MICROPROCESSOR-CONTROLLED THERMOGRAVIMETRIC SEPARATIONS *

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ABSTRACT

A microprocessor-controlled thermogravimetric analysis is described from a hardware standpoint. Features include increased automation, accuracy, reliability, speed of operation, and simplicity. Automation capabilities include thermocouple linearization to 0.1°C, multiple-step programming, automatic purge gas switching, temperature autocalibration, abscissa scaling, method storage and recall.

Examples illustrating the use of the new system include gravimetric separations of volatiles, organics, and fillers in polymer matrices.

INTRODUCTION

Thermogravimetry (TG) has been developing over a number of years as a research method used for characterizing weight loss behavior of organic, inorganic, and polymeric materials. More recently, TG has been developing as a useful tool for routine quantitative gravimetric analysis to separate complex mixtures according to differences in volatility, pyrolizability, oxidizability, or reducibility. As in gas and liquid chromatography, the use of multiple-step programs can be used to make separations more efficient and more reliable. The use of a microprocessor controller to direct changes in temperature and atmosphere allows a new dimension in TG analysis. With this new system, as seen in Fig. 1, complex separation programs can be directed with total automation. The result is improved reproducibility, greater flexibility, and less demand on operator time and expertise. Let us consider the salient features of this new microprocessor controlled TG apparatus and look at some examples of its performance.

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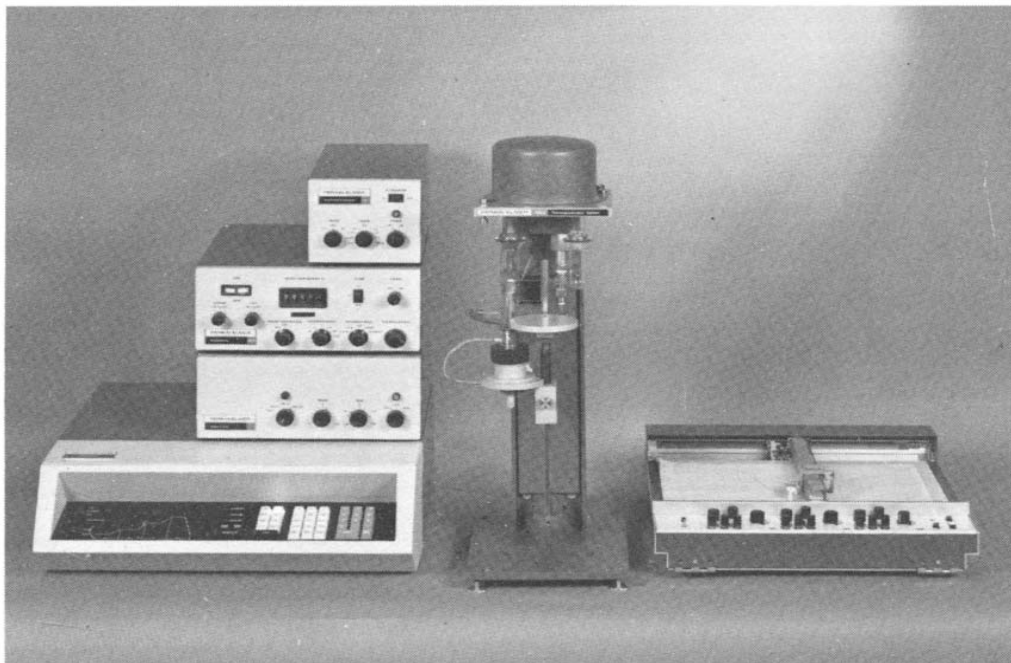
Fig. 1. Perkin-Elmer microprocessor-controlled TG apparatus.

INSTRUMENTATION

The balance

The recording microbalance used in the system is the Model AR-2 "Autobalance", a modern design making full use of the latest solid-state technology; even the optical system of the balance mechanism uses solid-state photo sources and sensors. The capacity and ultimate sensitivity of this balance are greater than would ever be required in a practical TG experiment. Some features of most importance in TG are

(a) The zero setting does not change when the sensitivity or recorder range of the balance is changed. This allows on-the-fly changes in sensitivity without loss of accuracy. This obviously desirable feature is, in fact, rather uncommon in balances used for TG. The mass calibration is similarly independent of range. The balance is calibrated with a 100 mg weight accurate to a few micrograms on the 100 mg range; the calibration then holds over all ranges.

