$$\mathbf{R}_0 = \boldsymbol{\delta} \qquad \text{(A14)}$$

$$\mathbf{R}_n = \left(\frac{1}{2}\right)^n \int_{t'}^{t} \int_{t'}^{t_1} \cdots \int_{t'}^{t_{n-1}} \dot{\mathbf{\Gamma}}_1 \bullet \dot{\mathbf{\Gamma}}_2 \bullet \cdots \dot{\mathbf{\Gamma}}_n \, dt_n \ldots dt_2 \, dt_1; \quad n \geqq 1 \qquad \text{(A15)}$$

and

$$\mathbf{S} = \sum_{n=0}^{\infty} \mathbf{S}_n \qquad \text{(A16)}$$

$$\mathbf{S}_0 = \boldsymbol{\delta} \qquad \text{(A17)}$$

$$\mathbf{S}_n = \left(\frac{1}{2}\right)^n \int_{t}^{t'} \int_{t}^{t_1} \cdots \int_{t}^{t_{n-1}} \dot{\mathbf{\Gamma}}_1 \bullet \dot{\mathbf{\Gamma}}_2 \bullet \cdots \dot{\mathbf{\Gamma}}_n \, dt_n \ldots dt_2 \, dt_1; \quad n \geqq 1 \qquad \text{(A18)}$$

where $\dot{\mathbf{\Gamma}}_i = \dot{\mathbf{\Gamma}}(X, t, t_i)$. Equations (A11) to (A18) may be proven, for example, by considering first an observer moving with a fluid particle and rotating with the vorticity of the fluid, and then rewriting the equations for a space fixed observer. An illustration of the use of Equations (A11) and (A13) to (A15) is given in Section 9.

THE AUTHORS

R. Byron Bird is Professor of Chemical Engineering at the University of Wisconsin and a member of the Executive Committee of the Rheology Research Center. He received his Ph.D. with Professor J. O. Hirschfelder in 1950 in physical chemistry and has been teaching at Wisconsin since 1953. Teaching assignments in Holland and Japan catalyzed his interest in Dutch and Japanese. Hiking and canoeing provide frequent relief from equations, symbols, and subscripts.

Ole Hassager is presently visiting assistant professor at the Department of Chemical Engineering, the University of Wisconsin. He recieived a M.Sc. degree at the Technical University of Denmark in 1970. He then went to work with Professor R. B. Bird of the University of Wisconsin where, despite frequent sailing on Lake Mendota, he received his Ph.D. degree in 1973.

Said Abdel-Khalik is a recent member of the RRC's canoeing team with a postdoctoral rank (Newtonian fluids only). He got his M.S. and Ph.D. degrees in Mechanical Engineering from Wisconsin under Professor M. M. El-Wakil. He did his undergraduate work at Alexandria University, Egypt.

JOURNAL REVIEW

A Semimicro Thermomechanical Technique for Characterizing Polymeric Materials: Torsional Braid Analysis

An overview of a nondestructive semimicro mechanical technique—pioneered, developed, and exploited by the author—which is used for characterizing phase transitions and transformations in polymeric materials is presented. Particular attention is given to literature published since January, 1972, which pertains to advances in automation, data acquisition and processing, and application to polymeric systems. The instrument has been consolidated as a powerful and convenient mechanical spectrometer in this short period.

JOHN K. GILLHAM

Department of Chemical Engineering
Princeton University
Princeton, New Jersey 08540

SCOPE

An understanding of the relationships between bulk properties and molecular architecture is a major goal of polymer science. Dynamic mechanical methods, particularly those involving low-deformation oscillatory experiments which are used to generate mechanical spectra, have been important in this endeavor. The mechanical spectra consist of two parameters, one related to the storage and the other to the loss of energy on mechanical deformation, which are presented as functions of temperature or time. Attempts are being made to relate (for example) the loss peaks to the onset of particular localized intra- and intermolecular motions on the one hand and to changes in macroscopic bulk properties on the other hand.

The torsional pendulum is commonly used for characterizing the thermomechanical behavior of polymeric materials. However, it would be used even more extensively were it not for problems with data reduction, difficulties with specimen fabrication, and the inherently low thermal conductivity of organic materials which limits the rate of heating and cooling during measurements. The tedium of the experiment has resulted in its scattered use by experimenters who have constructed their own apparatus. Although the torsional pendulum technique is old, in the field of plastics it only became a full standard (ASTM D-2236) of the American Society for Testing Materials in 1969.

In recent years a variant of the torsional pendulum method has emerged which avoids many of the difficulties associated with the parent instrument. The technique, torsional braid analysis (TBA), involves a torsional pendulum which uses a small composite specimen. The latter is prepared by soaking a multifilamented inert (glass) braid in a solution of the polymer and, after mounting in the apparatus, removing the solvent by heating. The natural frequency (approximately 1 Hz) and decay of intermittently induced free torsional oscillations are measured, and the calculated storage and loss parameters of the composite specimen are presented as a function of temperature or time. These spectra are interpreted in terms of the behavior of the polymer. The unique features of TBA are the ease of fabrication of the mounted specimen (which is generally the most difficult part of any mechanical experiment), and the ability to examine materials throughout the spectrum of mechanical states (glassy, rubbery, and fluid). The technique is therefore particularly suitable for the characterization of polymers which are available only in limited quantities and for the study of processes (such as cure) which convert liquids to solids. The ease of specimen fabrication and the reasonable rates of continuous change in temperature (as a consequence of the use of small specimens), coupled with recent developments in automation and in data acquisition and processing, render the TBA approach experimentally highly tractable. These developments and results obtained by exploitation of the ability of the technique to characterize supported specimens form subjects of this review.

CONCLUSIONS AND SIGNIFICANCE

An adaptation of the torsional pendulum operating throughout the temperature range −190° to 600°C, which is used for the facile thermomechanical characterization of small amounts of polymeric materials, is described. The composite specimen is easily prepared by impregnating an inert substrate with a polymer solution and thermally removing the solvent. Conversion of the damped mechanical oscillations to electrical analog signals is accomplished using a no-drag transducer which involves transmission of light through the linear-with-angle region of an optical wedge to a linearly responding vacuum phototube. The instrument has been automated with a laboratory-designed analog minicomputer which controls a repetitive sequence consisting of alignment of the transducer, initiation of free oscillations, and computation and immediate printout of the defining parameters of each wave. The apparatus also has been interfaced with a large centralized batch computer using a sensor computer in the laboratory as the digital front-end to a multilevel hierarchical system of computers. The latter is a flexible and powerful tool for data acquisition and processing and for development of instrumentation.

The technique has been used for investigating structure-property relationships, thermohysteresis effects, and the influence of chemical reactions in polymers. Applications to linear polymer systems which are discussed herein include amorphous polyolefins, isomeric polymethylmethacrylates, polycarborane-siloxanes, and aromatic polyimides. In each case, interrelationships between systematic changes in molecular structure and macroscopic response are obtained which lead naturally to more general considerations relating structure to properties. This experimental approach is particularly useful in monitoring systems throughout the liquid to solid change in state. This is exemplified by an analysis of the cure transitions of a thermosetting epoxy system which has provided a model encompassing the behavior of crosslinking systems in general.

The developments outlined in the present article show that the technique is particularly suitable as a tool for investigating materials available in limited quantities, for studying non self-supporting materials, and for investigating reactive polymeric systems. It should therefore appeal to the chemist who desires to gain a sophisticated insight into the behavior of molecules as materials and to those who seek to understand better the changes and properties of reactive systems. Since the development of the technique has taken place for the most part in the author's laboratories, the literature is largely his own. The availability of automated commercial instruments is beginning to provide a more diversified literature.

Characterization of polymeric solids by dynamic mechanical methods has been an important endeavor for the past twenty years. A main purpose has been to relate macroscopic bulk properties to molecular structure by correlating changes in each to the storage and dissipation of energy which are obtained from the stress-strain relationships of the low-deformation oscillatory experiments. An extensive review of the literature emphasizing the molecular basis of the mechanical spectra and also reviewing the theory of the experimental methods was published by McCrum et al. in 1967 whereas an important paper emphasizing bulk properties as the manifestation of the mechanical spectra was published by Boyer in 1968. A text published in 1974 by Nielsen brings the area up-to-date.

The freely oscillating torsional pendulum has been a favored tool for thermomechanical studies. Reasons for this include its inherent simplicity, the low frequency (~ 1 Hz) which permits direct correlation of the temperatures of phase transitions with static nonmechanical methods (for example, dilatometry and calorimetry), and the high resolution of the transitions which is a consequence of the Arrhenius type of frequency dependence. However, the technique presents a number of difficulties. Experiments usually have employed relatively large specimens which have been investigated over limited ranges of temperature. The long-time scale of the experiments is determined by the low thermal conductivity of the organic specimens and formidable data processing problems. The limited temperature range of study is the consequence of the long-time scale but also of an inability of materials to support their own weight at or near critical load-limiting transitions, such as the glass or melting transitions. A description of an adaptation of the torsional pendulum, torsional braid analysis (TBA), was published by Lewis and Gillham in 1962. The technique was refined (Gillham and Lewis, 1962) to use a small sample (~ 10 mg) of polymer (or oligomer) supported on an *inert* multifilamented substrate (the braid). Specimens are easily made by impregnating the braid from solution followed by drying in the apparatus. This type of anisotropic composite specimen has been employed in an attempt to minimize the contribution of the substrate to torsional deformation. Rigidity and loss moduli of the composite specimens are calculated from the damped oscillations of each wave and changes are interpreted in terms of the properties of the matrix. The size of the specimen permits experiments to be conducted at relatively rapid rates of temperature change (for example, $\Delta T/\Delta t = 2°C/\text{min.}$). The technique has the distinct advantage of being able to take measurements throughout the liquid, rubbery, and solid states. The ability to locate critical transitions and to measure changes in mechanical properties induced above the load-limiting transitions has taken the torsional pendulum technique into new areas. An extensive review of the first ten years' progress with the technique was published in 1972 by Gillham. An account of the present status of the instrumentation (including automation), methods used for data processing, and application to various polymeric systems forms the basis of the following account.

THE INSTRUMENT

A schematic diagram of the apparatus is shown in Figure 1. Free oscillations are initiated by step displacement of an upper gear which produces constant angular displacement of the lower inertial mass as a result of the latter's lag in rotational response. The natural frequency range of the vibrations is 0.1 to 2 Hz. Conversion of the damped oscillations to electrical analog signals is accomplished using a no-drag transducer (Gillham, 1972a). Light from a constant source is attenuated in passing through the linear-with-angle region of a pair of polarizers, one of which serves as the inertial mass of the pendulum; the attenuated light is sensed by a linearly responding vacuum phototube circuit. There are no electronic devices within the specimen chamber.

