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A COMPUTER AUTOMATED THERMAL ANALYSIS LABORATORY FOR POLYMER CHARACTERIZATION*

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ABSTRACT

Thermal methods of analysis can be used to measure a wide variety of physical and chemical properties of polymer systems. These properties are usually determined by making one or more transformations of the output from the TA instruments. Transformations that are commonly encountered include multiplication, integration, differentiation, logarithms, baseline subtraction and combinations of these to fit complex equations. In many cases, the calculations and/or replotting require more time than the operation time of the instrument.

This paper describes a software package that has been developed for use with a DEC PDP 11/40 computer system, which eliminates nearly all of the hand calculations and plotting that are normally encountered for DSC, TG, TMA and evolved gas techniques (TEA, TGC). The package consists of programs to perform direct data acquisition simultaneously from all the instruments, to transform the data as necessary, and to plot the TA curves in a form suitable for reporting. Substantial improvements in efficiency, accuracy and data analysis capabilities have been realized through automation of the TA laboratory. Specific examples of expanded capabilities for polymer characterization are described.

INTRODUCTION

Provision of thermoanalytical services for polymer characterization at a large technical center requires flexibility in both instrumentation and data analysis capabilities. Routine and non-routine analyses of a wide variety of polymer systems must be performed efficiently and reported in such a way that the requestors, who may not have a detailed knowledge of the instrument's operation, can understand and interpret the results. In most cases, this requires that personnel in the thermal analysis laboratory transform the output from the instruments to produce plots or tabulations of meaningful physical or chemical properties. These transformations and, in some cases,

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replots can be very time consuming and inaccurate when done by hand; therefore, it is advantageous to use a computer with plotting capabilities for this purpose. Direct instrument interfacing with on-line data collection and storage is desirable since this eliminates the need to transfer data manually to a computer system.

During the past two years, the Polymer Properties Group in Union Carbide Corporation has been involved in the automation of a variety of instruments used for polymer characterization including thermoanalytical devices. A PDP 11/40 minicomputer system with a real-time multitasking operating system was installed to perform data acquisition, data analysis and plotting for these instruments. This paper describes the FORTRAN IV software package that has been developed to automate the instruments in the thermal analysis laboratory (DSC, DTA, TG, TMA, evolved gas analysis) of this group.

Most of the TA automation described in the literature was developed for a specific instrument or application such as the analysis of rate data from dynamic heating experiments[1]. An exception to this is an automated thermoanalytical laboratory for general chemical testing described by Catalano and English[2]. They developed a custom computer system and a software package written in FOCAL to meet the needs at their facility. Our approach differs from theirs in that a commercially available computer system is employed with minimal modifications, and software is written in FORTRAN IV to make use of existing utility programs. Also, emphasis is placed on techniques and transformations that are encountered in polymer testing although the software is not restricted to that purpose.

EXPERIMENTAL

The commercial instrumentation in the thermal analysis laboratory consists of two DuPont Thermal Analyzers (Model 990) with cell bases and cells for differential thermal analysis (DTA), differential scanning calorimetry (DSC) and pressure DSC, plus attachable modules for thermogravimetry (TGA, Model 951), and thermomechanical analysis (TMA, Model 942). In addition, there are two free-standing instruments for evolved gas analysis; a thermal evolution analyzer (TEA, DuPont, Model 916) and a thermal gas chromatograph (TGC, SPEX Industries, Model MP-3). Instrument specifications can be found in sales literature from the manufacturers. The analogue outputs from the thermocouples and detectors in the respective instruments are connected by shielded cable to a multiplexed, flying capacitor A/D converter (12 bit, 24 channels, 200 Hz), which is part of the DEC Industrial Control Subsystem (ICS). A schematic of the computer hardware is shown in Fig. 1. In addition to the PDP 11/40 CPU, the hardware includes 96 KW of core, disc cartridge drives for on-line data storage of 4.8 MW, floppy disc drives for long term data storage and retrieval, various interactive terminals, and a GOULD 5000 electrostatic printer–plotter (1300 lines/min). The software supplied by the vendors includes: (1) a real-time multitasking operating system (DEC RSX-11D), which controls the dynamic allocation of resources to tasks on a proprity and time shared basis; (2)

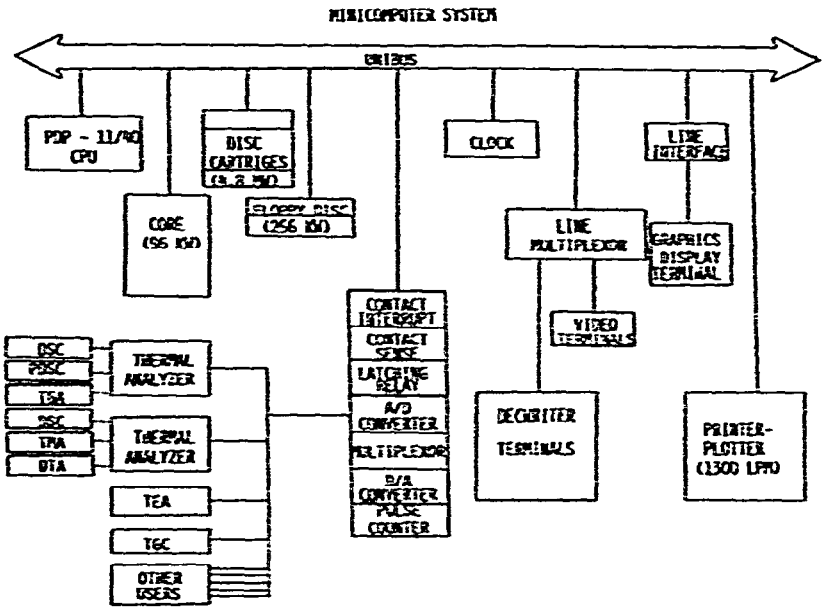

Fig. 1. Schematic of PDP 11/40 minicomputer system with interface to thermal analysis equipment.