(2) The weight suppression control is digital with four digit thumb-wheels and a two-digit vernier and with three full scale ranges (10, 100, and 1000 mg). This allows almost any desired fraction of any sample weight to be suppressed so that the remainder can be "blown-up" and displayed full scale. The precision and resolution of the suppression system are such that the suppressed weight is known with undiminished accuracy.

(3) The continuous "% sample weight" control has unusual range, spanning the full range of the sample weights between decade recorder ranges.

BALANCE ARM

ACTIVE
GAS
INLET

ANTISTATIC TUBE

ANTICONVECTION
SHIELD
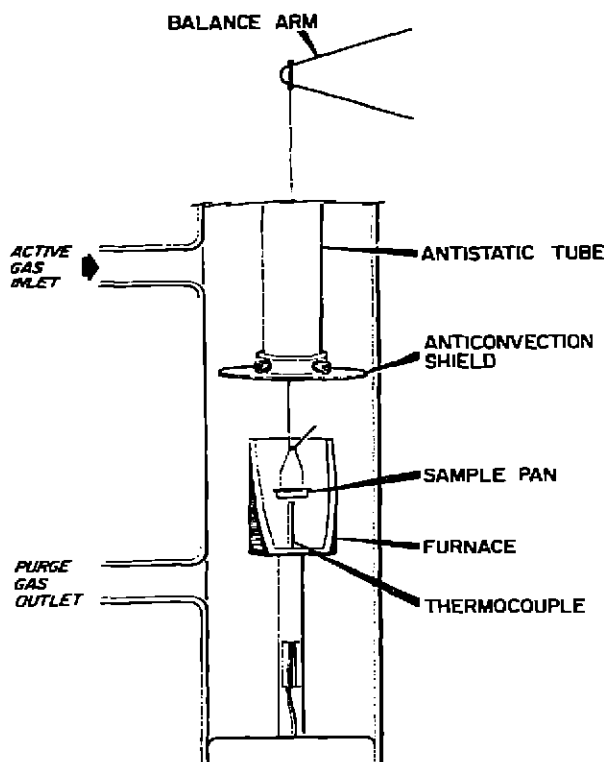
SAMPLE PAN

FURNACE

PURGE
GAS
OUTLET

THERMOCOUPLE

Fig. 2. Diagram of the Model TGS-2 furnace.

For example, with the recorder range on 10 mg, any sample weight between 1 and 10 mg may be displayed full scale on the recorder. In practice, this means that a very large class of TG applications may be run with an absolute minimum of balance adjustments.

(4) The balance mechanism in the Model TGS-2 is mounted to be virtually isolated from the furnace, thus minimizing possible effects, of heat, purge change, and decomposition products on the balance (see Fig. 2).

The design philosophy of some TG systems involves the use of a balance of marginal specifications presumably on the grounds that TG experiments are less demanding than some of the other applications of recording balances. While it is true that perhaps 75% of common TG experiments will not use the full capabilities of the Model AR-2 system, it is obviously a great advantage to have excess capacity and sensitivity so that the system does not impose limitations on the user in extending its applications to critical and demanding measurements. In ordinary TG applications, the benefits of the system are manifested by noise-free and highly linear weight measurements over a very broad range of sample sizes.

The furnace

The problems associated with furnace temperature control in a TG apparatus are those commonly encountered in any system involving a heat

source, a control temperature sensor, and a "load" which is to be maintained at, or programmed over, a range of temperature. If not properly designed, such systems are subject to phenomena such as overshoot, cycling, offset, "droop", and the like. Various kinds of controllers employing proportional band control with or without rate mode, with or without reset action, may be employed with varying degrees of success depending upon the basic design of the system components [1]. These problems in the temperature control arise because heat transfer is a naturally slow process, and there are inevitably thermal resistances between the heat source, the control sensor, and the load. The problems become magnified as the physical size of the system increases. The greater the thermal mass of the components, the greater the inability of the system to respond to a desired temperature change.

In a TG apparatus, the load, which is the sample and its container, is of low thermal mass. Most TG systems, however, employ a needlessly massive furnace which typically surrounds the sample area but is outside the sample space enclosure. This interposes large air-spaces and the hangdown tube wall, which together create a very large thermal resistance between the furnace and sample. This means that the sample temperature responds slowly to any change in furnace temperature. Conversely, a change in sample temperature caused by, for example, a strong exothermic reaction occurring in the sample itself is not rapidly dissipated to the surroundings. In short, the sample temperature is under poor control.

