Basic Rheology of Polymer Melts

An Introductory Polymer Science Experiment

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Polymer processing induces various levels of stress, strain, and strain rate. It is well known that the molecular structure of polymers plays an important part in the relationships among these different parameters (*1–6*). So, it is interesting to quantify its significance through rheology, which is the study of flow and deformation of matter.

The aim of this experiment is to introduce basic concepts concerning the rheological behavior of polymer melts, which are discussed elsewhere in the course. Viscoelastic properties are studied by means of dynamic mechanical testing, and attention is focused on various rheological quantities such as complex modulus, rubbery plateau modulus, complex viscosity, and Newtonian viscosity. In addition, time dependence and time–temperature correspondence may be explored by the building of an experimental “master curve”.

Basic Rheology (*1–6*)

Before exploring the viscoelastic properties of polymers, let us examine the response ε of ideal systems to a stress σ.

> An *ideal elastic body* obeys Hooke’s law: applied stress (σ) and induced strain (ε) are related by a unique modulus value E:

$$\sigma = E\varepsilon.$$

The elastic deformation is instantaneous and independent of time (wholly recoverable when the stress is removed). So, an ideal elastic element can be simulated by a spring.

> A *completely viscous response* is that of a Newtonian fluid, whose deformation (ε) is linear with time while stress (σ) is applied and is completely irrecoverable:
>
> $$\sigma = \eta\,(d\varepsilon/dt)$$
>
> where η is the viscosity of the fluid. A simple mechanical analogy of a Newtonian fluid is a dashpot.

Most polymeric materials are neither a liquid nor a solid. They have both viscous and elastic characters; that is, they exhibit a *viscoelastic behavior*, which is described by several mathematical models based upon an arrangement of the two idealized elements (“spring and dashpot”). If they are placed in series, the resulting *Maxwell element* exhibits flow plus elasticity on the application of stress; when the stress is applied, the spring elongates while the dashpot slowly yields. On the removal of the stress the spring recovers but the dashpot does not. The resulting strain is given by the equation

$$d\varepsilon/dt = \underbrace{(1/E)\,(d\sigma/dt)}_{\text{Hooke}} + \underbrace{\sigma/\eta}_{\text{Newton}}$$

Viscoelastic properties are investigated using rheological experiments such as dynamic mechanical testing, which offers a convenient way to assess time dependence of mechanical properties of polymers.

Basis of Dynamic Mechanical Testing

The material is subjected to an oscillatory stress, and the corresponding oscillatory response is monitored and analyzed. The effect of time dependence in linear viscoelastic material is exemplified by the *phase lag* observed between stress and strain, which varies according to test conditions (frequency, temperature). For instance, suppose that the time-dependent stress imposed on a polymeric sample is given as

$$\sigma(t) = \sigma_0 \sin(\omega t)$$

This function depicts a stress that oscillates from $+\sigma_0$ to $-\sigma_0$ with angular frequency ω.

Then, the resulting sinusoidal strain will lag the stress by some amount of time:

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t + \delta)$$

where ε_0 is strain amplitude.

For an elastic material (at any frequency), the stress and the strain maxima occur at the same time ($\delta = 0$); stress and strain are in phase. For a viscous liquid, the strain maximum lags the stress maximum by a phase difference of $\pi/2$. Thus, the phase angle δ changes reflect the time dependence of the viscoelastic properties of the polymer.

Therefore, no single parameter can be used to characterize the stress–strain relationship in viscoelastic material. The *complex dynamic modulus* (G^*) is resolved into two components using complex notation:

$$G^* = \sigma/\varepsilon = G' + iG''$$

The real part of the complex modulus (G') describes stress–strain relationships that are in phase. G' is called the *storage modulus* (or *elastic modulus*). The imaginary component (G'') characterizes the out-of-phase component and is named the *loss modulus* (or *viscous modulus*).