ICS/ICR subroutines to control the A/D converters and other instrument interfaces; (3) a FORTRAN Scientific Subroutines package from DEC; and (4) GOULD software to support printing and plotting. Again, the reader is referred to the manufacturers for detailed descriptions of the software.

DISCUSSION AND RESULTS

The complete software package that has been developed to support the thermoanalytical measurements is logically broken into three sections, data acquisition, calculations, and plotting (see Fig. 2). All of the programs are written in FORTRAN IV and employ special subroutines of the operating system (RSX-11D) to perform system directives and control of the ICS interface with the instruments. The plotting program relies on Calcomp compatible subroutines in the GOULD 5000 Plot Package. Information is passed from the acquisition stage to calculations and then to plotting by creation and on-line storage (Disk Cartridge) of data files, each representing a complete analysis. Together, the programs work to transform the analogue signals from the instruments into refined plots and/or tabulations of the desired properties as a function of time or temperature.

Data acquisition

Three main programs, TTYN07, TADAQ and TADA, are involved in the production of a complete data file for each analysis (see Fig. 2). Preliminary information concerning a new run is entered in a question–answer format by running TTYN07 at the terminal in the laboratory. An example of the communication between operator and computer is shown below (operator input is underlined).

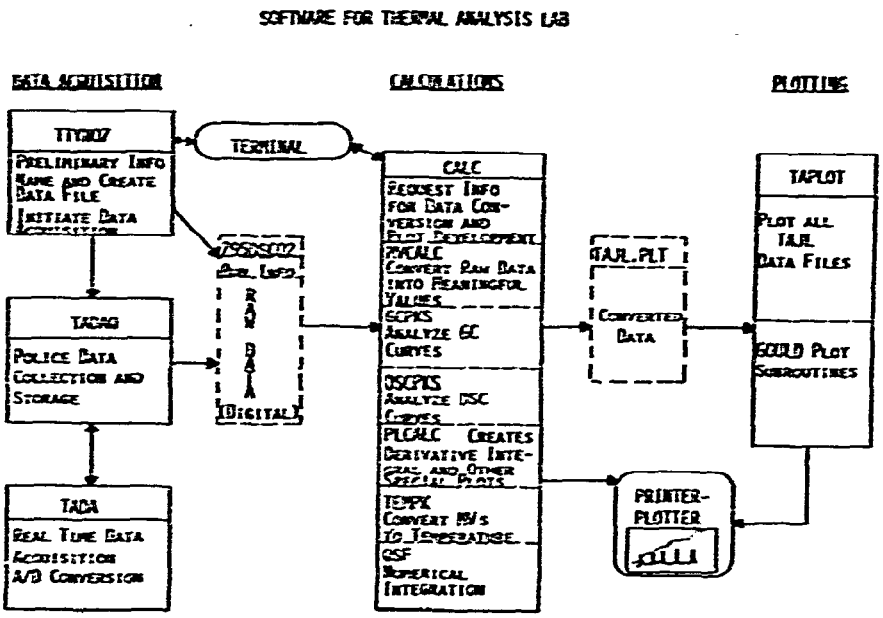

Fig. 2. Schematic of software package for thermal analysis laboratory.

THERMAL ANALYSIS DATA COLLECTION

ANALYSIS NO. = 795
SAMPLE ID = EXAMPLE
SAMPLE SIZE (MG OR MILS) = 3.55
SAME CONDITIONS AS LAST RUN? N
CHARGE NO. = 00000
TECHNIQUE = DSCO DSC1 TGA TMA TEA TCEG TCGC
NUMBER = 1 2 3 4 5 6 7
TECHNIQUE NUMBER = 1
HEATING RATE (DEG C/MIN) = 5
ATMOSPHERE AND PSI(PDSC ONLY) = N
COMMENTS: NONE
FILE NAME SEC/PT T OR HR WT ID NO
795DSC001.795 2 5.0 3.5 EXAMPLE
IS THIS RUN CHARGEABLE? N
IS THIS INFO CORRECT? Y
TTYNO7 — STOP
RUN STARTED – INST: 1
RUN COMPLETED – INST: 1

Normally, less than forty characters must be typed to enter the preliminary information, which is stored as a header in the same data file (795DSC001) that will be used to store the digital data gathered during the analysis. Files are named within TTYN07

by combining the analysis number, the instrument abbreviation and a run number, which is automatically incremented at each new run under the same analysis number. A directory of all runs is maintained which, when combined with the preliminary information stored in the data files, relieves the operator of virtually all bookkeeping functions. Communication between the operator and the computer is complete, until the next run, after the preliminary information is entered since data acquisition is automatically initiated by TTYN07 before this program exits.

Data collection and storage from the instruments is performed by two programs, one (TADA) operating in real-time and the other (TADAQ) in computer-time. This arrangement minimizes the size of the real-time program, which permanently ties up core during data collection, by relieving it of operations that can be made in computer-time. The main function of TADA is to perform the A/D conversion at fixed time intervals, usually every two seconds, for all analogue channels used by the TA instruments. TADA controls the gain of the A/D converter to maintain optimum resolution in the 12 bit digital output. The gain and digital reading for each channel are encoded into a single integer word (16 bit), which is sent to the computer-time program for examination. TADAQ is run periodically by TADA, usually at 20 sec intervals, and proceeds to sort and store, as necessary, all the data that has been sent since the last time it ran. Core is used briefly and is then recovered for use by other tasks. To perform its function, TADAQ keeps a continuously updated record of the status of all data collection in the TA lab. This includes instruments that are running, file names, data sampling rates, etc. Data storage is initiated for new runs based on information sent from TTYN07 and is stopped when the temperature reading from an instrument employing programmed heating stops increasing or after a fixed time interval specified by the operator for isothermal runs.