The furnace in the Model TGS-2 is an aluminum oxide cylinder about 1/2 in. in diameter and 3/4 in. long mounted on a ceramic stem inside the sample space (see Fig. 2). The cylinder is grooved and non-inductively wound with platinum wire, the leads of which feed through the ceramic stem and out through vacuum-tight seals to an external connection. The platinum wire and the grooves are coated and filled with flame-sprayed aluminum
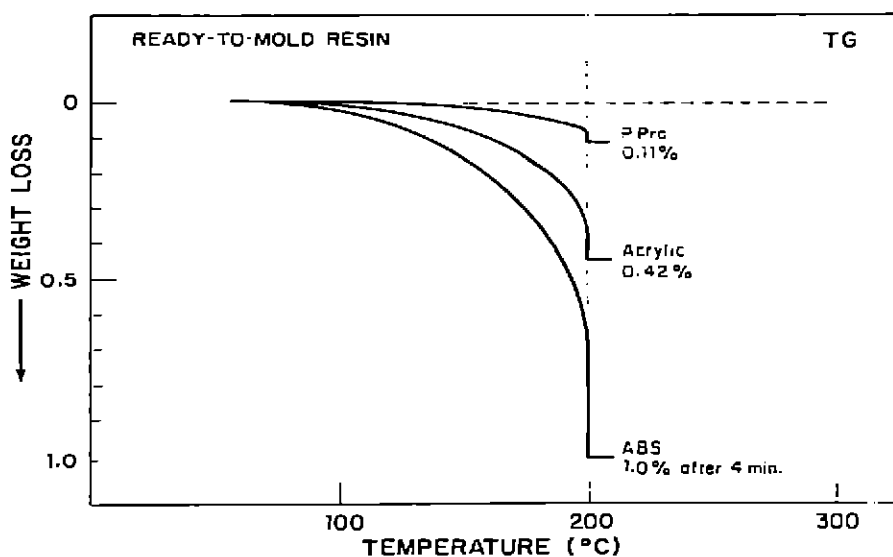

Fig. 3. Total volatile content at 200°C.

oxide for electrical insulation and optimum thermal contact of the wire with the furnace body. The platinum wire functions as both heater and temperature sensor in a novel electrical design which "time shares" the wire at high frequency. The resistance (temperature) of the platinum wire is sensed during one half of a cycle and compared with the desired program temperature. During the other half of the cycle, power is supplied to the wire such as to null the difference between actual and desired temperature. This control system is nearly ideal; thermal lags between heater and sensor are eliminated as they are the same element. The coupling of the wire with the furnace body is via highly conductive material and, being of truly low thermal mass, the furnace responds extremely rapidly to the demands of the programmer.

Since the sample is suspended in a platinum pan coaxially in the furnace space and only a few millimeters from the controlled furnace wall, it follows that the sample temperature is under comparatively excellent control. The practical effect is that samples can be scanned at rates many times faster than is common practice with conventional systems while maintaining comparable or better temperature control. This, combined with the rapid natural cooling rate of the furnace system, means that the sample throughput or workload can be several times greater without sacrifice of data quality.

Temperature measurement

The Model TGS-2 offers a choice of sample temperature measuring and recording systems. As with accurate differential scanning calorimetry, the relationship between the display temperature and the true sample temperature can be established by means of temperature standards, in this case, Curie point magnetic transition standards. The programmer controls can be adjusted to bring the indicated temperature closely in line with each of the standards over the temperature range. This method has been fully described elsewhere [2] and has been tentatively approved by the International Confederation of Thermal Analysis as the method of choice for the calibration of TG apparatus. Although the use of sharp magnetic transition standards allows as close an approach as seems possible to the establishment of a true sample temperature calibration, it has been argued that it is less convenient than a thermocouple readout from the vicinity of the sample. The TGS-2 provides a Type K chromel—alumel thermocouple in close contact with the sample pan so that at all times the operator can monitor the furnace temperature. As described in the next section, the microprocessor linearizes the thermocouple signal, scales it for recorder presentation, and uses it in an autocalibration routine.

The programmer

The most important instrumental development in the thermal analysis field in the last year has been that of microprocessor-controlled analyzers. Because of the relative complexity of many thermal analysis methods and because of the necessity of absolute reproducibility of program conditions, thermal analysis is a prime candidate for microcomputer control. Generally

speaking, the microcomputer allows more involved programs to be specified in advance and called up and executed absolutely reproducibly even by an unskilled operator. The result is a more efficient use of instrument and operator time and more reproducible analyses.

Some specific incremental capabilities afforded by the microcomputer are as follows.