Dynamic viscosity (η^*) is related to the complex modulus by

$$\eta^* = \sigma/(d\varepsilon/dt) = G^*/(i\omega) = \eta' - i\eta''$$

with $\eta'' = G'/\omega$ and $\eta' = G''/\omega$. Then, the real component of the complex viscosity (η') describes the viscous dissipation in the sample, while the imaginary component (η'') represents the stored elastic energy.

Furthermore, the *tangent* of the *phase angle* ($\tan\delta$) describes the balance between the viscous and elastic behaviors in a polymer melt:

$$\tan\delta = G''/G' = \eta'/\eta''$$

Time–Temperature Equivalence

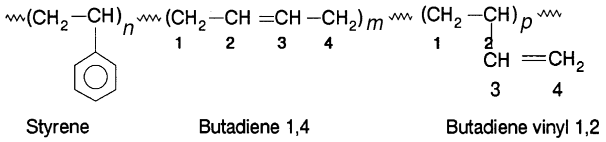
The description of the viscoelastic response of a polymer melt to small stresses is greatly simplified by the application of the time–temperature equivalence principle. Experimental data measured on accessible time scales at various temperatures can be used to build a master curve at a fixed temperature (reference temperature) over a very broad time scale. If data measured at a given temperature are simply shifted horizontally, a portion of the log data versus log frequency curve will superimpose itself upon a previously measured curve obtained at another temperature (small vertical adjustments are also sometimes necessary to take into account thermal expansion).

This experiment is devoted to the investigation of viscoelastic behavior of several styrene-co-butadiene random copolymers. This study points out the effects of the molecular characteristics of the samples (molecular weight and molecular weight distribution) on the readily measurable viscoelastic properties.

Experimental Procedure

Polymers

The samples were styrene-butadiene rubbers (SBR), kindly supplied by the Michelin Company. They were synthesized in solution via anionic polymerization and designated as B160, N120, and B310 (Table 1). All of these random copolymers have the same microstructure from ^{1}H NMR measurements (*7*) (see Scheme I).



Scheme I: Possible microstructure of styrene-co-butadiene copolymers.

Chemical composition: The two types of units are arranged at random along the chain with the same relative amounts of styrene (25%) and total butadiene (75%). *Configuration of butadiene units*: 60% 1,4 units, 40% vinyl 1,2 units. But, these samples have different molecular weights (M_w) and molecular weight distributions (MWD) (see Table 1).

SBR was chosen, but other polymers, such as polydimethylsiloxanes (PDMS), may also be used.

Instrumentation

Viscoelastic properties were investigated in oscillatory shear mode using a rotational controlled stress rheometer with parallel-plate geometry (StressTech Rheologica). The plates were 20 mm in diameter, and the gap between them was 2 mm (Fig. 1).

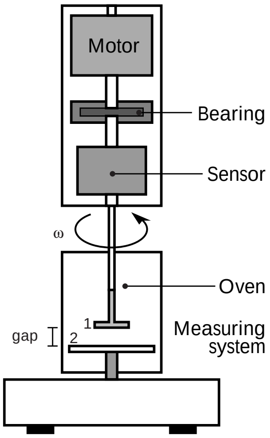


Figure 1. Schematic diagram of the rotational controlled-stress rheometer. (1) upper plate (20 mm in diameter), (2) lower plate.

Table 1. Molecular Parameters of Polymers

Sample	M_w[a]	M_n / M_w, MWD[a]	Shape
B160	160,000	2.1, broad	linear
N120	120,000	1.1, narrow	linear
B310	310,000	1.7, broad	linear

[a] From SEC measurements.

Procedure

First, the sample linearity response with respect to stress amplitude must be checked. The sample behavior at a stepwise changing stress amplitude (from 1 to 22.5 kPa) was analyzed at one frequency (1 Hz) under constant temperature (100 °C). The aim of this kind of measurement was to find a stress range inside which the measurement results were independent of the applied stress. This range is called the *linear viscoelastic region.*

Then, for each test temperature, a frequency sweep was run in the range 0.01–30 Hz. For each sample (B160, N120, and B310) and temperature (70, 100, and 130 °C), a suitable stress amplitude was selected in order to be within the limits of linear viscoelasticity and to work in the optimum torque range of the transducer. The viscoelastic properties (dynamic viscosity, phase shift, storage, loss, and complex modulus) were calculated as a function of frequency.

