3 Rheology Basics: Creep–Recovery and Stress Relaxation

The next area we will review before starting on dynamic testing is creep, recovery, and stress relaxation testing. Creep testing is a basic probe of polymer relaxations and a fundamental form of polymer behavior. It has been said that while creep in metals is a failure mode that implies poor design, in polymers it is a fact of life.¹ The importance of creep can be seen by the number of courses dedicated to it in mechanical engineering curriculums as well as the collections of data available from technical societies.²

Creep testing involves loading a sample with a set weight and watching the strain change over time. Recovery tests look at how the material relaxes once the load is removed. The tests can be done separately but are most useful together. Stress relaxation is the inverse of creep: a sample is held at a set length and the force it generates is measured. These are shown schematically in Figure 3.1. In the following sections we will discuss the creep–recovery and stress relaxation tests as well as their applications. This will give us an introduction to how polymers relax and recover. As most commercial DMAs will perform creep tests, it will also give us another tool to examine material behavior.

Creep and creep–recovery tests are especially useful for studying materials under very low shear rates or frequencies, under long test times, or under real use conditions. Since the creep–recovery cycle can be repeated multiple times and the temperature varies independently of the stress, it is possible to mimic real–life conditions fairly accurately. This is done for everything from rubbers to hair coated with hairspray to the wheels on a desk chair.

3.1 CREEP–RECOVERY TESTING

If a constant static load is applied to a sample, for example, a 5-lb weight is put on top of a gallon milk container, the material will obviously distort. After an initial change, the material will reach a constant rate of change that can be plotted against time (Figure 3.2). This is actually how a lot of creep tests are done, and it is still common to find polymer manufacturers with a room full of parts under load that are being watched. This checks not only the polymer but also the design of the part.

More accurately representative samples of polymer can be tested for creep. The sample is loaded with a very low stress level, just enough to hold it in place, and allowed to stabilize. The testing stress is then applied very quickly, with instantaneous application being ideal, and the changes in the material response are recorded.
Creep, recovery, and stress relaxation tests. (a) Creep testing is performed by applying a load or stress to a sample. (b) When the stress is removed and the material allowed to recover, this is called a recovery test. These two tests are often cycled. (c) Stress relaxation is the reverse of creep. Holding a sample at a set length, the change in stress as a function of time or temperature is recorded.
as percent strain. The material is then held at this stress for a period of time until the material reaches equilibrium. Figure 3.3 shows a creep test and the recovery step.

We can use creep tests in two ways: to gain basic information about the polymer or to examine the polymer response under conditions that approximate real use. In the former case, we want to work within the linear viscoelastic region so we can calculate equilibrium values for viscosity ($\eta$), modulus ($E$), and compliance ($J$). Compliance is the willingness of the material to deform and is the inverse of modulus for an elastic material. However, for a viscoelastic material this is not true, and a Laplace transform is necessary to make that conversion. As we mentioned in the
previous chapter, polymers have a range over which the viscoelastic properties are linear. We can determine this region for creep–recovery by running a series of tests on different specimens from the sample and plotting the creep compliance, $J$, versus time, $t$. Where the plots begin to overlay, this is the linear viscoelastic region. Another approach to finding the linear region is to run a series of creep tests and observe under what stress no flow occurs in the equilibrium region over time (Figure 3.4). A third way to estimate the linear region is to run the curve at two stresses and add the curves together, using the Boltzmann superposition principle, which states that the effect of stresses is additive in the linear region. So if we look at the 25 mN curve in Figure 3.4 and take the strain at 0.5 min, we notice the strain increases linearly with the stress until about 100 mN, where it starts to diverge, and at 250 mN the strains are no longer linear. Once we have determined the linear region, we can run our samples within it and analyze the curve. This does not mean you cannot get very useful data outside this limit, but we will discuss that later.