The apparatus is essentially a tube surrounded by a heating coil, cooling coils for liquid nitrogen, and a fluidized bed for heat transfer (Gillham and Lewis, 1962). It operates over a temperature range of −190° to 600°C with a temperature spread of ± 1°C over an 8-in. specimen. Through the use of a suitable controller/programmer, experiments may be carried out with increasing, decreasing, and isothermal temperature modes. Measurements have been made from 4°K in a suitable apparatus (Hiltner et al., 1974). The atmosphere is tightly controlled; inert, conditioning (Gillham et al., 1974b) or reactive gases (Roller and Gillham, 1972a; Roller and Gillham, 1973b), or a vacuum may be used.

The instrument has been automated (Bell et al., 1974) with a laboratory-designed and built, hard-wired analog minicomputer (Figure 1; controller/data analyzer) which controls a repetitive sequence which consists of alignment of the optical transducer by slow rotation of the pendulum head, initiation of free oscillations by step displacement of the pendulum head, and computation and immediate print-out on paper tape of thermocouple voltage logarithmic decrement, and period (P, s) for each damped wave. The latter two parameters are computed from the number of oscillations contained between measured boundary conditions within each wave (see below). The pattern of events is illustrated (Figure 2) in terms of a trace from a monitoring strip-chart recorder and the corresponding on-off electrical pulses of the controller/data analyzer. [The latter also provides immediate plotting on an XYZ plotter of the relative rigidity ($1/P^2$) and logarithmic decrement vs. temperature or time (Figure 1).]

The experiment has also been interfaced to a small real-

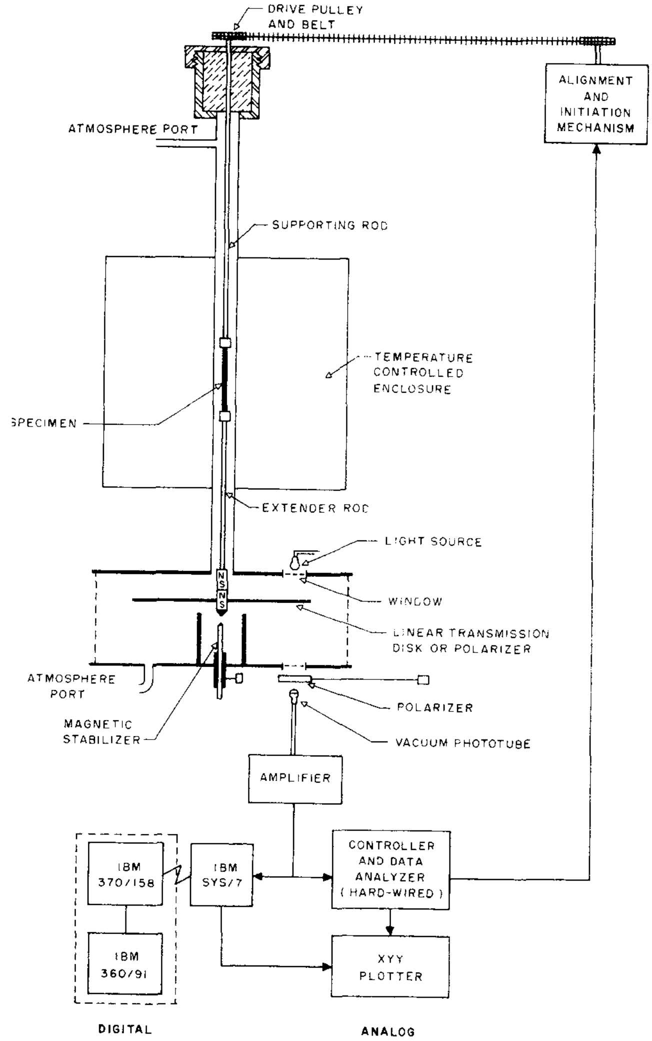


Fig. 1. Torsional pendulum and torsional braid apparatus.

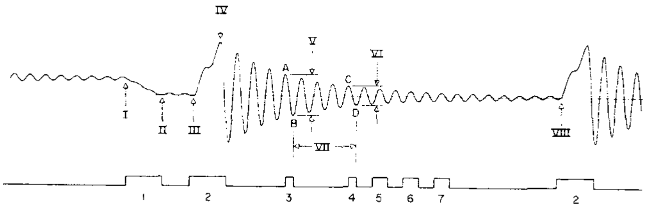


Fig. 2. Controller/data analyzer sequence.
Top. Strip-Chart Recorder: I. Previous wave decays, drift detected and correction begins; II. Polarizers correctly positioned; III. Wave initiating sequence begins; IV. Free oscillations begin; V. AB, first peak-to-peak amplitude less than initial boundary amplitude is measured; VI. CD, first peak-to-peak amplitude < 1/2 AB is measured; VII. Time interval between peaks *B* and *D* is measured; VIII. No drift correction required, wave initiating sequence re-starts. Bottom. Controller/Data Analyzer: 1. Polarizers positioned; 2. Wave initiated; 3. Peak-to-peak amplitude, AB, measured; 4. Peak-to-peak amplitude, CD, measured; 5. Period (sec.) printed; 6. Logarithmic decrement printed; 7. Temperature (millivolts) printed.

time computer in the laboratory which serves as the digital front-end to a hierarchical system of computers (Figure 1). This multilevel, flexible, and powerful hierarchical system permits computer-aided development of instrumentation, analysis of raw data, and graphical presentation of the final results. In principle, the real-time computer can also serve as controller and data analyzer in immediate time (Figure 1).

POLYMER/BRAID COMPOSITE SPECIMEN

The substrate used in a TBA experiment is a loose heat-cleaned glass braid (2 to 8 in. in length) containing about 3600 filaments (Gillham and Lewis, 1962). The large surface area of the assembly of filaments permits pickup of relatively large amounts of solution and minimizes flow due to gravity. The contribution of the substrate to torsional properties of the composite specimen is minimized by using multifilaments rather than a rod. A braid (Figure 3) is employed in an attempt to balance any twists in the component yarns. Solvent is removed from the solution-impregnated braid in situ by heating above the boiling point of the solvent and into the fluid state of the polymer (compatible with thermal stability). The apparatus can also accommodate homogeneous specimens (for example, film, Figure 3) for conventional quantitative torsional pendulum studies (as in ASTM D-2236).

DATA ACQUISITION AND REDUCTION

The response function of the torsional pendulum to mechanical excitation is described to good approximation by

$$\theta(t) = \theta_0 e^{-\alpha t} \cos(\omega t - \phi) \qquad (1)$$

which is a solution to the equation of motion with form

$$\frac{d^2\theta}{dt^2} + A_1 \frac{d\theta}{dt} + A_2 \theta = 0 \qquad (2)$$

where ϕ is a phase angle depending on the timing of data acquisition and θ_0, A_1 $(= 2\alpha)$ and A_2 $(= \omega^2 + \alpha^2)$ are constants. In complex format, the equation of motion is

$$I \frac{d^2\theta}{dt^2} + K(G' + iG'')\theta = 0 \qquad (3)$$

where $G'[= I/K\ (\omega^2 - \alpha^2)]$ and $G''[= 2\alpha I\omega/K]$ are the in-phase and out-of-phase shear moduli, respectively. G' and G'' are material parameters which relate directly to the energy stored and dissipated, respectively, on mechanical deformation. $\frac{1}{2}\ G'\epsilon^2$ is the energy stored in the cyclic experiment at strain ϵ and $\pi G''\epsilon^2_{\max}$ is an approximation for the energy dissipated per cycle, where $\epsilon_{\max}$ is the peak strain (Gillham, 1972a; Gillham, 1974).

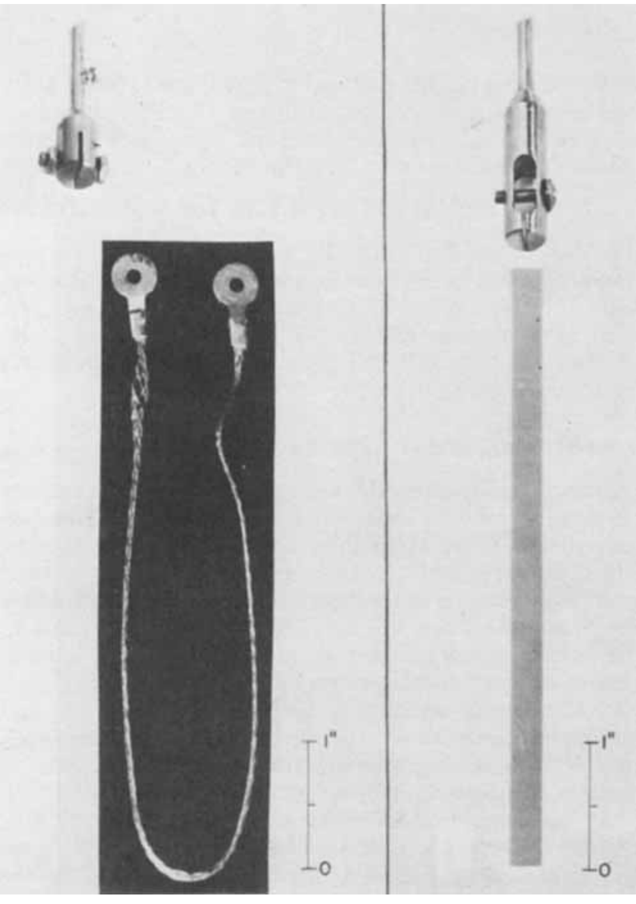


Fig. 3. Unimpregnated glass braid (left); polymer film (right).

Since an experiment may run over the course of several days and generate more than 1000 damped sine waves, manual techniques for reducing the experimental analog waves are slow and tedious. These traditionally involve measuring the decay of successive peak amplitudes to provide the logarithmic decrement $\Delta \equiv \ln[\theta_i/\theta_{i+1}]$ $(= 2\pi\ \alpha/\omega)$ and the period $P(\equiv 2\ \pi/\omega)$ for each wave. The data for torsional pendulum studies usually are presented as G' and Δ, G' and G'' $(\simeq G'\Delta/\pi)$ or as G' and $\tan\delta$ $(= G''/G')$. Due to the small size $(G' \simeq K_2LI/r^4P^2$ for a cylindrical specimen of radius r and length $L)$, irregular geometry, and composite nature of the specimens and in order to make data reduction tractable, simplified parameters have been used in torsional braid analysis until recently (Gillham, 1972a). These parameters, which refer to the composite specimen, are relative rigidity $\equiv 1/P^2$ and the mechanical damping index $\equiv 1/n$, where n is the number of oscillations counted for decay of a wave between two arbitrary but measured boundary amplitudes $[\Delta = 1/n \ln(\theta_i/\theta_{i+n})]$. The dedicated data analyzer referred to above (Bell et al., 1974), uses this procedure in computing the logarithmic decrement.

On-line computer data acquisition, reduction, and presentation constitute a powerful and also flexible method for tackling the formerly immense data processing problem (Gillham et al., 1974b; Hazony et al., 1974; Stadnicki et al., 1974). A data reduction program currently in use, which is written in Fortran and processed in the batch computer, employs a linear least squares fit of the differential form of the equation of motion [Equation (2)] to the digitized data. The results are presented directly in terms of numbers which are proportional to G' and G'' of the composite specimen of the experiment (simplified by omitting geometrical constants).

