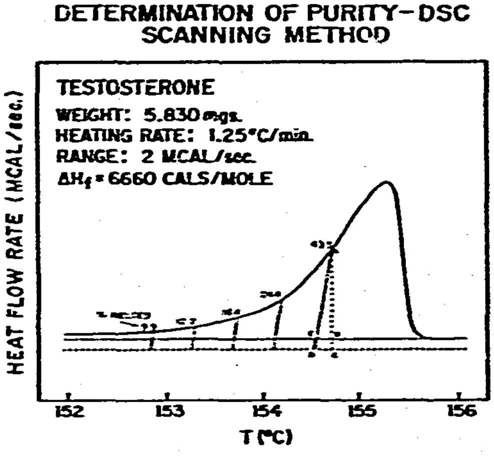


Fig. 5. Oxidative stability of polymers—DSC isothermal method.

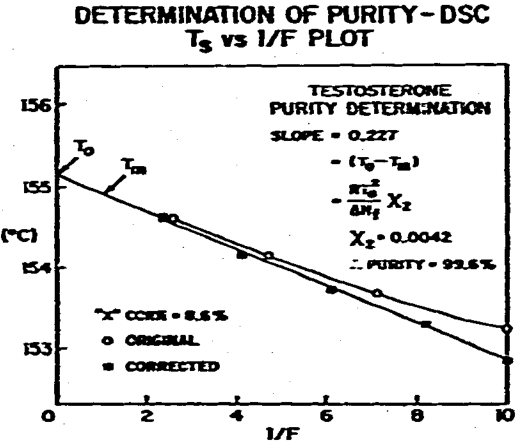
Fig. 6. Determination of purity—DSC scanning method.

This approach has the first advantage that all samples are examined under more nearly identical conditions. The second principal advantage is that the relationship between isothermal time and anti-oxidant effectiveness or anti-oxidant concentration is likely to be more nearly linear. The most obvious disadvantage is that no matter which temperature is chosen, some samples will oxidize in a short time while others will take an exceedingly long time. Thus, the time per analysis will be on the average much longer than for the continuously scanning procedure.

3E. Determination of purity—DSC

The well-known effect of impurities on the melting point of crystalline compounds provides the basis for various methods of purity determination. Some years ago[8,9] a particular method using the Perkin-Elmer DSC was proposed which has since found wide utility in the field. The DSC method, like all methods based upon melting point depression or melting range, depends upon the applicability of the Van't Hoff equation[10]. This first method, which perhaps may be called the scanning or dynamic technique, has since been supplemented by an additional method which perhaps may be called the step-wise melting method[11–13].

As illustrated in Fig. 6, the dynamic technique involves slowly scanning through the melting region of a relatively small sample in order to approach thermodynamic equilibrium. Sections are constructed as shown to correct for thermal resistances within the system, and the fraction melted at the indicated temperature is determined by dividing the area under the curve up to that temperature by the total peak area. A plot of the reciprocal fraction melted versus temperature is then made. As illustrated in Fig. 7, while theory predicts such a plot will yield a straight line, this is not always the case; the original data curve will be concave upward. This is attributed to the fact that not all of the initial melting was resolved from the baseline. Consequently, an area increment, or "*x*" correction must be added equally to each partial area as well



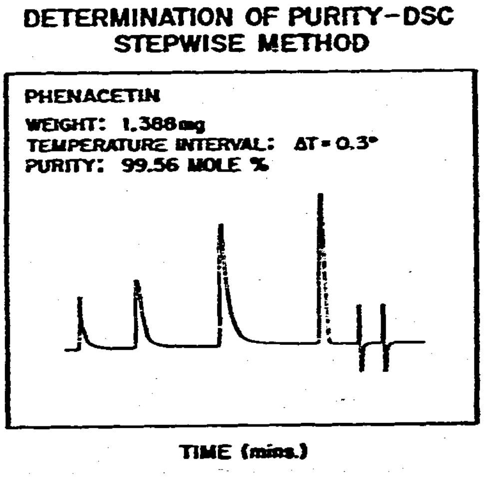


Fig. 7. Determination of purity—DSC T_s vs. $1/F$ plot.