Multiple-step programming. Analyses can be programmed to include iso-thermal dwell times, heating rate changes, preconditioning cycles, and burn-off cycles, all executed identically from run to run. This allows fast scanning rates through temperature ranges of no activity, coupled with low scanning rates over the critical regions of separation.

Automatic purge change-over. Changes in purge gas composition, flow rate or vacuum can be programmed into the analysis. A rapid purge-out of oxygen can easily be programmed into an oxygen-free analysis.

Recorder set-up. Zero suppression, temperature scale expansion, pen-lift control, and event mark intervals can be optimized and specified from the program. As a result, the output for a given analysis will be standardized and optimized.

Method storage. Heating rates, isothermal holding times and temperatures, purge switchover time, and recorder set-up parameters are all stored in a numbered "method file". Thus, once a thermal analysis method has been developed, it can be stored in its entirety in the memory of the microprocessor and recalled at any future time for use. This assures absolute repro-ducibility of even complex analyses.

Automatic temperature calibration. One of the necessities for absolute TA reproducibility is that the analyzers be properly calibrated. This calibration is done at the factory but should be "trimmed up" from time to time. Because this important step is an operator-intensive procedure, it has been preprogrammed into the System 4 controller so that the operator need only push the "calibrate" key to initiate a multiple point calibration routine. Approximately 20 min later, the analyzer is temperature calibrated iso-thermally and dynamically.

Memory protect and keyboard inhibit. All of the parameters in use, including the current temperature calibration parameters, and all of the parameters in the method file are protected from erasure even if there is a power outage or the instrument is temporarily turned off. Furthermore, if an instrument is to be used for one particular analysis, a method can be "locked in" using a hidden back-panel switch so that the parameters cannot be changed. The result is that methods once developed can be protected from erasure or modification both when in use and when the instrument is at rest.

The design of the System 4 microprocessor controller was such as to relieve the operator of much of the difficult and time-consuming aspects of instrumental set-up and operation, and yet provide the assurance that the analyses be performed reproducibly. With this in mind, it becomes possible to tailor TA methods to reduce analysis time and improve accuracy. The following areas are ones where new techniques involving microprocessor control can improve or extend present plastics analysis methods.

Separation of volatiles, polymers, and fillers

Thermogravimetric analysis is increasingly being used as a rapid, automated, gravimetric separation technique for assessing the amounts of various components in a polymer or elastomer blend. First, low heat, inert purge or vacuum are used to extract moisture, solvent, monomer, and low molecular weight additives. Moderate to high temperatures, together with inert purge, are used to depolymerize or pyrolize the polymer matrix quantitatively. High temperature switchover from inert to oxidizing atmosphere is used to separate carbon black, graphite, and molybdenum disulfide from the other fillers. High temperature switchover from carbon dioxide to nitrogen allows assessment of calcium and magnesium carbonate in inorganic filler materials.

Residual moisture, monomer, and solvent

Volatiles can cause a variety of problems in processing plastics. Even very low amounts of residual moisture, monomer or solvents can lead to the production of tiny bubbles which can ruin the performance or appearance properties of a molded part.

Using a good recording microbalance, together with a controlled atmosphere and elevated temperature, allows even very small amounts of volatile material to be detected and assessed. One technique which is accurate and easy to use involves the System 4, TGS-2 combination. The problems which normally limit the accuracy of a low-level volatile TG determination are first, uncertain weight losses due to poor atmosphere control over the sample during the sample preparation and loading state, second, uncertainty in the position of the true "no sample-weight-change baseline", and, finally, poor separation between volatilization and degradation weight losses. These sources of uncertainty can be greatly minimized using proper technique.

The simplest and most accurate technique involves zeroing the balance with a throw-away pan at the plastic processing temperature, loading the 20—50 mg sample and setting up the gravimetric scale (e.g. 1% of sample weight displayed full-scale with 100% weight suppression) with the sample external to the furnace, returning the furnace to surround the sample at an intermediate temperature (e.g. 50°C) with an inert purge, and, finally, programming to the processing temperature.

Using the proper set-up [3], the final displacement of the pan from the zero division line is exactly the percentage weight loss (e.g. 75 division displacement is 0.75% volatiles) (see Fig. 3). If the volatiles are more or less than anticipated, the weight scale can be simply expanded or compressed (e.g. 0.5% full-scale or 2.0% full-scale) to allow a reading of the final result. The pan containing the melted sample is now thrown away and a fresh pan inserted for the next sample. The turn-around time for the test is roughly 5—10 min depending on the time required for the samples to lose their volatile components. The method is applicable to most resin systems with a detectability of approximately 0.01%.