The laboratory experiment is interfaced to the immense power of a large-scale batch computer (IBM 360/91) for the purpose of on-line processing of large volumes of data by using two additional computers interconnected in a hierarchical fashion between the experiment and the batch computer (Figure 1). The actual data acquisition is performed by a small real-time computer (IBM System 7) situated in the laboratory which serves as the digital front-end for the system. Incoming analog signals are digitized and processed by the front-end computer for the purpose of setting the scan rate, phase angle, and amplitude boundary conditions. Trimming, coding for data management and shipping, and other requirements of final data reduction are also taken care of by the real-time computer. An intermediate computer (IBM 370/158) is used for data buffering and time matching in order to interface the vastly different timing requirements of the real-time and batch computers.

The advantages of the Hierarchical Computer System, as compared with use of a dedicated minicomputer, are twofold (Hazony et al., 1974): (1) maximum flexibility in the further development of the procedures for data acquisition and experimental control by the digital front end, and (2) the power of the central batch computer being the ultimate limitation on the magnitude and sophistication of the data reduction procedures. By separation of the two distinctly different functions, a high degree of optimization in the utilization of the resources of the hierarchical system can be achieved. For example, in the most flexible mode numerous simultaneous experiments can be accommodated by the laboratory computer. In the other extreme, the latter can function as a stand-alone machine dedicated to one experiment in immediate time (Figure 1).

Typical preprocessed digital data of a damped wave are shown in Figure 4. Typical thermomechanical spectra obtained using the hierarchical system of computers are displayed in Figure 5. In the latter, G'' is plotted vs. temperature for three isomeric forms of polymethylmethacrylate (see later).

Computer analysis of the data for different modes for presenting torsional pendulum data shows that internally consistent values for glass transitions of amorphous polymers are obtained by using dG'/dT and G'' and that use of the relative rigidity parameter ($1/P^2$) provides an accurate measure of the relative value of G'. The assignment of glass transition temperatures of amorphous polymers appears to conform to the following trend:

$$T(\tan\delta) = T(\Delta) \geqq T(\alpha) \geqq T(G'') = T(dG'/dT)$$

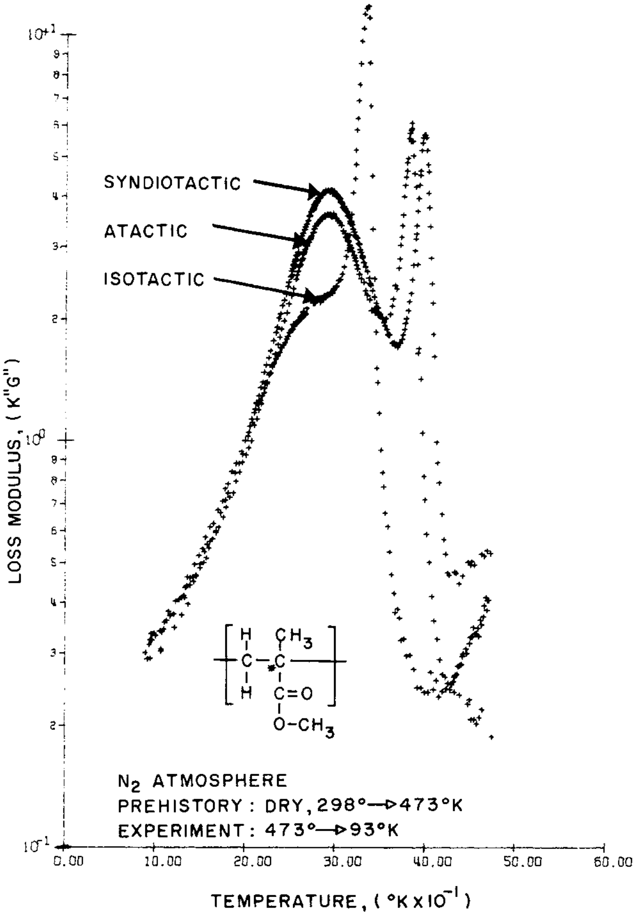


Fig. 5. Computer processed TBA data for three isomeric polymethylmethacrylates ($\Delta T/\Delta t = 2°C/\text{min.}$).

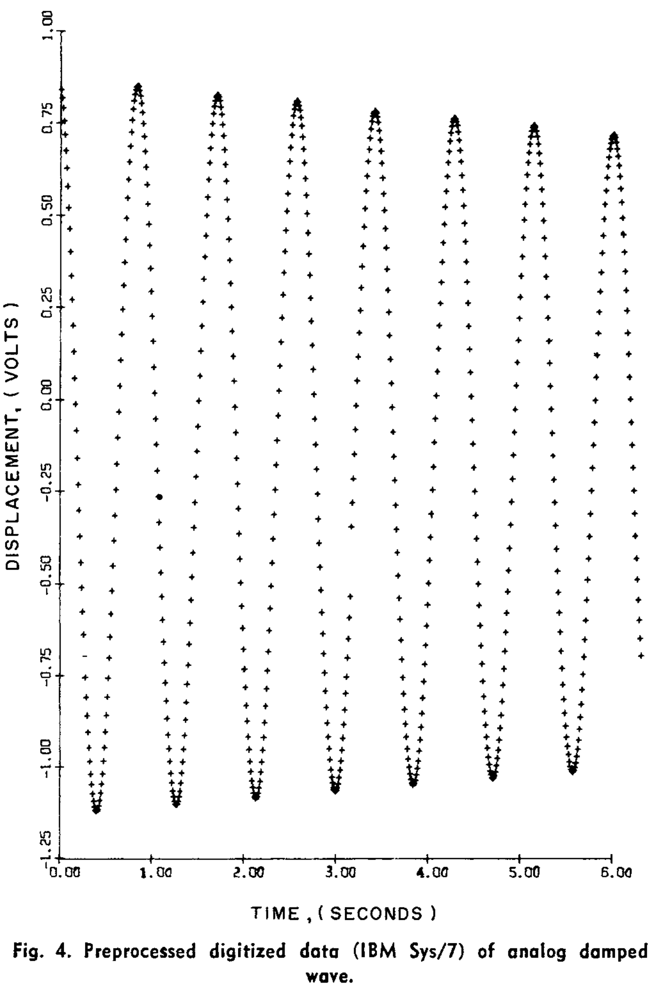


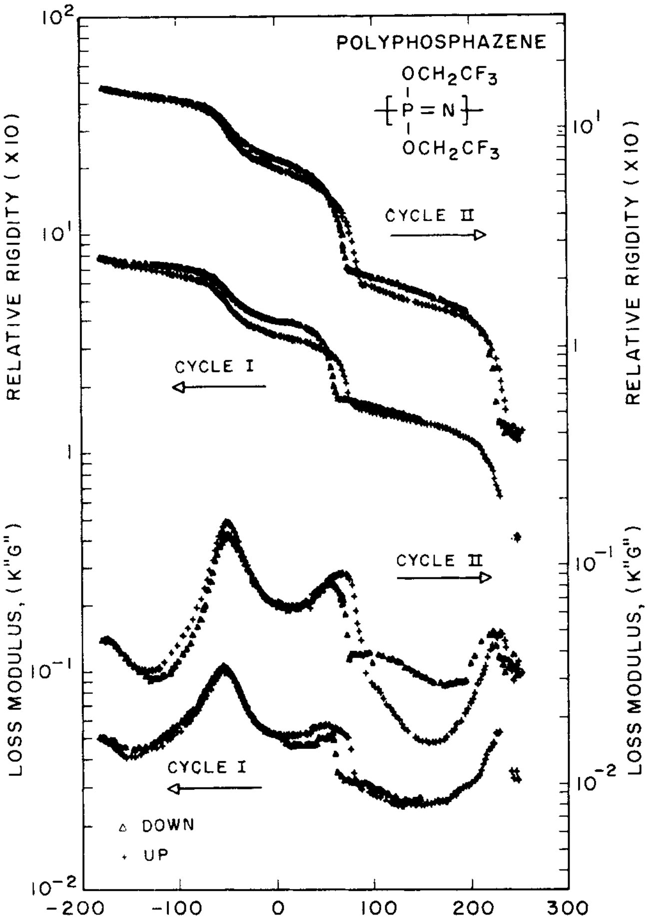
Fig. 4. Preprocessed digitized data (IBM Sys/7) of analog damped wave.

The data of the figures for this report were obtained using hand-reduction procedures except where noted to the contrary. [For purposes of clarification in comparing data, some of the figures (that is, 7, 9, 13, 14, 16) display curves of thermomechanical data which are displaced vertically by arbitrary amounts.]

THERMOMECHANICAL SPECTRA

Storage and loss functions are presented vs. temperature or time to provide thermomechanical spectra. The loss spectrum is characterized by a series of peaks each of which is attributed to the onset of motion of internal structural elements of the material. These loss peaks define the phase transitions and are accompanied by changes in the storage spectrum. A task of the developing applied science of mechanical spectroscopy of polymeric materials is to identify the underlying mechanisms of the intra- and intermolecular motions (which, in general, are less localized with increasing temperature) and to relate them to changes in macroscopic behavior.

As an example, the thermomechanical loss spectrum of each of the amorphous polymethylmethacrylates of Figure 5 (Gillham et al., 1974b) displays a sharp peak at the glass transition (T_g) and an intense "β" transition (T_β) in the glassy state. The latter is associated with the onset



He ATMOSPHERE
PREHISTORY : DRY, 25 → 150°C
EXPERIMENT :
150 → −180 → 250 → −180 → 250°C

Fig. 6. TBA data from dedicated data analyzer for a polyphosphazene ($\Delta T/\Delta t = 2°\text{C/min.}$).

of motions of the ester side groups with increasing temperature, whereas the glass transition is associated with the onset of longer range cooperative torsional motions of extended segments of the polymer chains. In terms of bulk properties many linear amorphous polymeric materials are, for example, brittle at temperatures below the β-peak, tougher above it, and solid only until the glass transition. Other macroscopic properties which can change significantly through secondary transitions in the solid state include adhesion, friction, creep, diffusion, etc. (Boyer, 1968). A major use of the torsional pendulum is to characterize phase transitions in solid polymeric materials. By using supported polymer samples, measurements can be made through the load-limiting transitions (T_g for amorphous, and the melting transition Tm for semicrystalline polymeric materials).

The ability to obtain data throughout load-limiting first-order transitions is exemplified by the thermomechanical spectra for a polyphosphazene with repeat structure —P(OCH$_2$CF$_3$)$_2$N— (Figure 6). [The spectra are for the continuous sequence $150 \rightarrow -180 \rightarrow 250 \rightarrow -180 \rightarrow 250°\text{C}$; they are separated into two parts for reasons of clarity.] The following transitions are observed: a single glassy-state relaxation at −180°C, a glass transition at −53°C, a first-order crystal to crystal transition with the transition measured at 58°C on cooling and at 68°C on heating, and a first-order crystal/melting transition with crystallization occurring at 223°C ($T_{\text{crystallization}}$) and subsequent melting occurring at 238°C (Tm). The data were obtained using the dedicated data analyzer (Connelly and Gillham, 1974).

