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SOME RECOLLECTIONS OF THERMAL ANALYSIS RESEARCH AT DU PONT

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INTRODUCTION

Thermal analysis has seen rapid growth in both instrumentation and applications during the past 25 years. The Du Pont Company has contributed significantly to this growth. Initial research into the technique began in the Polychemicals Department (later to become the Plastics Department and now Polymer Products Department) in the early 1950s and has continued there and in other departments since then.

The first commercial thermal analysis instrument manufactured by Du Pont was shipped in 1963, beginning an era of innovation, both inside the Du Pont Company and by the many users in a wide variety of applications throughout the world. Some of the historical events that occurred within Du Pont in the last 35 years are recollected here.

I. RESEARCH EFFORTS

In the early 1950s, scientists in the Du Pont Polychemicals Department began to see the need for thermal analysis in the characterization of polymers. J. Mitchell, Jr., Research Supervisor of Analytical and Physical Measurements, felt that precise measurement of thermal behavior would provide useful information, particularly since this would be helpful in defining the commercial utility of polymers. Du Pont scientists, and others, recognized the need for a technique which could meaningfully characterize small samples of polymers in an attempt to reduce the time, effort and high failure costs then associated with polymer research and development.

In 1952, M. Kohan first attempted to study thermal behavior using large thermocouples, 1 in. diameter × 8 in. test tubes as sample holders and a heating block which increased the sample temperature at a rate of $10°C\ h^{-1}$.

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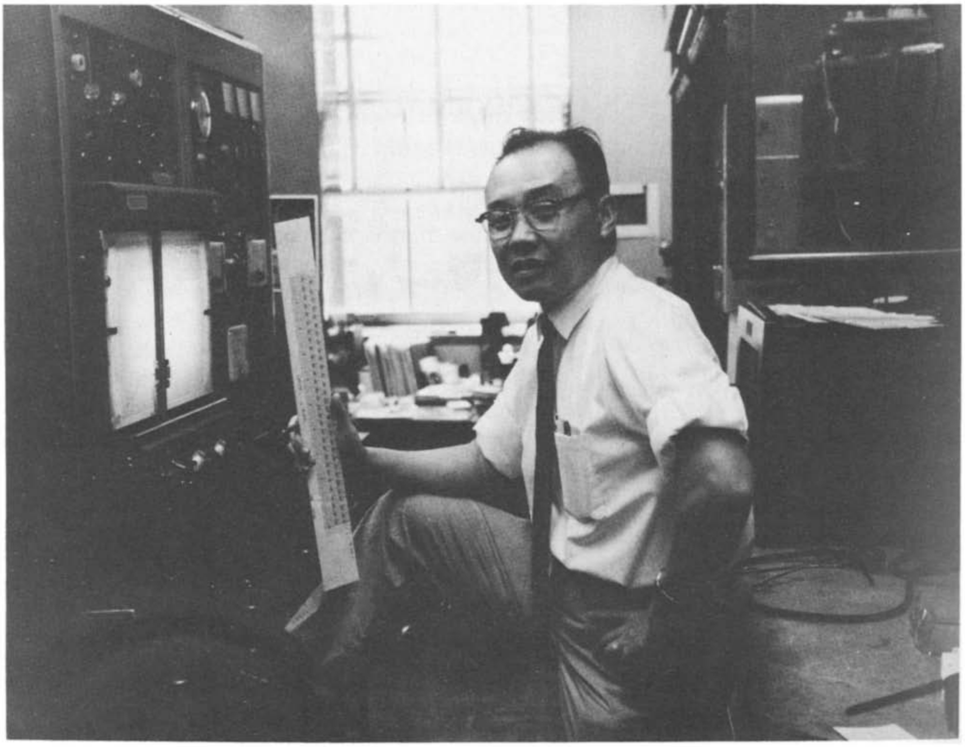

Fig. 1. The author (Jen Chiu), using an early model of a Differential Thermal Analysis apparatus in 1961.

This type of experimental equipment worked, but it was clearly slow and tedious, and the large samples made resolution poor. However, temperature measurements were obtained and the promise of the technique was demonstrated. In 1956 and 1957 D.R. Johnson applied thermo-optical analysis to the study of crystallization kinetics and nucleation of various nylons. He developed micro thermocouple technology for in-sample temperature measurements of milligram size samples thus making rapid and controlled observations possible. High speed, multi-pen recorders were used to record the fast transitions of crystallizations.

In 1958, D.A. Vassallo, a new scientist in Mitchell's group, undertook an assignment to scout for thermoanalytical equipment to further pursue this technique. Further studies had confirmed that, for polymer studies, small samples (mg) would be required to obtain the necessary resolution and precision [1,2]. Since no commercially available equipment was found to fit the needs, a Differential Thermal Analysis (DTA) system was designed and built which incorporated all components except the sample cell into a series of cabinets (Fig. 1). Temperature programmers previously developed for gas chromatography in this group served as a model for this new system, thus providing several selectable program rates. Small (28–40 gauge) chromel–alumel thermocouples were used for the ΔT and sample temperature signals. The sample thermocouple output was fed to the X axis of the built-in recorder to give a direct measure of sample temperature. Now, analysis times for DTA could be much shorter and data much more meaningful because the small sample sizes enhanced resolution. Early studies centered on the effects of heating rates and atmospheres and helped define experimental conditions for accurate and reproducible analyses. Vassallo also explored complementary techniques such as Thermal Evolution Analysis (TEA) to complement DTA and Thermogravimetric Analysis (TGA).