In addition to the three main programs, there are a number of minor programs that assist in the data collection process. One of these programs is used to print out messages on the terminal in the laboratory as specified by TADAQ, to inform the operator of the start and end of data collection on the instruments. Another program is run to give a complete picture of the status of data acquisition in the laboratory and to manually override data collection on specific instruments in case a run is to be aborted.

The entire package of programs produces a complete data file for each run with a minimal input and attention from the operator. The present software supports simultaneous data collection on four instruments and can be modified easily to support more instruments as the laboratory is expanded.

Calculations and plotting

A single program (CALC) is used to work-up and transform the data from all of the instruments in the laboratory. This requires a somewhat lengthy program, which is broken into six subroutines that are overlaid in core to minimize space requirements. A single program approach is used to avoid duplication that occurs if programs are written for each instrument or technique.

Most of the main program is involved in the input and output of data and in communications with the operator.

```
MCR>RUN CALC$
THERMAL ANALYSIS CALCULATIONS
ANALYSIS NO. = 795
DO YOU WISH TO PLOT ALL FILES? Y
DO YOU WISH TO SPECIFY PLOT LIMITS? Y
PLOT LIMITS – ENTER –999 FOR NO LIMIT

        LOW T, HIGH T, LOW Y, HIGH Y, LOW Y2, HIGH Y2
LIMITS = 0,200,–999
PLOT NUMBER = 2
DO YOU WISH TO SPECIFY DSC BASELINE? Y
BASELINE LIMITS
LOW T, HIGH T, MID T(-999 IF SINGLET)
LIMITS = 75,85,–999
DO YOU WISH TO INTEGRATE ANOTHER REGION? N
CALC COMPLETED FOR 795DSC001.795 EXAMPLE
CALC -- STOP
```

The information supplied by the operator directs the computer to the desired data files and specifies the type of transformations necessary to create a file of refined data for plotting. Routine plot files that can be obtained for all instruments include

Plot no.	*Description*
1	Converted instrument response vs. time or temperature
2	Converted response plus its integral vs. time or temperature
3	Converted response plus its derivative vs. time or temperature

Special plots such as log Y vs. $1/X$, log Y vs. log X and first- and second-order rate equations are available for selected techniques and will be described in the applications section. Options allow the operator to isolate selected regions of the data in both the X and Y directions for expanded plots.

A listing of the individual subroutines and their main functions is given below.

MVCALC. Converts the digital numbers stored in the raw data files into the physical property measure by the instrument (e.g. evolution rate of combustible organic for the thermal evolution analyzer) and the temperature of the sample at that time (using TEMPK). The program also isolates the desired plot region if this is specified.

PLCALC. Performs special transformations of the converted data from

MVCALC such as integrations (using QSF), differentiation, logarithms and others. This is the only subroutine that has to be modified for the addition of new transformations.

GCPKS and DSCPKS. Interpret and analyze GC and DSC data. These programs identify and resolve peaks, construct baselines, and integrate (using QSF) individual peaks to obtain concentrations or enthalpy changes.

TEMPK. A function subroutine containing third-order polynomial fits to type K thermocouple data used to convert from millivolts to temperature. The temperature is predicted to within ± 0.3°C between −150 and 600°C.

QSF. Canned numerical integration program from the DEC Scientific Subroutine package.

After the calculations and transformations are completed, the refined data are printed by the GOULD giving an 8½ × 11 in. tabulation of the results. Also, a plot file (TAJL.PLT) containing the *X*, *Y*1 and *Y*2 coordinates to be plotted plus descriptive information is stored on the disk. The calculation program will then either exit or cycle to another data file with the same analysis number and start again, depending on the options that are specified. A new plot file with the next higher version number is created for each data file that is calculated. The original data files remain on the disk and can be recalculated in as many ways as desired.

Plotting of the TAJL files on the GOULD is initiated by running the plotting program (TAPLOT)

```
MCR>RUN TAPLOT$
PLOT STARTED: [230,001]TAJL.PLT;001 795DSC001.795
PLOT FINISHED: [230,001]TAJL.PLT;001 795DSC001.795
TAPLOT — STOP
```

The program requires no input from the operator and continues to run periodically (ca. one minute intervals) until all versions of the TAJL files have been plotted. This allows unattended operation, which is desirable because of the time required to produce the finished plot (ca. 30 sec) and the large number of files that accumulate during normal operation of the laboratory. Also, plotting can be carried out at off-hours when the computer resources are not heavily used. Each TAJL file is deleted by TAPLOT after plotting, thereby freeing space on the disk for other uses.

All plots are produced on 8½ × 11 in. sheets and contain the information needed to identify the sample and run conditions. Labels on the *X* and two *Y* axes are selected automatically as prescribed by the instrument type and plot number. Two parameters (e.g. response and integral) can be plotted on a single graph and a table of data describing transitions (DSC) or component concentrations (GC) can be displayed on the plot.