Results and Discussion

Linear Viscoelastic Region of Sample B160

Elastic modulus as a function of applied stress is plotted in Figure 2. The sample B160 exhibits a constant *G′* in the 1–5-kPa range of applied stress. The end of the linear viscoelastic region is indicated by a decrease of *G′* value. So, all further experiments should be carried out using a stress value inside the limits of linear viscoelasticity.

Students can determine the linear viscoelastic region for each of the other samples. They observe that the linear viscoelastic regime range estimated for sample B160 is valid for samples N120 and B310. So, we can assume that the linear viscoelastic domain essentially depends on the microstructure of the material and not on molecular parameters.

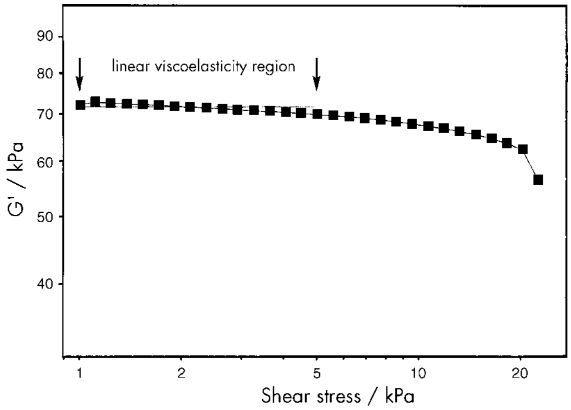


Figure 2. Dependence of the elastic modulus (*G′*) on applied stress for sample B160 at 100 °C. The frequency is 1 Hz.

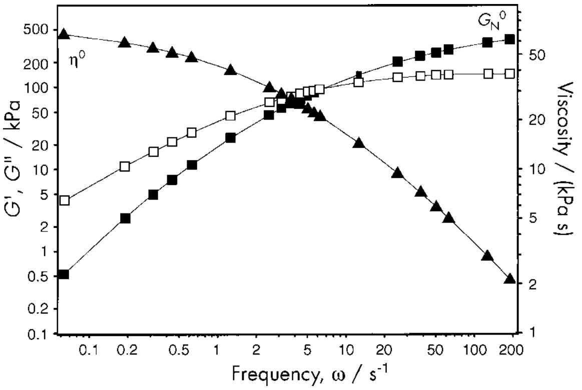


Figure 3. Double logarithmic plots of viscoelastic properties vs the frequency for sample B160 at 100 °C: G' (■), G'' (□), η^* (▲).

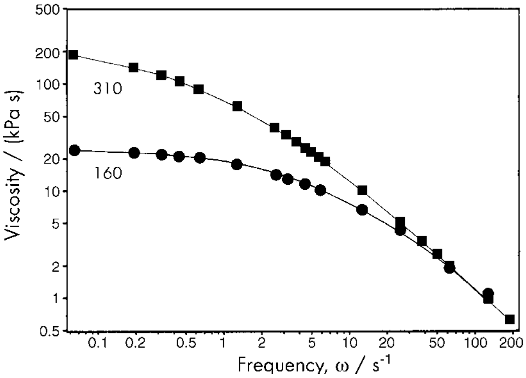


Figure 4. Molecular weight effects on the viscosity η' for B160 (●) and B310 (■) at 130 °C.

Viscoelastic Properties of Sample B160: Frequency Sweep

When the frequency is varying and the stress is kept constant (2 kPa), this results in a varying viscoelastic properties with the frequency N (Hz) = $\omega/2\pi$.

