

Chapter 2

Background to Polymers and Composites

2.1 Fibers

In view of their manufacturing process, such as drawing and extrusion for glass fibers and the sheet-like atomic structure of carbon and graphite fibers, these reinforcements are essentially transversely anisotropic about their longitudinal orientation (Hull 1981), in which direction they possess high stiffness and strength. In view of their small diameter, typically 8 μm , it has been possible to determine their longitudinal modulus only, while no direct data are available about their in-plane stiffnesses.

Typical values of experimental data are listed in Table 2.1

It is common practice to subject fibers to two kinds of treatments. The first one, called “sizing” aims at the polishing and smoothing of nicks and roughnesses over the fibers’ surfaces. The second treatment concerns the introduction of an interphase, usually a fraction of a micron thick, whose purpose is to enhance the chemical/physical binding between the polymeric binder and the embedded fibers.

2.2 Polymers

2.2.1 Material Aspects

Polymers are a large class of materials consisting of long chain molecular structures, up to 10^6 in molecular weights, where the basic component of these chains is a monomer. Consider for example the styrene monomer, where two carbon molecules are attached to each other by a double bond. Upon introducing a free radical catalyst, the double bond is opened, releasing a free electron and rearranging the bonding configuration as sketched below (Fig. 2.1).

Table 2.1 Longitudinal properties of some fibers

Fiber	E glass	S glass	Carbon AS4	Carbon T300
Longitudinal stiffness (GPa)	72	85	235	228
Longitudinal strength (MPa)	3,450	4,500	3,750	3,000
Longitudinal elongation to failure (%)	4.8	5.3	1.6	1.3
Density (g/cm ³)	2.55	2.5	1.8	1.75

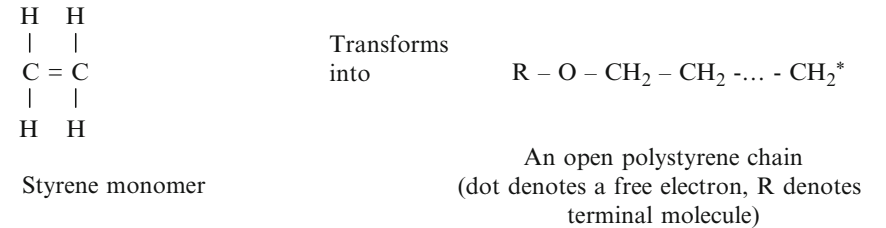


Fig. 2.1 The polymerization of polystyrene

The chain is terminated by linking the last CH₂ component to another free radical. The above scheme represents one form of a polymerization process.

In view of the aforementioned imperfections in the cross-linking process the glassy state still contains an overall amount of free volume $V_f \sim 0.025 - 0.03$, which is distributed throughout the polymer (Deng and Jean 1993; Dammert et al. 1999; Yampolskii 2007). It has been suggested that these micro volumes are located about chain ends.

A typical record of volumetric increase due to absorption of moist air is given in Fig. 2.2, where the gap between the data and the theoretical line accounts for water molecules that occupy the free volume.

It was noted that the glassy phase is not in a state of thermodynamic equilibrium and chain motions, though inhibited, still persist. These motions are not limited to the side groups alone, but involve several mechanisms within the backbone structure as well (Aklonis and MacKnight 1983). The above fluctuations are further arrested at a temperature ranging about $T_\beta < T_g$ where the polymer undergoes a secondary transition (The β transition).

Separately from the effects of temperature, the free volume V_f tends to diminish spontaneously with time toward a more compacted configuration. In that configuration chain mobility is further inhibited and creep is diminished. This tendency, called “aging,” is associated with embrittlement and reduction in polymer fracture toughness (Struik 1978).

The activity a_i of the i th component in a vapor mixture is defined by the ratio $a_i = P_i/P_T$, where P_i is its partial vapor pressure and P_T is the total pressure of the vapor mixture. For humid air, a_i of the water vapor is akin to relative humidity (RH) (Bond and Smith 2006). Note that RH is related to vapor pressure in tabulated form. The activity a is a measurable quantity and theoretically predictable (Flory 1953).

