

# CHAPTER I

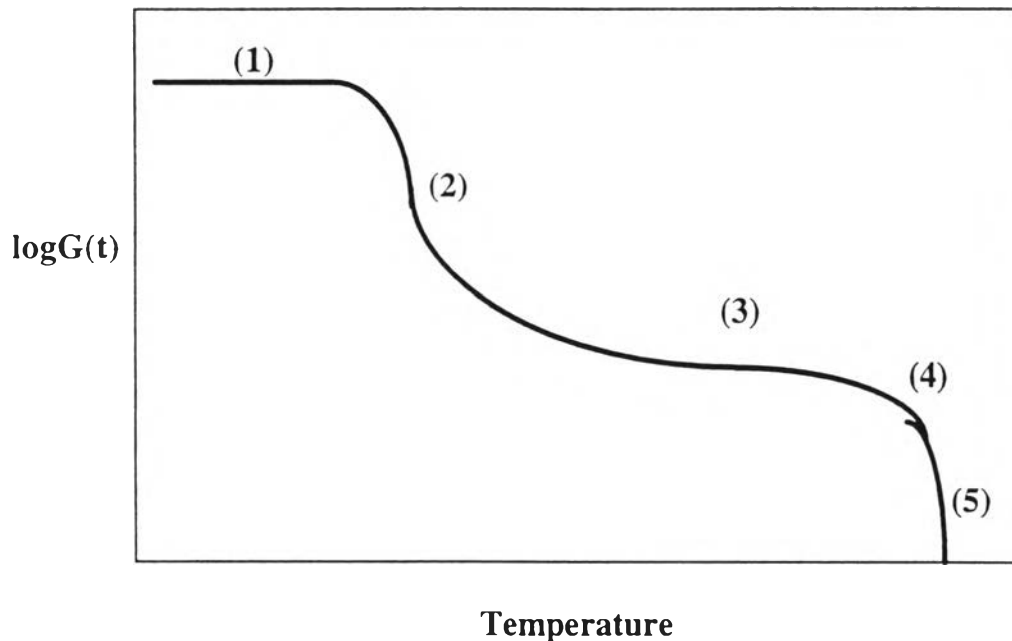
## INTRODUCTION

The properties of two types of ideal materials, the elastic solid and viscous fluid, are discussed in many text-books [Ferry 1980]. The elastic solid has a definite shape and is deformed by external forces into a new equilibrium shape. When these external forces are removed, the solid can reverse exactly to its original shape. The solid restores energy obtained from the work done by the external forces during deformation. This energy is then available to store the body to its original shape when these forces are removed. A viscous liquid, on the other hand, has no finite shape and flow irreversibly under the action of external force without storing energy. Real materials have properties which are intermediate between those of an elastic solid and a viscous liquid. The real materials are called viscoelastic materials. One of the most well known example is polymer materials.

### 1.1 Viscoelastic Behaviors

#### 1.1.1 The Temperature Dependence

The viscoelastic properties of polymer system can be affected remarkably by temperature or pressure changes. The five regions of viscoelastic behavior are briefly discussed to provide a broader picture of the temperature dependence of polymer properties [Sperling 1993].



**Figure 1.1** Schematic modulus-temperature curve for polymer materials.

#### *1.1.1.1 The glassy region*

Some polymers are glassy and brittle. Young's modulus for glassy polymers just below glass transition temperature is nearly equal for all polymers a few GPa. Moreover, the modulus is also nearly independent of temperature. In the glassy state, molecular motions are largely restricted to vibration and short-range rotational motions.

#### *1.1.1.2 The glass transition region*

Typically, the modulus drops by a factor of about 100 in a 20-30°C range. The behavior of polymers in this region is best described as leathery, although a few degree of temperature change will obviously affect the stiffness of the leather. The glass transition temperature,  $T_g$ , is defined as the temperature where the thermal expansion coefficient undergoes a discontinuity. Quantitatively, the glass transition region can be interpreted as the onset of long-range, coordinated molecular motion. While only 1- 4 chain atoms are involved in motion below glass transition temperature, some 10- 50 chain

atoms attain sufficient thermal energy to move in a coordinated manner in the glass transition region.

