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Introduction

The subject matter of this book is the response that polymers exhibit when they are subjected to external forces of various kinds. Almost without exception, polymers belong to a class of substances known as "viscoelastic bodies." As the name implies, these materials respond to external forces in a manner intermediate between the behavior of an elastic solid and a viscous liquid. To set the stage for what follows, it is necessary to describe in very general terms the types of forces to which the viscoelastic bodies might be subjected for characterization purposes.

Consider first the motion of a rigid body in space. This motion can be thought of as consisting of translational and rotational components. If no forces act on the body, it will maintain its original state of motion indefinitely in accordance with Newton's first law of motion. However, if a single force or a set of forces whose vector sum is nonzero act on the body, it will experience acceleration or a change in its state of motion. Consider, however, the case where the vector sum of forces acting on the body is zero and the body experiences no change in either its translational or rotational component of motion. In such a condition, the body is said to be stressed. If the requirement of rigidity is removed, the body will in general undergo a deformation as a result of the application of these balanced forces. If this occurs, the body is said to be strained. It is the relationship between stress and strain that is our main concern. Depending on the types of stress and strain applied to a body, we can use these quantities to define new quantities—material properties— that ultimately relate to the chemical and physical structure of the body. These material properties are referred to using the terms "modulus" and

"compliance." To understand in rough terms the physical meaning of the modulus of a solid, consider the following simple experiment.

Suppose we have a piece of rubber (e.g., natural rubber), ½ cm × ½ cm × 4 cm, and a piece of plastic (e.g., polystyrene) of the same dimensions. The experiment to be performed consists of suspending a weight (applying a force) of, say 1 kg, from each sample as shown in Figure 1-1.
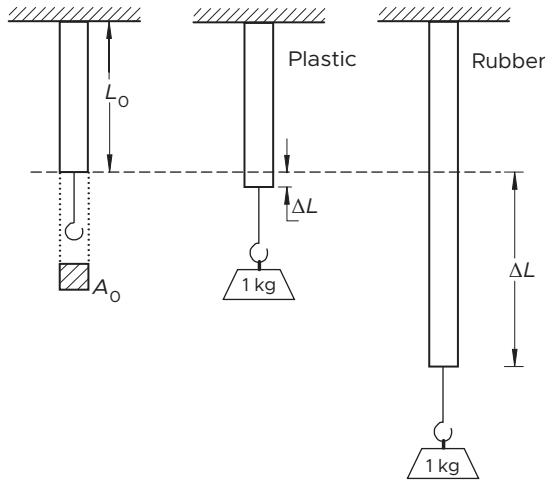

Figure 1-1. Deformation of samples made from plastic vs. rubber. As a reference, the undeformed shape for both samples is shown on the left side. A_0 refers to the cross-sectional area of the undeformed sample.

As is obvious, the deformation of the rubber will be much greater than that of the plastic. Using this experiment, we might define a spring constant k as the applied force f divided by the change in length ΔL

$$k = F / \Delta L \tag{1-1}$$

and use this number to compare the samples. However, to obtain a measure that is independent of the sample size, that is, a material property, as opposed to a sample property, we must divide the applied force by the initial cross-sectional area A_0 and divide the ΔL by the initial sample length L_0. Then, the modulus M is

$$M = \frac{F / A_0}{\Delta L / L_0} \tag{1-2}$$

Because ΔL is much larger for the rubber than for the plastic, from equation (1-2) it is clear that the modulus of the rubber is much lower than the modulus of the plastic. Thus, the particular modulus defined in equation (1-2) specifies the

resistance of a material to elongation at small deformations and is called the Young's modulus. It is normally given the symbol E. (See www.rheology.org for suggestions on standard nomenclature for viscoelastic quantities.)

Further experimentation, however, reveals that the situation is more complicated than is initially apparent. If, for example, one were to carry out the test on the rubber at liquid nitrogen temperature, one would find that this "rubber" undergoes a much smaller elongation than with the same force at room temperature. In fact, the extension would be so small as to be comparable to the extension exhibited by the plastic at room temperature. A more dramatic demonstration of this effect is obtained by immersing a rubber ball in liquid nitrogen for several minutes. The cold ball, when bounced, no longer has the characteristic properties of a rubbery object but, instead, is indistinguishable from a hard sphere made of plastic.

On the other hand, if the piece of plastic is heated in an oven to 130 °C and then subjected to the modulus measurement, it is found that a much larger elongation, comparable to the elongation of the rubber at room temperature, results.

These simple experiments indicate that the modulus of a polymeric material is not invariant, but is a function of temperature T, that is, $M = M(T)$.