The double logarithmic plots of the loss and storage moduli versus the frequency show a crossover between G' and G''. Thus, two distinct regions of viscoelastic behavior are observed in Figure 3:

- At low frequency $G' < G''$. The polymer melt's behavior is more viscous than elastic. This is the terminal region.
- Then $G' > G''$. The elastic character of the polymer melt becomes dominant. This is the transition zone.
- Finally G' reaches an invariant value called the *rubbery plateau modulus*, noted G_N^0.

One of the most typical effects in polymer viscoelasticity is the non-Newtonian character of the viscosity function. The dynamic viscosity (η^*) decreases as the frequency increases. At very low frequency, η^* tends toward an invariant value. So, below a critical frequency, η' is constant as a function of the frequency and the material exhibits a Newtonian behavior. The Newtonian viscosity of a polymer melt, η_0, is defined by the relation

$$\lim_{\omega\to 0} \eta^*(\omega) = \lim_{\omega\to 0} \eta'(\omega) = \eta_0$$

Effects of Molecular Weight (8–12)

Figure 4 plots η' versus the frequency for samples B160 and B310. It is noted that an increase in molecular weight causes a higher Newtonian viscosity.

Comparison of the viscosity function of these two samples checks the molecular-weight dependance of η_0. It is well known that η_0 may be related to the polymer's molecular weight M_w by the following equation (*1–5, 12*):

$$\eta_0(T) = A(T) \times M_w^{3.4}$$

Students can calculate and comment on the value of the ratios ($\eta_0/M_w^{3.4}$) for the two samples considered.

Moreover, since this equation exhibits the temperature dependence of viscosity, students can illustrate the drastic changes in viscosity with temperature for a given material by simply plotting complex viscosity versus frequency at different temperatures. Elsewhere, it is important to point out that the rubbery plateau modulus G_N^0 does *not* depend upon molecular weight (see Fig. 5).

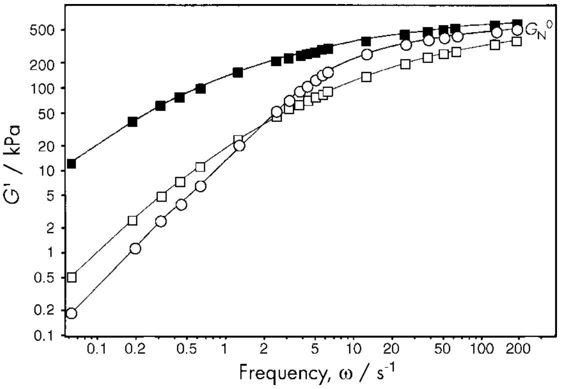


Figure 5. Double logarithmic plot of the elastic modulus vs the frequency for B160 (□), N120 (○) and B310 (■) at 100°C.

Effects of Molecular Weight Distribution (MWD) (12–15)

As regards the accuracy of size exclusion chromatography (SEC) measurements, the weight-average molecular weights of samples B160 and N120 are quite close in comparison with that of sample B310. Therefore we assume that only the molecular weight distribution differs for samples B160 and N120. Figure 6 illustrates the effects of MWD on the viscoelastic behavior of materials.

The narrower distribution displays Newtonian behavior until a higher frequency. Its fall-off in η' with frequency is then rapid, whereas for the broader distribution, the transition from the Newtonian plateau to the non-Newtonian regime is very smooth. See Figure 6A. For a given value of M_w, a sample with a broad molecular weight distribution exhibits more elastic character than one with a narrow MWD (lower tan δ value); see Figure 6B.

It is important to point out that the molecular polydispersity (MWD) does not affect the rubbery plateau modulus G_N^0 (Fig. 5).

