

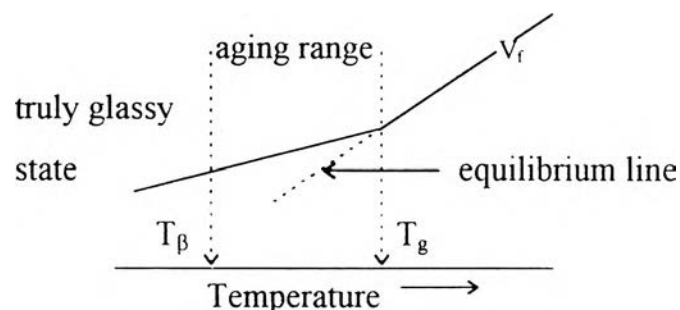
# CHAPTER I

## INTRODUCTION

### 1.1 Physical Aging

Physical aging is the phenomenon in which properties of a material change with time. It occurs when the materials undergo a slow process and attempt to establish an equilibrium. This gradual approach toward an equilibrium affects many properties of the material.

Physical aging is a gradual continuation of the glass formation that sets in around  $T_g$  (fig.1.1a) [L.C.E. Struik, 1978]. Therefore it affects all those temperature-dependent properties which change drastically and abruptly at  $T_g$ . During aging, these properties change in the same direction as during cooling through the  $T_g$  range; the material becomes stiffer and more brittle, its damping decreases, and so do its creep and stress-relaxation rates, dielectric constant, dielectric loss, and etc [L.C. E. Struik, 1978].



**Figure 1.1a** Temperature window of aging.  $T_g$  is the glass transition temperature,  $T_\beta$  the temperature of the highest secondary transition, and  $v$  the specific volume.

Fig.1.1a shows that amorphous solids are not in thermodynamic equilibrium at temperatures below their glass transition [F. Simon, 1931 and A.J. Kovac, 1964]. The materials undergo a slow change toward equilibrium, indicating that even below  $T_g$  molecular mobility is not quite zero but it is too low for complete relaxation to occur.

During physical aging, the molecular mobility decreases, and hence, the relaxation and retardation times characteristic of the viscoelastic behavior increase [S. Vleeshouwers, A.M. Jamieson, and R. Simha; 1989].

The effect of physical aging on viscoelastic properties was studied in the glassy state. Tensile creep was measured during isothermal physical aging; the sample is subjected to a series of creep experiments after quenching. It is the more convenient procedure for saving the time for the test. It should be noted that it is only useful for creep tests at small strains, i.e. in the range of linear viscoelastic behavior, and at constant aging temperature, i.e. isothermal. When tests are done at different aging temperatures, keeping the aging time constant, this method cannot be used of course [S. Vleeshouwers, A.M. Jamieson, and R. Simha; 1989]. It can be expected that the individual creep tests will not change the properties of the material for creep tests at low stress levels [L.C.E. Struik, 1978].

Struik [1978] investigated the effect of physical aging on creep compliance of many materials and found that the momentary creep curves (i.e., measured on a short time scale,  $t$ , relative to the aging times,  $t_a$ ) exhibit a universal shape. It can be implied that all relaxation times are identically shifted by temperature or thermal history [D.J. Plazek and J.H. Magill, 1968 and F.R. Schwarzl and L.C.E. Struik, 1967].

Williams, Landel and Ferry [W.L.F., 1955] found an approximately identical shift factor-temperature relation for all amorphous polymers, which could be expressed as a universal relationship, known as WLF equation :

$$\log a_T = C_1 (T - T_g) / [C_2 + (T - T_g)], \quad (1.1)$$

where  $C_1$  and  $C_2$  are constants and  $a_T$  represents the temperature variation of the segmental friction coefficient for mechanical relaxations, molecular relaxation process.

The value of  $a_T$  determines the amount of horizontal shift of the time scale for data determined isothermally in short time intervals. The WLF equation can be used to predict the shift factors for the superposition of low strain linear viscoelastic behavior of an amorphous polymer. The WLF equation has been applied successfully to describe the relaxation of polymers in the temperature range of  $T_g \pm 50$  °C [I.M. Ward and D.W. Hadley, 1993]. Commonly referred to as time-temperature superposition, it is quite applicable for the construction of relaxation-modulus master curves or extending creep data covering many decades of time [O. Olabisi, L.M. Robeson and M.T. Shaw, 1979].

### **Free Volume Theory**

In free-volume models, free volume  $V_f$  is related to specific volume  $V$  by

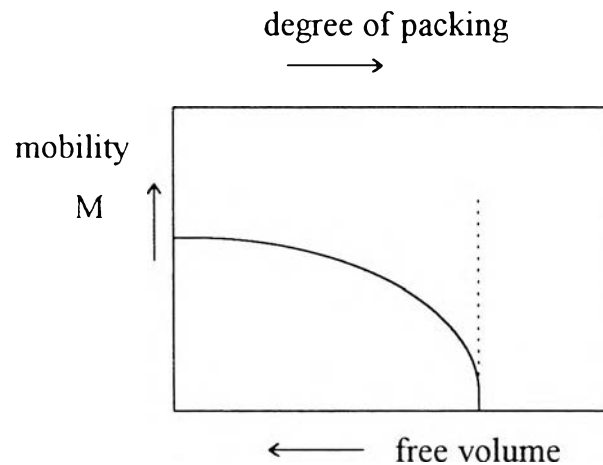
$$V_f = V - V_o(T), \quad (1.2)$$

The occupied volume,  $V_o$ , is a function of temperature only. The relationship between mobility and free volume can be related via a Doolittle equation :

$$\ln M = A - B/f(T, t_a), \quad (1.3)$$

where  $M$  is the mobility,  $A$  and  $B$  are constant, and  $f$  is the volume fraction defined by  $f = V_f/V$ .