Creep experiments can be performed in a variety of geometries, depending on the sample, its modulus and/or viscosity, and the mode of deformation that it would be expected to see in use. Shear, flexure, compression, and extension are all used. The extension or tensile geometry will be used for the rest of this discussion unless otherwise noted. When discussing viscosity, it will be useful to assume that the extensional or tensile viscosity is three times that of shear viscosity for the same sample when Poisson’s ratio, $\nu$, is equal to 0.5. For other values of Poisson’s ratio, this does not hold.

### 3.2 MODELS TO DESCRIBE CREEP–RECOVERY BEHAVIOR

In the preceding chapter, we discussed how the dashpot and the spring are combined to model the viscous and elastic portions of a stress–strain curve. The creep–recovery curve can also be looked at as a combination of springs (elastic sections) and dashpots (viscous sections). However, the models discussed in the last chapter are not adequate for this. The Maxwell model, with the spring and dashpot in series (Figure 3.5a) gives a strain curve with sharp corners where regions change. It also continues to deform as long as it is stressed for the dashpot continues to respond. So despite the fact the Maxwell model works reasonably well as a representation of stress–strain curves, it is inadequate for creep.

The Voigt–Kelvin model with the spring and the dashpot in parallel is the next simplest arrangement we could consider. This model, shown in Figure 3.5b, gives a curve somewhat like the creep–recovery curve of a solid. This arrangement of the spring and dashpot gives us a way to visualize a time-dependent response as the resistance of the dashpot slows the restoring force of the spring. However, it doesn’t show the instantaneous response seen in some samples. It also doesn’t show the continued flow under equilibrium stress that is seen in many polymers.

In order to address these problems, we can continue the combination of dashpots and springs to develop the four-element model. This combining of the various dashpots and spring is used with fair success to model linear behavior. Figure 3.5c
FIGURE 3.4 Linear region from creep–response. A plot of percent strain against time showing two methods of determining the linear region for a creep curve. One can look for the region where the equilibrium region shows no flow as a function of time or where the stress-strain relationship ceases being linear.
shows the model and the curve that results from it. This curve shows the same regions as seen in real materials, including a small instantaneous region, a leveling off of the equilibrium region, and a realistic recovery curve. We can use the four-element model to help us understand the strain curve. We can also add additional elements if needed to adjust the behavior and tie it back to structural units. This is a common approach, and Shoemaker et al. report the use of a six-element model to predict the behavior of ice cream where various parts of that mixture were assigned to specific elements of the model. For example, they assign the independent spring to ice crystals, the independent dashpot to butterfat, and the Voigt elements to stabilizer gels, air cells, and fat crystals. This approach doesn’t always work this well (and there are some doubts as to the validity of these assignments in this

FIGURE 3.5 Models for approximating creep–recovery response. Neither the Maxwell (a) nor the Voigt (b) model work well to explain creep. The four-element model (c) does a better job.
particular case too\(^9\)), and better approaches exist. While real polymers do not have springs and dashpots in them, the idea gives us an easy way to explain what is happening in a creep experiment.

### 3.3 ANALYZING A CREEP–RECOVERY CURVE TO FIT THE FOUR-ELEMENT MODEL

If we now examine a creep–recovery curve, we have three options in interpreting the results. These are shown graphically in Figure 3.6. We can plot strain vs. stress and fit the data to a model, in this case to the four-element model as shown in Figure 3.6. Alternately, we could plot strain vs. stress and analyze quantitatively in terms of irrecoverable creep, viscosity, modulus, and relaxation time. A third choice would be to plot creep compliance, \( J \), versus time.