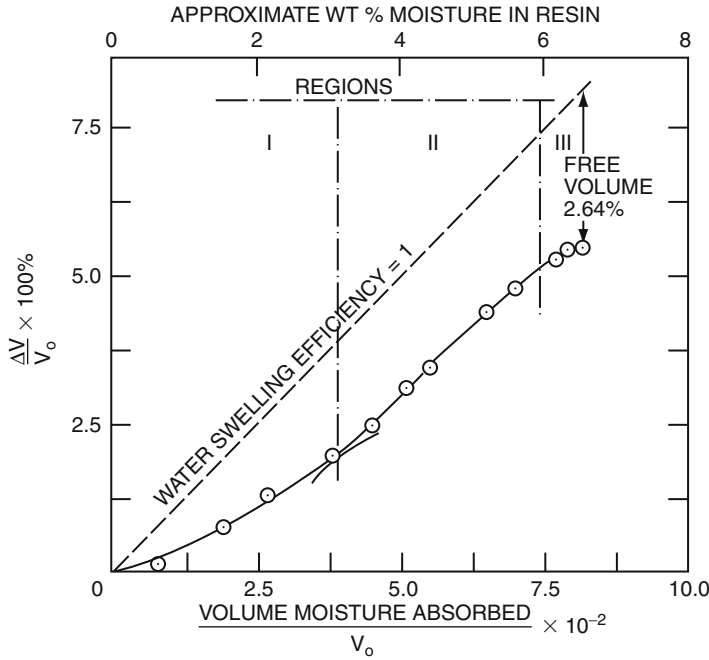


Fig. 2.2 Swelling behavior of Hercules 3501 epoxy resin immersed in water at 74°C. Swelling efficiency = 1 if the volumetric strain of the epoxy matches the volume of absorbed water. With kind permission from Springer Science + Business Media: Adamson (1980) figure 2

2.2.2 Mechanics Aspects of Glassy Polymers

In view of the presence of the free volume V_f , the macro-molecular polymeric chains still retain a certain degree of freedom of motion that allows for some configurational changes under loads. These changes may be viewed as occurring against viscous resistance and are therefore time dependent.

Consequently, the strain response to the application of, say, a unit step load is related by a time dependent creep compliance $D(t)$. Inversely, the stress associated with the application of unit strain is given by the relaxation modulus $E(t)$. These are shown schematically in Fig. 2.3.

When excited by thermal agitation, both creep and recovery quicken with temperature. In many cases, thermal effects are focused on time alone and can be accounted for by means of a temperature dependent shift factor $a_T(T)$, thereby $D(t) \rightarrow D(\xi)$, where $\xi = \xi(T) = t/a_T(T)$ and analogously for $E(t)$. This states that the time-dependent response at all temperatures is essentially the same,

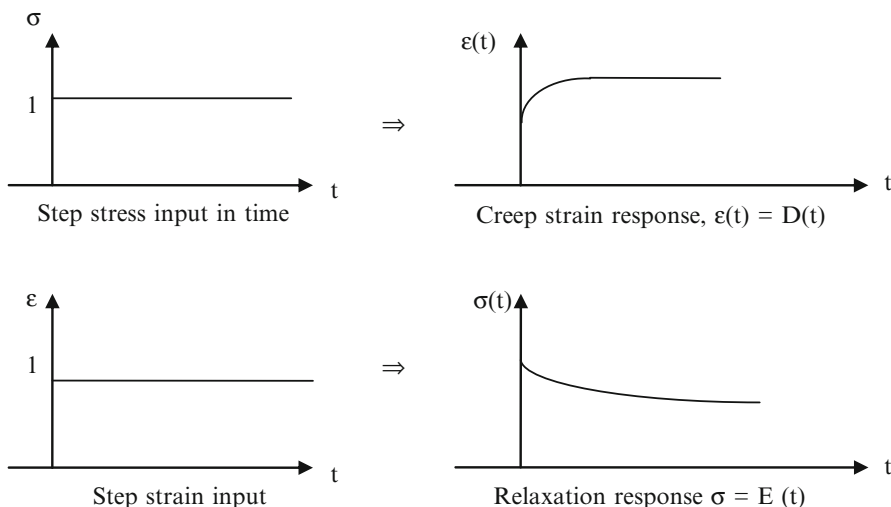


Fig. 2.3 Schematics of creep and relaxation viscoelastic response

except that the gears on the clock are to be adjusted with temperature to cause it to run faster or slower.¹

Viscoelastic response exhibits reversal effects that differ qualitatively from elastic behavior. Consider, for instance, the following cases (Fig. 2.4).