#### *1.1.1.3 The rubbery plateau region*

After the sharp drop of the modulus in the glass transition region, the modulus becomes almost constant again in the rubbery plateau region. In this region polymers exhibit long-range rubbery elasticity. Due to the fact that long polymer molecules are entangled, chain entanglement networks are formed to restrict the motion of the chains. The width of the plateau is governed primarily by the molecular weight of polymer; the higher molecular weight, the broader the plateau.

#### *1.1.1.4 The rubbery flow region*

In this region, the polymer is marked by both rubber elasticity and flow properties, depending on time scale of the experiment. For short time scale experiments, the physical entanglements are not able to relax, the material still behaves rubbery. For long times, the increased molecular motion imparted by the increased temperature permits the chain to move in a coordinated manner (depending on molecular weight) and to flow. It must be emphasized that this region does not occur for cross-linked polymers.

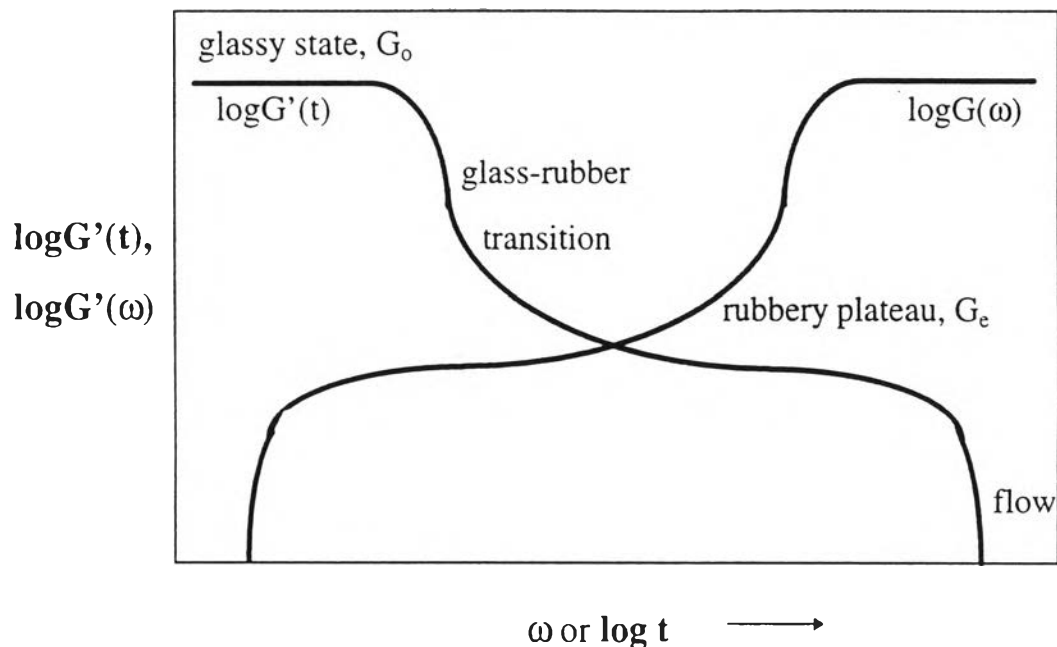
#### *1.1.1.5 The liquid flow region*

At still higher temperatures, the liquid flow region is reached. The polymer flows readily, often behaves like molasses. The increased energy allocated to the chain permits them to reptate out through entanglements rapidly and flow as individual molecules.

### 1.2.2 The Time Dependence

The viscoelastic properties of polymer system also depend on the time scale or frequency scale of the experiment. The polymers can behave as glassy solid, viscoelastic solid, rubber or viscous liquid depending on the time or frequency scale of the experiment [Mark et al. 1987]. Figure 1.2 show the

variation of shear modulus with time or frequency at a constant temperature over a very wide time or frequency scale.