In 1961, Jen Chiu took over the Thermal Analysis research program from Vassallo (who was transferred to Polyolefins Production Laboratory at the Sabine River Plant) and developed an improved DTA cell [3,4]. This cell gave high sensitivity and resolution, good atmosphere control, quick cooling, fast change of thermocouples and freedom from cell cleanup. Initially this cell was used as a reaction vessel for identification of organic compounds by forming and characterizing their derivatives simultaneously in the DTA cell. The instrument control and recording system was also reduced to a more compact bench model (Fig. 2). Further developments of this prototype equipment at Polychemicals led to commercialization of the Du Pont Model 900 DTA (see Section II, Commercialization Activities).

While the model shown in Fig. 2 allowed analysis of samples from −100 to 500°C, there was also a need to study thermally stable polymers and inorganic compounds. Another cell was developed [5] which allowed operation up to 1100°C without significant loss of resolution or sensitivity. This cell was made interchangeable with the original cell, to allow use of the same programmer/recorder facilities. It also permitted operation at reduced pressures as low as 1.3 Pa.

After thermal analysis had been shown to be feasible and practical via DTA, interest in measuring other properties of materials as a function of temperature increased. Johnson, Tabeling and Szabo had developed a Thermogravimetric Analyzer (TGA) to study weight change as a function of temperature (or of time at a constant temperature) either in a controlled dynamic or static gas environment, or in vacuum [6]. This technique had already been applied to compare thermal stabilities and decomposition kinetics. Many other useful applications were investigated in the early 1960s, including analysis of effects of additives, characterization of copolymers and polymer blends [7], kinetic studies, and various other factors affecting thermal stability.

By this time, measurement of the electrical properties, including conductivity of a polymer at various temperatures, was common in the polymer industry, but the study of polymer structure and behavior by conductivity changes had not been fully developed. A cell was developed that would

Fig. 2. A more compact early model of a Differential Thermal Analyzer in 1962.

perform simultaneous, dynamic DTA and Electrothermal Analysis (ETA) [5]. Changes in both heat content and electrical conductivity could be measured continuously as a function of sample temperature. In some instances, ETA was able to detect thermal transitions not detectable by DTA.

Extensive data essential to polymer research were now being generated by DTA, TGA and ETA. The desire to extend this, and to further reduce analysis time via increased sample throughput resulted in an effort to simultaneously study these three and also Derivative Thermogravimetric Analysis (DTG) to monitor changes in enthalpy, conductivity, weight and rate of weight change [8]. These combined techniques were found to be valuable in studying complex systems involving consecutive or overlapping thermal events since each technique provides information not readily revealed by the others.

By the mid 1960s, many trends in thermal analysis concepts and instruments for materials characterization were developing [9]:

Expansion of applications
Modular approach
Combined techniques
Dynamic calorimetry
High-speed analysis
Automated continuous analysis
Comprehensive theories
Dynamic organic analysis

An innovative approach was the combination of techniques. A thermal analyzer was visualized coupled to a gas chromatograph, infrared spectrometer or mass spectrometer. This would allow the investigator to separate and identify components previously evolved from the thermal analyzer according to thermal stability. The initial step toward realization of these combined or "hyphenated" techniques was first described in 1968 [10] and demonstrated the successful combination of thermogravimetric analysis and gas chromatography (Fig. 3). This method followed weight changes of a sample as it was heated under controlled conditions, collected the volatiles during significant events as detected by the TGA, then analyzed them intermittently by GC. This new technique featured precise control of temperature and atmosphere and used minimal thermal energy to perform pyrolysis. Therefore, this reduced the production of secondary products and provided simple and reproducible GC scans. Impurities, such as solvents, monomers, additives, etc., could be analyzed separately from the polymer matrix. Both quantitative and qualitative information on the various components in the sample were obtained. As research on this method continued, it led to development of an improved, all metal coupler to replace the glass system previously used [11]. The new apparatus was semi-automatic, easy to operate and adaptable to most commercial TGA and GC instruments (Fig. 3).

By the late 1960s, good calorimetric data (another trend predicted in 1965) were being obtained using commercially available instruments. Heats of transition and reaction in solid and relatively nonvolatile liquid systems were being measured. Similar measurements were also needed on volatile systems (e.g. heat of polymerization of volatile monomers). These determinations were hampered, however, by lack of commercially available sealable sample containers which would withstand pressure build-up during the analysis. A sealed glass ampoule technique was developed [12] and was demonstrated to be useful for determining heats of polymerization using a