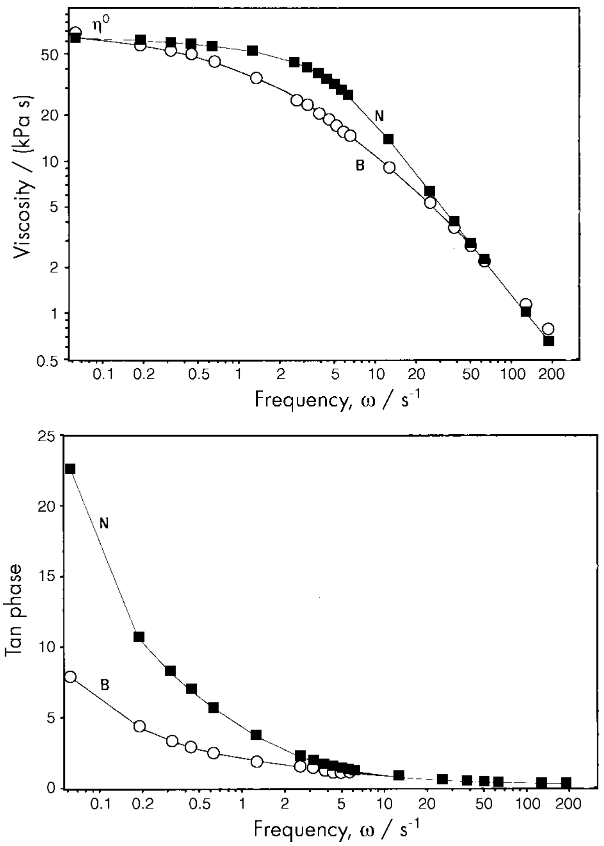


Figure 6. Molecular weight distribution effects on (A) the viscosity η′ and (B) the tangent of the phase angle (tan δ) for B160 (○) and N120 (■) at 100°C.

Application of the Time–Temperature Equivalence Principle

The time–temperature correspondence principle may be applied to a series of overlapping plots of log modulus versus log frequency at various temperatures to yield a master curve, as shown in Figure 7B. In this figure, 100 °C has been chosen as the reference temperature.

Figure 7A plots curves obtained by direct evaluation of $G'(\omega)$ and $G''(\omega)$ from experiments performed at three different temperatures. It shows that the frequency of a given modulus increases as temperature increases. Table 2 clearly shows that the ordinate of the crossover point, called the *crossover modulus*, is invariant with experimental temperature, whereas the abscissa changes strongly. Thus, if the data measured at 70 °C (below the reference temperature) are simply shifted horizontally to higher frequency, a portion of this latter curve superimposes itself upon the previously measured curve at 100 °C. At the same time, data measured at 130 °C (above the reference temperature) are shifted to lower frequency to produce

Table 2. Coordinates of Crossover Point of *G′*(ω) and *G″*(ω) Curves for Sample B160 vs Temperature

