

Long term performance of polymers

1.0 Introduction

Polymer materials exhibit time dependent behavior. The stress and strain induced when a load is applied are a function of time. In the most general form can be thought of as a 3 dimensional surface. The stress-strain-time relationship, or constitutive law, can be determined by loading a polymer specimen with constant stress (creep) or constant strain (stress relaxation or isometric). We can also construct isochronous curve by cross section of the surface with constant time levels as shown in Figure 1.

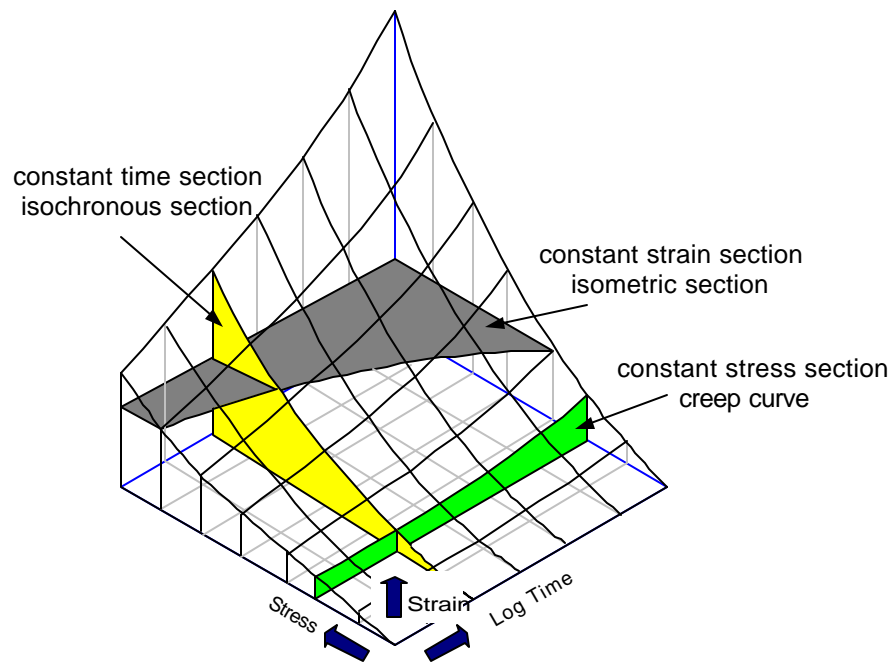


Figure 1. Constant stress-strain-time coordinates [1]

1.1 Creep, constant load

When a plastic material is subjected to a constant load, it deforms continuously (Figure 2). The initial strain is roughly predicted by its stress-strain modulus. The material will continue to deform slowly with time indefinitely or until rupture or yielding causes failure. The primary region is the early stage of loading when the creep rate decreases rapidly with time. Then it reaches a steady state which is called the secondary creep stage followed by a rapid increase (tertiary stage) and fracture. This phenomenon of deformation under load with time is called creep. Of course, this is an idealized curve. Some materials do not have secondary stage, while tertiary creep only occurs at high stresses and for ductile materials. [1] All plastics creep to a certain extent. The degree of creep depends on several factors, such as type of plastic, magnitude of load, temperature and time. The standard test method for creep characterization is ASTM D2990. In this

test procedure, the dimensional changes that occur during time under a constant static load are measured.