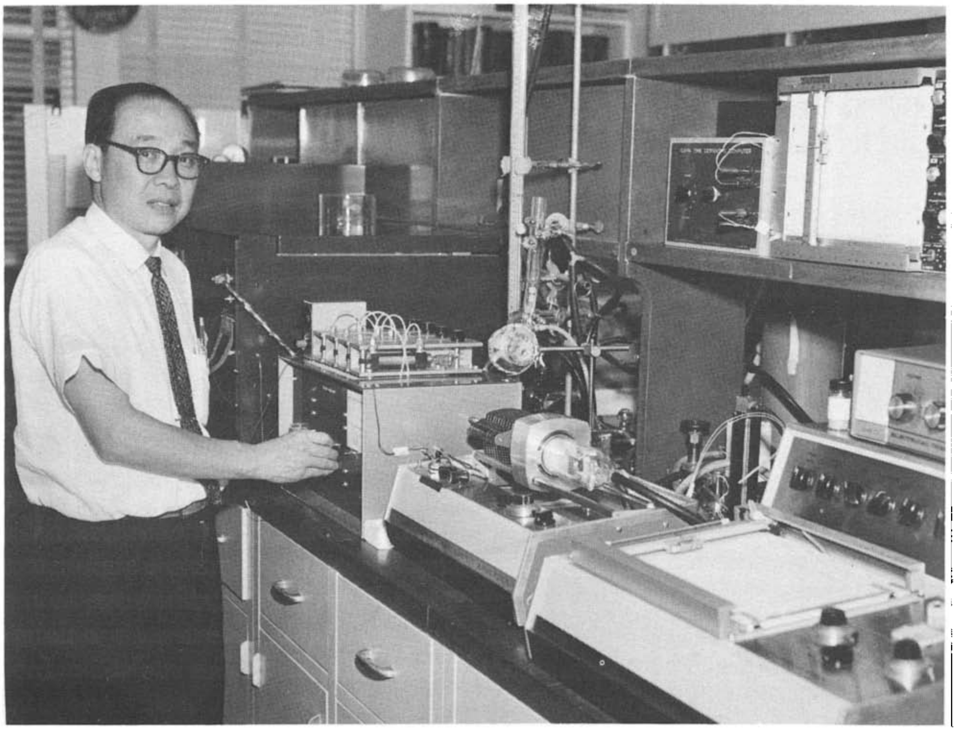

Fig. 3. A combined TGA–GC system used in the author's (Jen Chiu) laboratory. A semi-automatic interface was used.

commercially available calorimeter cell. The procedure was simple and good precision was achieved (3%). The sample container was disposable or could be used to keep the sample for other analyses. This technique was later extended for use with the Differential Scanning Calorimeter (DSC) cell [13].

By the early 1970s, four factors had contributed to the significant growth of thermal analysis techniques [14].

High resolution and rapid analysis had been available since small samples and small thermocouples had been used and continued to improve with the development of improved systems, both for DTA and for Differential Scanning Calorimetry (DSC) [15,16].

More modules for analysis of multiple properties of materials were becoming commercially available and techniques now included Thermomechanical Analysis (TMA) (originally studied by R.R. Garrett in the Du Pont Elastomers Department) [17] and Thermal Evolution Analysis (TEA) in addition to DTA, DSC, TGA and ETA [18]. This development of additional modules contributed significantly to the growth of thermal analysis. Once the original financial commitment to the programmer/recorder console had been made for one technique, addition of other modules became relatively inexpensive and increased the laboratory's capability significantly.

Coupling to other techniques, as mentioned, permitted identification of components separated by thermal analysis. Coupling of thermogravimetric analyzers to gas chromatographs [11], mass and infrared spectrometers, and photometers was being reported. For those laboratories with limited instrument capability, a simple cold trap or bubbling technique could be used to collect volatiles for wet analysis, or to be sent to other facilities for later study.

Computer analysis of thermal analysis data was used to reduce the time necessary to perform complex or tedious calculations and to permit calculation of more involved parameters (such as absolute purity of organic materials and kinetics of cure or decomposition). At the Du Pont Experimental Station, J.S. Fok and E.A. Abrahamson [19] developed a central computer system for use by all research laboratories. This system provided both a real time operating system and data acquisition and reduction for many types of analytical instruments, including thermal analyzers. Up to 200 instruments could be handled directly. Several data analysis programs were written and used, including determination of temperature and heat of transition, calorimetric purity, and specific heat. A study of the effects of both sample and instrument parameters (data acquisition) on results of purity determinations by DSC using both on-line and time-shared computer systems was made [20]. It showed that accurate and precise results could be obtained.

Meanwhile, interest continued in extending conductivity and resistivity measurements to dielectric measurements to provide more information on segmental molecular motions and relaxation phenomena [21]. As an absolute (non-differential) measurement, the electrothermal technique is not subjected to heating rate restrictions, sloping baselines or reference material requirements. This technique detected very subtle transitions such as the beta transition due to motions of polar side groups in poly(methyl methacrylate), and also provided a method to determine the plastic flow temperature above the glass transition for amorphous polymers (which had not been detectable by DTA/DSC).

Another measurement of interest, thermal conductivity of solids, was made possible using a commercial DSC with some modifications [22]. Thermal conductivity is of interest for many applications, including analysis of construction materials used in a thermal environment where heat transfer, insulation and storage are of concern, and for use in determination of hazard potential of materials. Although thermal conductivity measurements on solids were possible before this study, the new technique was the first to demonstrate high sensitivity, sample versatility, a broad temperature range, precision of better than 3% and utility for routine determinations.