Fig. 8. Determination of purity—DSC stepwise method.

as the total area in order to linearize the plot. This "x" correction is well known and presents only minor difficulties in the determination of purity.

At the "Pittsburgh" Conference in 1972, Staub and Perron[11] proposed a modification of the dynamic DSC method which involves the step-wise melting of the sample in a few tenths of a degree steps. Further discussions of this method have been presented by Gray[12] and by Gray and Fyans[13].

Typical results for the step-wise purity technique are illustrated in Fig. 8, where a phenacetin sample of 99.56 mole % purity was step-wise scanned at a ΔT interval of 0.3 degrees. The calculation procedures for handling the step-wise purity method have been discussed elsewhere[11–13] and will not be reviewed here. I think, however, that both methods have found wide acceptance in the field with perhaps the dynamic method the more popularly employed because of the shorter analysis time and the greater experience with the dynamic method among investigators.

4. THERMOMECHANICAL ANALYSIS

The following examples are meant to suggest some areas of ASTM testing where TMA may improve the speed and reliability of testing.

4A. Expansion coefficient—TMA

Perhaps one of the more important physical properties for plastics when used as potting materials or for printed circuit boards is the expansion coefficient. Frequently, in these types of applications, epoxy resins are used.

The general expression for the average coefficient of expansion, is

$$\alpha = \Delta L/(L_{20}\Delta T)$$

where

α = expansion coefficient
L_{20} = length at 20°C
ΔL = change in length
ΔT = temperature interval

Since the TMS-1 continuously monitors the change in length as a function of temperature, it is an ideal technique for measuring the expansion coefficient. An example of this measurement made on an epoxy printed circuit board is shown in Fig. 9. Note also that the glass transition temperature, as evidenced by a change in slope of the trace, is simultaneously measured by this technique.

4B. Flexure analysis—TMA

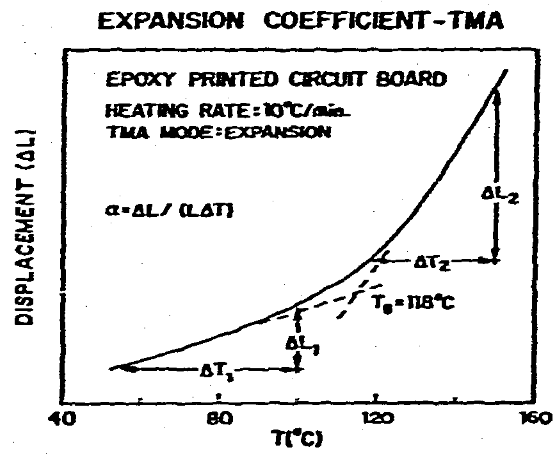
An additional useful standard measurement that may be performed by TMA on a "micro" scale is the deflection temperature of plastics under load (ASTM D 648). This analysis may be performed using the Flexure Analysis Accessory Kit available for use with the TMS-1.

The object of the test is to determine the temperature at which the test specimen has deflected 0.25 mm (0.010 in.) when under stresses of 18.5 kg cm^{-2} (264 psi) and 4.6 kg cm^{-2} (66 psi). Having measured the sample's dimensions, the required loading is calculated as follows:

$$P = \frac{2Sbd^2}{3L}$$

where P = load
S = desired stress
b = width of sample
d = depth of sample
L = length between knife edges

Sample dimensions are typically 0.2 in. long, 0.15 in. wide and 0.020 in. thick. Since these dimensions are not critical, there is no need to compression mold samples as in the ASTM method. In fact, the compression molding itself might well impart thermal history effects which would confuse the results.



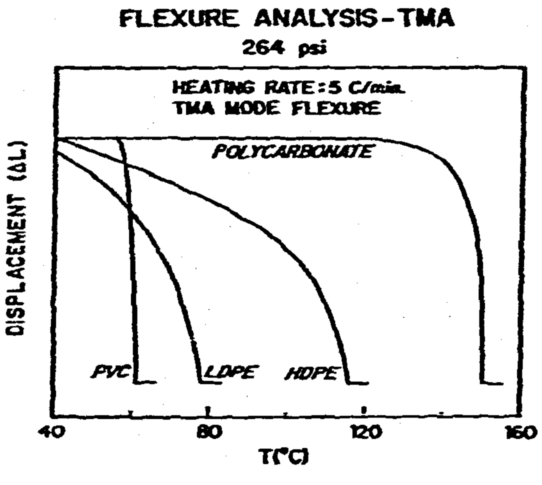


Fig. 9. Expansion coefficient—TMA.