**Figure 1.2** Schematic modulus- time (frequency) curve for uncross-linked, amorphous polymers with high molecular weight and narrow molecular weight distribution.

The time scale is inversely proportional to the frequency scale of the experiment, ( $\omega = 1/t$ ). For short time scale experiment polymer is in glassy state with very high and nearly constant value of shear modulus. It is time independent. The limit of  $G(t)$  for  $t = 0$  is equal to the limit of  $G'(\omega)$  for  $\omega = \infty$  and equal to the instantaneous modulus  $G_0$ . At intermediate time the shear modulus drops rapidly at glass-rubber transition region.  $G(t)$  depends heavily on the time scale, this is the generally situation of viscoelastic behavior. The  $G(t)$  shows nearly constant value,  $G_e$ , at rubbery plateau region due to the effect of entanglement networks. It is time independent. At very long time  $G(t)$  drops again and finally approaches a straight line with innumerable value of slope in the flow regime or terminal zone.  $G(t)$  is time dependent and decreases as  $t^2 \propto 1/\omega^2$ .

## 1.2 Time-Temperature Superposition

The most widely used procedure for the treatment of the viscoelastic functions of amorphous polymers and other materials is time-temperature superposition. According to this procedure, different isothermal viscoelastic data, each obtained over a narrow frequency, or time range, are superposable by shifting each point of the curve by the same amount shift factor,  $a_T$ , along the frequency or the time axis to obtain master curve or reduced curve extending over a wider range than original data. The master curve is then used to predict the behavior of materials, notably polymers, to frequencies or time otherwise inaccessible to experiment.

The criteria for applicability of the method of preparing master curve [ Ferry 1980] are: (a) the shapes of adjacent curves must match to others; (b) the same value of  $a_T$  must superpose all viscoelastic data; (c) the temperature dependence of  $a_T$  must have a reasonable form consistent with experience.

The shift factor  $a_T$  is defined as the relaxation time scale ratio :

$$a_T = \lambda(T)/\lambda(T_o) \quad (1.1)$$

where  $\lambda$  is the relaxation time and  $T_o$  is the reference temperature.

It can be also defined as the frequency at loss peak ratio :

$$a_T = \omega_{\max}(T)/\omega_{\max}(T_o) \quad (1.2)$$

where  $\omega_{\max}$  is the frequency at the loss peak and  $T_o$  is reference temperature.

## 1.3 The William - Landel - Ferry Equation ( WLF equation )

The WLF equation is a universal equation used to express a general curve  $a_T(T)$  for many polymers. The origin of WLF equation is elucidated by order of molecular dimensions or small voids associated with packing irregularity in the framework of free volume theory.

Total free volume per gram,  $v$ , is the sum of the free volume per gram,  $v_f$ , and the occupied volume,  $v_o$ , which includes not only the volume of the molecules as represented by their van de Waals radii but also the volume associated with vibrational motions. The occupied volume increases with temperature.

The specific volumes are normalized by the volume  $v_g$  at  $T_g$ . Thus the fractional free volume,  $f$ , a dimensionless number, is  $v_f/v_g$ . It may be assumed that  $f$  increase linearly with temperature in accordance with the relation :

$$f = f_o + \alpha_f(T-T_o) \quad (1.3)$$

where  $f_o$  is the fractional free volume at a reference temperature  $T_o$  and  $\alpha_f$  is thermal expansion coefficient.

The fractional free volume is related with the time required to reach a voluminal equilibrium. The lower the temperature, the smaller the fractional free volume, the longer the time required to reach the equilibrium. Therefore, the relaxation time scale is inversely proportional to the fractional free volume.

The shift factor  $a_T$  which is defined as the relaxation time scale ratio can be defined in form of steady state shear viscosity,  $\eta_o$  :

$$a_T = \eta_o T_o \rho_o(T) / \eta_{oo} T \rho(T) \quad (1.4)$$

where  $\eta_{oo}$  is the steady state shear flow viscosity at reference temperature  $T_o$  and  $\rho_o$  is the density of polymer at the reference temperature  $T_o$ .