Dynamic Mechanical Analysis (DMA) of polymers became available in 1976 [23], allowing measurement of viscoelastic properties of polymers. This became an area of intense interest for polymer characterization.

Thermal evolution techniques initially involved monitoring of materials thermally evolved from a sample on controlled heating, and detection and identification of the off gases using vacuum gauges, electrochemical devices, and thermal conductivity as well as flame ionization detectors [24]. The ability of any thermal technique to characterize complex polymer systems is greatly enhanced when spectroscopic methods are added for identification of evolved gases. One study resulted in development of a thermal evolution–differential trapping–mass spectrometric technique [25]. This system involved heating the sample under controlled temperature and pressure conditions, condensing the evolved gases in traps maintained at various temperatures, continuously monitoring the pressure changes at strategic locations and analyzing the selectively trapped volatiles by mass spectrometry. This system provided preliminary separation of thermal events by thermal evolution, which avoided the complex mass spectra often resulting from conventional total pyrolysis. The added feature of differential trapping also allowed further separation of products according to volatility, and selective removal of certain components prior to mass spectrometric analysis.

Because the information obtained by mass spectrometric analysis of volatiles was found to be so useful in polymer characterization, direct coupling of a thermogravimetric analyzer to a mass spectrometer was investigated. Coupling techniques developed included total condensation and continuous monitoring for a wide variety of applications [26,27]. This work was later expanded to include TGA–GC–MS [28] where the TGA functioned as a sample conditioner or reactor, the GC to separate volatiles and the MS as an identification instrument.

Another area of research in hyphenated techniques resulted in development of a coupled TGA–photometric system by Levy and Loehr to study polymer combustion [29]. The photometric system measured smoke generation simultaneously with weight loss. The technique was further extended by Johnson and Chiu [30] to measure ignition temperature and smoke density simultaneously with weight loss and rate of weight loss. This type of information can be useful in studying the effect of flame retardants, particularly for rapid screening of different compositions and comparison of sample behavior. Also, TGA has been coupled to an infrared spectrophotometer by D.E. Smith, a summer employee in the Plastics Department, in order to distinguish blends of two homopolymers from their copolymers [31].

Not all hyphenated techniques involve spectrographic or photometric systems. A technique of coupling automatic titration to TGA was developed [32] which allowed quantitative determination of a selected component in the volatiles produced under precise heating conditions in a TGA. This system was found to be effective in polymer compositional studies using both acidimetric and ion-selective electrode titration methods. An example

TABLE 1

Predictions of future trends

1. High resolution using large samples
2. More modules
3. Computer-controlled sampling and analysis
4. Automated process stream analysis
5. High-speed analysis
6. Disposable units
7. More hyphenated techniques
8. Expanded applications
9. Improved performance

of the latter is a convenient determination of vinyl chloride/vinyl acetate copolymers. Later work extended the concept to sample systems where released volatiles cause fouling of the sensing electrodes. The electrodes were

Fig. 4. Past and present members of the Thermal Analysis Laboratory of the Polymer Products Department at the Du Pont Experimental Station. First row (from left to right), J.H. Taylor, M.J. Vilone, Jen Chiu, S.G. Fischer-Drowos, C.B. Ireland, C.S. McLaren. Second row (from left to right), R.T. Cole, E.F. Palermo, F.P. Hytrek, L.H. McCormack, R.A. Parkinson, B.B. Johnson, A.J. Beattie, P.G. Fair. Third row (from left to right), E.G. Clark, M.J.C. Panco, W.N. Cawthray, R.W. Koveleski, W.J. Pangonis.

replaced by a dipping probe colorimeter and the titration end point was indicated by a color change [33].

In 1981, R.C. Johnson and V. Ivansons in the Central Research and Development Department developed multiple sample instruments for DSC and DTA [34]. The microprocessor controlled DSC cell allowed three samples to be run simultaneously for improved throughput. Also, because all samples experienced the same thermal history, more dependable intercomparisons of samples could be made by including reference or quality control materials and calibration standards. The five-sample DTA cell allowed very rapid determination of phase diagrams.

The research aspects of thermal analysis have grown consistently in the last decade. This trend is expected to continue, and new concepts are forecast, as outlined in Table 1. Several of these are worth explaining. High resolution using large samples will be needed for accurate analysis of non-homogeneous materials. More modules are expected to be developed as new measurements become practical. Computers now not only process data, but control the programming of several modules simultaneously and computer controlled sampling should be the next breakthrough available. High speed analysis is always of interest to increase laboratory throughput. More hyphenated techniques will continue to be developed to give more thorough interpretation of results.

Thermal analysis has been a subject of intense and successful research at Du Pont for many years and this is also expected to continue. At the Polymer Products Department (previously Polychemicals and Plastics Departments), the thermal analysis group has grown from the original one-man laboratory to more than ten. A recent picture (taken in April 1985) of some past and present members of this group is shown in Fig. 4.