In Figure 3.6a, we show the relationship of the resultant strain curve to the parts of the four-element model. This analysis is valid for materials in their linear viscoelastic region and only those that fit the model. However, it is a simple way to separate sample behavior into elastic, viscous, and viscoelastic components. As the stress, \( \sigma_o \), is applied, there is an immediate response by the material. The point at which \( \sigma_o \) is applied is when time is equal to 0 for the creep experiment. (Likewise for the recovery portion, time zero is when the force is removed.) The height of this initial jump is equal to the applied stress, \( \sigma_o \), divided by the independent spring constant, \( E_1 \). This spring can be envisioned as stretching immediately and then locking into its extended condition. In practice, this region may be very small and hard to see, and the derivative of strain may be used to locate it. After this spring is extended, the independent dashpot and the Voigt element can respond. When the force is removed, there is an immediate recovery of this spring that is again equal to \( \sigma_o / E_1 \). This is useful, as sometimes it is easier to measure this value in recovery than in creep. From a molecular perspective, we can look at this as the elastic deformation of the polymer chains.

The independent dashpots contribution, \( \eta_1 \), can be calculated by the slope of the strain curve when it reaches region of equilibrium flow. This equilibrium slope is equal to the applied stress, \( \sigma_o \), divided by \( \eta_1 \). The same value can be obtained determining the permanent set of the sample, and extrapolating this back to \( t_0 \), the time at which \( \sigma_o \) was removed. A straight line drawn for \( t_0 \) to this point will have

\[
\text{slope} = \frac{\sigma_o(t_0)}{\eta_1} \tag{3.1}
\]

The problem with this method is that the time required to reach the equilibrium value for the permanent set may be very long. If you can actually reach the true permanent set point, you could also calculate \( \eta_1 \) from the value of the permanent set directly. This dashpot doesn’t recover because there is nothing to apply a restoring force to it, and molecularly it represents the slip of one polymer chain past another.

The curved region between the initial elastic response and the equilibrium flow response is described by the Voigt element of the Berger model. Separating this into individual components is much trickier, as the region of the retarded elastic response...
is described by the parallel combination of the spring, $E_2$, and dashpot, $\eta_2$. In addition, some contribution from the independent dashpot exists. This region responds slowly due the damping affect of the dashpot until the spring is fully extended. The presence of the spring allows for a slow recovery as it pushes the dashpot back to its original position. Molecularly, we can consider this dashpot to
represent the resistance of the chains to uncoiling, while the spring represents the thermal vibration of chain segments that will tend to seek the lowest energy arrangement.

Since the overall deformation of the model is given as

$$\varepsilon(f) = \left(\frac{\sigma_o}{E_1}\right) + \left(\frac{\sigma_o}{\eta_1}\right) + \left(\frac{\sigma_o}{E_2}\right)\left(1 - e^{-t/(\eta_2/E_2)}\right)$$

(3.2)

we can get the value for the Voigt unit by subtracting the first two terms from the total strain, so

$$\varepsilon(f) - \left(\frac{\sigma_o}{E_1}\right) - \left(\frac{\sigma_o}{\eta_1}\right) = \left(\frac{\sigma_o}{E_2}\right)\left(1 - e^{-t/(\eta_2/E_2)}\right)$$

(3.3)

The exponential term, $\eta_2/E_2$, is the retardation time, $\tau$, for the polymer. The retardation time is the time required for the Voigt element to deform to 63.21% (or $1 - 1/e$) of its total deformation. If we plot the log of strain against the log of time, the creep curve appears sigmoidal, and the steepest part of the curve occurs at the retardation time. Taking the derivative of the above curve puts the retardation time at the peak. Having the retardation time, we can now solve the above equation for $E_2$ and then get $\eta_2$. The major failing of this model is it uses a single retardation time when real polymers, due to their molecular weight distribution, have a range of retardation times.

A single retardation time means this model doesn’t fit most polymers well, but it allows for a quick, simple estimate of how changes in formulation or structure can affect behavior. Much more exact models exist, including four-element models in 3D and with multiple relaxation times, but these tend to be mathematically nontrivial. A good introduction to fitting the models to data and to multiple relaxation times can be found in Sperling’s book.