The molecular mobility of polymer chain at any temperature depends primarily on the free volume remaining [Ferry 1980]. The steady state shear viscosity can be expressed in terms of  $v_f$ . This principle was applied long time ago to the shear viscosity of simple liquids by Batchinski [Batchinski 1913] and more recently by Doolittle [Doolittle 1957] with an empirical equation which was found to represent with high accuracy viscosities of ordinary liquids of low molecular weight :

$$\ln \eta_0 = \ln A + B(v - v_f)/v_f \quad (1.5)$$

where A and B are empirical constants.

The combination of equation (1.4) and (1.5) yields another form of logarithmic shift factor :

$$\log a_T = (B/2.303)[1/f - 1/f_0] + \log (T_0 \rho_0 / T \rho). \quad (1.6)$$

In practice, this equation is almost always used without the last term :

$$\log a_T = (B/2.303)[1/f - 1/f_0] \quad (1.7)$$

By substitution equation (1.3) into (1.6) :

$$\log a_T = -(B/2.303)(T - T_0) / [f_0 / \alpha_f + (T - T_0)]. \quad (1.8)$$

WLF equation can be rewritten from equation (1.8) in the form :

$$\log a_T = -C_1^0 (T - T_0) / C_2^0 + (T - T_0), \quad (1.9)$$

where the constants are

$$C_1^0 = B/2.303 f_0 \quad (1.10)$$

$$C_2^0 = f_0 / \alpha_f. \quad (1.11)$$

Values of  $C_1^0$  and  $C_2^0$  refer to an arbitrary reference temperature  $T_0$  which is usually somewhere within a temperature range of experimental interest.

If  $T_0 = T_g$  the values of  $C_1^g$  and  $C_2^g$  are universal for many polymers; they are 51.6 and 7.4 K respectively [Ferry 1980]

Shift factor from the WLF equation is not applicable below  $T_g$  but usable in the vicinity of 100 °C from  $T_g$  or in the terminal zone in which the internal molecular motion of the system does not depend heavily on temperature. In the glassy zone and for crystalline polymers, where sensitive temperature dependences are involved, some modification of the WLF is therefore necessary.

## 1.4 The Coupling Model of Relaxation

It was stated by Ngai and Plazek in 1986 that the temperature dependences in softening and terminal zones are different. And the shift factor obtained for the  $\alpha$ -relaxation process,  $(a_T)_\alpha$ , shows a stronger temperature dependence than that obtained for the  $\eta$ -relaxation process,  $(a_T)_\eta$ . Therefore, the shift factor  $(a_T)_\alpha$  does not obey a single WLF equation because for  $\alpha$ -relaxation the viscoelastic behavior depends only on the segmental motion of the local chain and its free volume is small and can be affected a great deal by a small temperature change. But for the  $\eta$ -relaxation, the chain reptation dominates and there are several modes of molecular motions including side chain motions and segmental motions. The free volume is relatively large in the  $\eta$ -relaxation or equilibrium state.

Since all of the molecular motions contributing to the deformation do not have the same temperature dependence, temperature reduction of the data to a single master curve continuously above and below  $T_g$  can only be achieved empirically. But the shift factors  $(a_T)_\alpha$  below  $T_g$  will not obey the WLF equation.

A generally applicable model of relaxation in complex systems has been proposed and applied in diverse disciplines [Ngai & Plazek 1986]. This model is known as “The Coupling Model” proposed by Ngai and Plazek in 1986.