II. COMMERCIALIZATION ACTIVITIES

As noted previously, and as described by Gee and Tyler [35], the beginning of the instrument business at Du Pont occurred when company scientists first found it necessary to design and develop their own specific instruments to ensure proper product knowledge and process characterizations. Several groups had suggested that Du Pont make and sell these instruments for use by other research laboratories. In the late 1950s interest in product diversification was high, and in 1960, the Du Pont Engineering Department initiated a study of their own recommendations and those by Plastics Department and Remington Arms personnel to diversify by entering the instrument business. This study uncovered more than 510 candidate instruments and devices developed by company researchers and resulted in a formal proposal to commercialize selected instruments from this list. Management approved the proposal in June 1961 and authorized US $1.9

Fig. 5. Judy Clark of the Polychemicals Department at Du Pont using an early model of the Du Pont 900 DTA.

million of venture capital with an objective of developing a successful business within three years. The venture was formally constituted in the Development Department in August 1961 and work was begun immediately to develop market information and marketing expertise along with the production facilities needed for a new business.

Two products were selected for initial commercialization, one being the Differential Thermal Analyzer. By spring of 1962 several key personnel had joined the group, including J.C. Metzger, Venture Manager; R.A. Piper, Marketing Manager; J. Johnston, Jr., Engineering Manager; D.R. Johnson, Product Manager; and D.M. Barton, Manufacturing Manager. Work was in progress to develop the design used initially by Chiu (Fig. 2) and put it into production. Instrument design and engineering consultants were hired to combine a functional instrument with an attractive design and work was contracted to area engineering shops (such as All American Engineering) when facilities were not available in-house. The model 900 Differential Thermal Analyzer (Fig. 5) was introduced to the market at the Instrument Society of America Exhibit in October 1962, and was chosen as one of the top 20 instruments shown that year [36].

In-house experience again proved beneficial as Du Pont scientists were able to provide applications expertise in use of DTA for fundamental and applied research on many materials. Several of the early marketing representatives had prior experience in various company research laboratories and were able to demonstrate the ability of the DTA to solve industrial problems. The first commercial instrument was delivered to the Du Pont Niagara Falls plant in January 1963. Shortly afterwards, the first "outside sale" was made to Phillips Petroleum in Oklahoma where it was used to study polyethylene.

Initial customer response to the new instrument was good, but most prospects wanted to see results on their own problem samples. This led to two sales support activities:

(1) development of the Applications Lahoratory, where scientists analyzed samples for potential customers to show utility; and

(2) "in-house" demonstrations, either at the customer's laboratory or in the Applications Laboratory, to evaluate utility and simultaneously show how easy the instrument was to operate.

Again, the focus was on problem solving, and most demonstrations involved analyzing "good" versus "bad" samples, or showing change in some property related to processing, additive content (e.g. plasticizer), etc. The ability of the DTA to show second order transitions (such as glass transitions) of polymers provided a new and simple way to study these parameters and apply them to practical problems in the plastics industry. Early sales were encouraging as 65 units were sold in the first year growing to 95 in the second year.

Another area where company expertise was valuable was in scouting for other companion products for the 900 DTA. The original 900 programmer/recorder design featured a plug-in cell for two reasons: so a second cell could be used while the first was cooled down to minimize system down-time between samples; and, so other plug-in cells or modules could be used. Early work in the Plastics Department had already indicated a need to measure other properties in addition to transition temperatures, so provision for "plug-in modules" was made early. Since TA was a new technique, it was recognized that this modular concept would provide for economic addition of other techniques as modules to the programmer/recorder. Based on both in-house needs and market research, Thermogravimetric Analysis (TGA) was chosen as the next technique to be developed thus permitting study of weight changes as a function of temperature. Development criteria for a TGA module specified that it be of a horizontal design to allow gas flow without the aerodynamic forces of drag and minimize problems associated with buoyancy. (This feature proved to be doubly useful later when interest in hyphenated techniques started; the horizontal design facilitated coupling the TGA to a variety of other instruments.) The 950 TGA was launched at ISA in 1963 and then exhibited at the Pittsburgh Conference early in 1964 [37]. This marked the realization of the modular concept.

During this time, several accessories for the 900 DTA were being developed, many based on designs developed in the Plastics Department. In the first two years (1962–1963), the visual cell and standard cell cooling jacket were introduced, as well as two new cells: the intermediate temperature cell, extending operation to 850°C and the high temperature cell, allowing operation to 1200°C. Work on additional modules was also in progress, and a Thermal Penetrometer was developed and introduced, to measure softening of materials.

In 1965, several new products and accessories were added to the product line. A "remote cell adapter" allowed convenient use of the standard and intermediate DTA external to the programmer (connected by a 6 ft. cable) for isolation of the cell, for safety or convenience. A flow accessory (for atmosphere control) and a quick-cool accessory broadened the types of operation possible with the standard DTA cell. A time base generator allowed operation of the X–Y recorder with time on the X-axis, to measure transition times under isothermal conditions.

Two of the more significant additions, however, were the Calorimeter Cell and the Electrothermal Analyzer (ETA). The calorimeter cell, provided as a module for the 900, was based on the design of Boersma [38], and provided accurate measurement of quantitative DTA data from −100 to 700°C. Holders for sample and reference were located in separate cavities in a heating block, with good resistance to heat transfer, providing good quantitative results. The ETA cell accessory, based on Chiu's design [5], was used for electrical resistance measurements. Both of these products, although novel at the time of introduction, enjoyed only moderate popularity and were later discontinued. However, several of the features of the calorimeter cell base were later incorporated into development of improved remote cell bases.