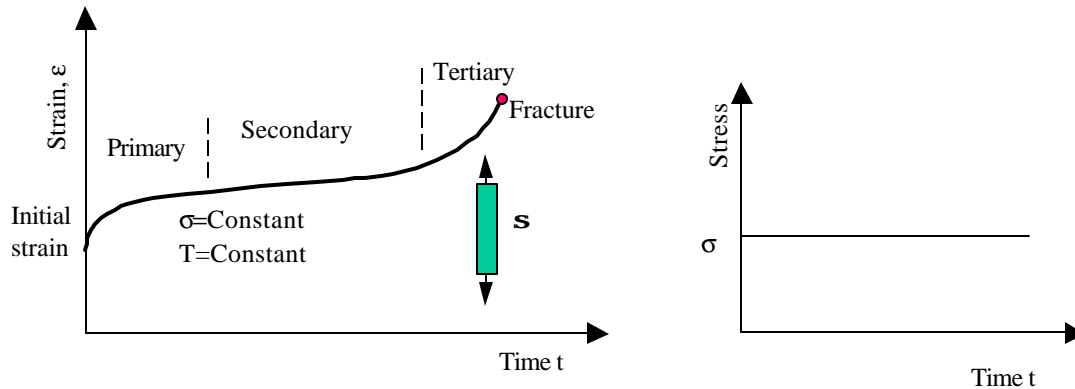


Figure 2. Creep curve for plastics, a constant load is applied [1]

If the applied load is released before the creep rupture occurs, an immediate elastic recovery equal to the elastic deformation, followed by a period of slow recovery is observed (Figure 3). The material in most cases does not recover to the original shape and a permanent deformation remains. The magnitude of the permanent deformation depends on length of time, amount of stress applied, and temperature.

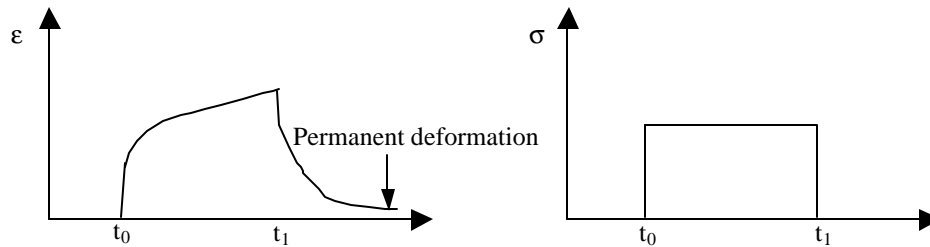


Figure 3. Creep curve with recovery. A constant load is applied at t_0 and removed at t_1

The creep rupture is basically similar to a creep test with the exception that it is continued until the material fails. Since higher loads are used, creep rates are higher and the material fails in a shorter time (usually terminated in 1000h [1]). This test is useful in establishing a safe envelope inside which a creep test can be conducted. The basic information obtained from the stress rupture test is the time to failure at a given stress. Based on this data, a safe stress can be determined below which it is safe to operate, given the time requirement of the end use application. The construction of the creep rupture envelope is shown in Figure 4. Test is conducted under constant stresses and the points of the onset of tertiary stage are connected to form the creep rupture envelope.

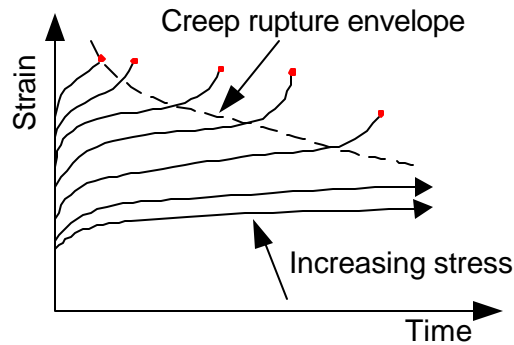


Figure 4. Creep rupture envelope [1]

1.2 Stress relaxation, constant strain

Stress relaxation is defined as a gradual decrease in stress with time under a constant deformation or strain. This behavior of polymer is studied by applying a constant deformation to the specimen and measuring the stress required to maintain that strain as a function of time.