### 3.4 Analyzing a Creep Experiment for Practical Use

The second of the three methods of analysis, shown in Figure 3.6b, is more suited to the real world. Often we intentionally study a polymer outside of the linear region because that is where we plan to use it. More often, we are working with a system that does not obey the Berger model. If we look at Figure 3.6, we can see that the slope of the equilibrium region of the creep curve gives us a strain rate, $\dot{\varepsilon}$. We can also calculate the initial strain, $\varepsilon_o$, and the recoverable strain, $\varepsilon_r$. Since we know the stress and strain for each point on the curve we can calculate a modulus ($\sigma/\varepsilon$) and, with the strain rate, a viscosity ($\sigma/\dot{\varepsilon}$). If we do the latter where the strain rate has become constant, we can measure an equilibrium viscosity, $\eta_e$. Extrapolating that line back to $t_o$, we can calculate the equilibrium modulus, $E_e$. Percent recovery and a relaxation time can also be calculated. These values help quantify the recovery cure: percent recovery is simply how much the polymer comes back after the stress
is released, while the relaxation time here is simply the amount of time required for
the strain to recover to 36.79% (or \(1/e\)) of its original value.

We can actually measure three types of viscosity from this curve. The simple
viscosity is given above, and by multiplying the denominator by 3 we approximate
the shear viscosity, \(\eta_s\). Nielsen suggests that a more accurate viscosity, \(\eta_{irr}\), can be
obtained by inverting the recovery curve and subtracting it from the creep curve.
The resulting value, \(\Delta \varepsilon\), is then used to calculate a strain rate, multiplied by 3 and
divided into the stress, \(\sigma_o\). Finally we can calculate the irrecoverable viscosity, \(\eta_{irr}\),
by extrapolating the strain at permanent set back to \(t_f\) and taking the slope of the
line from \(t_o\) to \(t_f\). This slope can be used to calculate an irrecoverable strain rate,
which is then multiplied by 3 and divided into the initial stress, \(\sigma_o\). This value tells
us how quickly the material flows irreversibly.

If we instead choose to plot creep compliance against time, we can calculate
various compliance values. Extrapolating the slope of the equilibrium region back
to \(t_o\) gives us \(J_{e0}\), while the slope of this region is equal to \(t/\eta_0\). The very low shear
rates seen in creep, this term reduces to \(1/\eta_0\). We can also use the recovery curve
to independently calculate \(J_{e0}\) by allowing the polymer to recover to equilibrium.
Since we know

\[
\lim_{t \to \infty} J_t(t) = J_{e0} \quad \text{for} \quad \dot{\varepsilon}(t) = \dot{\varepsilon}_\infty
\]

then we can watch the change in \(J_t\) until it is zero or, more practically, very small.
This can be done by watching the second derivative of the strain as it approaches
zero. At this point, \(J_t\) is equal to \(J_{e0}\). If we are in steady state creep, the two
measurements of \(J_{e0}\) should agree. If we actually measure the \(J_{e0}\), we can estimate
the longest retardation time (\(\lambda_o\)) for the material by \(\eta_0 \cdot J_{e0}\).

### 3.5 OTHER VARIATIONS ON CREEP TESTS

Before we discuss the structure–property relationships or concepts of retardation
and relaxation times, let’s quickly look at variations of the simple creep–recovery
cycle we discussed above. As we said before, a big advantage of a creep test is its
ability to mimic the conditions seen in use. By varying the number cycles and the
temperature, we can impose stresses that approximate many end-use conditions.

**Figure 3.7** shows three types of tests that are done to simulate real applications
of polymers. In **Figure 3.7a**, multiple creep cycles are applied to a sample. This can
be done for a set number of cycles to see if the properties degrade over multiple
cycles (for example, to test a windshield wiper blade) or until failure (for example
on a resealable o-ring). Creep testing to failure is also occasionally called a creep
rupture experiment. One normally analyzes the first and last cycle to see the degree
of degradation or plots a certain value, say \(\eta_e\), as a function of cycle number.