In 1966, the 940 Thermomechanical Analyzer (TMA) [39] evolved from the Thermal Penetrometer concept and allowed measurement of expansion of samples in addition to softening or penetration. It was based on a moveable core transformer. Newer modules and many accessories would later be developed which would make the TMA a very versatile instrument (e.g. dilatometer, fiber and film probes, stress relaxation, etc.).

In 1967, the 920 Thermograph was introduced. This was a low cost thermal analyzer for routine applications where the versatility of the 900 DTA was not needed. This economical product had modest sales and was eventually discontinued.

A significant achievement in the area of calorimetric analysis was achieved in 1967 when the Differential Scanning Calorimeter (DSC) cell was introduced [16]. This cell used a thermoelectric disc made of constantan as both the major path of heat transfer to and from the sample and also has one-half of the differential measuring thermocouple. It operated on the principle of a heat-flow analog of an electrical bridge circuit. Good quantitative data were

Fig. 6. The Du Pont 990 Thermal Analyzer.

obtained as easily as with the DTA cell, and a versatile pan-type system provided convenient sample handling. This cell could be plugged into the 900 programmer directly or used with the remote cell adapter. Also in 1967, a new DTA cell extending operation to 1600°C was introduced. Transition temperature measurements could now be made from −180 (using the DSC cell) to 1600°C using this cell, giving the system a widely versatile range of applicability. In 1970, DSC capability was extended further with the introduction of a Pressure DSC Cell [40] which allowed analysis of samples under reduced (to 1.3 Pa) or elevated (to 7 MPa) pressure.

The instrument business, like so many others, constantly changes as new technology becomes available and user needs are identified. Success depends largely on continuing to provide state-of-the-art, competitive products. In 1971, the Model 990 Thermal Analyzer (Fig. 6) programmer/recorder replaced the 900. Innovative features of the 990 included a larger (11 × 17 in.) recorder with 2 pens, allowing simultaneous display of either the *Y* axis signal at two sensitivities or the derivative of the signal (now huilt into each module). This unit also allowed either sample temperature or time to be displayed on either the *X* or *Y* axis. Upgraded analysis modules (951 TGA, 942 TMA and Cell Base II for DTA/DSC Cells) originally accompanied this programmer. Improvements and additions continued: in 1976, the 943 TMA became available with accessories for stress relaxation, fiber tension, parallel plate rheometry and a new furnace extending operation to 1200°C. The 910 cell base, with a preamplifier to extend DSC sensitivity by a factor of 2 became available in 1977. The 916 Thermal Evolution Analyzer (TEA) to measure organic carbon evolved from a sample, was available from 1970 to 1979.