Plasticizers in plastics, plastisols, and rubber

A second type of low molecular weight component present in plastics and
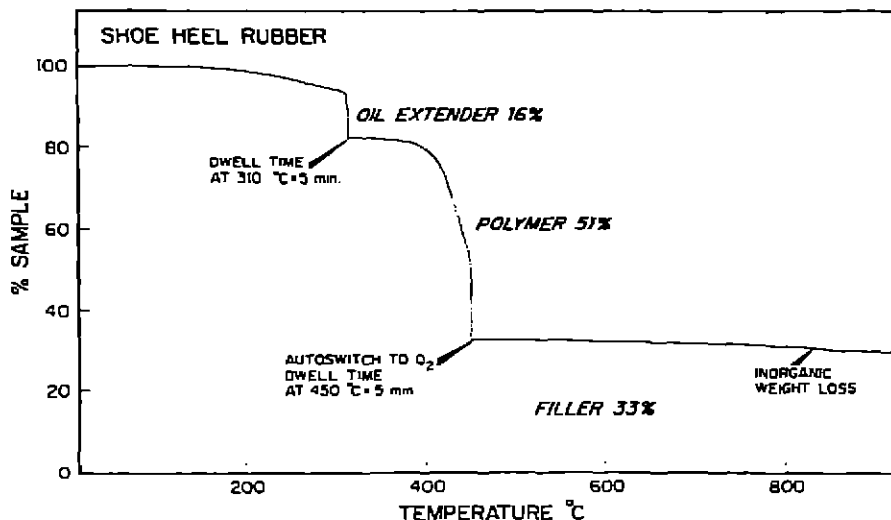
Fig. 4. Separation of highly filled polymers and elastomers.

elastomer formulations is that of plasticizers. These monomeric components are added to modify the viscoelastic properties of the blend to make it more flexible, deformable, and processable. These additives are generally lower in thermal stability than the polymer components and can generally be separated from the polymers using an inert purge atmosphere and a somewhat elevated temperature. Two types of materials, viz. rubber and vinyl, are frequently and extensively plasticized.

Rubber formulations often contain up to 20% petroleum, which acts as a lubricant to reduce internal friction and flexcracking, while at the same time promoting flexibility and adhesive friction. Figure 4 shows a separation of ordinary shoe heel rubber into its primary components of extender, polymer, and filler. In this case, a small sample of 1—10 mg of rubber is placed in the TG pan and the weight expanded to 100 divisions. The temperature program calls for a fast heating rate in an inert atmosphere with brief dwell times at 310 and 450°C to allow time for the oils and polymer, respectively, to volatilize. After this, the purge is switched to air and the T-program continued to detect any carbon black or polymer pyrolysis products. Using the microprocessor programmer, this separation could be performed with total automation in about 20 min. That is, every 20 min the operator could file the results of the analysis and load another sample.

The separation of phthalate plasticizers from vinyls and plastisols is carried out in a similar way. Figure 5 shows a step-wise analysis of upholstery vinyl, this time presented in a time-base (strip chart recorder) format. Separation of the dioctyl phthalate (DOP) plasticizer is complete in 4—5 min at 200°C. When this same separation is performed on a series of identical samples at different isothermal temperatures, the half-life for residency time for DOP can be obtained as a function of temperature. Plotting the data on a semi-log plot (T vs. log t) the life expectancy can be predicted at the end-use temperature [4].
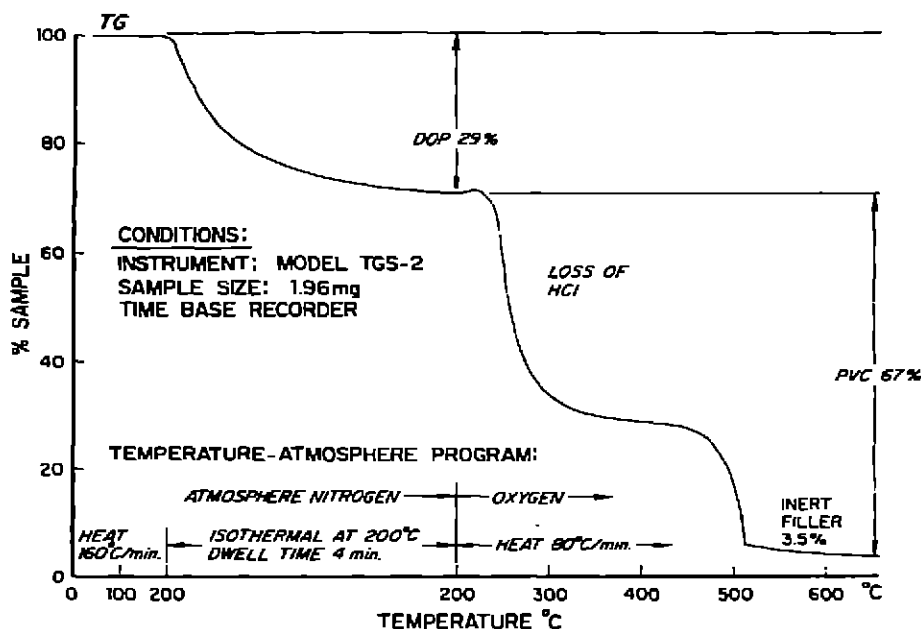
Fig. 5. Determination of dioctyl phthalate plasticizer in polyvinyl chloride.

