CREEP COMPLIANCE MEASUREMENTS BY THERMOMECHANICAL ANALYSIS—PARALLEL PLATE RHEOMETRY (TMA–PPR)*

R. B. Prime

IBM (H20–025), SAN JOSE, CA 95193, U.S.A.

A method is described for measurement of creep compliance and apparent viscosity of thermoplastic materials above their glass transition temperatures. The method utilizes a standard thermomechanical analyzer (TMA) with minor modifications. Small samples in the shape of a flat-ended cylinder are compressed isothermally between parallel plates consisting of a special probe and the base of the sample platform. Previously derived physical relationships and experimental restraints are employed. Results are reported for a polystyrene standard and an electrophotographic toner at several temperatures. Standard time-temperature superposition techniques were used to construct creep compliance master curves for the toner. It is demonstrated that TMA is ideally suited for this type of measurement.

Two types of parallel plate rheometer experiments are possible: (a) when the sample fills the space between the plates and exudes from between them after the load is applied (constant sample radius, equal to radius of plates); and (b) when the radius of the test plates is larger than that of the sample throughout the test and the sample volume is constant. The Wallace plastimeter is representative of the first (a) and the Williams plastimeter of the second (b). Both methods require a flat-ended cylindrical sample. Viscosities from 10^1 to 10^8 Pa·s** can be measured with low shear rates of 0.0001 to 1 s^{-1} being generated.

In this paper, the method (b) TMA–PPR technique is employed in the measurement of creep compliance and apparent viscosity of a polystyrene reference material and an electrophotographic toner. In a separate study [1] it was shown that the time-temperature dependencies of both noncontact and hot-roll fixing of the toner to paper were identical to the time-temperature dependencies of the toner rheology measured by TMA–PPR.

* Presented at the 7th ICTA in Kingston, Ontario, Canada.
** 1 Pa·s = 10 Poise.

Parallel plate rheometry is not a new technique. Its use for measuring "plasticity" of unvulcanized rubber stocks dates back to the 1920's. Theoretical solutions for the rate of approach of two parallel plates separated by a viscoelastic medium date back even further [2–6]. The technique has been applied in several polymer and nonpolymer applications.

Sone [7] applied the method (b) technique, and oscillating plate and cone-and-plate viscometry to the rheological properties of butter. Shama and Sherman [8] used parallel plate rheometry to study aging (staling) of cake and margarine. Dienes and Klemm [5] determined the viscosity-temperature behavior of polyethylene and vinyl chloride-acetate resin compounds from method (b) measurements. Dienes [9] further showed that parallel plate rheometry was also capable of measuring elastic and delayed elastic components of deformation. He applied the technique to polyethylene, vinyl chloride-acetate, and cellulose ester compounds. Longworth and Morawetz [10] measured melt viscosities of styrene homopolymers and copolymers with methacrylic acid over a wide range of shear rates, using the method (b) technique. Cessna and Jabloner [11] pioneered in the application of thermomechanical analysis (TMA) to parallel plate rheometry. Utilizing a DuPont Thermomechanical Analyzer and method (a) technique they investigated the early stages of curing of several polyaromatic thermosetting resins.

Background theory

Parallel plate rheometry measures the approach of two parallel plates moving toward each other under the action of a force with a viscoelastic medium between them. The experiment measures creep compliance of the viscoelastic medium, $J(t)$, which is the time-dependent strain relative to a constant stress*.

$$J(t) = \frac{\text{strain } (t)}{\text{stress}} = J_g + \Sigma J_i(1 - e^{-t/\tau_i}) + t/\eta \tag{1}$$

In noncross-linked thermoplastic materials, such as those investigated in this study, the deformation can be separated into an elastic component (J_g, the glassy compliance), a time-dependent elastic component (characterized by a distribution of relaxation times, τ_i), and a viscous or nonrecoverable component (t/η, where η is the viscosity).

* In the parallel plate method, stress is only approaximately constant, decreasing through the test. In this study the stress decrease ranged from 0.1% at 48° to 56% at 130°.