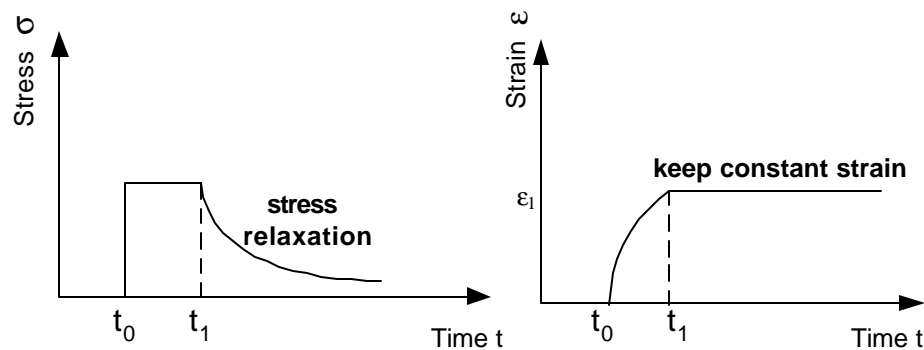


Figure 5. Stress relaxation of plastics

Stress relaxation test can be used for some practical applications. For example, low stress relaxation is desired for threaded bottle closures. The stress data obtained from stress relaxation test can be used to calculate transient modulus for plastics design by simply dividing the stress at a particular time by the applied strain. The 3 dimensional stress-strain-time relationship can also be constructed by stress strain relaxation test as shown in Figure 1. However, stress relaxation test is more difficult to perform than creep test and has limited practical applications. As a result, stress relaxation test D2991 is dropped by ASTM in 1992.

1.3 Design with plastics

Design with plastics can be divided into two categories, design for strength and design for stiffness. The strength of a component is limited by the yield strength and

rupture resistance of the material from which it is made. As shown in Figure 4, a creep rupture envelope can be obtained from creep test. For a expected life time, the maximum stress allowed (σ_4) can be decided from the creep rupture envelope line. Design for stiffness with creep curves proceeds by establishing the maximum strain acceptable ϵ_{\max} , thereby establishing a horizontal line on the creep diagram correspondingly. The expected lifetime t_L of the part is also determined, and the maximum stress permissible is found on the creep curve at the intersection of these two lines.

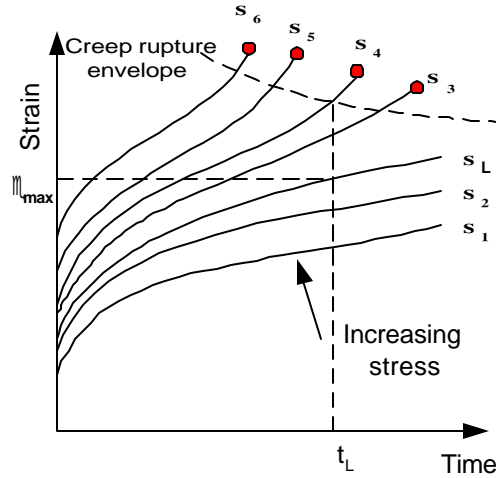


Figure 5. Design criteria by creep curves

As shown in Figure 5, many combinations of σ and time will yield this maximum strain. For a desired lifetime t_L , however, there is one maximum level σ_L which satisfies the maximum strain. Design basis selection depends on the specific application. Usually, strain or dimension requirement is more critical, and design for stiffness is favored in this case. If the dimension precision of the component under discussion is not so important compared as strength, design for strength is then used accordingly. For complicated structures, both can be used for design criteria to ensure successful material performance during service time.

2.0 Objective

Since the pressure loads of the heat exchanger are nearly constant over time, creep behavior, i.e. strain under constant load, is the main consideration for our structure design. Our goal is to get stress-strain-time relationship (constitutive law) and creep rupture data for our design basis. Since the service time is very long, 10 years, property prediction methods should be used for obtaining constitutive law. Time temperature superposition is one of the most important methods to predict long term properties using short duration tests. By creep test data in one or two months, creep behavior after some years can be predicted with acceptable accuracy. There are several test methods for evaluating long term properties of materials, including creep test ASTM-D2990, stress relaxation test D2991, hydrostatic test D1598, D2837, and DMA (Dynamic Mechanical Analysis). [1-6] In the following sections, constitutive law for creep behavior is

described, methods for superposition of time-temperature data are presented and test standards evaluating creep behavior are summarized.

3.0 Linear and nonlinear viscoelasticity

The time dependent material behavior is often referred to as *viscoelasticity*. If a constant load σ_1 is applied to a viscoelastic specimen, the time dependent strain is recorded as ϵ_1 as shown in Figure 7(a). After some period of time, the load is removed. Suppose the specimen is allowed to recover and a larger stress σ_2 is applied. The time dependence of the strain ϵ_2 is shown in Figure 7(b).