After assessing the % plasticizer, the separation can be continued to determine other components such as functional fillers and ash discussed below.

Polymer blend analysis

In cases where polymer blends consist of materials of substantially different thermal or oxidative stability, it is often possible to derive a technique for quantitatively separating and assessing the components. For example, Brennan [5] has demonstrated the complete gravimetric separation of polytetrafluoroethylene and acetal blend using an air purge and a moderate heating rate. In most systems, the separation is not complete; that is, there is overlapping of the weight loss regions for the components. In these cases, it is preferable to develop a quantitative analytical DTG technique using as reference standards samples of known composition.

Separation of functional fillers: carbon, carbonate, and MoS_2

In most cases, the organic material in a formulation can be separated from the inorganic components using moderate heat (500—600°C) and an inert or weakly oxidizing atmosphere. The total filler content can then be read from the recorder chart. For some polymers (e.g. some epoxies), these conditions will result in pyrolytic reduction of the polymer to carbon, which would preclude simple separation from carbon fillers. In this case, it is necessary to prepare unfilled polymer samples and run these under the desired separation conditions to determine the residue left by pyrolysis. The filled samples can then be corrected for this effect.

Once the organic material has been removed, the remaining fillers can often be further separated by further heating or by changing the purge atmosphere.
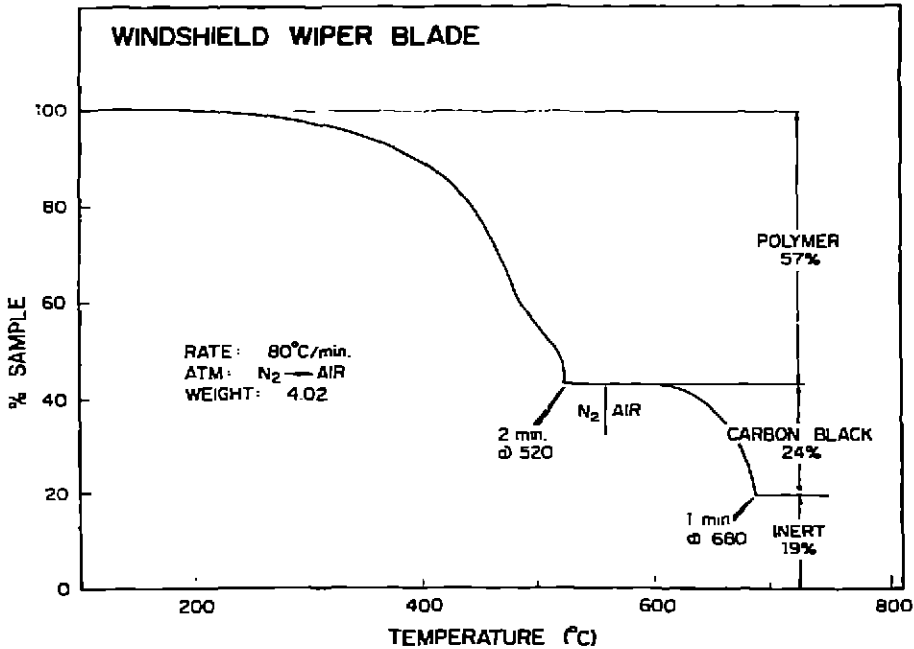
Fig. 6. TG separation of finished rubber product.