You can also vary the temperature with each cycle to see where the properties
degrad as temperature increases. This is shown in **Figure 3.7b**. The temperature
can be raised and lowered, to simulate the effect of an environmental thermal cycle.
It can also be just raised or lowered to duplicate the temperature changes caused by
FIGURE 3.7 Examples of types of creep tests: (a) Multiple creep–recovery cycles, (b) multiple creep cycles with overlaying temperature ramp, and (c) heat-set cycle.
FIGURE 3.7 (Continued).
placing the part into a specific environment, such as a gasket in a pump down an oil well or a plastic pipe in an Alaskan winter. This environmental testing is not limited to temperature, as creep–recovery tests can also be run in solvents or in controlled atmospheres.

You can also vary the temperature within one creep cycle, as shown in Figure 3.7c. This is the equivalent of the rubber industry’s heat-set test, used for materials that will be heated and squeezed at the same time. The creep stress is applied and the material is heated to a set temperature and cooled back to room temperature while still under the load. The stress is removed and the amount of recovery recorded.

A final comment on creep testing is that the American Society for Testing and Materials (ASTM)\textsuperscript{12} does have standard procedures for creep tests that supply guidelines for both testing and data interpretation. The main method for plastics is D 2990-91. It covers tensile, compressive, and flexural creep and creep rupture.

3.6 A QUICK LOOK AT STRESS RELAXATION EXPERIMENTS

The conceptual inverse of a creep experiment is a stress relaxation experiment (Figure 3.8a). A sample is very quickly distorted to a set length, and the decay of the stress exerted by the sample is measured. These are often difficult experiments to run, because the sample may need to be strained very quickly. They do provide some very useful information that complements creep data. Creep data and stress relaxation data can be treated as mainly reciprocal,\textsuperscript{13} and roughly related as

\[
\left(\frac{\varepsilon_t}{\varepsilon_0}\right)_{\text{creep}} \approx \left(\frac{\sigma_t}{\sigma_0}\right)_{\text{stress relax}}
\]

The analysis of the stress relaxation curve is shown in Figure 3.8a and is analogous to the creep analysis. One interesting application of the stress relaxation experiment exploits the relationship that the area under the stress relaxation curve plotted as $E(t)$ versus $t$ is the viscosity, $\eta_0$. Doing experiments at very low strain, this allows us to measure the viscosity of a colloid without destroying its structure.\textsuperscript{14}

A special type of stress relaxation experiment with immense industry applications is the constant gauge length experiment.\textsuperscript{15} This is shown in Figure 3.8b. A sample is held at a set length with a minimal stress and then the temperature is increased. As the material responds to the temperature changes, the stress exerted by it is measured. The shrinkage or expansion force of the material is recorded. The experiment may be done with thermal cycles to determine if the same behavior is seen during each cycle.

3.7 SUPERPOSITION — THE BOLTZMANN PRINCIPLE

The question sometimes arises of how strains act when applied to a material that is already deformed. Boltzmann showed back in 1876 that the strains will add together linearly and a material’s stress at any one time is a function of its strain history.
Sample would be distorted to length $y'$ and held.

(a) Classical Test

Sample would be distorted to length $y'$ and held.

(b) Constant Gauge Length

FIGURE 3.8 Stress relaxation experiments: (a) Analysis of a classical stress relaxation experiment where the sample is held at length, $l$, and the stress changes are recorded, (b) a constant gauge length experiment where the sample is held at length, $l$, and the temperature increased.
This applies to a linear response, no matter whether any of the models we discussed is applied. It also works for applied stress and measured strain. There is time dependence in this, as the material will change over time. For example, in stress relaxation the sample will have decreasing stress with time, and therefore in calculating the sum of the strains one needs to consider this decay to correctly determine the stress. This decay over time is called a memory function.16

The superposition of polymer properties is not just limited to the stress and strain effects. Creep and stress relaxation curves collected at different temperatures are also superpositioned to extend the range of data at the reference temperature. This will be discussed in detail in Chapter 8.