Applications

DSC, PDSC, DTA. The output from the DuPont DSC can be converted to sample specific heat by a simple multiplicative transformation involving experimental

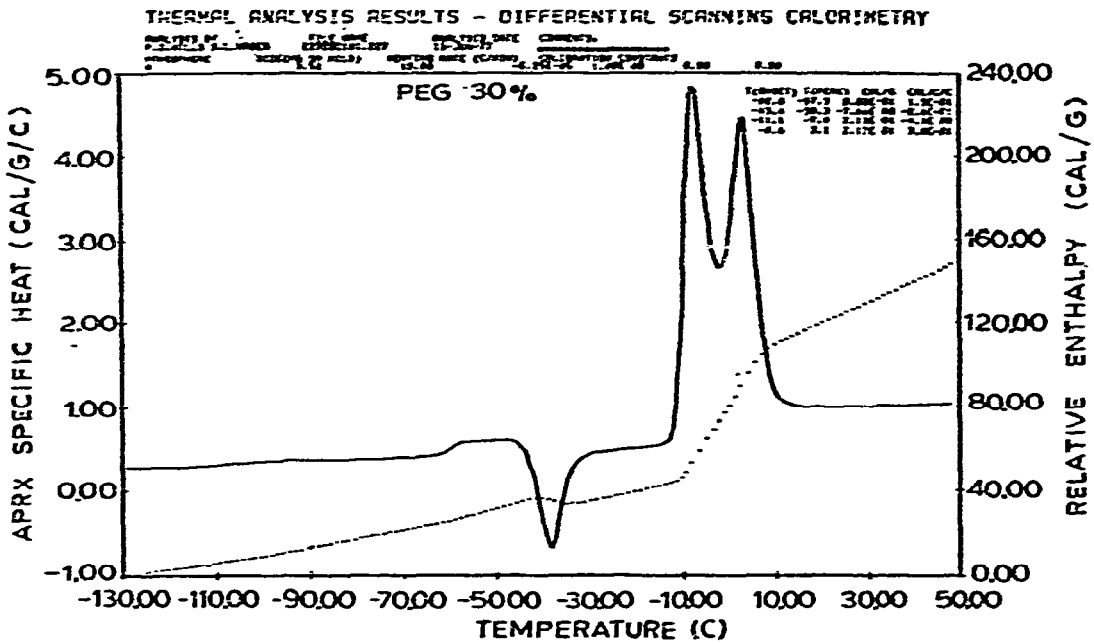

Fig. 3. Differential scanning calorimeter curve for 30% solution of polyethylene glycol in water. Computer label identifies sample and conditions. —, Specific heat (left axis); ..., relative enthalpy (right axis).

parameters (instrument response, sample weight, heating rate) plus subtraction of baseline offset. Careful baseline correction is required when absolute specific heats are desired while approximate corrections are suitable when the magnitudes of transitions are of interest. The enthalpy change represented by a peak in a DSC curve is obtained by construction of a baseline under the peak followed by integration with respect to time.

The most common application of DSC in polymer characterization is in the measurement of phase transitions. Figure 3 shows the computer output for DSC analysis of a 30% solution of polyethylene glycol in water in which a number of transitions are observed. These include a weak glass transition at $-62°C$ [T (onset)], an exothermic peak due to crystallization at $-43°C$, and melting peaks at $-11°C$ (water + polymer)[3] and $-1°C$ (free water). The shift in specific heat and the enthalpy change through each transition are tabulated on the plot with the onset and peak temperatures.

Information concerning the sample identification and run conditions is printed at the top of each plot as demonstrated in Fig. 3. This heading has been deleted from the remaining examples for publication.

TG. The DuPont Thermogravimetric Analyzer continuously measures the weight of a sample during warm-up or at constant temperature. No transformations of the instrument output are necessary for routine measurements; however, the capability for full scale expansion of selected regions of the curve is often useful. Figure 4 shows the weight loss and rate of weight loss for an ethylene–vinyl acetate copolymer

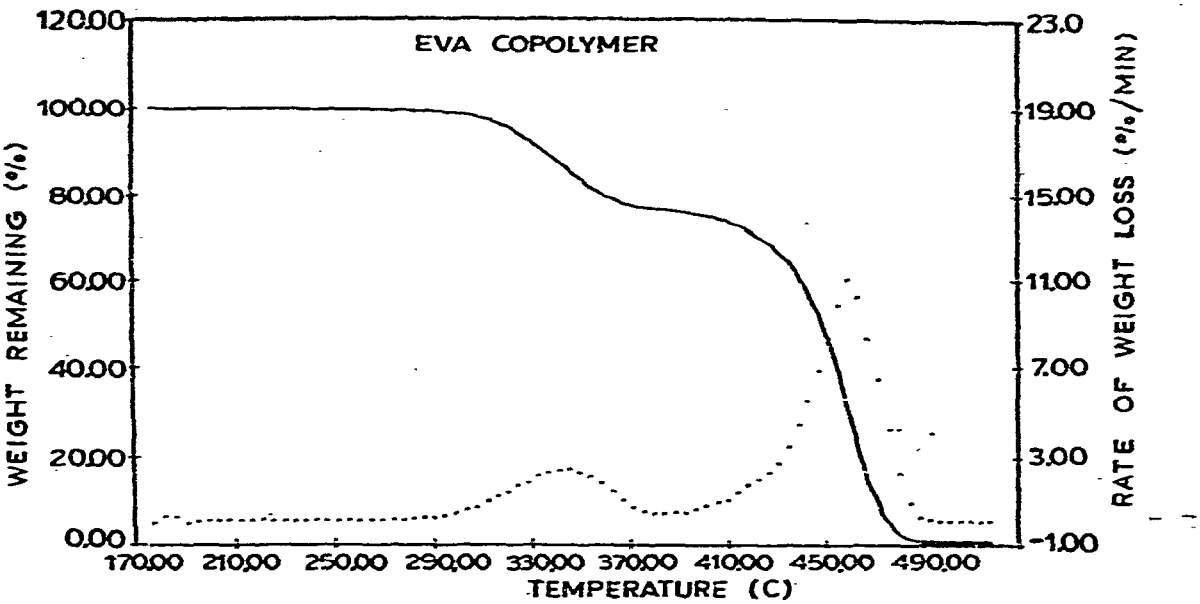

Fig. 4. Thermogravimetric analysis curve for ethylene–vinyl acetate copolymer (30% VA); 20.1 mg; 5°C/min; in nitrogen. —, Weight remaining (left axis); ..., rate of weight loss (right axis).