As described earlier, two types of experiments are possible: (a) when the sample fills the space between the plates and exudes from between them after the load is applied and (b) when the radius of the test plates is larger than that of the sample throughout the test and the sample volume is constant. Dienes and Klemm [5] describe the physics of both types of experiments. However, the solution they present is subject to the limiting condition that the separation of the plates h must be small compared to the sample radius R; Dienes and Klemm suggested that h should be less than $R/10$. Gent [6] modified the basic equation to avoid this limitation. The creep compliance, in terms of Gent's modified equation and method (b) measurements becomes

$$J(t) = \frac{3V}{F}\left\{\left(\frac{1}{h} - \frac{1}{h_0}\right) + \frac{V}{8\pi}\left(\frac{1}{h^4} - \frac{1}{h_0^4}\right)\right\} \tag{2}$$

where h_0 is the initial sample height ($=$ plate separation at $t=0$), h is the sample height at time t after the load is applied, V is the sample volume (constant), and F is the applied force. Gent demonstrated the applicability of Equation 2 over the entire deformation range with experimental measurements (Method b) of a coal-tar pitch sample of $h_0/R_0 = 3.9$. Independent measurements of viscosity were in excellent agreement with results from the parallel plate method. Note that the solution given by Dienes and Klemm [5] does not include the term $(1/h - 1/h_0)$.

In this study, measurements were made according to method (b), and the TMA–PPR data converted to creep compliance by means of Equation 2. At high temperatures and/or long times a predominantly viscous region could be identified, where the slope of the creep compliance curve, $\log J(t)/\log t = 1$. Under these conditions $J(t) \cong t/\eta$, which provides for the measurement of viscosity. The mean shear rate associated with the viscosity measurements was calculated from the following relationship given by Longworth and Morawetz [10]

$$\dot{\gamma} = \frac{2\pi^{1/2}h_0^{5/2}F}{3V^{3/2}\eta} \tag{3}$$

where $\dot{\gamma}$ is the mean velocity gradient in the direction parallel to the plates. The mean shear stress was calculated as $\bar{\tau} = \eta\dot{\gamma}$.

Experimental

1. *Materials.* Materials used in this study were a narrow molecular weight polystyrene and an electrophotographic toner. The polystyrene was Waters Associates Standard No. 25710: $M_n = 49{,}000$, $M_w = 51{,}000$. The toner was IBM

790 toner, for use in the IBM 3800 Printing Subsystem. It is a blend of thermoplastic resins and carbon black. By DSC the toner exhibits a T_g between 65–70°, and a secondary transition between 90–100°.

2. *Test specimens.* The test specimens were right circular cylinders, which were molded at 100°C using the simple mold depicted in Figure 1. Samples of radius 2.55 ± .03 mm were prepared. Sample heights varied between 1.3 and 4.4 mm, with taller samples generally used at lower temperatures. Sample weights and volumes
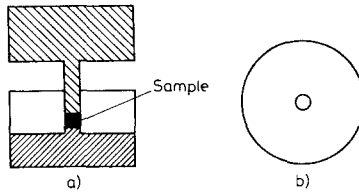
Fig. 1 Schematic for three-section mold used to prepare TMA–PPR samples. (a) cross-sectional view. (b) top view of center section. Sample diameter was 5 mm for this work; 2 mm diameter samples for higher pressure studies were prepared with a similar mold

were measured to ensure the absence of air bubbles. It was observed that temperature gradients in the sample could be kept to < 1° at temperatures between 55 and 112°, providing sample thickness was < 4 mm.

3. *Instrumental.* Measurements were made using a Perkin-Elmer TMS–1 Thermomechanical Analysis System. A special probe was made with an enlarged flat circular foot ($\simeq 4$ mm in radius); see Figure 2. A special device was constructed for applying the load to the sample. The device is attached to the TMA analyzer and greatly facilitates the addition and removal of weights to the TMA sample loading pan. Brass washers were epoxied to the weights so that they could be lowered onto the loading pan by means of the hook-chain-dial mechanism of the loading device. Temperature calibration was accomplished by step-heating of naphthalene and benzoic acid pellets.