The torsional pendulum and TBA methods produce very similar results in spite of the composite nature of the TBA specimens. Illustrative of this is a comparison (Gillham, 1972a) of torsional pendulum data on an intractable (infusible and insoluble) polyimide film, and TBA data on a cured polyimide-forming varnish which presumably has the same composition. After preheating the varnish and film to 300°C and cooling to −190°C in an attempt to subject both materials to the same prehistory, the polymers appeared (Figure 7) to be thermomechanically similar, with loss maxima peaking at about −90°, +30°, +200°, and +400°C. The rigidity modulus of both materials displayed a steady decline from −180°C to about 400°C, with subtle inflections corresponding to the loss peaks, and then displayed a small increase. The relatively large decrease in rigidity, together with the relative magnitude of the 400°C loss region, marked the glass transition region. The shape of the loss peak and the corresponding upturn in rigidity indicated further that chemical reactions involving chain-stiffening and/or crosslinking occurred in the T_g region where molecular motion and diffusive processes increase by orders of magnitude. The cooling curves, after heating to 500°C, show that for both polymers the thermal cure raised and broadened the T_g region. On the other hand, although the damping shoulder at 200°C had disappeared, the lower two peaks remained after heating to 500°C. Thermo-

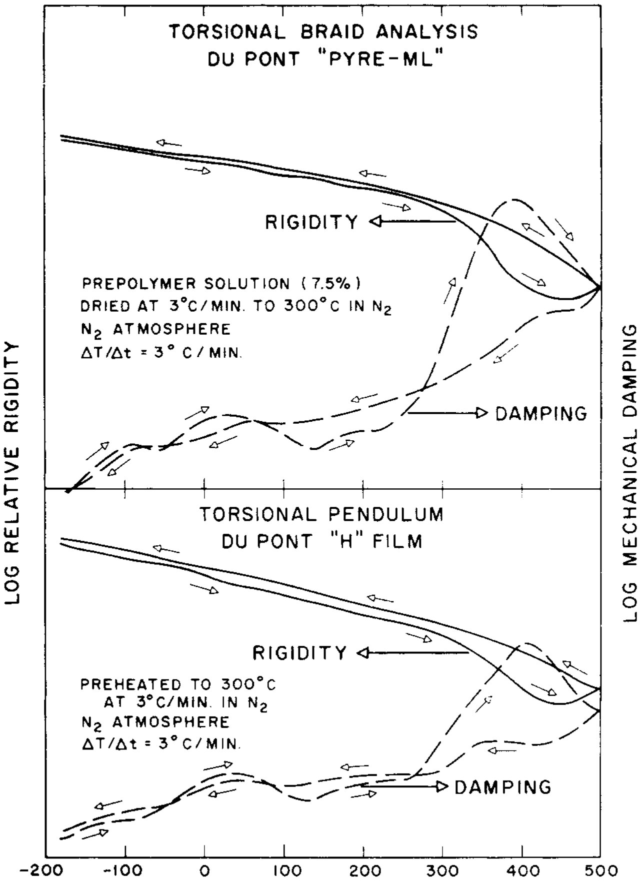


Fig. 7. Upper figure: Thermomechanical behavior (TBA) of a cured polyimide-forming varnish. Lower figure: Thermomechanical behavior (torsional pendulum) of a polyimide film.

mechanical spectra are often sufficiently complex to serve as fingerprints of the combined effects of composition and thermal prehistory.

TECHNIQUE

Thermomechanical measurements are inherently more sensitive than the more usual thermal techniques for investigating temperature dependent properties, and, in revealing changes in mechanical terms, are of special interest to applied polymer scientists. As an example of sensitivity and correlation with other techniques, the thermomechanical spectra of a specimen of highly acetylated cellulose triacetate, together with the corresponding results for specimens with the same prehistory obtained by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), are presented in Figure 8 (Gillham, 1972a). The T_g in the vicinity of 190°C is accompanied by a drastic decrease in rigidity, a prominent maximum in damping, and an endothermic shift in DTA. The subsequent increase in rigidity at temperatures above 200°C is attributed to crystallization and/or chain-stiffening processes and is accompanied by an exothermic maximum (DTA). *Tm* at 290°C is accompanied by an abrupt decrease in rigidity, a maximum in damping, and an endothermic maximum (DTA). The subsequent increase in rigidity, decrease in damping, exotherm (DTA) and weight loss (TGA), are attributed to crosslinking and/or chain-stiffening processes.

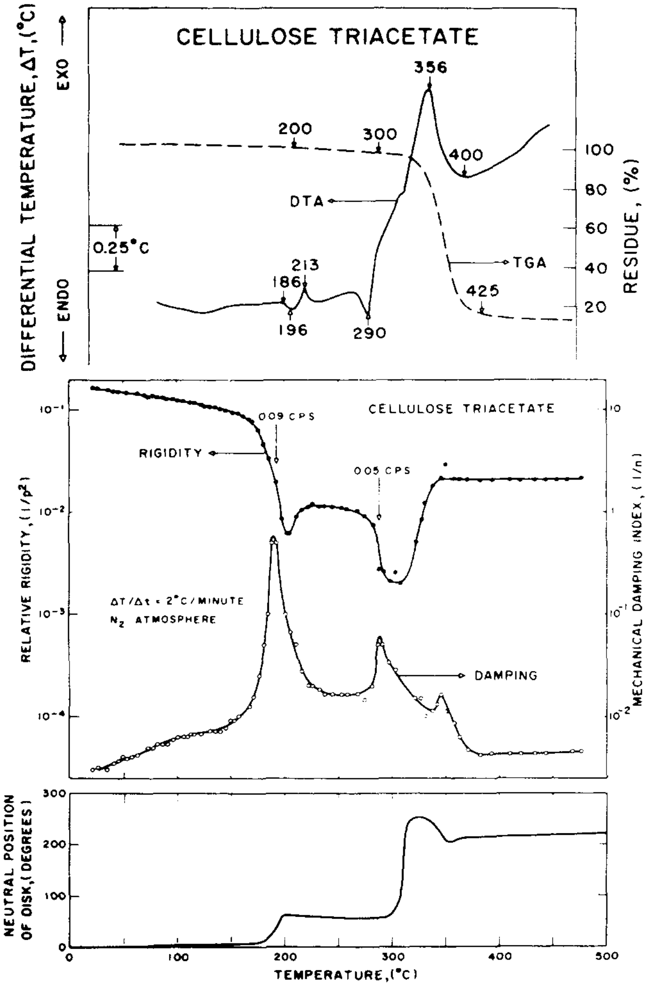


Fig. 8. Comparison of thermomechanical (TBA), differential thermal analysis (DTA) and thermogravimetric analysis (TGA) data for cellulose triacetate. The bottom figure shows the twisting which the composite TBA specimen undergoes with changing temperature (even in the absence of oscillations).

The bottom diagram of Figure 8 shows the angular drift of the neutral position of the inertial mass vs. temperature for a cellulose triacetate/glass braid specimen. The specimen was not oscillated. The motion is a consequence of stresses which develop in the composite specimen. The sense of the drift correlates with expansion or contraction of the matrix. It is observed that drifts which correspond to T_g and *Tm* are in the opposite sense to the processes corresponding to crystallization and crosslinking. [It is the occurrence of this twisting phenomenon which necessitated the incorporation into the instrumentation of a self-aligning mechanism for the optical transducer (Figure 2).]

There are many advantages of working with small specimens with an essentially nondestructive technique. Among these is the relatively rapid approach to thermal equilibrium of the specimen with the environment. This permits thermomechanical experiments to be undertaken over extended ranges of temperatures in a reasonable time scale. It permits the acquisition of data at both increasing and decreasing temperatures which often reveals features which might be ignored by a unidirectional experiment. (Most mechanical apparatus operate in one direction of temperature change.) Thermohysteresis can arise in polymeric materials from physical time-dependent phenomena such as crystallization/fusion (Connelly and Gillham, 1974; Gillham, 1972a; Gillham and Benci, 1974; Roller and Gillham, 1973a; Schoff and Gillham, 1974), dry atmosphere/water vapor (Gillham, 1972a; Gillham et al., 1972; Gillham et al., 1974b; Krug and Gillham, 1973), annealing/cracking (Gillham et al., 1974b; Kiran et al., 1974; Udipi and Gillham, 1974), and from chemical reactions (Gillham, 1972a; Gillham et al., 1972; Gillham and Glazier, 1972; Roller and Gillham, 1972a; Roller and Gillham, 1973a; Schoff and Gillham, 1974), not to mention incorrect assignments of temperature. Lack of thermohysteresis is a good test of reversibility and also often distinguishes amorphous from semicrystalline materials (Connelly and Gillham, 1974; Gillham and Benci, 1974; Martin and Gillham, 1972; Kiran et al., 1974; Roller et al., 1973; Udipi and Gillham, 1974). A more subtle advantage in using small specimens is the ability to remove (by heating the polymeric matrix to a fluid state) tenaciously held foreign materials such as water, solvent and monomer, the presence of which alters the mechanical spectra. An important advantage of the procedure which is used for examining small supported samples stems from the coupling of the preparation of the specimen with the experiment. This provides a high degree of control over the prehistory, a factor which strongly influences the results. Working with small samples also presents problems as examples, development of instrumentation required the innovation of a no-drag transducer for converting the mechanical oscillations into electrical analog signals, and the use of nitrogen as an inert atmosphere must be accompanied by careful drying since water vapor can condense at low temperatures and affect the data (Gillham, 1972a; Gillham et al., 1972; Krug and Gillham, 1973).

As an example of the influence of small amounts of water, a sample of xylan (hemicellulose) has been investigated (Gillham, 1972a). A specimen was prepared from an aqueous solution (10%) by impregnating a braid and heating to 140°C and then cooling to 25°C in flowing nitrogen. Hi-Pure nitrogen was used as the environment throughout drying and collecting data. The thermomechanical data (Figure 9) are for the temperature sequence 25 → −180 → 400°C. Differences in behavior between cooling below 25°C and subsequent heating are

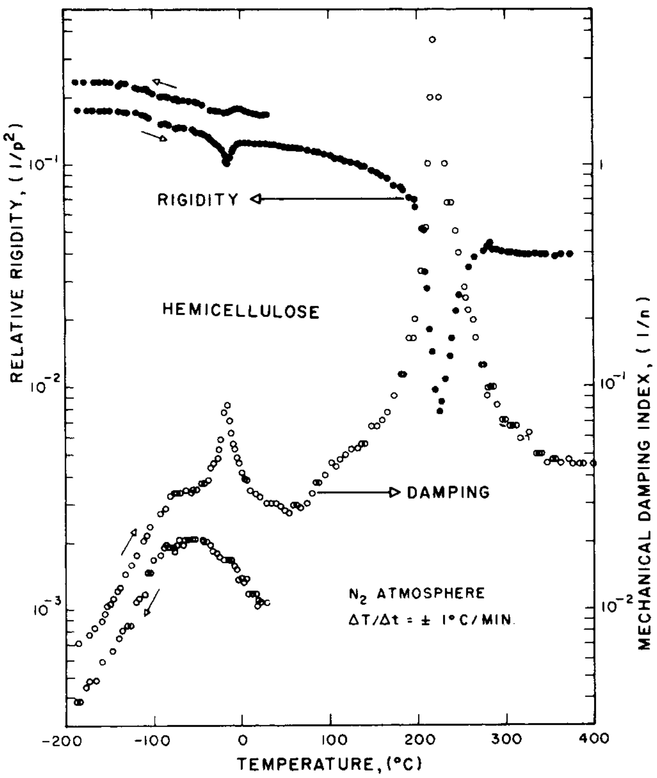


Fig. 9. Hemicellulose (Xylan): Thermohysteresis due to water vapor (TBA).

the consequence of small amounts of water. It appears that, on cooling, water vapor freezes out on the cooler walls of the specimen chamber, and the thermomechanical spectra reflect the behavior of the drier material. On warming, the specimen is colder than the walls of the chamber and water transfers to the polymer, especially towards 0°C. This water plasticizes the polymer and produces the changes in rigidity and damping which are observed just below 0°C. When the nitrogen gas was further dried before being used, the responses on cooling and subsequent heating were the same.