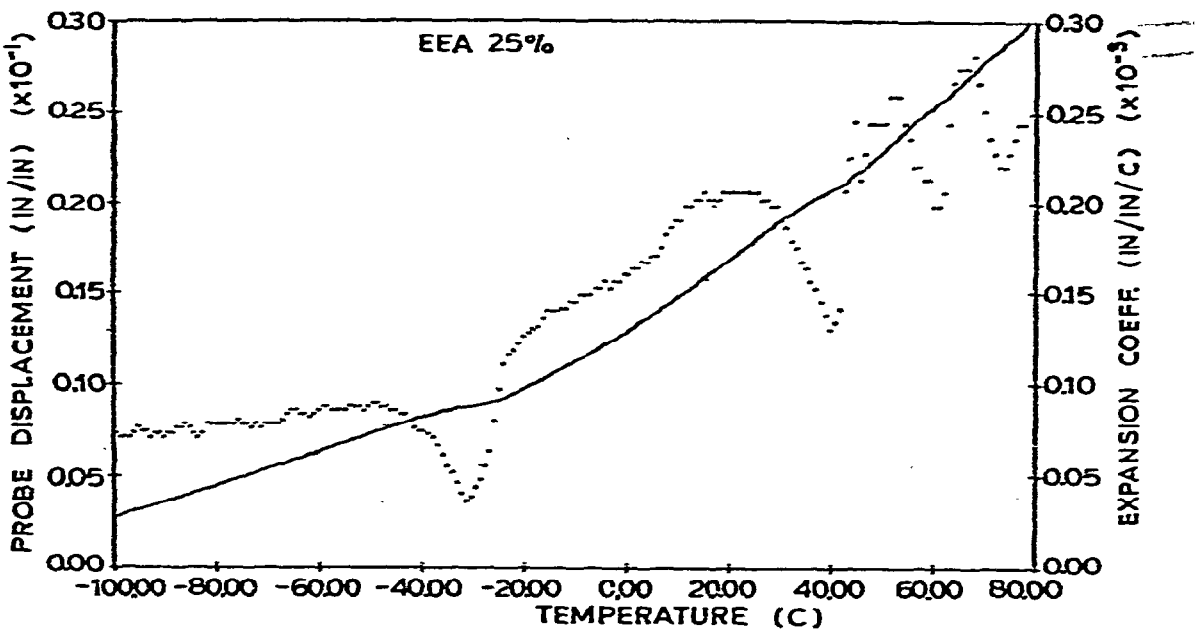

Fig. 5. Thermomechanical analysis curve for ethylene–ethyl acrylate copolymer (25% EA) measured in expansion mode; 214 mil plaque; 5°C/min; in nitrogen. —, Plaque expansion (left axis); ..., expansion coefficient (right axis).

(30% VA) heated at 5°C/min. The weight loss near 330°C is due to the loss of acetic acid from the side chains[4].

TMA. The output from the LVDT in the DuPont TMA can be converted to fractional expansion of the sample and, by differentiation, to expansion coefficient as a

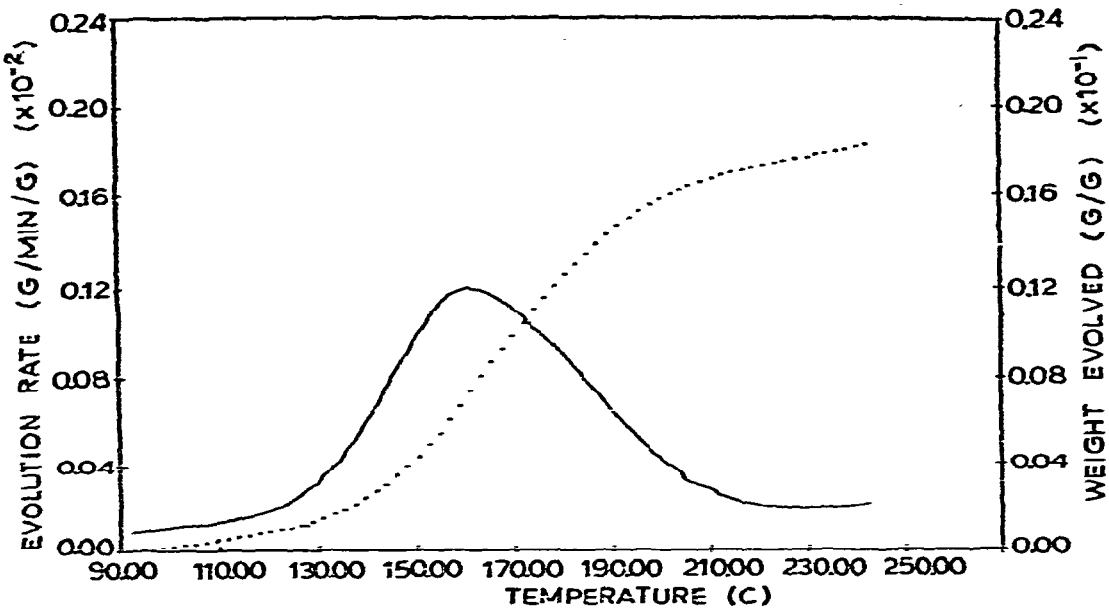

Fig. 6. Thermal evolution analysis curve showing by-product formation during crosslinking of thermosetting resin; 18.1 mg; 4°C/min; in nitrogen. —, Evolution rate (left axis); ...., weight evolved (right axis).