Fig. 10. Flexure analysis at 264 PSI—TMA.

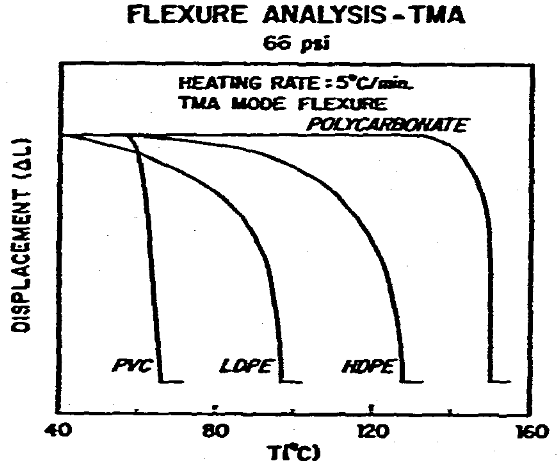
Because of the greatly reduced size of the sample and the improved thermal coupling, program rates considerably higher than the specified 2°C min^{-1} were found quite satisfactory. Illustrated in Fig. 10 are superimposed thermograms of high and low density polyethylene, PVC, and polycarbonate at 264 psi, run so that 0.010 in. deflection will be 50% of full scale on the recorder. Under either stress, the gradual softening of the first order melting behavior of the polyethylene is dramatically different from the abrupt softening of the second order glass transitions in the PVC and polycarbonate samples. Also, as illustrated in Fig. 11, the identical samples run at 66 psi, indicate that the second order transitions are only slightly influenced by loading as shown in Table 1.

TABLE 1

FLEXURE ANALYSIS—TMA

Sample	*Deflection T (°C)*	
	66 psi	*264 psi*
Low density P-E	89	67
High density P-E	119	105
PVC	62	60
Polycarbonate	147	146

Hence the flexure mode provides a very definite and precise means of determining the flexure properties and also the glass transition temperature for samples which can be prepared in sheet form.



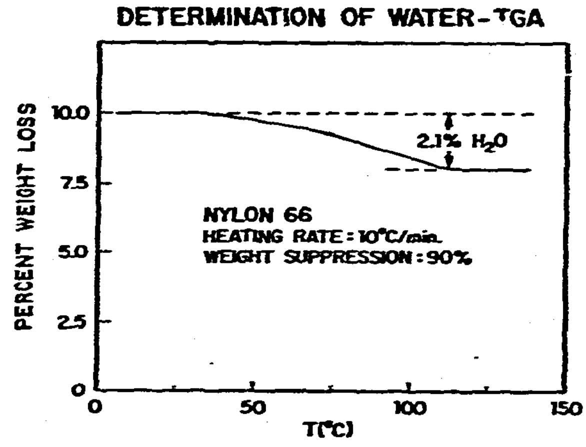


Fig. 11 Flexure analysis at 66 PSI—TMA.

Fig. 12. Determination of water—TG.

5. *Thermogravimetric analysis—TG*

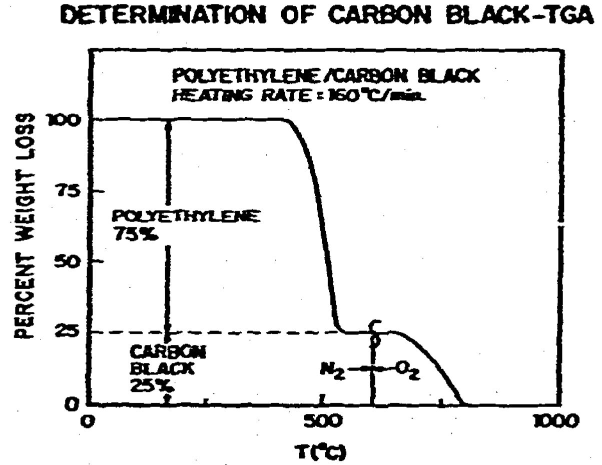
Recent advances in TG as exemplified by the new Perkin-Elmer Model TGS-2, thermogravimetric system, have led to not only improvements in the quality of results but also have greatly simplified the operation of the instrument and the actual running of samples. The following examples are an attempt to indicate some areas of ASTM testing where TG may simplify and improve the speed and reliability of the testing.