Carbon black

Carbon (e.g. carbon black, furnace black, carbon fibers, and graphite) can be quantitatively separated from inorganic fillers by switching the purge atmosphere from inert to oxidizing at a moderate temperature (600—700°C) while holding the temperature program isothermal or heating slowly. A
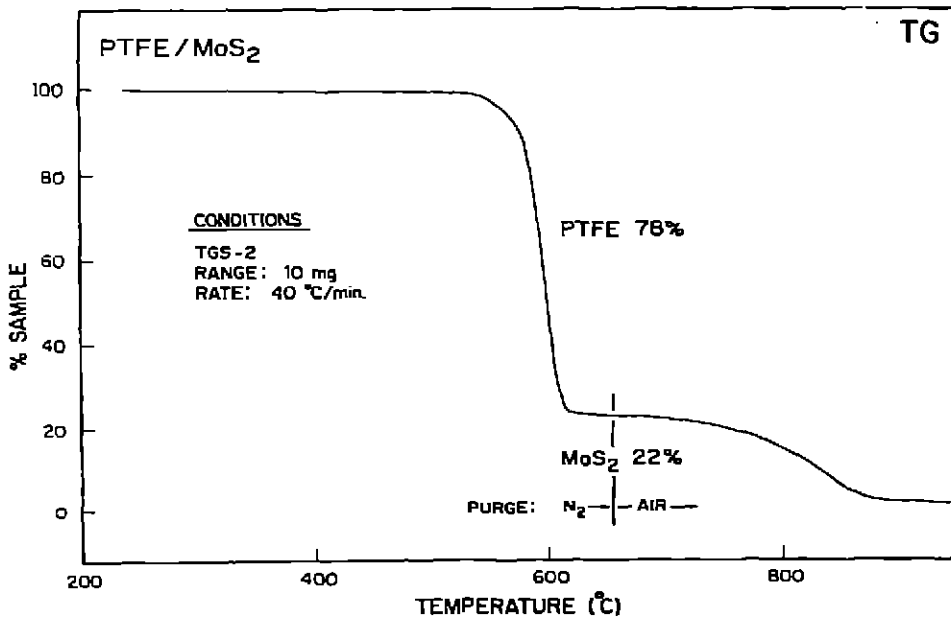

Fig. 7. Determination of molybdenum disulfide in polymer formulations.

simple example of this type of analysis is that of carbon black content in automotive rubber formulations (see Fig. 6). In this case, the sample can be heated rapidly in nitrogen to 520°C and held until the polymer and other organics have been volatilized. The purge is then switched to air and the heating resumed to burn off the carbon. A brief dwell point at 680°C is provided to assure combustion of the carbon. A wide range of elastomer formulations have been separated using basically this technique [6].

Molybdenum disulfide

MoS_2 is sometimes added to engineering thermoplastics to improve frictional properties. In an inert purge atmosphere, MoS_2 is stable up to at least 950°C; in air, it is converted to a more volatile form which then sublimes from the sample. Thus, MoS_2 can be separated from polymer—filler substrates using basically the same method as for carbon. Figure 7 shows the separation of PTFE from MoS_2: pyrolysis of PTFE, purge gas switch to air, and sublimation of the molybdenum. To minimize the condensation of the molybdenum products in the analyzer, a fast purge rate and small sample size is recommended.

Calcium carbonate

A few inorganic fillers can be identified and quantitatively determined in the presence of other inorganic fillers through an inorganic decomposition, usually the loss of CO_2.