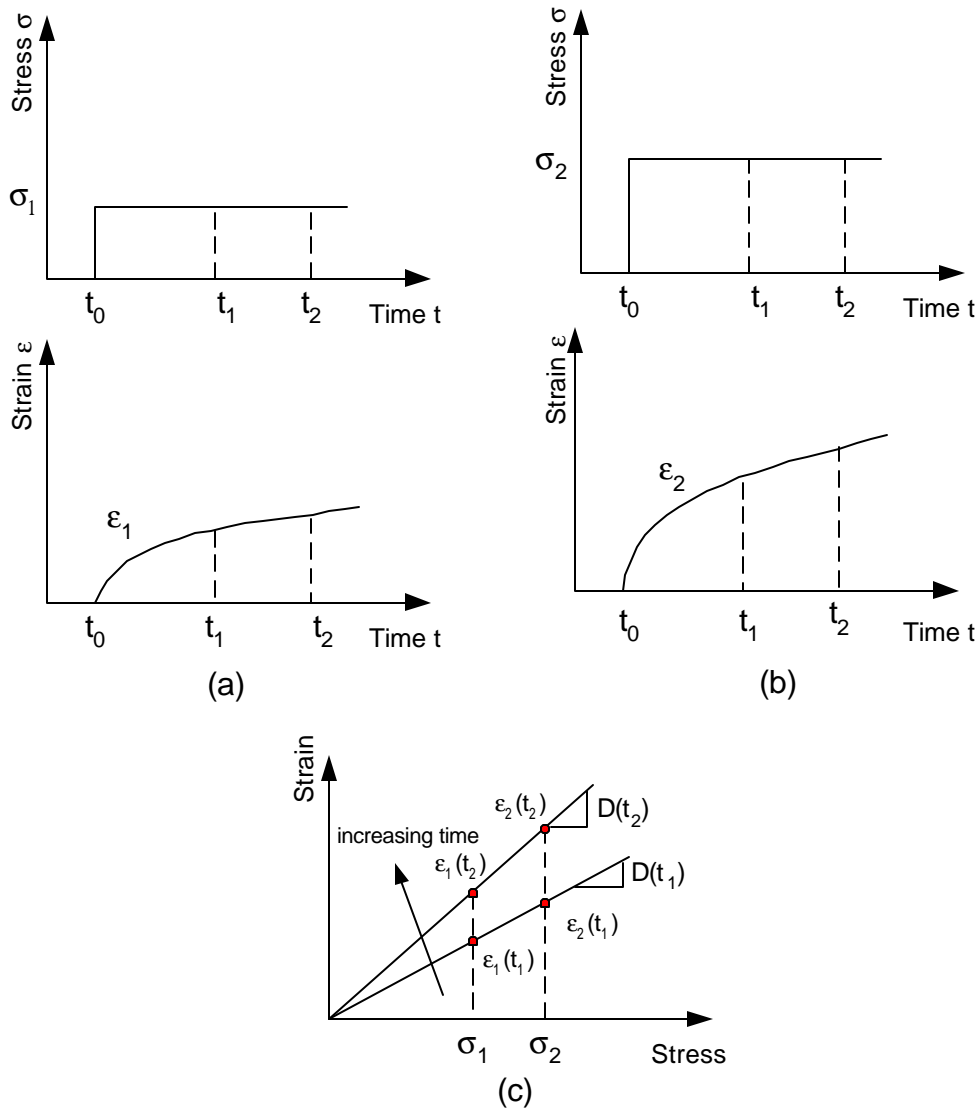


Figure 7. Linear viscoelastic creep: (a) constant stress σ_1 applied at time t_0 leads to time dependent strain $\epsilon_1(t)$; (b) a higher stress applied at t_0 leads to time dependent strain $\epsilon_2(t)$; (c) from (a) and (b) the strains at t_1 and t_2 are linear in the stress [7]