2.3 Effects of Fluids: Fundamental Aspects

When polymers are exposed to ambient fluids or vapor, the highly mobile and generally small molecules of the ambient phase penetrate the polymer by means of what may be conceived as a random walk process. This process proceeds until the attainment of equilibrium. Equilibrium may be formally attributed to a balance in internal and ambient chemical potentials in the absence of flux.² Alternately, it is possible to associate equilibrium with the state where fluid molecules became

¹ It should be noted that $a_T(T)$ is obtained from isothermal creep data, plotted against $\log t$ and collected over a wide temperature range. These isothermal plots are then coalesced to form a “master curve” by shifting parallel to the horizontal $\log t$ axis. This procedure is not error free. To verify its validity, it is necessary to conduct transient temperature tests and compare the resulting data with computational predictions. For temperatures sufficiently below T_g the shift factor function $a_T(T)$ is given by the Arrhenius expression of the form $a_T(T) = A \exp(-B/T)$.

² The chemical potential μ , which is conjugate to the fluid concentration m , is a measure of the energy required to increase the concentration while holding other thermodynamic variables constant. Originally introduced by Gibbs, it was defined by means of the Gibbs free energy function G , i.e., $\mu = \partial G / \partial m$. But other forms of energy can be used.

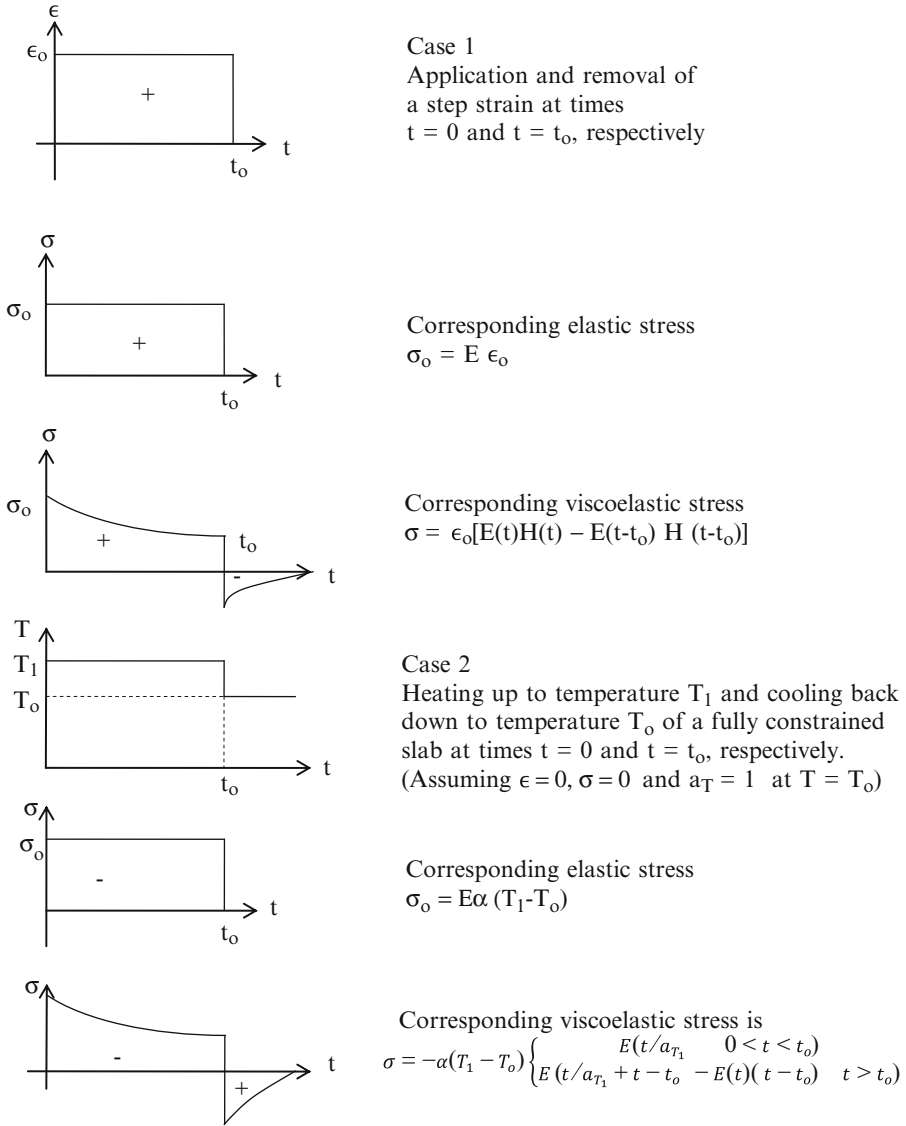


Fig. 2.4 Comparative elastic and viscoelastic responses to strain and stress inputs. Sign reversals occur in the viscoelastic case

attached to all available chemical sites within the polymeric chains and filled to capacity all the accessible free volume within the polymer.