3.8 RETARDATION AND RELAXATION TIMES

We mentioned in Section 3.4 that one of the failings of the four-element model is that it uses a single retardation where most polymers have a distribution of retardation times. We also mentioned that we could estimate the longest retardation time from the creep compliance, \( J \), versus time plot. The distribution of retardation times, \( L(t) \), in a creep experiment or of relaxation times, \( H(t) \), in a stress relaxation experiment are what determines the mechanical properties of a polymer. One method estimates \( L(t) \) from the slope of the compliance curve against log (time) plot, and \( H(t) \) is similarly obtained from the stress relaxation data. Below \( T_g \), these are heavily influenced by the free volume, \( v_f \), of the material. There is considerable interest in determining what the distribution of relaxation or retardation times are for a polymer, and many approaches can be found.17 Again, Ferry16 remains the major lead reference for those interested in this topic.

If you know the retardation time or relaxation time spectra, it is theoretically possible to calculate other types of viscoelastic data. This has not reduced to practice as well as one might hope, and the calculations are very complex. Neither \( L(t) \) nor \( H(t) \) are routinely used in solving problems. Methods also exist of calculating a discrete spectrum of relaxation and retardation times.18

3.9 STRUCTURE–PROPERTY RELATIONSHIPS IN CREEP–RECOVERY TESTS

The effects of various structural and environmental parameters on creep–recovery tests are well known.19 Temperature may be the most important variable, as most materials show markedly different behavior above and below \( T_g \) (Figure 3.9a). The glass transition, \( T_g \), of a polymer, where the polymer changes from glassy to rubbery, is where chains gain enough mobility to slide by each other. Below the \( T_g \), the behavior of the polymer is dominated by the free volume, \( v_f \), which limits the ability of the chains to move. In glassy polymers below the \( T_g \), where little molecular motion occurs, the amount of creep is small until the deformation is great enough to cause crazing.20 Decreasing the ability of the chains to move, by lowering the temperature, increasing the pressure, annealing, increasing the degree of crystallinity, increasing the amount of cross-linking, or decreasing the free volume will decrease the amount of creep.
As the polymer temperature approaches the temperature of its glass transition, the amount of creep becomes very temperature-dependent. As we exceed the $T_g$, the effects of other structural parameter appear. Amorphous polymers without cross-linking have a strong dependence on molecular weight in the amount of flow seen at equilibrium. Branching changes the amount of creep, but the effect is difficult to summarize as depending on the branch length and degree of branching. For example, the amount of flow can be either increased or decreased depending on whether the branches are long enough to entangle. Plasticizers increase the creep. Plasticization acts by lowering the $T_g$, increasing the molecular weight between entanglements, and diluting the polymer. These effects also decrease the recovery. Time can also affect recovery as long creep experiments allow more chains to disentangle and slip, lowering recovery.

Cross-linked polymers show a very specific curve with a flat equilibrium region, because the cross-links do not allow flow. As shown in Figure 3.9b, recovery is normally quite high. While some creep does occur if times are long enough and the cross-link density low enough, in highly cross-linked materials no creep is seen. For highly crystalline polymers below $T_g$, we see creep responses similar to those seen in a cross-linked polymer because the crystals act as cross-links and restrain flow. As crystallinity decreases, the material becomes less rigid. However, these materials are very sensitive to thermal history between the $T_g$ and the melt because of changes to the crystal morphology.

### 3.10 THERMOMECHANICAL ANALYSIS

Thermomechanical analysis (TMA) involves applying a static force to a sample and watching the dimensional changes. In some cases, as in testing a sample in flexure or compression, it could be viewed as a creep test with varying temperature.
A more common use of TMA is the measure of the thermal expansion of a specimen. Since the basis of TMA’s operation is the change in the dimensions of a sample as a function of temperature or time, a simple way of looking at TMA is as a very sensitive micrometer. Several testing approaches exist and are shown in Figure 3.10. Although it is not normally discussed in a development of DMA, its dependence on the same free volume effects that lead to relaxation and retardation times indicate that a discussion of the basics of this technique should be included here.