An investigation of the temperature dependence of the modulus of our two samples is now possible. At temperature T_1, we measure the modulus as before, and then increase the temperature to T_2, and so on. Schematic data from such an experiment are plotted in Figure 1-2. The temperature dependence of the modulus is so great that it must be plotted using a logarithmic scale. (This large variation in modulus presents experimental problems that will be treated subsequently.) The region between the vertical dashed lines represents normal-use temperatures and, consistent with the opening experiment, we find that in this range the plastic has a high modulus while the rubber has a relatively low modulus. Upon cooling, the modulus of the rubber rises markedly, by as much as four orders of magnitude, indicating that the rubber at lower temperatures behaves like a plastic. The nearly constant modulus for the rubber is evidenced at higher temperatures. This behavior is discussed in detail in Chapter 6. At low temperatures, the modulus–temperature behavior for the plastic is seen to be quite similar in shape to that of the rubber except that the large drop, called the glass transition, occurs at higher temperatures, resulting in the high modulus observed at room temperature. At ~100 °C it is clear that the modulus of the plastic is close to that of a rubber, agreeing with the results of one of the earlier "experiments" in this discussion. At yet higher temperatures, the
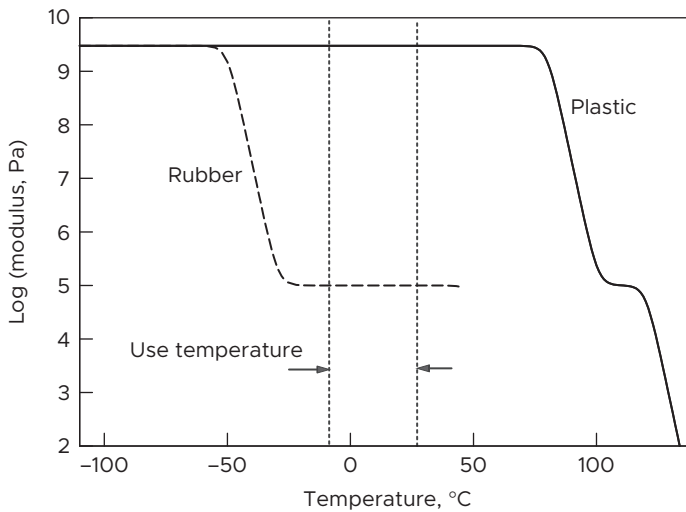
Figure 1-2. Schematics of the modulus vs. temperature behavior for a rubber and a plastic over a broad temperature range.

plastic's modulus drops once again; this is the region where the material can be easily molded.

One more type of deformational experiment remains to be discussed. Consider a material like pitch or tar, which is used as a roof coating and is applied at elevated temperatures. Our test is similar to the standard experiment done above, utilizing the same size sample at room temperature. First, we suspend the 1-kg weight from the sample and observe the small resultant extension; the modulus calculated according to equation (1-2) is high. However, if the sample is left suspended in this vertical position for several hours, the result is a considerable elongation of the sample. Now application of equation (1-2) gives a very low value for the modulus. Thus, the modulus measurement on the short timescale of a few seconds resulted in a high value while the modulus measurement on the longer time scale of hours resulted in a low modulus. This apparent discrepancy is accounted for by realizing that the modulus is a function of time as well as temperature; this has been found to be the case generally for polymeric materials. Strictly then, the measurements spoken of earlier in this chapter and depicted schematically in Figure 1-2 should have some time associated with each modulus value. (Time represents the duration between the application of the force and the measurement of the extension.) It is convenient to pick the same constant time for all measurements, so one might consider the constant time in Figure 1-2 to be 10 seconds.
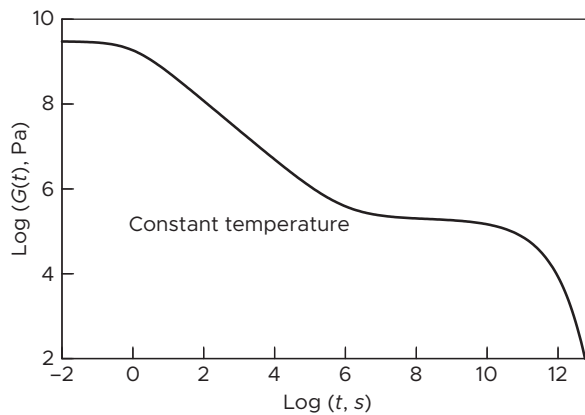
Figure 1-3. Schematic modulus–time* curve for a polymer at constant temperature.

As is evident from the above discussion, it should be possible to measure the behavior of a material as a function of time at constant temperature. A schematic modulus–time behavior is shown in Figure 1-3. The modulus is seen to fall from its initial high value by about three orders of magnitude to a modulus indicative of a rubber and, after evidencing a plateau, fall again. The ordinate here is log t; at the chosen temperature, an experiment lasting for 1 to 30 minutes would characterize this material as a plastic. However, in an experiment lasting 10^8 minutes (200 years), the material would "look like" an elastomer. Longer measurements would correspond to still softer materials. Methods for obtaining curves of the type shown in Figure 1-3 are discussed in Chapter 4, as well as methods of converting from modulus–time behavior to modulus–temperature behavior and vice versa.