5A. Determination of moisture—TG

One area of concern, particularly in the textile industry, is the determination of moisture in textile fibers which may affect their handling and physical properties. Using modern, highly sensitive thermogravimetric instrumentation, this determination is relatively straight-forward as illustrated in Fig. 12, which shows a scan of Nylon 66 staple fiber for adsorbed water determination. One particular advantage of the TGS-2 is the ability to electronically suppress a large portion of the total sample weight to observe small and subtle changes in a sample's behavior under high sensitivity conditions.

5B. Determination of carbon black—TG

Carbon black is frequently added to polymers to improve some specific physical properties or simply as a bulk filler material. In many cases the percentage of carbon black in a polymer matrix may be determined by TG. An example of this procedure is illustrated in Fig. 13. In this example, the percentage of carbon black in polyethylene was determined. The procedure is relatively simple and straight-forward. The material to be checked is placed in the sample pan of the TGS-2 and the system is purged with an inert gas such as nitrogen. When the purging cycle is completed, the system is programmed rapidly to about 600°C in nitrogen to pyrolytically decompose the polyethylene. In this instance the polyethylene is pyrolytically decomposed completely to gaseous products such that the residue is carbon black. The percentages may be read directly from the y-axis of the recorded thermogram. Many users find it convenient to switch the purge gas at this point to either air or oxygen to combust the carbon black to leave the sample pan completely clean for the next determination (heating to 1000°C speeds the combustion of the carbon black, reducing the experimental time).



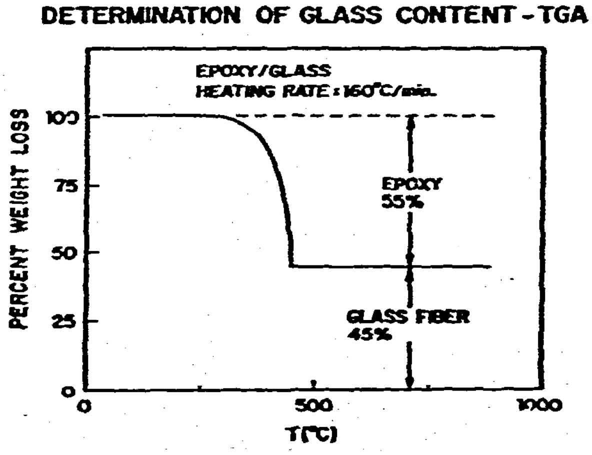


Fig. 13. Determination of carbon black—TG.

Fig. 14. Determination of glass content—TG.

5C. Determination of glass content—TG

In some instances, glass or glass fibers are used with plastics to improve some physical properties particularly tensile strength and dimensional stability. One particularly important use of glass fibers is found in the printed circuit board industry where glass fibers are used in conjunction with a thermosetting resin, generally epoxy, to not only improve general physical properties but also to reduce the expansion coefficient of the printed circuit boards.

In a manner very similar to the previous example, TG may be used to determine the percentage glass imbedded in a plastic matrix. Figure 14 illustrates this determination for the glass content of an epoxy printed circuit board. As in the previous example, the y-axis was set at 100% full scale for direct percentage recording. In this instance either air or nitrogen may be used to combust the epoxy as there is no weight loss associated with the glass fibers. Another advantage of the TGS-2 may be utilized in this measurement and that is the ability to heat the sample at rates of up to 320°C min^{-1}. Using the high heating rate we are able to heat the sample to 1000°C in about 3 min, thus greatly reducing the analysis time.

6. CONCLUSIONS

Modern thermal analysis instrumentation such as DSC, TMA, and TG often speeds and simplifies some previously rather difficult analysis without sacrificing the accuracy of the results and in some instances actually improving upon them and as such deserves some consideration as a supplement to or replacement for some ASTM testing standards. The previous examples are merely suggestions, of couse, as any standards adopted by ASTM must survive the detailed scrutiny and testing by the interested ASTM Committees.

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