The technique of TMA was probably developed from penetration and hardness tests and first applied to polymers in 1948. It is still a very commonly used method. As discussed above, the $T_g$ in a polymer corresponds to the expansion of the free volume, allowing greater chain mobility above this transition. We will discuss thermal transitions at length in Chapter 5, but we need to mention here that the transitions are caused by increases in the free volume of the material as it is heated (Figure 3.11a). Seen as an inflection or bend in the thermal expansion curve, this change in the TMA can be seen to cover a range of temperatures (Figure 3.11b), of which the $T_g$ value is an indicator defined by a standard method. This fact seems to get lost as inexperienced users often worry why perfect agreement isn’t seen in the value of the $T_g$ when comparing different methods. The width of the $T_g$ transition can be as important an indicator of changes in the material as the actual temperature. Other commonly used TMA methods such as flexure (Figure 3.11c) and extension (Figure 3.11d) also show that the $T_g$ occurs over a range of temperatures. This is also seen in the DMA data (Chapter 5) as well as in the DSC.

TMA allows the calculation of the coefficient of thermal expansion (CTE) or, more correctly, the thermal expansivity from the same data as used to determine the $T_g$ (Figure 3.11b). Since many materials are used in contact with a dissimilar material...
FIGURE 3.11 Transitions in TMA: (a) Changes occur in the free volume, (b) standard method for measuring the $T_g$ by the CTE in expansion (note that the $T_g$ occurs over a range of temperatures and not at a specific temperature, although the method picks a temperature as an indicator), (c) the $T_g$ can be measured in penetration, (d) the $T_g$ and heat-set temperatures are shown in extension. A flexure cure is not shown but would look similar to the curve in (c).
(c) $T_g$ in Flexure  

(d) $T_g$ and Heat Set in Extension

FIGURE 3.11 (Continued).
in the final product, knowing the rate and amount of thermal expansion by the CTE helps design around mismatches that can cause failure in the final product. These data are only available when the $T_g$ is collected by thermal expansion in a technique formally called thermodilatometry. Different $T_g$ values are seen for each mode of testing (flexure, penetration, or expansion), as they each measure a slightly different effect. It is also important to remember that anisotropic materials will have different CTEs depending on the direction in which they have been measured (Figure 3.12a). For example, a composite of graphite fibers and epoxy will show three distinct CTEs corresponding to the $x$-, $y$-, and $z$-directions, because the fibers have different orientation or packing in each axis. Blends of liquid crystals and polyesters show a significant enough difference between directions that the orientation of the crystals can be determined by TMA. Similarly, oriented fibers and films show a different CTE in the direction of orientation.

The study of bulk or volumetric expansion is referred to as dilatometry and can also be done in a TMA. This technique, which involves measuring the volumetric change of a sample, is traditionally applied to liquids. Boundy and Boyer used it extensively to measure initial rates for bulk polymerization of styrene. Because of the great difference in density between a polymer and its monomer, very accurate measurements are possible at very low degrees of conversion. When a total change in size is needed, for example in anisotropic or heterogeneous samples or in a very odd-shaped sample, a similar technique is used with silicon oil or alumina oxide as a filler. This is shown in Figure 3.12b. Volume changes like this are especially important in curing studies where the specimen shrinks as it cures. The shrinkage of a thermoset as it cross-links often leads to cracking and void formation, and measurement of the amount of shrinkage is often critical to understanding the process.
NOTES

1. J. Sosa, *University of Houston Short Course on Polymer Analysis*, Houston, TX, 5 May 1994.
8. C. Shoemaker et al., *Society of Rheology Short Course on Food Rheology*, S. Rheology, Boston, 1993.
12. The ASTM can be reached at ASTM Committee on Standards, 1916 Race Street, Philadelphia, PA, 19103. Standards are republished yearly.
16. We are not going to address the Boltzmann principle in detail, as it is beyond the scope of this book. Interested readers are referred to Ferry, op. cit.


30. W. Brostow et al., paper in review.