4. *Test procedure and data analysis.* An outline of the TMA–PPR test procedure is given below. A N_2 purge of 35 cc/m was used. For the studies reported here, a force of 4.91×10^4 dynes (50.1 g load) was applied to the samples, producing an initial pressure of $2.40 \pm .04 \times 10^4$ Pa ($3.48 \pm .06$ psi):

a) Place test specimen between parallel plates of the TMA, as illustrated in Figure 2. Approximately zero load should be on the sample*. Place thermocouple close to sample and at approximately one-half the sample height.

---

* A set of washers of differing weights, which could be added to the sample loading tray, was found to be useful in obtaining zero load.

b) Raise furnace assembly and heat to a temperature somewhat below the test temperature. Add the weight to the sample loading tray and remove after a short time. The time and temperature should be just sufficient to allow the sample to
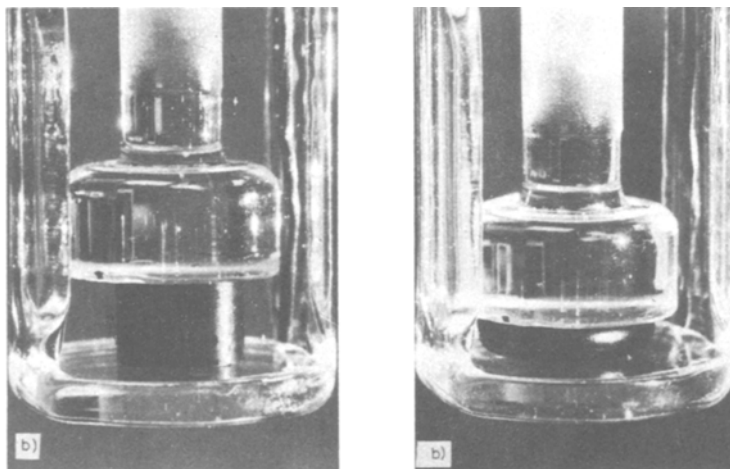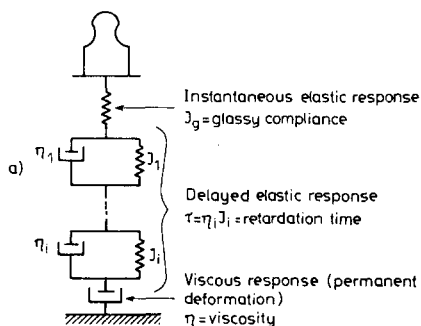

Fig. 2 Creep compliance measurements. a) Spring and dashpot model representing elastic, time-dependent elastic (viscoelastic) and viscous components of the deformation. b) Illustration of TMA technique at beginning and end of measurement

"mold" to the TMA–PPR faces without causing significant change in sample height. Allow sample to recover viscoelastically (2–15 hours). Heat to the test temperature. When the temperature is stable ($\simeq 10$ m), lower the weight onto the sample loading pan and record sample height versus time. A fast recorder chart speed is recommended for the early portions of the experiment.

c) A computer program was used to convert the TMA–PPR data to creep compliance via Equation 2. Input into the computer was the probe displacement-

time data, the instrument sensitivity, room temperature sample height, the change in sample height on heating to temperature, sample diameter, sample mass, and load on the sample. Output included plots of h *vs.* t, $J(t)$, and pressure versus time. If a viscous region of the creep compliance curve could be identified, the program would also compute the slope ($\Delta \log J(t)/\Delta \log t$), the apparent viscosity, mean shear rate, and mean shear stress.

Results

1. *General.* Figure 2 illustrates the TMA–PPR measurement. Figure 3 shows the h versus time data for a toner sample at 103.5°; Figure 4 shows the same data converted to creep compliance. At these conditions the toner exhibits viscoelastic response over approximately the first 400 seconds, beyond which the response is purely viscous. Apparent viscosity, mean shear rate, and mean shear stress were calculated for the viscous region and are presented in Table 1. Since parallel plate
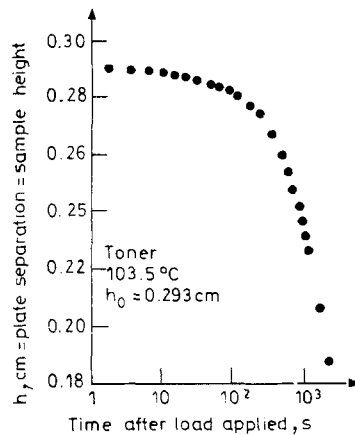