### 1.4.1 Relaxation in Simple System

We consider the thermal relaxation and viscous deformations of a linear polymer melt of monodisperse high molecular weight entangled molecules which are assumed to be normal modes (primitive modes). An example of such a primitive mode is the terminal Rouse mode (free Rouse



mode). Its primitive relaxation rate,  $W_o$ , is the same for all chains and inversely proportional to the primitive relaxation time,  $\tau_o$ .  $\tau_o$  of Rouse mode for terminal relaxation was derived and found to be [ Ngai & Plazek, 1986 ] :

$$\tau_{oi} = a^2 M^2 \zeta_o / 6\pi^2 M_o^2 kT i^2, \quad i = 1, 2, 3, \dots \quad (1.12)$$

where  $M$  is molecular weight,  $\zeta_o$  is the primitive friction factor for the Rouse beads,  $a$  is the effective bond length,  $M_o$  is the molecular weight of the repeat unit, and  $i$  is number of mode.

#### 1.4.2 Relaxation in Complex System

Relaxation in complex system, the primitive species can be coupled via molecular, ionic, electronic or other interactions with the complex environment and with one another. Relaxation of the primitive species must involve sequential, cooperative, or tandem adjustments and response of its complex environment. The primitive relaxation rate,  $W_o$ , will be slowed down at time longer than a time,  $t_c$ , at crossover frequency,  $\omega_c$  ( $t_c = \omega_c^{-1}$ ). In general, the reduction of  $W_o$  is a function of time :

$$W(t) = W_o f(t) = 1/\tau^*, \quad (1.13)$$

where  $\tau^*$  is the effective relaxation time,  $f(t) = 1$  for  $\omega_c t \ll 1$ , and  $f(t) < 1$  for  $\omega_c t \gg 1$ . Hence,

$$\begin{aligned} W(t) &= W_o, \quad \omega_c t \ll 1 \\ &= W_o (\omega'_c t)^{\beta-1}, \quad \omega_c t \gg 1, \end{aligned} \quad (1.14)$$

where  $\omega_c$  is the crossover frequency,  $\omega'_c$  is related to  $\omega_c$  by a constant factor of  $\exp(\gamma)$  with  $\gamma = 0.577$ ,  $\beta$  is a coupling parameter or the bandwidth of distribution spectrum of relaxation time, and  $\beta-1$  is proportional to the strength of the coupling of the primitive species with the environments. The relaxation quantity  $Q$  is described by the equation :

$$dQ/dt = -W(t)Q. \quad (1.15)$$

If  $\omega_c/W_0 = \omega_c\tau_0 \gg 1$  ; log-time relaxation behavior, the relaxation is dominated by the fractional exponential of Kohlrausch :

$$Q(t) = Q(0)\exp[-(t/\tau^*)^\beta], \quad (1.16)$$

where the effective relaxation time is defined as :

$$\tau^* = [\beta\omega_c^{(\beta-1)}\tau_0]^{1/\beta}. \quad (1.17)$$

### 1.4.3 Application of the Coupling Model of Relaxation in Complex System

Concerning with the problem of different temperature dependences of shift factors  $(a_T)_\alpha$  and  $(a_T)_\eta$ , we will discuss this problem in the framework of coupling model. Assuming that the molecular processes involved in the  $\alpha$  and  $\eta$ -relaxations are different in nature, so the molecular interactions or coupling with the respective environment will also be different. Hence, the corresponding coupling parameter  $\beta_\alpha$  and  $\beta_\eta$  are not expected to be the same value. The quantity  $\beta$  can be obtained from a fit of the fractional exponential of Kohlrausch (equation 1.16) to the time dependences of stress relaxation measurements :

$$G(t) = G(0)\exp[-(t/\tau^*)^\beta]. \quad (1.18)$$

*1.4.3.1  $\eta$ -relaxation* According to the primitive Rouse mode for terminal relaxation, the primitive relaxation  $\tau_{oi}$  is the longest for  $i = 1$  and decreases rapidly to zero with increasing  $i$ . The effective terminal relaxation and flow are then mostly due to the mode  $i = 1$ .