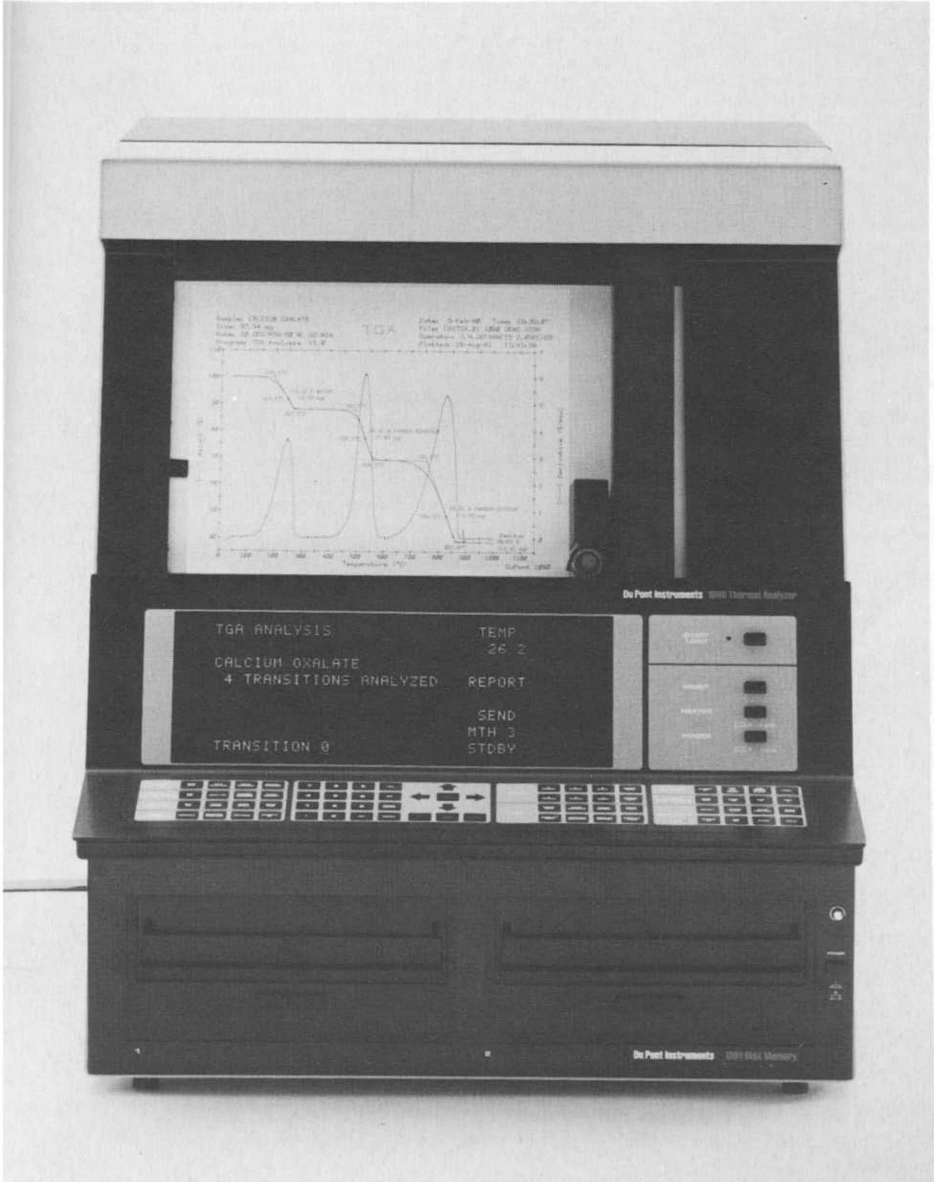

Fig. 7. The Du Pont 1090 Thermal Analyzer.

A very significant module, the 980 Dynamic Mechanical Analyzer (DMA) was introduced in 1976 [41]. It was now possible to obtain information related to modulus and damping of viscoelastic materials quickly and easily. The 980 DMA measured resonant frequency and damping of a mechanical oscillator containing the sample which was set into oscillation and maintained in that state. The 981 DMA [42] allowed quantitative calculation of flexural storage modulus (calculated from the resonant frequency), flexural loss modulus, and damping (tan delta). Further refinements in hardware and calculations continued to appear, each providing improved performance and more meaningful data [43,44]. These types of measurements provide information on very subtle second order transitions (beta and gamma transitions), and other molecular motions in viscoelastic materials. Although these analyses had been possible before, they usually required expensive, standalone instruments and the measurements were often time-consuming and tedious.

In the late 1970s, as thermal analysis became more commonly used and applications became more complex, calculation of data became a limiting factor in many analyses. Instruments had been refined for rapid analysis with quick turn-around between samples, but data reduction was often time-consuming and tedious. Some applications, such as determination of absolute purity or reaction kinetics by DSC, required elaborate data handling. In the early 1970s, the 915 Computer Interface was available as an analog/digital converter for use with in-house computers as data analyzers. By the late 1970s programmable calculators gained popularity as on-line

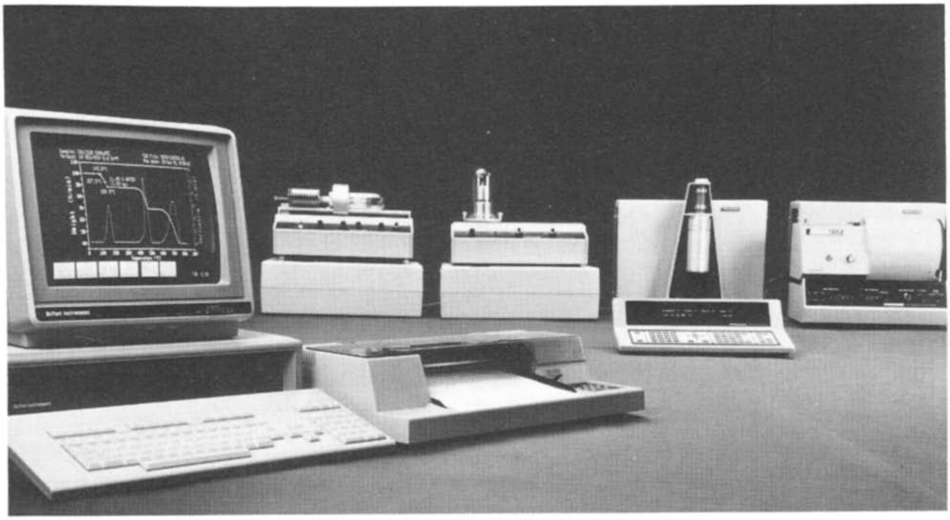

Fig. 8. The Du Pont 9900 Thermal Analysis System which can operate four modules simultaneously.

data acquisition and analysis devices. Both of these methods were obviously limited by the user's ability to write his own programs to handle the calculations. The 1090 Thermal Analyzer (Fig. 7) was developed by engineers under the direction of J.S. Fok and introduced in 1979. It featured microprocessor control of data acquisition and analysis. (The R90 low cost programmer for routine analysis, introduced in 1978, used microprocessors for programming control but had no data analysis capability.) The 1090 used a dual floppy disc system, and a digital plotter, and included many software programs for both simple and complex data handling. The 1090 was a successful product until new technology resulted in the development of the 9000/9900 Computer–Thermal Analyzer in 1984 (shown with all the modules in Fig. 8). This latter system incorporated a professional computer into the thermal analyzer and offered simultaneous operation of up to four modules, sophisticated data analysis, user programmability, a CRT for real time display or to facilitate data handling, and several other attractive features.