function of temperature. Figure 5 shows the converted TMA data for expansion of an ethylene–ethyl acrylate copolymer (25% EA). The curves show a change in expansion coefficient at ca. −35°C due to a low temperature transition and an increasing expansion rate accompanied by large fluctuations above RT probably due to gradual melting of crystalline domains in the polymer.

TEA. Output from the flame ionization detector in the thermal evolution analyzer is converted to evolution rate of combustible organic from the sample during warm-up by multiplying by a response factor and normalizing per gram of sample. Integration of the curve gives the weight evolved as a function of time or temperature.

A useful application of the TEA for polymer characterization is in the study of crosslinking reactions. Figure 6 shows the formation of a volatile by-product during crosslinking of a thermosetting resin. The evolution rate plus the integral supplies information about the extent of the reaction plus data on the reaction rate and concentration as a function of temperature. These data can be used to predict approximate kinetic parameters[5] (k, $t_{1/2}$, n, A, E_a) by fitting to the Arrhenius equation.

TGC. The thermal gas chromatograph carries the TEA measurements one step further in that the evolved products are trapped and then backflushed into a GC column for resolution of individual components. This technique is similar to pyrolysis GC except for the capability of slow controlled degradation with trapping. The computer converts the data collected from the TC and flame ionization detectors into elution rates and integrates the peaks to obtain component concentrations.

TGC and similar pyrolysis GC techniques have been used by several investi-

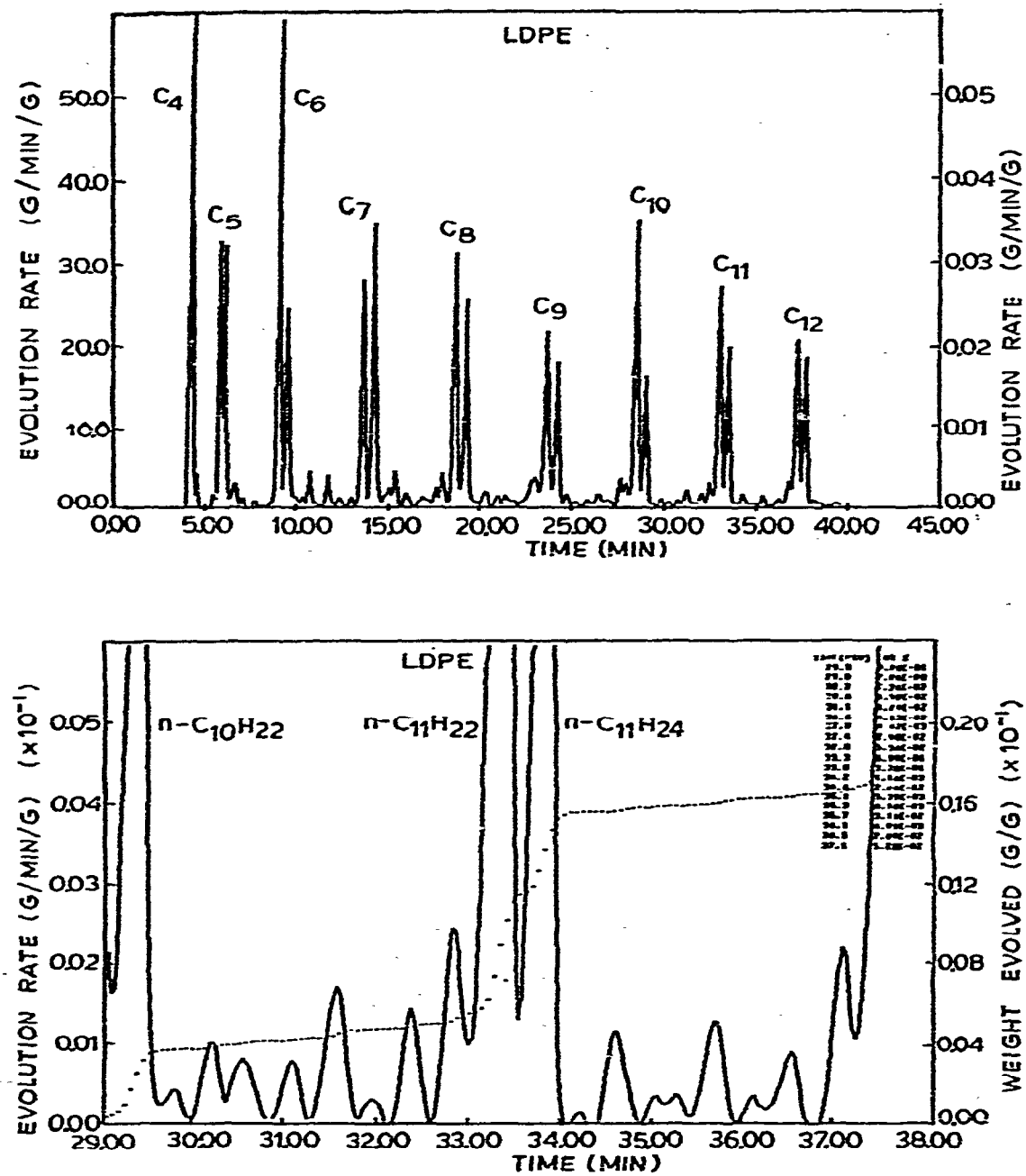

Fig. 7. GC of products from controlled degradation of low density polyethylene measured by thermal gas chromatography; lower curve shows expansion of selected region; 5.52 mg, decomposed at 32°C/min in helium; 30 ft. OV-101 column programmed at 4°C/min; 20 cc/min carrier flow. —, Elution rate (left axis); ..., weight evolved (right axis).