Regarding sea water, this fluid consists of about 3.5% of chemical elements, of which 30% are sodium and 55% chloride. Most of these elements are nearly entirely

ionized. Both freezing temperature and density vary with salinity (Neumann and Pierson 1966).

The ingress of water is associated with increased separation between the molecular chains, thereby inducing expansional strains. This phenomenon, called plasticization, enhances chain mobility in a manner akin to that of rising temperature. It was therefore possible to associate the creep and relaxations of “wet” polymers with concentration dependent a “hygral” shift factor $a_H(m)$ analogous to $a_T(T)$. Typically, the plasticization process is thermodynamically reversible.

It is worth noting that fluids suppress the level of the dry T_g . This reduction is commonly related by (McKague et al. 1978)

$$T_{gw} = \frac{\alpha_p V_p T_{gp} + \alpha_m V_m T_{gm}}{\alpha_p V_p + \alpha_m V_m},$$

Where, T_{gw} is T_g of the wet polymer and α , V , T_g denote coefficient of thermal expansion, volume fraction, and glass transition temperature, respectively. Subscripts p and m refer, in turn, to the polymer and fluid.

It was noted that in some circumstances, T_g has a weak inverse dependence on temperature as well (Zhou and Lucas 1999). The time-dependent aging of polymers, caused by the spontaneous collapse of free volume, is associated with material embrittlement and a decrease in T_g .

2.4 Fiber Reinforced Composites: Basic Considerations

The basic elements of composite materials are the uni-directionally reinforced ply or strand. Plies are thin plates (or shells), with a typical thickness $h = 0.125$ mm, containing randomly arrayed fibers running parallel to each other, all embedded in a polymeric resin. Typical values of the fiber volume fraction \bar{V}_f range between 40 and 60%. Strands are essentially uni-directional elements, with varying values of thickness and width, both of which are much shorter than the strand’s length, and a similar range of \bar{V}_f .

Each of the above elements can be viewed as being transversely isotropic about the common fiber direction, say x_1 , thus characterized by five material constants, say E_{11} , E_{22} , G_{23} , G_{12} , and ν_{12} , where $x_2 - x_3$ is the plane of isotropy and ν_{12} is the Poisson’s ratio that expresses the strain $-\epsilon_2/\epsilon_1$, due to σ_1 . For in-plane problems, say within the $x_1 - x_2$ plane, G_{23} is globally irrelevant. Similarly, only two thermal and two hydral expansional coefficients are of interest, namely α_1 , $\alpha_2 (= \alpha_3)$ and β_1 , $\beta_2 (= \beta_3)$, respectively.

Typical values of material properties are given in Table 2.2 for several fiber reinforced polymeric composites

Table 2.1 suggests that the effect of % volumetric water gain is approximately equivalent to that of temperature excursion exceeding 100°C.

Table 2.2 Material properties of several uni-directionally reinforced composites

Property	E-glass/ epoxy	S-glass/ epoxy	Carbon/epoxy A54/3501-6	Carbon/epoxy IM6/SC 1081
V_f (%)	55	50	63	65
Density ρ (g/cm ³)	2.1	2	1.58	1.6
E_{11} (GPa)	3.1	43	142	177
E_{22} (GPa)	8.6	8.9	10.3	10.8
G_{12} (GPa)	3.8	4.5	7.2	7.6
ν_{12}	0.28	0.27	0.27	0.27
α_1 (10 ⁻⁶ /°C)	7	5	-0.9	-0.3
α_2 (10 ⁻⁶ /°C)	21	26	27	30
β_1 (%)	0	0	0.01	0
β_2 (%)	0.3	0.3	0.3	0.3

β_1 and β_2 are per 1% of volume of water uptake at saturation, i.e., composite added weight gain/composite dry weight

Plies and strands are exceedingly weak in their transverse, in-plane directions. Strength enhancement can be achieved by strand weaving or through across-the-thickness stitching. In addition, considerations of cost and versatility in manufacturing suggest that swirl mat and randomly oriented chopped strand mats may have potential advantages.