T/°C	*G′* = *G″*/ kPa	ω/s^{-1}
70	75	1.44
100	77	6.94
130	79	22.1

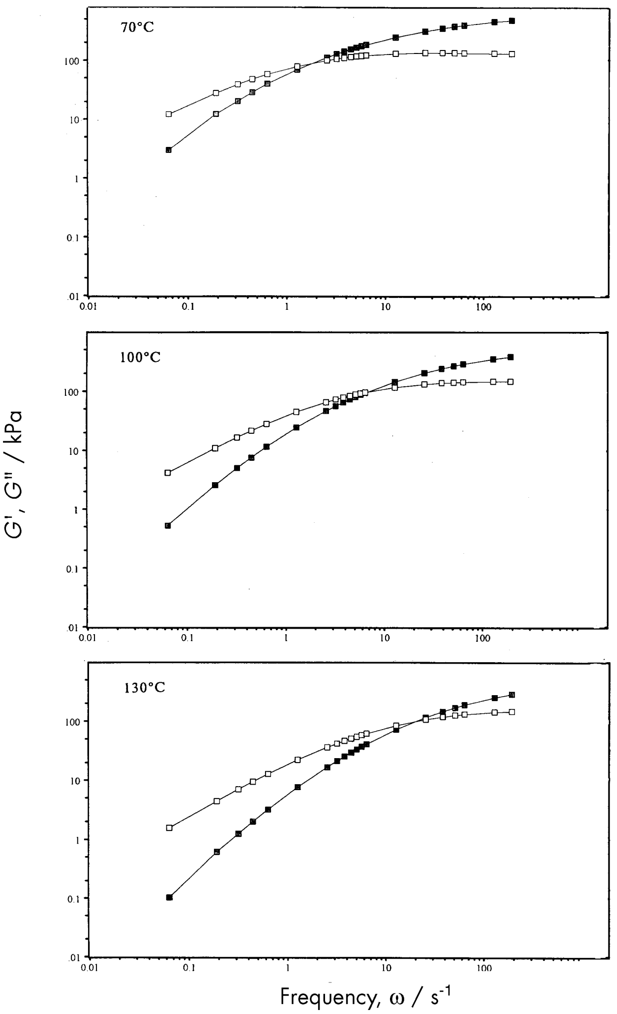


Figure 7A. Building *G′*, *G″* master curves from experimental data for the material B160: *G′*, *G″* vs frequency at different temperatures. Solid symbols correspond to *G′*, open symbols to *G″*.

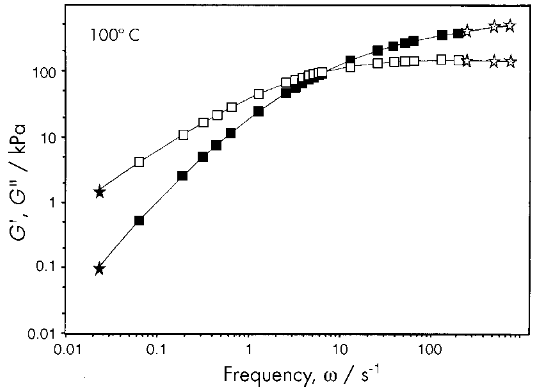


Figure 7B. Building *G′*, *G″* master curves from experimental data for the material B160: Master curves at 100 °C of *G′* (■) and *G″* (□). Stars are extrapolated values.

the master curve. In this way, Figure 7A reports experimental data measured on an accessible time scale at various temperatures. With the help of the time–temperature correspondence principle, such data are used to build a master curve at a fixed temperature over a broader time scale (Fig. 7B).

Since mechanical properties of polymers depend on both time and temperature, the applicability of the principle of time–temperature equivalence simplifies dynamic mechanical measurements. Temperature changes are reflected as time-scale changes (frequency) and vice versa. Thus, an experimental master curve may depict the behavior of a polymer at any time and any temperature.

Conclusion

In summary, students realize that polymer melts have both viscous and elastic characters and that frequency sweep is a powerful tool for investigating the viscoelastic properties of a material. This practical experiment is not devoted to the study of the molecular structure–processability relationships, but students can understand that molecular weight and molecular weight distribution effects are very significant in the processing of a given polymer. For instance, injection molding requires that viscous character prevail: polymer melts must be fluid to flow inside the mold. Therefore, materials with low molecular weight and narrow MWD are chosen. A high molecular weight combined with a broad MWD results in a highly viscous melt with a more elastic character. This kind of sample is quite convenient for blow molding, which involves stretching of the sheet. The melt spinning process needs low viscosity to improve the speed of spinning. However, the stretching of the fiber implies a high elasticity of the polymer melt, so the operator uses a low molecular weight material with a broad MWD.

The complexity of the experiment can be varied depending on the time allotted to it and to the course interests. We choose to study molecular weight and its distribution effects, but many other variables could also be considered, such as microstructure and chain architecture, which affect the value of the rubbery plateau modulus G_N^0, the additive concentration, or solvent dilution (*5, 12, 16*).

On other hand, mechanical properties of polymers vary greatly with time and temperature. The attention of students is attracted to their time dependence and the applicability of the time–temperature correspondence principle. The last experiment clearly shows that temperature changes are reflected as time-scale changes and vice versa: students build a master curve simply by horizontal shifts of their experimental data. Moreover, this shifting may be represented as a division of the time scale as a factor a_T, and the time–temperature equivalence principle may be stated quantitatively in terms of the WLF relationship that analytically expresses the temperature dependence of the shift factor a_T.

Acknowledgments

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