gators[6] to study the products from decomposition of polyethylene. These techniques have been suggested as viable methods for measuring branching in polyethylene. Figure 7 shows GC curves of the products from decomposition of a LDPE sample obtained with our automated system. The capability for curve expansion (Fig. 7,

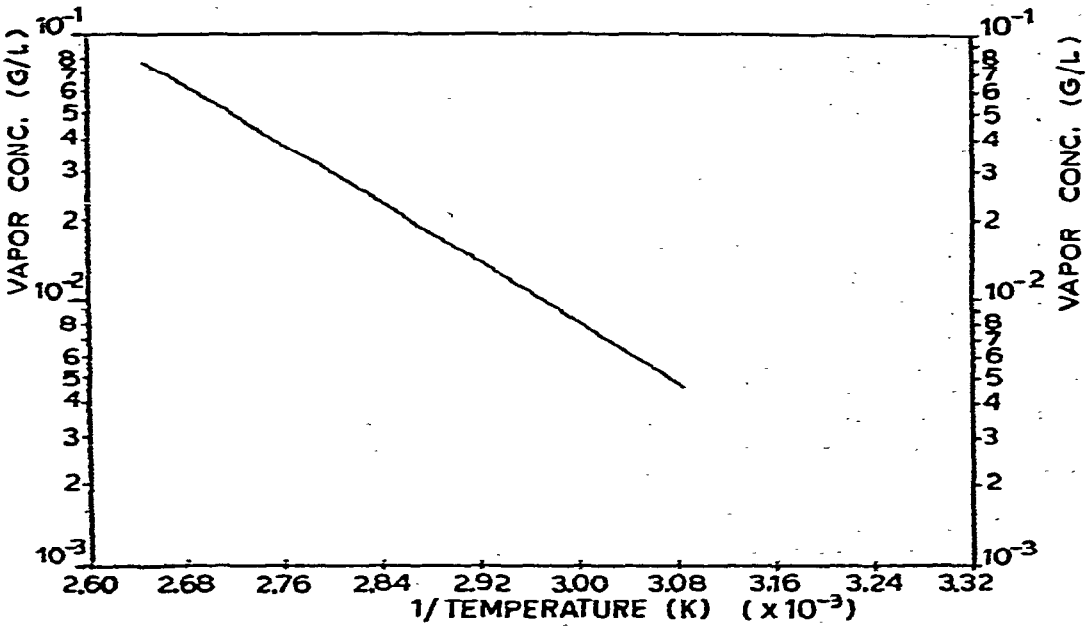

Fig. 8. Equilibrium concentration of acrylate vapor over photocure system containing acrylate solvent; vapor pressure probe; N_2 purge 1 cc/min; 2°C/min.

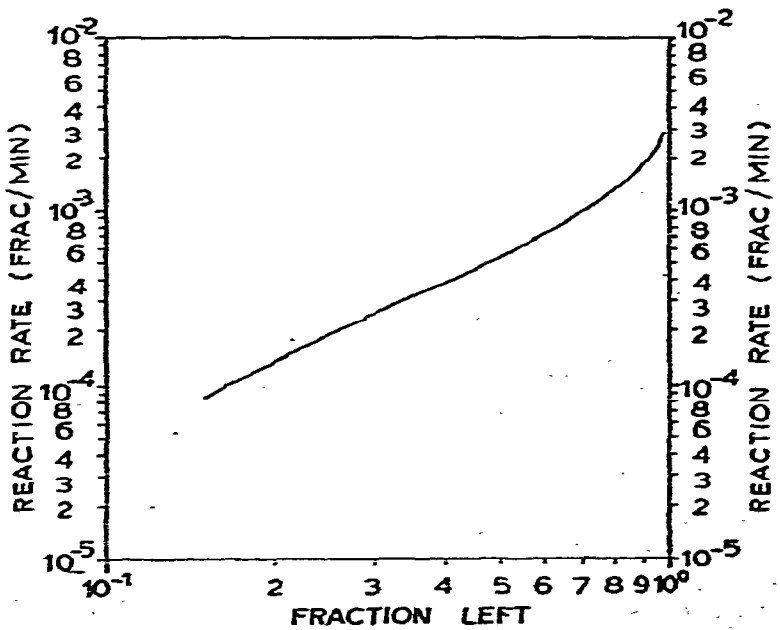

Fig. 9. Log reaction rate vs. log concentration plot obtained by transforming TEA measurements of the rate of formation of by-product during crosslinking of thermosetting resin; isothermal 110°C; 20.0 mg; in nitrogen.

bottom curve) is useful in this application since many of the small intermediate peaks are isomers that form from branches in the polymer chain and thus may be useful indicators of branch concentration. The amounts of the individual components are tabulated on the expanded plot (small print) and a line integral (dotted) is shown which supplies information about the cumulative weight evolved.

Special techniques. In addition to the normal types of plots that have been described, there are a number of unique transformations and plots that have been built into the system.