If at a particular time t_1 and t_2 after loading, ϵ_1 and ϵ_2 are linear with the magnitude of correspondent stresses, σ_1 and σ_2 , the stress strain relationship can be given by

$$\frac{\epsilon_1(t_1)}{\sigma_1(t_1)} = \frac{\epsilon_2(t_1)}{\sigma_2(t_1)}, \frac{\epsilon_1(t_2)}{\sigma_1(t_2)} = \frac{\epsilon_2(t_2)}{\sigma_2(t_2)} \quad (3)$$

Thus, if at an arbitrary time t , the strains at the two stresses can be expressed as

$$\frac{\epsilon_1(t)}{\sigma_1(t)} = \frac{\epsilon_2(t)}{\sigma_2(t)} \quad (4)$$

The strains in the two experiments are proportional to the imposed stresses. In general, for stress σ , the creep compliance $D(t)$ can be given as the ratio of strain to stress at a certain time.

$$D(t) = \epsilon(t) / \sigma \quad (5)$$

This property is often characterized as *linear viscoelasticity*. In the linear range, the compliance is independent of stress, which means that the compliance is the same whether stresses used in the creep test are σ_1, σ_2 or other stress levels. Figure 8(c). The strain range in which a specimen is linear viscoelastic can be determined by a creep test. A transition from linear to nonlinear viscoelasticity is shown in Figure 9.

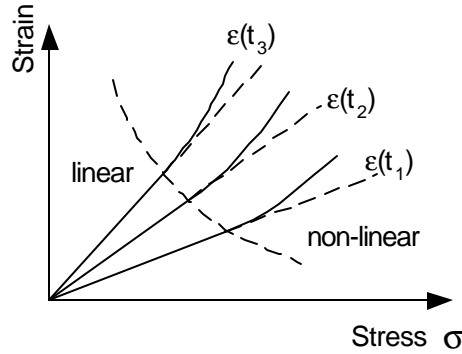


Figure 9. Linear-nonlinear transition of stress strain relationship with respect to different time levels [7]

(Isochronous creep curve, data are taken from creep test at different stresses)

However, polymers generally exhibit linear viscoelastic property at low stresses such that the corresponding strain is below $\sim 0.5 \times 10^{-2}$. At higher stress levels, the material will assume *nonlinear viscoelastic* behaviors which will not obey the linear relation between stress and strain described by equation (4).

Since nonlinear behavior is very important to determine material behavior at moderate or higher stress levels, some models have been suggested for different kind of polymers. [8-15]

4.0 Creep models:

Although creep data are most accurately presented as the plot of strain vs. time for various stresses and temperatures, many theoretical and empirical relations have been suggested for the dependence of creep strain on stress and temperature for plastics.

A simple model is a Kelvin (or Voigt) unit [16], which consists of a Hookean spring and a Newtonian dashpot as show in Figure 9. The spring models the elastic response while the dashpot models the viscous (or time dependent) response to load.

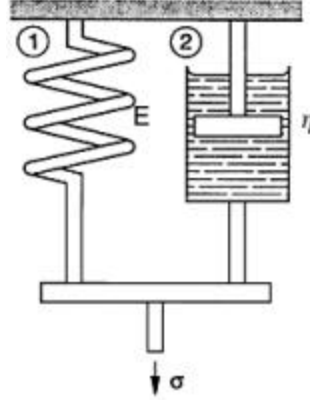


Figure 9. Schematic diagram of Kelvin model [16]

The governing equation for Kelvin model is:

$$\mathbf{s} = E\mathbf{e} + \mathbf{h}\dot{\mathbf{e}}, \quad (1)$$

E and η are the viscosity and Young's modulus respectively. Using the above equation, the strain in a creep test (constant stress) in the Kelvin model can be solved for as

$$\mathbf{e}(t) = \frac{\mathbf{s}_0}{E}(1 - e^{-t/\tau}), \quad \tau = \eta/E, \quad (2)$$

where τ is called the relaxation time at which the strain is 63.2% of \mathbf{s}_0/E .