A simple example of filler separation is that of $CaCO_3$ in a mineral-filled thermoset polyester (see Fig. 8). The separation involves rapid heating in air to 420°C, a brief dwell time to assure polymer combustion, then rapid heating to 750°C with a brief dwell time to allow for carbonate decomposition.
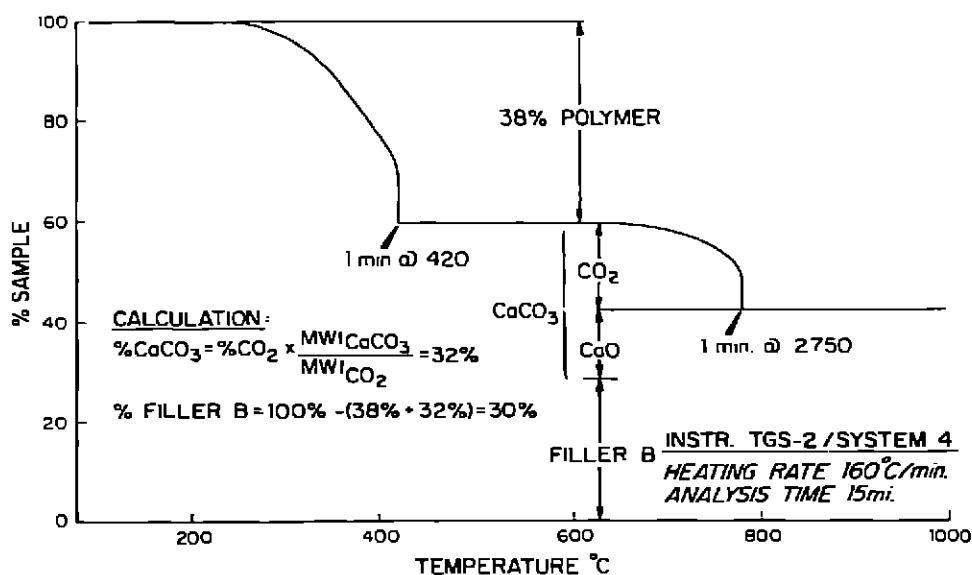
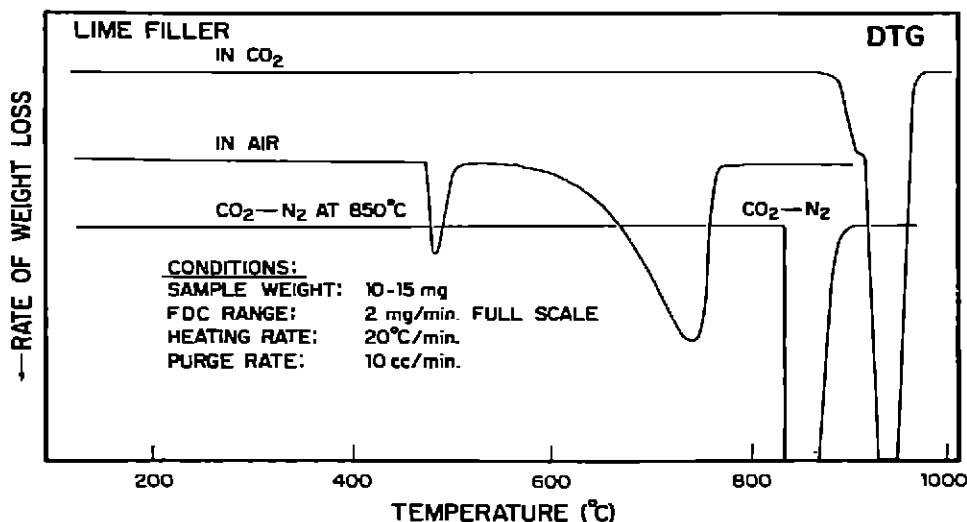Fig. 8. Thermoset polyester—filler analysis. Determination of carbonate filler.

Fig. 9. Suppression of carbonate decomposition with CO_2 purge.

Finally, a brief heating above 750°C establishes the absence of any further inorganic weight loss. The weight loss between 600 and 750° is due to the loss of CO_2 from $CaCO_3$ and can be seen in this sample to be 15% of the original sample weight. From the decomposition stoichiometry and the molecular weight, the weight of $CaCO_3$ can be calculated as 32%. By subtraction, the other inorganic filler is determined to be 30%. The analysis is quick, of the order of 15 min, and can be completely automated using the microprocessor controller.

Occasionally, it is difficult to completely pyrolize or oxidize other components in the polymer matrix without decomposing the less stable carbonates. In order to prevent the overlapping of these phenomena, the pyrolysis can be performed in an atmosphere of CO_2 with small percentages of oxygen added for desired combustion. The atmosphere of CO_2 suppresses to over 850°C the decomposition of the carbonates, which are the principle sources of inorganic weight loss in the temperature region of 400—1000°. Figure 9 shows the thermal decomposition of a commercial limestone filler under various purging atmospheres using the TGS-2 in the DTG mode. Under an atmosphere of air or nitrogen (middle curve) there is an inorganic weight loss due to a magnesium carbonate component. This would interfere with a normal polymer—filler separation. Run in a CO_2 atmosphere, this decomposition is suppressed to a sufficiently high temperature to allow separation of the other components (see Fig. 9, top curve). The best conditions for separating out the carbonate components is seen in the lower curve. Here a purge-gas switchover from CO_2 to any other gas allows immediate and unambiguous conversion of the carbonate components. This type of mid-analysis, atmosphere change-over can, of course, be conveniently automated using a microprocessor programmer.

In conclusion, the techniques of thermal analysis are continuing to expand their utility in the area of plastics analysis, the microprocessor con-

trol provides a capability for making thermal methods faster, simpler, and more reliable [7].

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