(*1*) log Y vs. $1/T$. This plot is used mainly to display vapor pressure or equilibrium vapor concentration measured by TEA with the vapor pressure probe. Figure 8 shows the equilibrium concentration of an acrylate monomer in the vapor phase over a photocurable coating system containing the acrylate solvent. The information gained from these types of measurements can be useful for developing low volatility systems and for designing equipment to maintain safe levels of the vapor during application.

(*2*) log Y vs. log X. This plot can be used for displaying reaction data gathered at constant temperature. For example, the evolution of volatile by-product during curing of thermosetting resins, as was described previously, can be monitored over time at constant temperature. This data can then be plotted as log reaction rate vs. log concentration, as shown in Fig. 9, to determine the order of the reaction or to show how the rate varies with concentration.

(*3*) log Y vs. X. Applications of this plot include display of first-order reaction data (isothermal) and unsteady state diffusion of a volatile gas out of polymer pellets

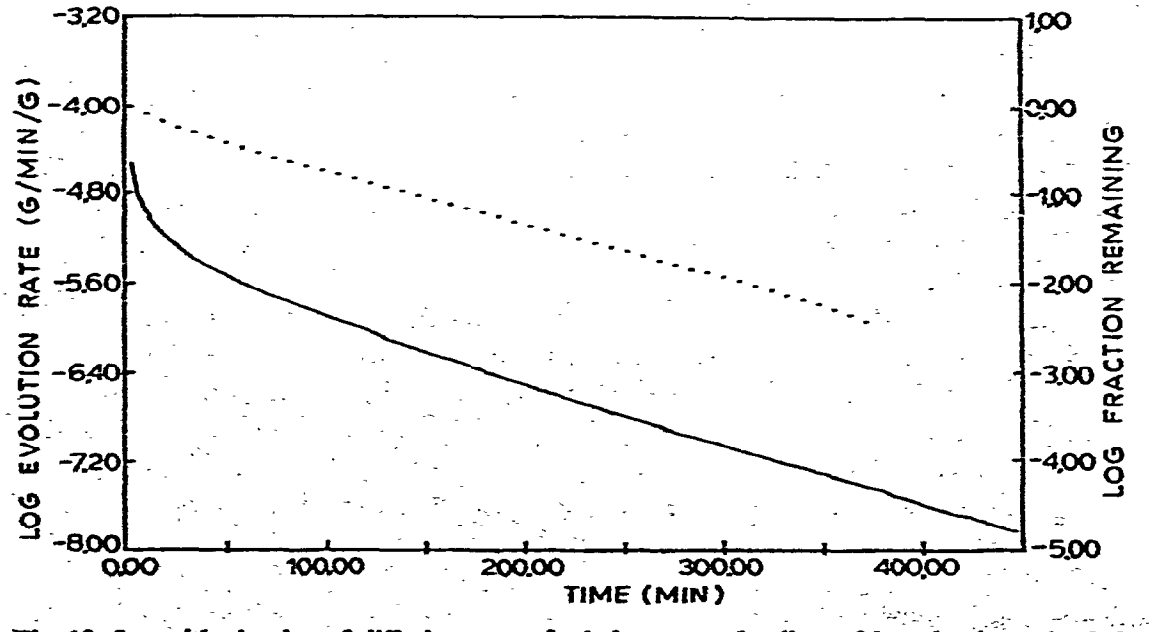

Fig. 10. Logarithmic plot of diffusion rate of ethylene out of pellets of low density polyethylene measured by TEA; isothermal 62°C; in nitrogen; external sample holder containing 7.5 g of resin. —, log evolution rate (left axis); ..., log fraction remaining (right axis).

or films. In these cases, Y is either concentration remaining or evolution rare and X is time. Figure 10 shows the evolution of ethylene from pellets of low density polyethylene at 62°C measured by TEA. The diffusion constant can be obtained from the slope of the curve at long time or by fitting the entire curve to the unsteady state diffusion equation for gases in spherical particles[7]. Solubility of ethylene in polyethylene also can be obtained by plotting the integral of the evolution rate data and measuring or extrapolating to long times. Data from these measurements can be used to design devolatilization equipment and prescribe safe handling proceduers for the resin[8].

Addition of plots. The variety of plots that have been described represents only a fraction of those that can occur in thermal analysis measurements. To provide for the development of new plots as needed, the software was written so that only PLCALC need be modified to perform the required transformations of the data. Generally, less time is needed to modify the software than would be required to transform and plot two files by hand.

CONCLUSIONS

A complete software package for use with a PDP 11/40 minicomputer has been developed to automate a thermal analysis laboratory involved in polymer characterization. The main attributes of this system are given below.

(*1*) One set of programs performs direct data acquisitions and storage, calculations and plotting for all of the TA instruments. Data is stored on-line until the finished plot is generated and then can be archived or deleted.

(*2*) Use of the entire package requires no knowledge of programming and minimal training.

(*3*) Virtually all bookkeeping is done by the computer with safeguards to avoid incorrect or lost information.

(*4*) A variety of data transformations and plot options are available for best display of the results. Plots are created on 8½ × 11 in. sheets for immediate reporting.

(*5*) The entire package is written in modular form for easy modification or expansion.

The automated system has been working smoothly for almost a year. Already we have realized substantial improvements in productivity by elimination of hand calculations and plotting and through reductions in repeated analyses. Accuracy of the data has been improved and the capability for transforming and displaying data has been enhanced. More data interpretation can be made by the submittors of samples since refined plots of physical properties are reported rather than recorder charts of the instrument output.

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