Fig. 3 Plate separation = sample height data for toner at 103.5°·h_0 = 0.293 cm at temperature

Table 1 Viscosity data for IBM 790 toner from TMA–PPR data. η_a = apparent viscosity, $\bar{\gamma}$ = mean shear rate, $\bar{\tau}$ = mean shear stress, slope = $\Delta \log J(t)/\Delta \log t$

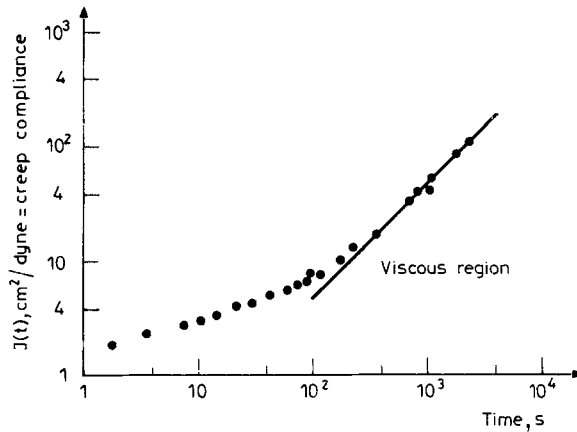| T, °C	h_0, at T, cm	Slope	η_a, Pa s	$\dot{\gamma}$, s^{-1}	$\bar{\tau}$, Pa
103.5	0.293	1.04	2.85×10^7	0.00067	1.91×10^4
110.8	0.229	0.99	1.51×10^6	0.0099	1.52×10^4
111.0	0.134	0.98	1.80×10^6	0.0050	0.91×10^4
121.0	0.203	1.02	2.33×10^5	0.059	1.38×10^4
130.0	0.155	0.98	7.24×10^4	0.139	1.00×10^4

Fig. 4 Creep compliance of toner at 103.5 °C, from Equation 2 and data of Figure 3. Region of constant slope = 1 identifies viscous portion
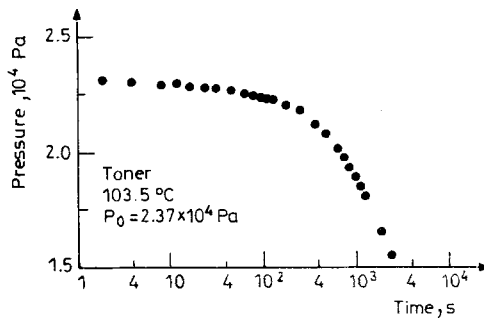

Fig. 5 Pressure profile through TMA–PPR experiment. Toner at 103.5°, $P_0 = 2.37 \times 10^4$ Pa

rheometry is a constant force measurement, the pressure decreases throughout the experiment. The pressure-time profile corresponding to the data of Figures 3 and 4 is shown in Figure 5.

2. *Polystyrene*. The TMA–PPR method was tested for accuracy by measuring the narrow molecular weight polystyrene at two temperatures, and comparing the results against accepted data [12]. As shown in Figure 6, the comparison is excellent. Agreement between log viscosity is $\simeq 1\%$. It is concluded that the TMA–PPR method is capable of generating quantitative rheological data.