STRUCTURE-PROPERTY RELATIONSHIPS

The availability of a semimicro thermomechanical technique using easily fabricated specimens extends the applicability of dynamic mechanical methods to a host of materials made by the polymer chemist (usually on a small scale). Series of structurally related polymers are being collected by this laboratory, studies of which are providing insights into the molecular basis of thermomechanical behavior in terms of relaxations which are easily located by low frequency dynamic mechanical methods. The particular interests of the author in the use of polymers as high performance engineering materials, combined with the versatility and the wide temperature range of the instrument, have led to research activities on the particular polymeric materials (polycarboranesiloxanes, polyimides, and epoxies) which form the subjects of some of the following topics. The high quality of data has also led to reexamination of more conventional polymers (for example, polyolefins and polymethylmethacrylates).

Amorphous Polyolefins

Two series of linear polyolefins with repeat structures $-[(CH_2)_mC(CH_3)_2]-$ and $-[(CH_2)_mC(CH_3)(C_2H_5)]-$, where $m = 1$, 2 and 3, have been examined (Martin and Gillham, 1972; Hiltner et al., 1974). These polymers are of fundamental importance to polymer science and yet have been neglected because of synthetic difficulties. A reason for their importance lies in the systematic in-chain variation of one $—CH_2—$ between the repeat units of consecutive members since it is the structure and influence of the main chain per se which is central to polymeric behavior. The temperatures of transitions for nonpolar amorphous polymeric materials are determined by the inherent flexibility of the individual molecules and by geometrical intermolecular interactions (packing). The thermomechanical spectra of the amorphous polyolefins (not shown) reveal that the glass transition temperatures of each series increase from the first to the second member and then decrease to the third member. The values of T_g for the first and second series are $-65(m = 1)$, -7 $(m = 2)$, and -15°C $(m = 3)$, and -20 $(m = 1)$, $+5$ $(m = 2)$ and -15°C $(m = 3)$, respectively. If the order of the flexibility of individual nonpolar molecules increases with increasing values of m, the maximum temperatures for the transitions (at $m = 2$) must arise from a dominance of geometrical intermolecular factors over flexibility. Geometrical interlocking of parts of adjacent molecules is considered to be at a maximum for the second member of each series where an examination of molecular models reveals the presence of a rather specific snug fit which is looser for higher members. The postulate of different mechanisms for the glass transitions of the first members in comparison with the later members of both series is supported by measurements of the apparent activation energies of the relaxations (determined dielectrically). For example, the activation energies for the glass transitions of the first series are 22 kcal/mole $(m = 1)$, 48 kcal/mole $(m = 2)$, and 44 kcal/mole $(m = 3)$, respectively. Either the dominant role of intermolecular geometrical interactions on the nature of transitions in the amorphous phase of solid polymers is a neglected principle of polymer science, or current ideas on intramolecular flexibility need to be reexamined.

Stereoregular Polymethylmethacrylates

The thermomechanical loss spectra of the isomeric polymethylmethacrylates in Figure 5 (Gillham et al., 1974b) show the significant influence of tacticity on the glass transition temperature. The syndiotactic polymer has its T_g some 65°K higher than that of the isotactic material. (The similarity of the thermomechanical spectra of the atactic and syndiotactic polymers is because there are only small differences between them in tacticity.)

The loss spectra show that the relative intensity of the β-peak decreases with increasing isotactic content. The speculation could be made that a completely isotactic polymer would not display a β-process (the isotactic content of the isotactic polymer was 96%). The similar shape of the G'' vs. T curves for the three polymers indicates further that the basic mechanism of the observed β-process is the same for the three polymers and supports the validity of extrapolating in this fashion. The absence of a β-peak is noted (Hiltner et al., 1974) for polyisobutylene, $-[CH_2C(CH_3)_2]-$, which also has an anomalously low glass transition temperature. The latter has been attributed to a lack of spacial sites for geometrical intermolecular interlocking along the molecules (Martin and Gillham, 1972) and this reason may be a factor contributing to the low T_g of isotactic polymethylmethacrylate (Kiran et al., 1974).

The ratio T_β/T_g (°K) provides a measure of the degree of coupling between the motions which give rise to the two transitions. For many amorphous polymers, the ratio is about 0.75. The value for syndiotactic polymethylmethacrylate is 0.74, that for the isotactic polymer is higher (> 0.84). High coupling in isotactic polymer is also revealed by the increase in intensity of the T_g loss peak parallelling the decrease in intensity of the β-peak with increasing isotacticity. Relatively lower intermolecular restrictions to motion of the backbone skeleton together with higher intramolecular restrictions to motion of the ester groups (until T_g) in the isotactic polymer could be responsible for these observations. A helical model is suggested for the molecular conformation of the isotactic polymer in the amorphous solid state.

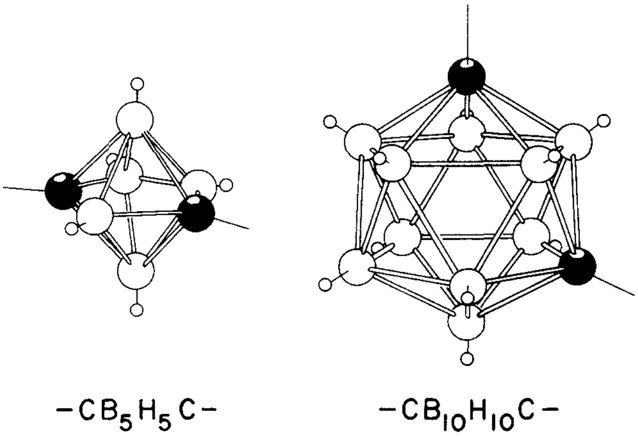


Fig. 10. Carborane cages. Incorporation in the polymer chains is through the two carbon (black) atoms.

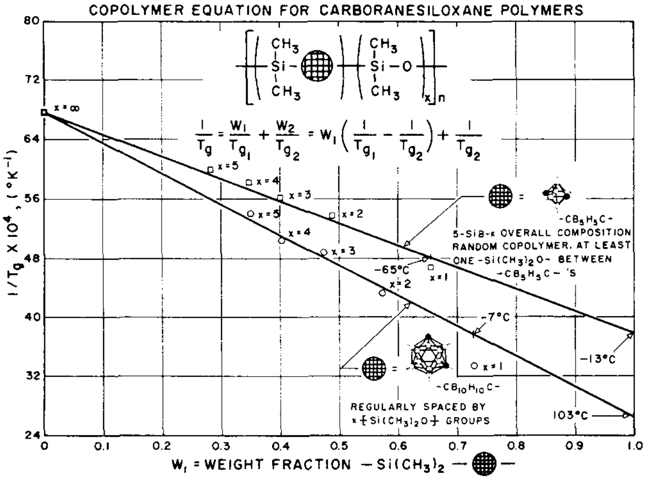


Fig. 11. 10-SiB-X polymers as copolymers of 10-SiB-0 and 10-SiB-∞. Also: 5-SiB-X polymers as copolymers of 5-SiB-0 and 5-SiB-∞. Glass transition temperatures fit the copolymer equation.

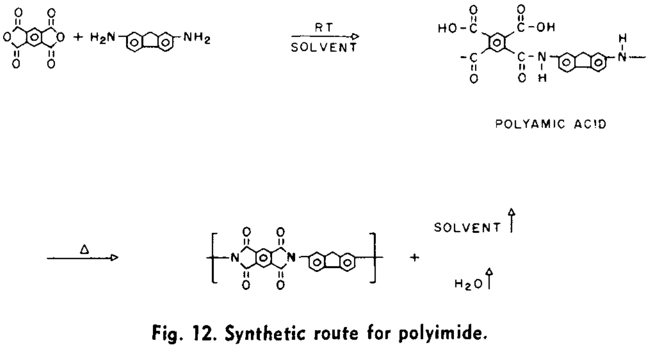


Fig. 12. Synthetic route for polyimide.

Carborane-Siloxane Copolymers

Linear polycarboranesiloxanes containing rigid carborane cages (Figures 10 and 11) and flexible siloxane in-chain linkages (Figure 11) have been synthesized recently as precursors which, when crosslinked, provide high temperature elastomers. In an inert atmosphere some of the linear materials are stable to about 500°C. The structure of "10—SiB—X" polymer (Figure 11) can be considered to be an alternating copolymer of $(Si(CH_3)_2—O)_x$ and $—CB_{10}H_{10}CSi(CH_3)_2—$ linkages. On the same basis, a "5—SiB—X" polymer (Figure 11) is a random copolymer of $—CB_5H_5CSi(CH_3)_2—$ and, on average, "X" dimethylsiloxane linkages. Since most of these linear materials have low glass transition temperatures, they are fluids at room temperature and are particularly suitable for characterization using a supported technique (Roller and Gillham, 1972, 1973, 1974).

Systematic relationships between molecular structure and physical material behavior have been established. For example, values of the glass transition temperatures for members of both the 10—SiB—X and 5—SiB—X series fit well (Figure 11), a copolymer transition vs. structure equation, $1/T_g = W_1/T_{g1} + W_2/T_{g2}$, where W_1 and W_2 are the weight fractions (which vary with X) of the two components in the copolymer, T_g is the glass transition temperature of the copolymer, and T_{g1} and T_{g2} are the glass transition temperatures of the homopolymers of each of the components of the copolymers. The steeper slope of the 10—SiB—X plot shows that the larger carborane cage is more influential in raising the glass transition when incorporated with siloxane linkages.

In the 10—SiB—X series, a glassy-state transition temperature (T_s) decreases from −90°C for 10—SiB—1, to −120°C for 10—SiB—2, to −140°C for 10—SiB—3, 10—SiB—4, and 10—SiB—5. This suggests that the limiting structure of the series, 10—SiB—∞ (that is, polydimethylsiloxane), should have a glassy-state relaxation at −140°C, which is masked by the glass transition at −125°C, and that the glassy-state relaxation is due to motion of part of the $+Si(CH_3)_2—O)$ unit. The motion is restricted by proximity of the carborane cages (in 10—SiB—1 and 10—SiB—2). The smaller and less influential $—CB_5H_5C—$ cage does not affect the glassy-state transition of the 5—SiB—X polymers, which all display T_s in the range −140 to −145°C.