Further improvements continued to be developed, often based on ideas and concepts generated by users within Du Pont. In 1982 the 912 Dual Sample DSC was introduced, based on the design suggested by R.C. Johnson and V. Ivansons in Du Pont's Central Research and Development Department [34].

III. MISCELLANEOUS

Du Pont's contribution to the development of thermal analysis as a technique goes beyond just research in industrial departments or commercialization of instruments. For example, in the 1960s, few vehicles existed for exchange of ideas and dialogue between users. In 1967 and 1969, Du Pont sponsored two users' meetings in Wilmington to provide an open forum for exchange of ideas, presentation of papers on research, and information on new instruments, etc. Both were highly successful, well attended, and well received. Once the North American Thermal Analysis Society (NATAS) was founded in 1969 these meetings were no longer needed, but they served to fill a void in the early days of TA.

Internally, scientists at the Du Pont Experimental Station formed a Thermal Analysis Discussion Group in 1974 which has continued to hold monthly meetings. Many Du Pont scientists are active in both NATAS and ICTA (International Confederation for Thermal Analysis). Jen Chiu and R.C. Johnson have served as NATAS Presidents in 1977 and 1985, respectively, and Jen Chiu served as ICTA councilor from 1977 to 1980 (Fig. 9). Jen Chiu, R.C. Johnson and P.S. Gill were elected NATAS Fellows in 1981, 1984 and 1985. Jen Chiu was a recipient of the Mettler Award and NATAS Outstanding Service Award in 1982. Also, Du Pont scientists have been

Fig. 9. The Council of the International Confederation for Thermal Analysis, Bayreuth, Germany, 1980. First row (from left to right), W.D. Emmerich (Germany), H. Kambe (Japan), H.G. McAdie (Canada), G. Lombardi (Italy), O.T. Sørensen (Denmark). Second row (from left to right), J.P. Redfern (U.K.), R. Otsuka (Japan), Jen Chiu (U.S.A.), E.L. Charsley (U.K.), J. Rouquerol (France), J.L. Holm (Norway). Third row (from left to right), H.J. Seifert (Germany), F. Paulik (Hungary), S.St.J. Warne (Australia), J. Šesták (Czechoslovakia), C.B. Murphy (U.S.A.), P.D. Garn (U.S.A.).

instrumental in informing and fostering the Thermal Analysis Forum of the Delaware Valley. Jen Chiu, P.F. Levy, G.J. Sloan and R.L. Blaine served as Presidents in 1977, 1981, 1984 and 1985, respectively. R.L. Blaine served as Chairman of ASTM's Committee E-37 on Thermal Measurements for several years and was elected an ASTM Fellow in 1982. P.S. Gill organized a TA course for the Society of Plastics Engineers. I.M. Sarasohn (with Professor W.W. Wendlandt of the University of Houston) has been giving American Chemical Society (ACS) TA courses for many years.

Du Pont has continued to foster overall development of thermal analysis and, in 1976, established the "Du Pont Award" for recognition of excellence in research or development in TA. The award is given at the International Conference on Thermal Analysis (ICTA) meeting and the recipient is chosen by the Awards Committee of ICTA. Those honored so far have been Paul Garn (1976), Gianni Lombardi (1979), Patrick Gallagher (1982), and Robert Mackenzie (1985).

SUMMARY

Du Pont has left its mark in the development of modern thermal analysis in many areas over the years. Some of the more significant research events which occurred are summarized in Table 2. Milestones in the instrument business are summarized in Table 3. All efforts have been well supported by the corporation and contributions to the technology are expected to continue.

TABLE 2

Milestones—TA research at Du Pont

1961	High Resolution Differential Thermal Analysis (DTA) to 500°C using milligram samples
1963	Thermogravimetric Analysis (TGA)
1964	Thermomechanical Analysis (TMA)
1965	High Resolution DTA to 1100°C Electrothermal Analysis (ETA)
1967	High Resolution Differential Scanning Calorimetry (DSC)
1968	Combined TGA–Gas Chromatography (GC)
1970	Sealed sample holders for calorimetric measurements on volatile samples
1972	TGA–Photometric Analysis
1976	Dynamic Mechanical Analysis (DMA)
1980	TGA–Mass Spectrometry (MS)
1982	Multiple Sample DSC and DTA
1983	TGA–Titrimitry
1984	TGA–GC–MS

TABLE 3

Milestones—Commercialization of instruments

1962	900 Differential Thermal Analyzer (DTA) introduced; represented achievement of good resolution using small samples in a commercial instrument
1963	950 Thermogravimetric Analyzer (TGA); first non-DTA module, modular concept realized
1964	940 Thermomechanical Analyzer (TMA)
1967	Differential Scanning Calorimeter (DSC) Cell; good quantitative data
1971	990 Thermal Analyzer
1976	980 Dynamic Mechanical Analyzer (DMA); first non-classical TA module; extended routine TA into field of rheological measurements
1979	1090 Thermal Analyzer; computerized programmer and data analyzer
1984	9000/9900 Computer Thermal Analyzer

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