Therefore the effective relaxation time  $\tau^*$  can be defined as :

$$\tau^*_{\eta} = [\beta_{\eta}\omega_c^{(\beta_{\eta}-1)}\tau_{o1}]^{1/\beta_{\eta}}. \quad (1.19)$$

Its contribution to the zero shear viscosity :

$$\eta \propto G_N^0\tau^*_{\eta}\Gamma(1/\beta_{\eta})/\beta_{\eta}, \quad (1.20)$$

where  $G_N^0$  is the plateau modulus and  $\Gamma$  is the gamma function and therefore

$$\eta \propto [M^2 \zeta_0(T)]^{1/\beta_\eta}. \quad (1.21)$$

The shift factors  $(a_T)_\eta$  can be defined for a reference temperature  $T_0$  as :

$$a_{T\eta} = \eta(T)/\eta(T_0) = [\zeta_0(T)/\zeta_0(T_0)]^{1/\beta_\eta}. \quad (1.22)$$

So

$$d \ln a_{T\eta} / d(1/T) = (1/\beta_\eta) [d \ln \zeta_0(T) / d(1/T)]. \quad (1.23)$$

1.4.3.2  *$\alpha$ -relaxation* The primitive friction factor is assumed to be the same for both the  $\alpha$  and  $\eta$ -relaxations. It is further assumed that stress relaxation assume the form of equation (1.18). Then the temperature dependence of the shift factor  $a_{T\alpha}$  for the same reference temperature  $T_0$  is

$$a_{T\alpha} = [\zeta_0(T)/\zeta_0(T_0)]^{1/\beta_\alpha}. \quad (1.24)$$

So

$$d \ln a_{T\alpha} / d(1/T) = (1/\beta_\alpha) [d \ln \zeta_0(T) / d(1/T)]. \quad (1.25)$$

Combining equations (1.22) and (1.24), (1.23) and (1.25), respectively, we arrive at :

$$\beta_\alpha \ln a_{T\alpha} = \beta_\eta \ln a_{T\eta}, \quad (1.26)$$

where

$$[d \ln a_{T\alpha} / d(1/T)] / [d \ln a_{T\eta} / d(1/T)] = \beta_\eta / \beta_\alpha. \quad (1.27)$$

Both relations are called coupling model. The coupling model thus can explain quantitatively the different temperature dependences in  $\alpha$  and  $\eta$ -relaxation processes.

### 1.5 Polymer Blends

Polymer blending is a common way to find the new materials that are required to meet needs and can usually be implemented far more rapidly and economically than a development of new chemistry.

Blending of thermoplastic polymers can improve mechanical properties such as toughness, and is usually the main reason for the development of novel plastic alloys and blends [Foke & Hope 1993]. Others reasons for blending two or more polymers together include: (i) to improve the polymer's processability, e.g. for the high temperature polyaromatic thermoplastic, (ii) to enhance the physical and mechanical properties of the blends, making them more desirable than those of the individual polymers and (iii) to meet the market demand such as the plastic recycling process blending.

For polymer blends, a distinction must be made between miscible blends and immiscible blends. A necessary condition for miscibility is  $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} < 0$  [Mark et al. 1988]. Miscible polymer blends show flow behavior which is equivalent with homopolymer flow behavior. The blends which consist of two miscible polymers can usually be characterized by a single intermediate glass transition temperature ( $T_g$ ), although the width of the glass transition temperature region may be broad.

In this study, PMMA and SAN were prepared in sheet form and their viscoelastic properties were measured and analyzed. The choice of the PMMA/SAN blends system was based on several important factors [Rusin 1990]: PMMA is a high performance polymer which has UV light stability and good thermal and weathering resistance. But disadvantages of PMMA are its lack of abrasion resistance, limited stress-crack resistance and flammability. While SAN has good environmental stress-crack resistance and low price. But it does not have such a high transparency or such good weathering properties as PMMA. So, some mechanical properties of PMMA can be improved by blending with SAN and vice versa.

### **1.6 Research Objectives**

The objectives of this thesis research are to investigate the continuity of the time-temperature superposition for PMMA, SAN and PMMA/SAN miscible blends at temperatures above and below  $T_g$ . In addition, we will test the coupling model of relaxation to account for the different temperature dependences of viscoelastic properties in the glassy and the terminal zones.