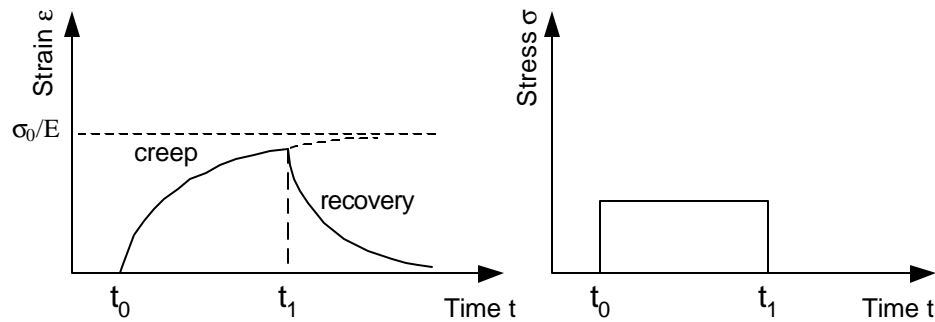


Figure 7. Creep and creep recovery response of Kelvin model

Figure 7 shows the creep and recovery curve of Kelvin model. This is a two-element-model. A large number of spring/dashpot components are usually needed to

reasonably describe creep behavior over decades of time. [1] These models can be used to construct constitutive law. And the unknown material constants, i.e. E and η can be curve fit from experimental data. Since different plastics show different creep properties, many models, which describe the relationship between stress, strain, time and temperature, have been suggested. [17-24]

5.0 Superposition Principles

There are two superposition principles, which are important in predicting creep behavior of plastic materials under various test conditions. The first of these is the *Boltzmann Superposition Principle*, which describes the response of a material to different loading histories. The second is the *Time Temperature Superposition Principle* or the WLF equation, which describes the equivalence of time and temperature.

The Boltzmann superposition principle states that the response of a material to a given load is independent of the response of the material to any load, which is already on the material. The deformation of a specimen is directly proportional to the applied stress, when all deformations are compared to equivalent times. It is only valid in linear viscoelastic region. For the case of creep, the total strain may be expressed by

$$\mathbf{e}(t) = D(t - \mathbf{t}_1)\mathbf{s}_1 + D(t - \mathbf{t}_2)(\mathbf{s}_2 - \mathbf{s}_1) + \dots + D(t - \mathbf{t}_i)(\mathbf{s}_i - \mathbf{s}_{i-1}) \quad (6)$$

or

$$\mathbf{e}(t) = \int_{-\infty}^t D(t - \mathbf{t})d\mathbf{s}(t) \quad (7)$$

where $D(t) = 1/E(t)$ is the compliance function, which is a characteristic of the polymer at a given temperature and initial stress. Figure 9 shows the creep curve by Boltzmann superposition principle.

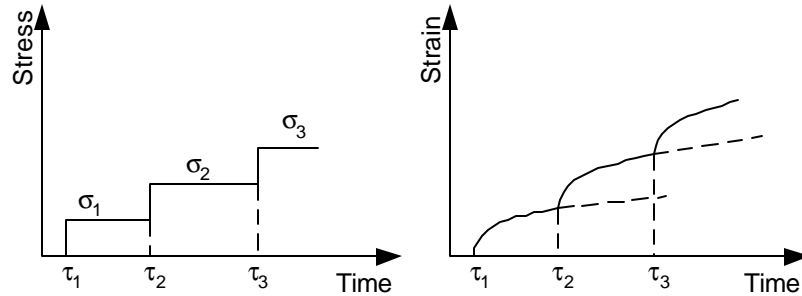


Figure 9. Boltzmann superposition principle

At time τ_1 , stress σ_1 is applied and the strain induced can be given by

$$\mathbf{e}_1(t) = \mathbf{s}_1 D(t) \quad (8)$$

According to linear viscoelasticity, the compliance $D(t)$ is independent of stress, i.e. $D(t)$ is the same for all stresses at a particular time. If stress increment $\sigma_2 - \sigma_1$ is applied at time τ_2 and the strain increase due to stress increment $\sigma_2 - \sigma_1$ is

$$\mathbf{e}_2(t) = D(t - \mathbf{t}_2)(\mathbf{s}_2 - \mathbf{s}_1) \quad (9)$$

Likewise, the strain increase due to $\sigma_3 - \sigma_2$ can be given by

$$\mathbf{e}_3(t) = D(t - \mathbf{t}_3)(\mathbf{s}_3 - \mathbf{s}_2) \quad (10)$$

Further strains induced by stress increment which can be positive or negative, are added to give equation (6) or (7).