3. *Toner*. Creep compliance of IBM 790 toner was measured over a wide range of temperatures and pressures. Data at an initial pressure of 2.4×10^4 Pa (3.5 psi) and over a temperature range of 48–130° are shown in Figure 7. At 48° an estimate of the glassy compliance, $J_g \cong 1 \times 10^{-10}$ cm^2/dyne, is obtained; the Young's
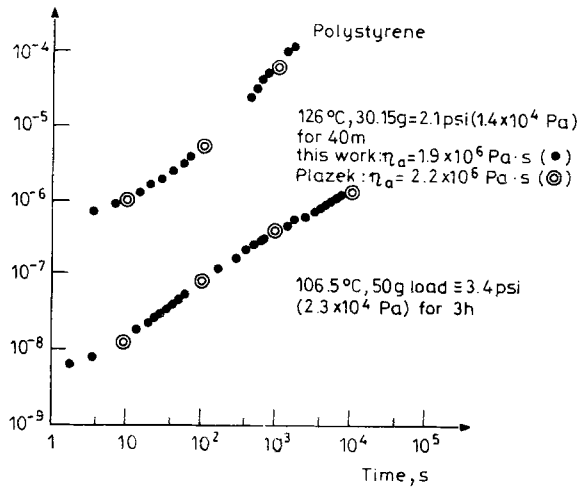
Fig. 6 Creep compliance of polystyrene reference material. ● 50,000 MW, this work (TMA–PPR) ◎ 46,900 MW (Reference 12)
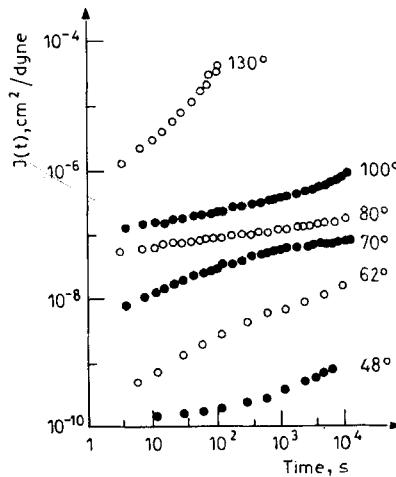

Fig. 7 Creep compliance curves for IBM 790 toner. Initial pressure = 2.4×10^4 Pa

modulus is the reciprocal of J_g. At longer times viscoelastic behavior is observed. Between 62 and 100° the deformation is predominantly viscoelastic, while at 130° it is mostly viscous.

Time-temperature superposition [13, 14] was used to generate a master curve by shifting the creep compliance curves along the time axis until they overlapped. Note that the creep compliance data have been normalized for temperature. The extent of
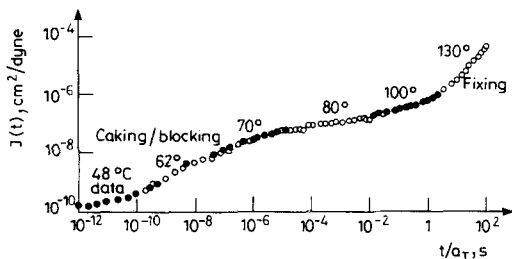
Fig. 8 Creep compliance master curve for toner, from data of Figure 7, plotted against reduced time t/a_T, for $T_0 = 130°$
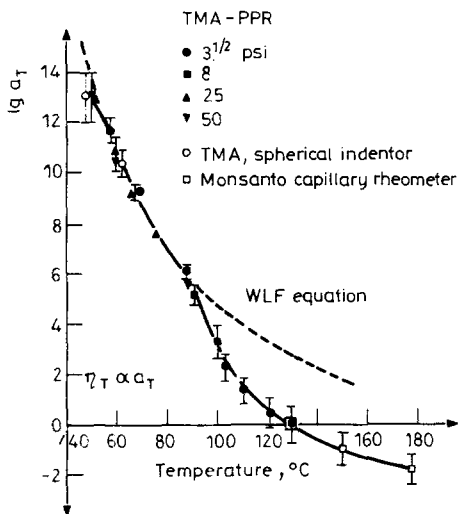

Fig. 9 Shift factor—temperature curve for IBM 790 toner. $a_T = 1$ at $130°$ (arbitrary)

the shifting is the shift factor a_T, where a_T is a ratio of corresponding times for the same behavior to occur at different temperatures. The shift factor is arbitrarily chosen to have a value of unity at some reference temperature. Figure 8 is the master curve obtained by shifting the creep compliance data of Figure 7; note that the elastic and viscous regions are separated by $\simeq 14$ decades of time.

Figure 9 is the shift factor-temperature curve, obtained from several TMA–PPR and capillary rheometer measurements. The significance of this curve is that it relates time and temperature. For electrophotographic toners this is important both at low temperatures where caking (or blocking) is a concern, and at high temperatures where fixing occurs. As an example, from Figure 9 it would be expected that the same amount of flow that occurs in the nip of a hot roll fuser in

10 ms at 140°C would require 20 msec at 130°C. An interesting aspect of the shift factor curve is the deviation from the standard WLF [14] behavior of unfilled, monocomponent polymers (dashed line) at $\simeq 90°$. This is attributed to the multi-component nature of toner, where one of the components functions as a solid diluent.