Although the transition-structure copolymer relationship applies to the 10—SiB—X polymers and to the more random 5—SiB—X polymers, it does not apply to physical blends (each prepared from a homogeneous solution of both component polymers in chloroform). Binary mixtures do not form solid solutions with intermediate transitions but reveal the transitions which are characteristic of the individual components. It appears that bulk mixtures of even structurally similar polycarboranesiloxanes are incompatible and form separate phases.

Polyimides

Polyimides (see Figures 13 and 14 for examples of chemical structure) are used as rigid polymeric materials for high temperature applications. The partially double-stranded nature of the structures is responsible for the rigidity of the materials at high temperature—but also for their intractability which creates processing problems. They are therefore formed in situ from solutions of metastable, but thermally reactive, precursor polymers which in turn are synthesized from monomers. An example of the reaction scheme is shown in Figure 12. A number of difficult problems are encountered in attempting to deduce structure-property relationships for these high-temperature polymers. These include: (1) determination of the thermal procedures for effecting complete reaction, (2) freezing-out competing reactions, (3) elimination of difficult-to-remove solvents, (4) the effect on reaction rate of vitrification in the curing process which occurs when the maximum temperature of the cure is less than the maximum glass transition temperature of the desired product (see "The Thermosetting Process") and (5) the effects of thermal reactions which occur in the vicinity of the high glass transition temperatures. In spite of these complications, definite structure-dependent similarities and differences in thermomechanical behavior have been obtained (Gillham et al., 1972; Gillham and Gillham, 1973).

The thermomechanical behavior of two series of polyimides [see Figures 13 and 14 for structure and cure (captions)] supports the prediction which can be made on the basis of the relative flexibilities of the molecules that there would be several distinct types of behavior. Polymers formed using benzophenone tetracarboxylic acid dianhydride (Figure 13) would be expected to be more flexible than those formed using pyromellitic acid dianhydride (Figure 14) since the former is less double-stranded with rigid linkages than the latter. Polyimides derived from benzophenone tetracarboxylic acid dianhydride do have lower glass transition temperatures and soften more through them than do the corresponding polyimides made from pyromellitic acid dianhydride. On the other hand, the presence of methylene vs. carbonyl linkages in the backbone has less influence on the molecular flexibility and intermolecular forces, and hence on the thermomechanical behavior. Indeed, for a given anhydride, very similar thermomechanical behavior is displayed by polyimides synthesized from fluorenediamine [Figures 13 and 14, ⑤] and fluorenonediamine [④]. Again, similar thermomechanical spectra are displayed by polyimides synthesized from p,p′-methylenedianiline [②], p,p′-diaminobenzophenone [③], and also from p,p′-diaminodiphenylether [①]. Further, as would be anticipated on the basis of intramolecular flexibility, polyimides ①, ② and ③ differ as a group from polyimides ④ and ⑤ (Figures 13 and 14).

The thermomechanical spectra of the benzophenone tetracarboxylic acid dianhydride-derived polyimides have the same form as do those of simpler amorphous polymers (such as the polymethylmethacrylates) in displaying as main features a glassy-state (T_β) peak and a glass transition region. The ratio T_β/T_g (°K) of approximately 0.7 is about that found for amorphous linear polymers. Although the thermomechanical spectra of the pyromellitic acid dianhydride-derived polyimides display the usual pattern when the diamine residue is the rigid fluorenediamine or fluoroenonediamine residue, polymers formed from p,p′-diaminodiphenylether, p,p′-methylenedianiline and p,p′-diaminobenzophenone (and also benzidine [⑥]) display multiple damping peaks. Since insertion of pyromellitic acid dianhydride vs. benzophenone tetracarboxylic acid dianhydride residues can result in more complexity than is produced by the other changes in molecular architecture, it may well be that this special influence is due to the high density of polar carbonyl groups in the very rigid dianhydride residue which drastically affects intermolecular interactions and controls the thermomechanical

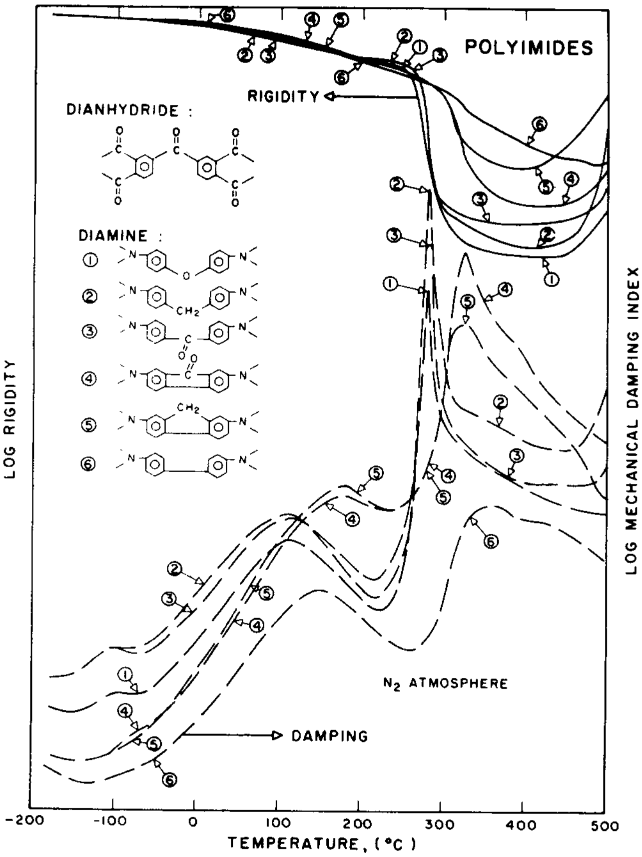


Fig. 13. Polyimides based on benzophenone tetracarboxylic acid dianhydride: effect of structure on thermomechanical behavior (TBA).
Prehistory: 25 → 300 → −180°C ($\Delta T/\Delta t = 2$°C/min.)
Experiment: −180 → 500°C ($\Delta T/\Delta t = 3$°C/min.)

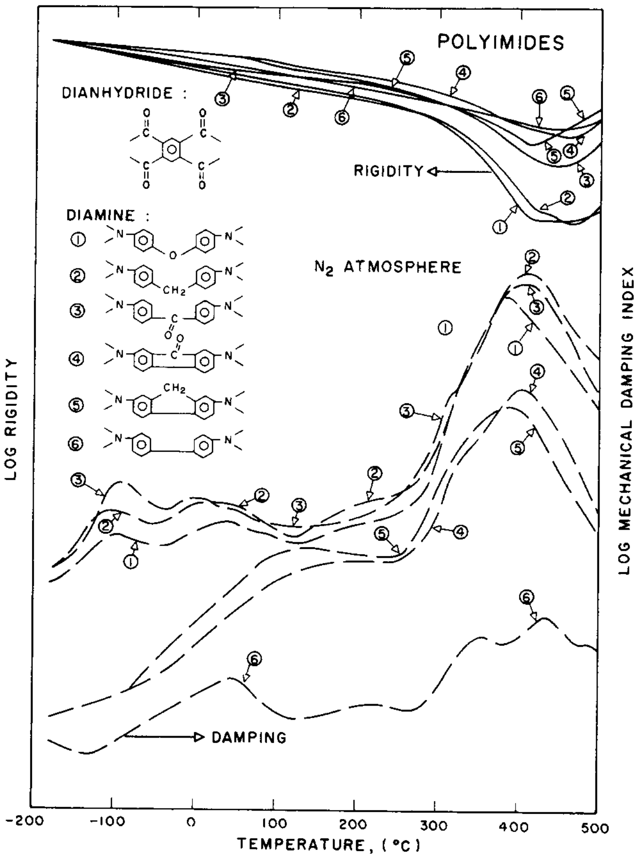


Fig. 14. Polyimides based on pyromellitic dianhydride: effect of structure on thermomechanical behavior (TBA).
Prehistory: 25 → 300 → −180°C ($\Delta T/\Delta t = 2$°C/min.)
Experiment: −180 → 500°C ($\Delta T/\Delta t = 3$°C/min.)

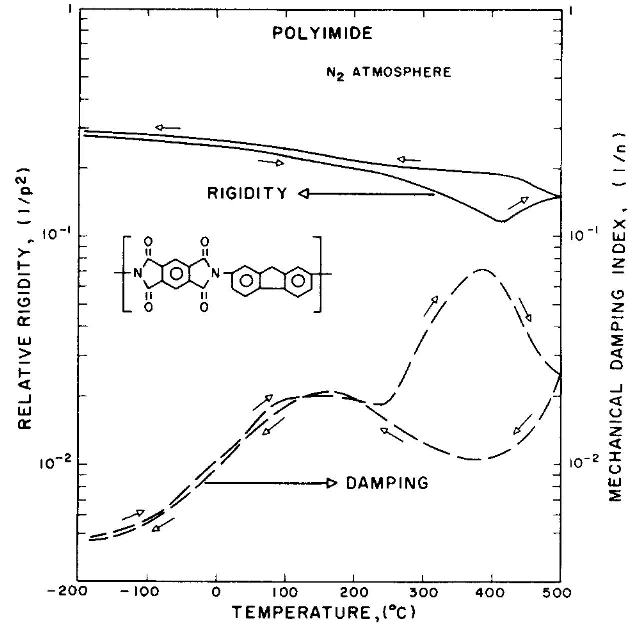


Fig. 15. Polyimide: Effect of heating to 500°C (TBA).
Prehistory: 25 → 300 → −180°C ($\Delta T/\Delta t = 2°C/\text{min.}$)
Experiment: −180 → 500 → −180°C ($\Delta T/\Delta t = 3°C/\text{min.}$)

behavior in the glassy state.

Chemical reactions are held responsible for the increase in rigidity which occurs above the glass transitions of the polyimides. These can be used to alter the thermomechanical behavior in a constructive manner. An example follows (Gillham et al., 1972; Gillham and Gillham, 1973).

The thermomechanical spectra (Figure 15) of a polyimide during the sequence −180 → 500 → −180°C, show that the T_g was shifted from about 350° to above 500°C, whereas the glassy state relaxation (with a damping peak at about 150°C) was virtually unaffected by treatment to 500°C. Crosslinking and/or chain-stiffening reactions occur (increasing the modulus above 400°C) which affect the longer range motions associated with T_g, and yet are insufficient in the time-temperature scale of the experiment to affect the more localized motions associated with the glassy-state relaxation. Since the damping peak in the glassy state (150°C) was observed after cure to 300°C and also after heating to 500°C, it represents a relaxation of the polyimide material per se. The controlled pyrolysis to 500°C resulted in a new material which differed in having a higher load-limiting T_g region, but had much the same thermomechanical properties as its percursor polyimide in the glassy state. That is, thermally-induced chemical reactions can be regulated so as to preferentially freeze-out longer range relaxations, thereby extending the glassy-state behavior and the utility of the material to higher temperatures. An important task of thermomechanical analysis is to derive processing procedures for optimizing thermomechanical response of materials (Gillham, 1972b).