Uni-directionally reinforced strands are the essential components in the manufacture of woven composites. In similar manner, the uni-directional reinforced plies are the basic building blocks of laminates. The latter contain a lay-up of several, multi-oriented plies and are formed by the application of a prescribed regime of pressure and temperature within an autoclave or a vacuum press.

A state of plane stress is considered to hold for the in-plane response of thin plates. Consequently, the stress-strain relations for a uni-directionally reinforced ply, with fibers parallel to the x_1 direction, employing truncated notation, read

$$\begin{aligned}\sigma_1 &= Q_{11}\varepsilon_1 + Q_{12}\varepsilon_2, \\ \sigma_2 &= Q_{12}\varepsilon_1 + Q_{22}\varepsilon_2, \\ \sigma_6 &= Q_{66}\varepsilon_6.\end{aligned}\tag{2.1}$$

Where, $Q_{11} = \bar{m}E_{11}$, $Q_{22} = \bar{m}E_{22}$, $Q_{12} = \bar{m}\nu_{12}E_{22} = \bar{m}\nu_{21}E_{11}$, $Q_{66} = G_{12}$, where, $\bar{m} = 1/(1 - \nu_{12}\nu_{21})$ with $\nu_{21} = \nu_{12}(E_{22}/E_{11})$ typically, $1.004 < \bar{m} < 1.015$.

Laminate theory, which derives from expressions for the off-axis stiffnesses when plies are oriented at various angles about common laminate axes, say x and y , is well developed and available in many textbooks.

When subjected to ambient temperature and/or moisture, the individual multi-oriented plies within a laminate cannot expand freely and impose mutual constraints on each other by means of internal residual stresses.

Consider, for example, a symmetric, cross-ply laminate $[90^\circ/0^\circ/0^\circ/90^\circ]$ or, in laminate jargon $[90^\circ/0^\circ]_s$. Let all plies be saturated with moisture (or fluid) at a uniform concentration m .

For the 0° plies, expressions (2.1) read

$$\begin{aligned}\sigma_1^0 &= Q_{11}(\varepsilon_1 - \beta_1 m) + Q_{12}(\varepsilon_2 - \beta_2 m), \\ \sigma_2^0 &= Q_{12}(\varepsilon_1 - \beta_1 m) + Q_{22}(\varepsilon_2 - \beta_2 m).\end{aligned}\quad (2.2)$$

While for the 90° plies one has

$$\begin{aligned}\sigma_1^{90} &= Q_{12}(\varepsilon_2 - \beta_1 m) + Q_{22}(\varepsilon_1 - \beta_2 m), \\ \sigma_2^{90} &= Q_{11}(\varepsilon_2 - \beta_1 m) + Q_{12}(\varepsilon_1 - \beta_2 m).\end{aligned}\quad (2.3)$$

In the absence of applied stress $\sigma_1^0 + \sigma_1^{90} = 0$ and $\sigma_2^0 + \sigma_2^{90} = 0$. Thereby, it follows that

$$\begin{aligned}(Q_{11} + Q_{22})\varepsilon_1 + 2Q_{12}\varepsilon_2 &= A(Q; \beta)m, \\ 2Q_{12}\varepsilon_1 + (Q_{11} + Q_{22})\varepsilon_2 &= A(Q; \beta)m,\end{aligned}$$

Where, $A(Q; \beta) = (Q_{11} + Q_{12})\beta_1 + (Q_{12} + Q_{22})\beta_2$.

Thus

$$\varepsilon_1 = \varepsilon_2 = \beta^+ m, \quad (2.4)$$

Where

$$\beta^+ = A(Q; \beta)/(Q_{11} + Q_{22} + 2Q_{12}). \quad (2.5)$$

For most composites $\beta_1 \approx 0$ and $Q_{11} \gg Q_{22} + 2Q_{12}$, thus approximately

$$\beta^+ \sim \beta_2(Q_{12} + Q_{22})/Q_{11}, \text{ i.e., } 0(\beta_2/10). \quad (2.6)$$

A similar result holds for the case of thermal expansion.

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