The time-temperature WLF superposition principle describes the equivalence of time and temperature. This superposition is used to describe temperature dependent behavior in stress relaxation. Figure 10 shows relaxation modulus curves for time temperature superposition. Relaxation curves made at different temperatures are superposed by horizontal shifts along a logarithmic time scale to give a single master curve covering a large range of times.

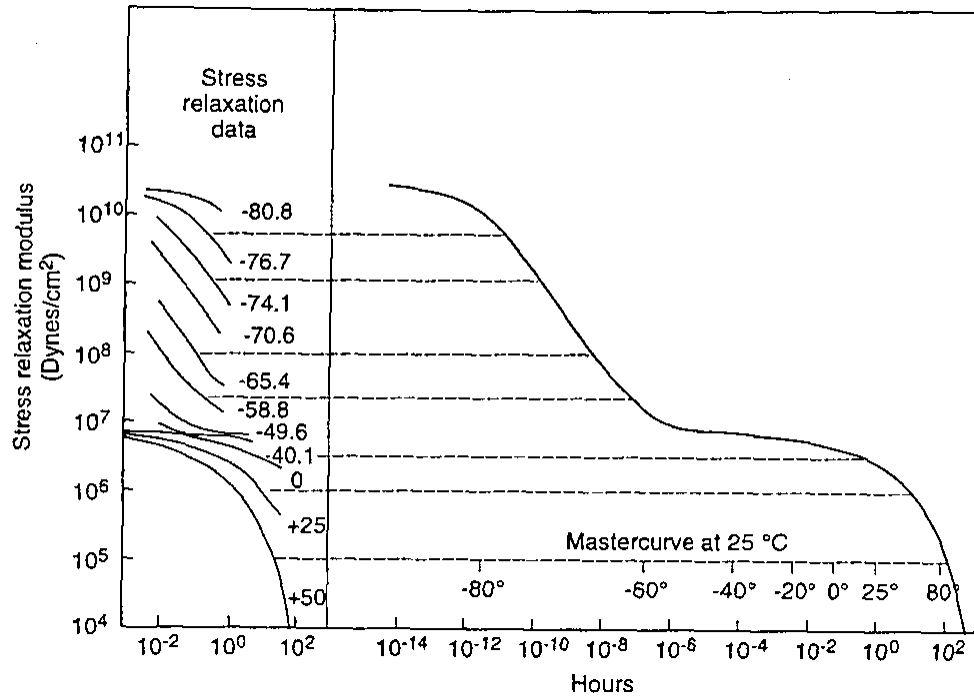


Figure 10. Relaxation modulus curves for polyisobutylene and corresponding master curve at 25 °C [24]

The shifting factor can be expressed as

$$\log a_T = -\frac{C_1(T - T_{ref})}{C_2 + (T - T_{ref})} \quad (11)$$

which is called WLF equation. $\log a_T$ is the amount of horizontal shift to be applied to a particular data. If the reference temperature is chosen as glass transition temperature, $C_1 = 17.44\text{K}$ and $C_2 = 51.6\text{K}$ for equation (11) fit well for a wide variety of polymers.

Similar method can also be used for creep behavior. Experimental curves are first obtained at a series of temperatures over a specific time period, and the values of compliance are plotted. Then the curve at some temperature is chosen as reference. The curves are then shifted one by one along the log times scale until they superimpose. Curves above the reference temperature are shifted to the right, and those below are shifted to the left. This method is very important because it can be used to predict long

term properties with short test duration. For example, figure 11 shows the creep compliance of polyisoprene at different temperatures and master curve obtained (several master curves are listed in figure 11(b) for comparison between different molecular weight of polyisoprene)