The Thermosetting Process

Analysis of the isothermal cure of epoxide resin/hardener systems in which low molecular weight liquids are converted to crosslinked solids reveals that there are three different types of dynamic mechanical behavior for thermosetting systems depending on the temperature of cure (Babayevsky and Gillham, 1973). This is illustrated in Figure 16 for the cure of a cycloaliphatic epoxide/aliphatic anhydride system (Gillham et al., 1974a).

The first type of behavior occurs at low temperatures and is characterized by the occurrence of a single damping peak *B* which is accompanied by a one-step increase in rigidity. As the temperature of cure is increased, a second damping peak *A* becomes resolvable. The rigidity curves then display a two-step increase corresponding to the damping peaks *A* and *B*. This represents the second type of behavior on isothermal cure. Increasing the temperature further results in a broadening of damping peak *B*, and the first step of the two-step increase in rigidity becomes relatively more dominant. Above a certain temperature, only a single damping peak *A* and a corresponding one-step increase in rigidity are observed. This corresponds to the third type of behavior on isothermal cure. At still higher cure temperatures, damping peak *A* is not completely definable due to the high rate of reaction.

Damping peak *A* and its corresponding increase in rigidity are associated with the gel point of the reactive system (the structural transition from linear and branched molecules into the macromolecular network), whereas damping peak *B* and its corresponding increase in rigidity are associated with vitrification (transition to the glassy state).

1. $T_{cure} < T_{gg}$. The first type of behavior is a result of an increase in molecular weight of the prepolymer which causes its transformation from the fluid to the glassy state before the onset of gelation. This behavior occurs until the temperature of isothermal cure is equal to the glass transition temperature T_{gg} of the reactive system at its gel point. At this temperature of cure, the processes of vitrification and gelation occur together. This follows since vitrification occurs when the glass transition temperature $T_g(t)$ of the reacting system equals the temperature of cure and since (for a given crosslinking system) gelation occurs at a constant conversion which is independent of temperature.

Before the occurrence of vitrification, the rate of reaction in the liquid state fits the Arrhenius relationship, the activation energy for which can be obtained by measuring times to gelation at isothermal temperatures of cure above T_{gg}. After vitrification, the rate of reaction is essentially quenched. A reactive thermosetting system should be stored at temperatures well below T_{gg} so as to avoid gelation and thereby provide a long shelf-life for processing.

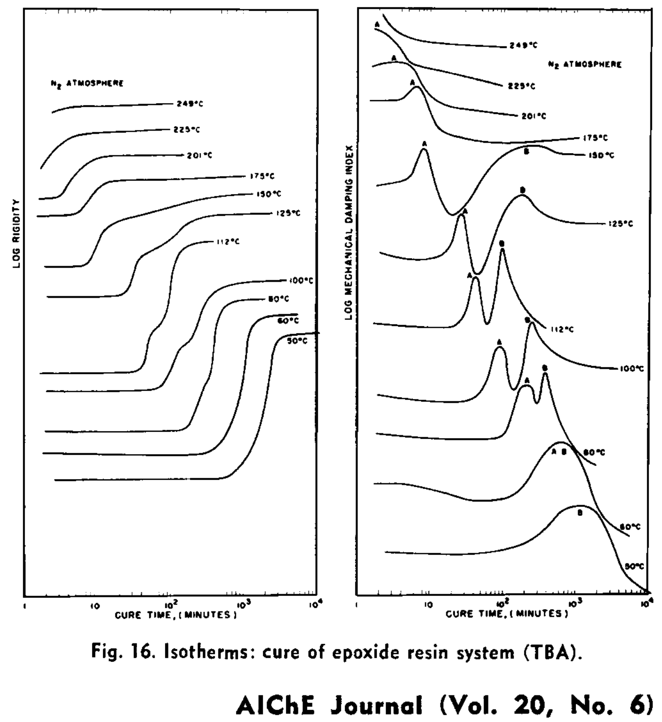


Fig. 16. Isotherms: cure of epoxide resin system (TBA).

This is presumably the basis of the technology of B-staging in the thermosetting industry in which a reactive system is partially reacted to a metastable but thermally processable solid intermediate which is later converted in situ to the end product.

2. $T_{gg} < T_{cure} < T_{g\infty}$. The second type of behavior occurs when the temperature of cure exceeds T_{gg} and is below $T_{g\infty}$ (the maximum glass transition temperature of the crosslinking system), in which temperature region the reactive system passes through gelation before vitrifying. Vitrification in this region is due mainly to an increase in crosslink density after gelation. The material changes from the fluid to the rubbery and then to the glassy state in passing through the two transitions.

A consequence of vitrification is that the system can only be completely cured by heating above $T_{g\infty}$. A convenient method for measuring the value of $T_{g\infty}$ is to obtain the thermomechanical behavior after curing or post-curing above $T_{g\infty}$.

3. $T_{cure} > T_{g\infty}$. The third type of behavior occurs when the temperature of isothermal cure exceeds the glass transition temperature of the fully crosslinked system $T_{g\infty}$ for above this temperature vitrification cannot occur.

The time of occurrence of gelation decreases with increasing isothermal temperature of cure according to the Arrhenius relationship since the conversion at the gel point is constant. However, the time of occurrence of vitrification reflects a competition between the increased rate constants for reaction with increased temperature in the pre-gel region, the influence on rate constants of increasing crosslink density prior to vitrification, and the increased chemical conversion necessary for vitrification to occur at higher temperatures. The time to vitrify can pass through a minimum as a consequence of decreases in reaction rate at high conversion (Gillham et al. 1974a). Schematic plots displaying times to gel and times to vitrify vs. temperature of isothermal cure are shown in Figure 17 which also displays extrapolations (dashed lines) to low temperatures of the gelation curve (using the Arrhenius relationship) and the vitrification curve (linear). These extrapolated curves intersect at T_{gg} which provides an accurate method for determining this new transition.

The significance of these findings lies in the generalizations which have been developed for reactive crosslinking systems. These depend on the existence of two critical temperatures T_{gg} and $T_{g\infty}$ for isothermal cure and the three types of behavior which can be obtained by curing below, between, or above these two critical temperatures.

The influence of the reactants on the nature of the cure is determined not only by the inherent reactivity of the functional groups, but also by the geometry and polarity of the growing chain segments which determine the transition temperatures (T_{gg}, T_g, $T_{g\infty}$) of the reactive systems and therefore the type of behavior experienced in isothermal cure. For example, for highly crosslinked or rigid-chain polymeric systems $T_{g\infty}$, or even T_{gg}, can be above the limits of thermal stability, and then only type 1 and type 2, or only type 1, behavior would be observed. Only type 3 behavior can be observed at $T_{\text{cure}} \geqq$ room temperature for reactive prepolymer systems if $T_{g\infty}$ is below room temperature (as for elastomers).

COMMENT

The TBA approach to the characterization of polymeric materials has evolved from what many would consider to be a rash proposition, that is, that the behavior of a polymer as a material could be gleaned from the behavior of a crude composite specimen. Only experience with a wide range of viscoelastic materials could show the general usefulness of the technique. This task involved refining the initial concept by using an inert substrate and necessitated development of instrumentation, which later included automation. The use of computer systems for data processing rendered the experiment tractable and more sophisticated but also provided an opportunity for introspection. On the basis of investigations of a wide range of materials, the contention of the author is that the results which have been obtained by, and the concepts which have evolved from, using the technique have provided originality and stimulus to currently important areas of the science of polymeric materials.

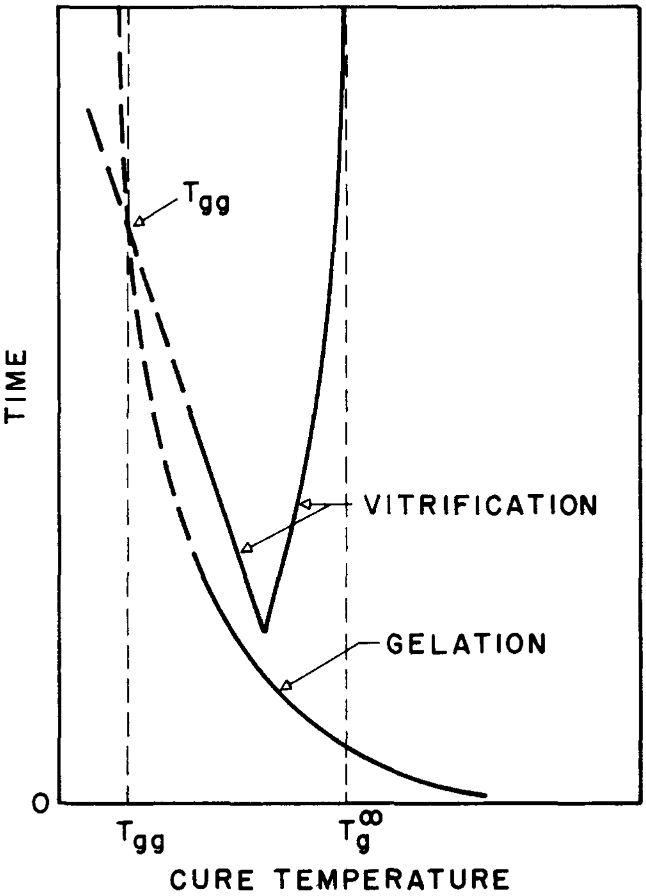


Fig. 17. Thermosetting epoxide resin: Time to gel and time to vitrify vs. isothermal cure temperature.

To the author, the most important contribution of the type of approach that is represented by TBA is the juxtapositioning of the chemistry, characterization, processing, and properties of polymeric materials. This places the technique in a position of great utility for both pragmatic and theoretical polymer science and engineering.

ACKNOWLEDGMENT

Financial support of the Air Force Materials Laboratory, Chemistry Branch of the Office of Naval Research and the National Aeronautics and Space Administration is acknowledged. Appreciation is extended to H. C. Gillham for his technical advice in the preparation of this review.