Toner viscosity data are presented in Table 1. The non-Newtonian nature of toner is exemplified by the dependence of viscosity on shear rate (111° data). Note, by comparison with Eq. 1 and from the definition of the shift factor as a ratio of times that, when the deformation is predominantly viscous, the shift factor measures the temperature dependence of viscosity.

Discussion and conclusions

By comparison with reference data for polystyrene, it was shown that the TMA–PPR technique can yield quantitative rheological data. The utility of the technique was demonstrated by generating the complete creep compliance master curve for an electrophotographic toner, and by showing that the time-temperature shift factors (a_T) from TMA–PPR measurements were identical to those for noncontact and hot-roll fixing of the toner to paper. Rigid temperature control, precise measurement of sample thickness with time, and modern data collection and analysis capabilities makes thermomechanical analysis an ideal method for parallel plate rheometry.

* * *

References

1 R. B. Prime, Photo. Sci. Eng., 27 No. 1 (1983) 19.
2 M. J. Stefan, Akad. Wiss. Wien Math., Naturwiss, K1. Abt. IIa, 69 (1874) 713.
3 A. Healy, I.R.I. Trans., 1 (1926) 334.
4 J. R. Scott, I.R.I. Trans., 7 (1931) 169.
5 G. J. Dienes and H. F. Klemm, J. Appl. Phys., 17 (1946) 45.
6 A. N. Gent, Br. J. Appl. Phys., 11 (1960) 85.
7 T. Sone, J. Phys. Soc. Japan, 16 (1961) 961.
8 F. Shama and P. Sherman, Soc. Chem. Ind. SCI Monograph ‖ 27 (1967) 77.
9 G. J. Dienes, J. Colloid Sci., 2 (1947) 131.
10 R. Longworth and H. Morawetz, J. Poly. Sci., 29 (1958) 307.
11 L. C. Cessna, Jr. and H. Jabloner, J. Elastomers Plast., 6 (1974) 103.
12 D. J. Plazek, J. Phys. Chem., 69 (1965) 3480.
13 J. D. Ferry, Viscoelastic Properties of Polymers, (2nd Edition) John Wiley, New York 1970, Chapter 2C.
14 J. D. Ferry, R. F. Landel and M. L. Williams, J. Appl. Phys., 26 (1955) 359.

Zusammenfassung — Eine Methode zur Messung der Kriechnachgiebigkeit und der scheinbaren Viskosität von thermoplastischen materialien oberhalb deren Glasumwandlungstemperaturen wird beschrieben. Es wurde ein thermomechanischer Standardanalyzer (TMA) mit geringfügigen Abänderungen benutzt. Kleine Proben in Form eines Zylinders mit ebenen Enden werden zwischen einer speziellen Sonde und der Basis der Probenplatte isotherm gepreßt. Vorausgehend abgeleitete physikalische Beziehungen und experimentelle Einschränkungen werden berücksichtigt. Ergebnisse werden für einen Polystyrolstandard und einen elektrophotographischen Toner und verschiedene Temperaturen angegeben. Standard-Techniken der Zeit-Temperatur-Überlagerung werden herangezogen, um Kriechnachgiebigkeitskurven für den Toner zu konstruieren. Es wird gezeigt, daß TMA für diesen Typ von Messungen ideal geeignet ist.

Резюме — Описан метод измерения деформационной ползучести и кажущейся вязкости термопластмасс выше их температуры стеклования. В методе использован с незначительными изменениями стандартный термомеханический анализатор (ТМА). Небольшие образцы в форме плоских цилиндров изотермически сжимаются между параллельными пластинками, состоящие из специальной пробы и опорной площадки образца. Использованы ранее установленные физические взаимосвязи и экспериментальные ограничения. Приведены при нескольких температурах результаты измерения для полистирола и электрофотографического виража. Стандартные методы наложения время — температура были использованы для построения эталонных кривых деформационной ползучести для виража. Показано, что метод ТМА идеально приемлемый для такого типа измерений.