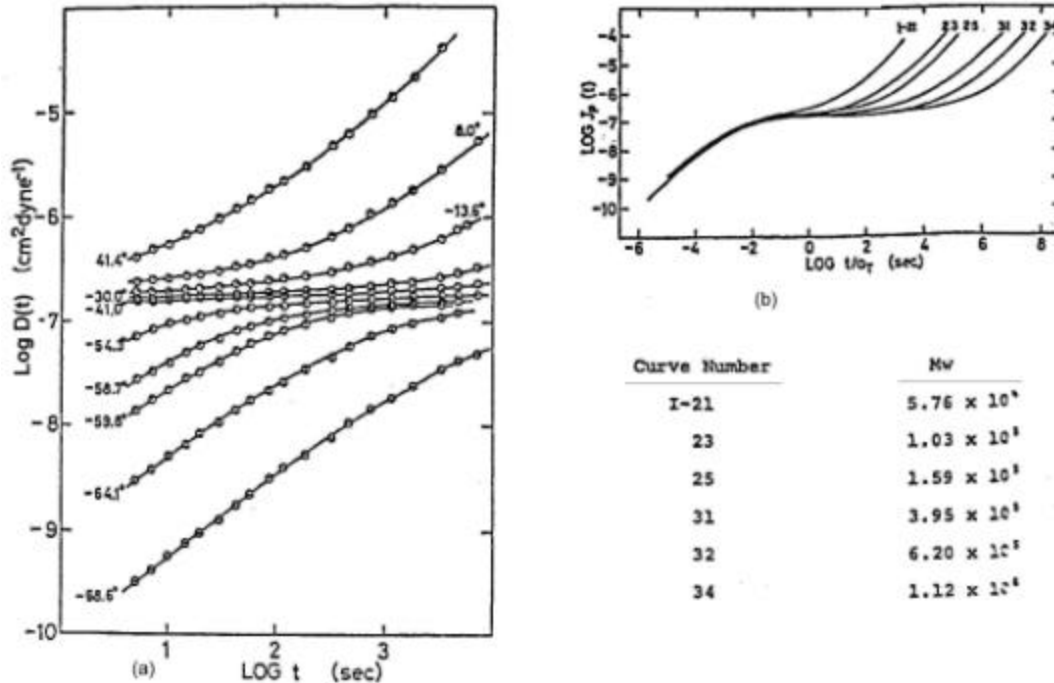


Figure 11. (a) Creep compliance of polyisoprene at different temperatures. Data for molecular weight 1.12×10^6 ; (b) Master curves for creep compliance of Polyisoprene with different molecular weight at reference temperature of -30°C [26]

Our problem is expected to use nonlinear viscoelastic model. Material behavior can not be predicted with simple linear model. Time temperature superposition has to be used to shorten test duration.

6.0 Test summary

The main considerations for test selection is test duration, creep rupture and constitutive law, working with film specimen and water immersion or humidity control. Currently, available tests include standard creep test ASTM-D2990, stress relaxation test ASTM-D2991, DMA frequency scan, hydrostatic test ASTM-D1598, D2837.

6.1 ASTM D2990 test terminology and data presentation

D2990 consists of measuring the extension or compression as a function of time and time-to-rupture, or failure of a specimen subject to constant tensile or compressive load under specified environmental conditions.

Creep modulus—the ratio of initial applied stress to creep strain

Creep strain—the total strain, at any given time, produced by the applied stress during a creep test

Deformation—a change in shape, size or position of a test specimen as a result of compression, deflection or extension

Compression—in a compressive creep test, the decrease in length produced in the gage length of a test specimen

Deflection—in a flexural creep test, the change in mid-span position of a test specimen

Extension—in a tensile creep test, the increase in length produced in the gage length of a test specimen

Stress—for tensile or compressive creep, the ratio of the applied load to the initial cross-section area.

Creep curves can be presented in a comprehensive way, in constant stress-strain-time coordinates, as shown in Figure 1. From a set of creep curves at various stresses it is possible to construct isochronous stress-strain curves by drawing lines at fixed times (0, 1, 10, 100h). The resulting curves are the isochronous stress-strain plots.

The isometric plots of the creep data are generated by taking a constant strain section of the creep curves and by plotting the stress as a function of time. Figure 1 shows the constant stress-strain-time coordinates.