NOTATION

$A_1 \quad = 2\,\alpha$
$A_2 \quad = \omega^2 + \alpha^2$

G' = elastic shear modulus
= in-phase shear modulus
= modulus
= rigidity
= storage modulus
G'' = damping
= loss modulus
= out-of-phase shear modulus
Hz = hertz, cps
I = inertial mass of oscillating system
K, K_2, K'' = constants depending on the geometry of the oscillating system
n = number of oscillations between two boundary amplitudes
P = period of oscillation, s
t = time
$T(\alpha)$ = T_g determined from the maximum in α
T_β = β-relaxation temperature
$T(\Delta)$ = T_g determined from the maximum in Δ
$T(\tan\delta)$ = T_g determined from the maximum in $\tan\delta$
$T_{\text{crystallization}}$ = crystallization temperature
T_{cure} = temperature of isothermal cure
$T(dG'/dT)$ = T_g determined from the maximum in dG'/dT
$T(G'')$ = T_g determined from the maximum in G''
T_g = glass transition temperature
T_{g1} = T_g of homopolymer 1 in degrees Kelvin
T_{g2} = T_g of homopolymer 2 in degrees Kelvin
T_{gg} = T_g of thermosetting system at gel point
Tm = melting transition temperature
T_s = glassy-state transition temperature
$T_g(t)$ = T_g of reacting system at time t
$T_{g\infty}$ = maximum T_g of crosslinked network
W_1 = weight fraction of comonomer 1 in copolymer
W_2 = weight fraction of comonomer 2 in copolymer

Greek Letters

α = damping coefficient
Δ = logarithmic decrement
$\tan\delta$ = tangent of angle between cyclic stress and strain vectors = G''/G'
ϵ = shear strain
$\epsilon_{\max}$ = maximum shear strain
θ = angular displacement, radians
θ_0 = angular displacement at $(\omega t - \phi) = 0$, radians
ϕ = phase angle with reference to $t = 0$, radians
ω = frequency of oscillation, radians per second

LITERATURE CITED

Babayevsky, P. G., and J. K. Gillham, "Epoxy Thermosetting Systems: Dynamic Mechanical Analysis of the Reactions of Aromatic Diamines with the Diglycidyl Ether of Bisphenol A," *J. Appl. Polymer Sci.*, **17**, 2067 (1973).

Bell, C. L. M., J. K. Gillham, and J. A. Benci, "Development of a Fully Automated Torsional Pendulum with Built-In Data Reduction Facilities," *Am. Chem. Soc., Polym. Preprints*, **15**(1), 542 (1974); Soc. Plastics Engineers, Annual Tech. Conf., San Francisco, Cal., *SPE Tech. Papers*, **20**, 598 (1974).

Boyer, R. F., "Dependence of Mechanical Properties on Molecular Motion in Polymers," *Polym. Eng. Sci.*, **8**, 161 (1968).

Connelly, T. M., and J. K. Gillham, "Polyphosphazenes: Thermomechanical Transitions," *Amer. Chem. Soc., Polymer Preprints*, **15**(2), 458 (1974).

Gillham, J. K., "Torsional Braid Analysis. A Semimicro Thermomechanical Approach to Polymer Characterization," *Critical Rev. Macrom. Sci.*, **1**, 83 (1972a).

———., "Optimization of the Thermomechanical Behavior of a Poly(Chromium (III) Trisphosphinate)," *J. Appl. Polymer Sci.*, **16**, 917 (1972b).

———., "Torsional Braid Analysis of Polymers," *J. Macrom. Sci.,-Physics*, **B9**(2), 209 (1974).

Gillham, J. K., and A. F. Lewis, "Thermal Isomerization of Poly(triallylcyanurate) using a Dynamic Mechanical Method," *Nature*, **195**, 1199 (1962).

Gillham, J. K., and K. C. Glazier, "Thermomechanical Behavior of 'BBB' Polymer," *J. Appl. Polymer Sci.*, **16**, 2153 (1972).

Gillham, J. K., K. D. Hallock, and S. J. Stadnicki, "Thermomechanical and Thermogravimetric Analyses of Systematic Series of Polyimides," *ibid.*, **16**, 2595 (1972).

Gillham, J. K., and H. C. Gillham, "Polyimides: Effect of Molecular Structure and Cure on Thermomechanical Behavior," *Polymer Eng. Sci.*, **13**, 447 (1973).

Gillham, J. K., and J. A. Benci, "Thermomechanical Behavior of Uncrosslinked 1,5-Polypentenamers," *J. Appl. Polymer Sci.*, **18**, in press (Dec., 1974).

———., and A. Noshay, "Isothermal Transitions of a Thermosetting System," *ibid.*, **18**, 951 (1974a).

Gillham, J. K., S. J. Stadnicki, and Y. Hazony, "Low Frequency Thermomechanical Spectrometry of Polymeric Materials: Computerized Torsional Braid Experiments—III. Tactic Polymethylmethacrylates," *Am. Chem. Soc., Polymer Preprints*, **15**(1), 562 (1974b).

Hazony, Y., S. J. Stadnicki, and J. K. Gillham, "Low-Frequency Thermomechanical Spectrometry of Polymeric Materials: Computerized Torsional Braid Experiments—I. Overview," *ibid.*, 549 (1974).

Hiltner, A., E. Baer, J. R. Martin, and J. K. Gillham, "Low Temperature Relaxations in Amorphous Polyolefins," *J. Macromol. Sci.,-Physics*, **B9**(2), 255 (1974).

Kiran, E., J. K. Gillham, and E. Gipstein, "Thermomechanical Behavior of Tactic Methacrylate Polymers," *ibid.*, 341.

Krug, R. R., and J. K. Gillham, "Thermomechanical Behavior of Poly-L-Alpha-Alkyl-Amino Acids in Dry and Moist Nitrogen," *J. Appl. Polymer Sci.*, **17**, 2089 (1973).

Lewis, A. F., and J. K. Gillham, "Novel Technique for Following the Rigidity Changes Accompanying the Curing of Polymers," *ibid.*, **6**, 422 (1962).

Martin, J. R., and J. K. Gillham, "Amorphous Polyolefins: A Relationship Between Molecular Structure, Submolecular Motion and Mechanical Behavior," *ibid.*, **16**, 2091 (1972).

McCrum, N. G., B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York (1967).

Neilsen, L. E., *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York (1974)

Roller, M. B., and J. K. Gillham, "Thermomechanical Behavior of Poly(Carborane-Siloxane)s Containing —CB_5H_5C— Cages," *J. Appl. Polymer Sci.*, **16**, 3073 (1972a).

————., "High-Temperature Elastomers: Glass Transition-Structure Correlations for Two Systematic Series of Linear Poly(Carborane-Siloxane)s. I.," *ibid.*, **16**, 3095 (1972b).

————., "High-Temperature Elastomers: Glass Transition-Structure Correlations for Two Systematic Series of Linear Poly(Carborane-Siloxane)s. II. Incompatibility," *ibid.*, **16**, 3105 (1972c).

————., "High-Temperature Elastomers: A Systematic Series of Linear Poly(Carborane-Siloxane)s Containing Icosahedral —$CB_{10}H_{10}C$— Cages. I. Thermomechanical Behavior in Nitrogen," *ibid.*, **17**, 2141 (1973a).

————., "High-Temperature Elastomers: A Systematic Series of Linear Poly(Carborane-Siloxane)s Containing Icosahedral —$CB_{10}H_{10}C$— Cages. II. Thermo-Oxidative Behavior", *ibid.*, **17**, 2623 (1973b).

————., "Linear Polycarboranesiloxanes", *Polymer Eng. Sci.*, **14**, 567 (1974).

————., and J. P. Kennedy, "Thermomechanical Behavior of a Polynorbornadiene," *J. Appl. Polymer Sci.*, **17**, 2223 (1973).

Schoff, C., and J. K. Gillham, "Fluorocarbon Bibenzoxazole Polymers: Transitions and Stability," *Am. Chem. Soc., Polymer Preprints*, **15**(2), 451 (1974).

Stadnicki, S. J., J. K. Gillham, and Y. Hazony, "Low Frequency Thermomechanical Spectrometry of Polymeric Materials: Computerized Torsional Braid Experiments—II. Data Processing," *ibid.*, **15**(1), 556 (1974).

Udipi, K., and J. K. Gillham, "Poly(ethylene carbonate) and Poly(propylene carbonate): Transitions and Thermomechanical Spectra," *J. Appl. Polymer Sci.*, **18**, 1575 (1974).

THE AUTHOR

John K. Gillham received his Bachelor of Arts in Natural Sciences from Cambridge University in 1953 and the Ph.D. in Chemistry from McGill University in 1959. He spent six years at the Stamford Research Laboratories of the American Cyanamid Company working on new polymers. A year's leave spent in the Department of Chemical Engineering at Princeton University was followed by his joining that department where he is an associate professor. His teaching and research responsibilities are in the field of polymeric materials. He is involved in the commercialization of his TBA technique and in consulting with the Polymer Industry.

Development of the TBA technique has not been without the raised eyebrows of colleagues; appellations have included, "Wet Sock Technique" and, more politely, "Chemistry on a String." The synthetic polymer chemist has been interested in his molecules as molecules, whereas the polymer physicist is content to spend his life with polystyrene. John Gillham covers the territory in between.

Dynamic Meniscus Profiles in Free Coating III Predictions Based on Two-Dimensional Flow Fields

One challenging problem in liquid-gas, interfacial phenomena is the prediction of the size and location of a flowing meniscus because it involves surfaces which are highly curved. The paper presents one aspect of this problem. A numerical method is presented for predicting the dynamic meniscus profiles—specifically those distorted considerably by flow. The geometry considered to provide these free (liquid-gas) surfaces is coating of a moving sheet by upward withdrawal from a finite bath. The predicted profiles agree with data taken with a glycerine-water solution and with viscous oils.

The method predicts the three parameters (coating thickness and two others) which are the minimum number of parameters necessary to describe the dynamic-meniscus profiles for this geometry. The numerical method is iterative, it simultaneously predicts the flow field in the bath, and it is based on the two-dimensional Navier-Stokes equations and appropriate boundary conditions. The interfacial boundary condition used for iteration is the normal stress condition which is composed of pressure, surface tension, and viscous terms.

CHIE Y. LEE
and
JOHN A. TALLMADGE

Department of Chemical Engineering
Drexel University
Philadelphia, Pennsylvania, 19104

SCOPE

This paper is concerned with the simultaneous prediction of dynamic meniscus profiles and flow fields in free coating of sheets by withdrawal from finite baths. The free coating geometry has been used commercially for photographic emulsions, galvanized steel, drawn glass plates, electroplating rinses, and other applications and is often followed by a film reduction device. In these and other coating geometries, there is a need for minimizing coating nonuniformities. The study of dynamic meniscus profiles and their flow fields is considered relevant to understanding the nature of flow instabilities, which in turn are believed to give rise to film nonuniformities.

The first objective of this paper is to present a numerical technique, based on two-dimensional flow, for predicting the dynamic meniscus profiles in terms of three parameters, the film coating thickness and the size and shape of the meniscus. The technique simultaneously predicts the flow fields and involves a search for minimum error in terms of two parameters which are related to shape and coating thickness. The error is calculated using a pressure error integral over the meniscus, which is based on the normal stress boundary condition along the meniscus interface. The major subroutine is a stream function-vorticity iteration for each assumed profile.

Most previous theoretical work in free coating has concentrated on the prediction of one dependent variable, coating thickness, as a function of one independent variable, the capillary number. The method described in this paper describes the prediction of three dependent parameters as a function of four independent parameters; the latter are Reynolds number *Re*, capillary number *Ca*, bath depth, and bath width.

The second objective of this paper is to compare the predicted results with experimental profiles, using data obtained from photographs of coating on a continuous belt device.

Correspondence concerning this paper should be addressed to J. A. Tallmadge. C. Y. Lee is with DeLaval Corporation, Pleasant Valley, New York.