Another experiment is often carried out in laboratories dealing with the physical properties of polymers. This is the determination of the temperature at which the material properties change from those of a plastic to those of a rubber. This temperature is known as the glass transition temperature and is a characteristic property of each substance. The glass transition temperature is given the symbol T_g. In Figure 1-2, for example, it is clear that at about 90 °C, the modulus of the plastic exhibits a steep decrease. Careful analysis of the curve in this region, however, indicates no abrupt change in modulus but

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* Books concerning the mechanical properties of polymers invariably have graphs that use log scales, and this one is no exception. The argument for the log function should be dimensionless, but such is not the custom. Thus, for example, log (G, Pa) should be interpreted as log [(G, Pa)/1 Pa].   In this volume, "ln" represents natural logarithm, whereas "log" stands for logarithm to base 10. The usual bracket hierarchy {[( )]} is used as needed.
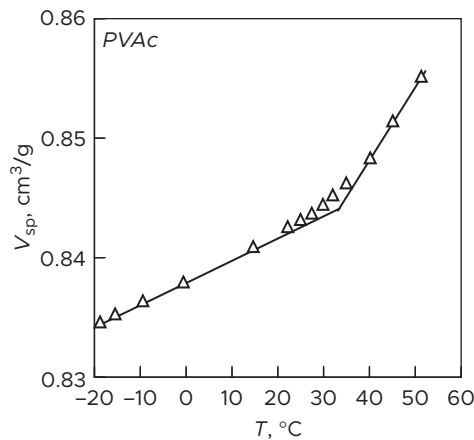
Figure 1-4. Specific volume data for poly(vinyl acetate) used to determine its T_g. [Kovacs (1958).[1] Copyright 1958, John Wiley & Sons.]

rather a smoothly varying change. From this experiment, it would seem that the glass transition occurs over a range of temperatures rather than at a single temperature. Experimentally, it has been found that the coefficient of expansion of a substance undergoes a more abrupt change in the region of the glass transition. The temperature at this change is often defined as T_g. An example of the data obtained in the determination of a glass transition temperature by this method is presented in Figure 1-4. The volume of a sample is measured as a function of temperature using a dilatometer, care being taken to change the temperature slowly and at an essentially constant rate. The temperature at which there is a change in slope (due to a discontinuity in the coefficient of expansion) is taken as T_g. In the example shown in Figure 1-4 for poly(vinyl acetate), T_g is about 34 °C. (See Problem 1-4.)

PROBLEMS

1-1. Snip a rubber band to form a single strand. Grip each end of this strand between the thumb and index finger of each hand, and apply an increasing force.

(a) Describe what your fingers are doing to maintain your grip as the strand is elongated. Draw a force balance on the gripped part of the sample at one end.

(b) Sketch a mechanical device that might be able to act similarly.

(c) Scribe *gauge marks* across the strand spaced about 4 cm apart. (Hint: a ball-point pen works well.) Carefully measure the actual length (L_0) between the marks with no tensile force applied. Now hold the strand against a scale and

stretch to the maximum extent, L. Calculate the extension ratio, $\lambda = L/L_0$. Hold the stretched position for about a minute and then release the sample. Measure quickly the distance between the gauge marks. Comment.

1-2. Sketch on Figure 1-2 the expected behavior if the elastomer were not crosslinked.

1-3. In Figure 1-3, the time scale extends to 10^{12} s. Calculate the equivalent value in years. With this value in mind, how might the researchers have gathered the long-time data? (Hint: see Chapter 4.)

1-4. (Challenging) As can be seen from Figure 1-4, the v_{sp} vs. T response is not exactly two intersecting straight lines. Instead, a curved section of data connects the two lines. The precision of the T_g depends quite strongly on the precisions of the two lines, which in turn depend on the number of data points used to determine their locations. Advantageous for finding the intersection would be a single function that fits the entire set of data while yielding straight lines well away from the curved section. Suggest how a suitable function might be found. (Hint: think in terms of the derivative of this function and how it should behave.)

1-5. Figure 1-4 is a plot of specific volume vs. temperature for poly(vinyl acetate) (PVAc), which is a common polymer. Being common, it is quite likely that the PVT (pressure–volume–temperature) response of PVAc has been recorded in the form of reducing parameters for an *equation of state*. In fact, reducing parameters for the Sanchez–Lacombe equation of state can be found in the *Polymer Handbook*.[2] Use the listed reducing parameters and the Sanchez–Lacombe equation of state to calculate the specific volume of PVAc as a function of temperature between 35 and 100 °C. Compare with the data in Figure 1-4. (Hint: the equation is nonlinear in v_{sp}, but linear in T, which suggests that T could be solved for at various values of v_{sp}. Discard the values that are outside the suggested temperature range.)

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www.rheology.org is the web site of The Society of Rheology. It gives current information on many aspects of the deformation and flow of materials.

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2. P. Zoller in *Polymer Handbook, 3rd Edition*, J. Brandrup and E. H. Immergut eds., Wiley, New York, 1989, p VI/475–VI/483.