The transport mobility of polymer chains in a closely packed system primarily depends on the degree of packing or in other words, on the free volume,  $V_f$  (See fig.1.1b).

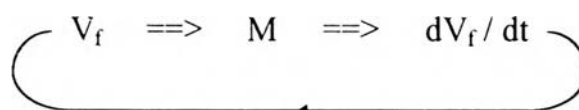


**Figure 1.1b** The free volume concept.

With increasing degree of packing, the mobility decreases, at first slowly, but later on at an ever increasing rate. At a critical degree of packing, the mobility steeply falls to zero.

During aging, in which polymer is kept at  $T_1$  after cooling from a temperature  $T_0$  above  $T_g$  to a temperature  $T_1$  below  $T_g$ , the transport mobility

M, identified with the segmental mobility (i.e. the rate factor for changes in chain configuration), decreases simultaneously with the free volume,  $V_f$ , of the Doolittle's equation. The changes in  $V_f$  determine M (fig.1.1b), while M determines the rate  $dV_f / dt$  at which  $V_f$  changes. So we have the following closed-loop scheme [L.C.E. Struik, 1978] :



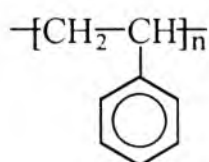
This closed-loop scheme implies that the volume-relaxation process is basically non-linear. This is essential for an understanding of aging. When the polymer is cooled to some temperature  $T_1$  below  $T_g$ , the mobility M will be small, but not zero. At this stage  $V_f$  is greater than it would be at equilibrium, the volume will continue to decrease slowly.

This construction will be accompanied by a decrease in the mobility, M, with concomitant changes in all those properties of the glassy polymer, undergo aging [L.C.E. Struik, 1978].

In this study, the influence of physical aging on the creep compliance was studied in the linear viscoelastic range for PS/PPO blend systems.

## 1.2 PS - PPO

### Polystyrene

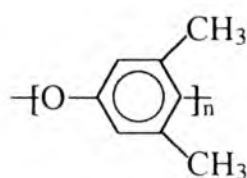


Polystyrene, PS, is a typical rigid plastic. The high rigidity is due to bulky side groups on the polymer chain resulting in high  $T_g$  values. PS has a glass transition temperature of about 100 °C. Although completely amorphous ( $T_g = 85$  °C), its bulky rigid chains (due to phenyl-phenyl interactions) impart good strength with high dimensional stability. High rigidity and high resistance to deformation of PS lead to high moduli.

PS is a very good electrical insulator, has excellent optical clarity due to the lack of crystallinity, possesses good resistance to aqueous acids and bases. Commercial PS have number-average molecular weight in the range of 50,000 - 150,000.

PS has some limitations. It can be attacked by hydrocarbon solvents, has a poor weatherability (UV, oxygen, and ozone attack) due to the labile benzylic hydrogens, is somewhat brittle, and has poor impact strength due to the stiff polymer chains.

#### **Poly (2,6-dimethyl-1,4-phenylene oxide)**



Poly (2,6-dimethyl-1,4-phenylene oxide), PPO, has a glass transition temperature of about 200 °C. Because of high  $T_g$ , PPO is difficult to be processed. PPO, because of higher monomer cost and a more difficult polymerization procedure, is significantly higher in cost than PS. Thus, combinations of these two polymers allow a balance in the price/performance

profile, with PPO yielding advantages in higher  $T_g$  and better impact strength while PS offers a very important price advantage. The blending, physical mixed of different materials, can be used to improve the properties of materials.

The blends of PS/PPO can be classified as engineering plastics because of the improved heat distortion temperature, toughness, flame resistance and creep resistance.

### 1.3 Tensile Creep

The tensile creep can be used to characterize the influence of physical aging related to viscoelastic properties [J.D. Ferry, 1980].

In a tensile creep study, a constant stress,  $\sigma$ , is applied within a short time and strain,  $\epsilon(t)$ , is measured as a function of time. The tensile creep compliance  $D(t)$  is defined as

$$D(t) = \epsilon(t) / \sigma. \quad (1.4)$$

For studying physical aging effects, the momentary creep curves would be fitted to an empirical equation for the creep compliance :

$$D(t) = D(0) \exp [(t/t_0)^\beta], \quad (1.5)$$

where  $D(0)$  is the compliance after an aging time  $t_a$ , immediately after applying;  $\beta$  is the scaling exponent and  $t_0$  is the characteristic time, dependent on aging time and temperature. Values for  $\beta$  and  $t_0$  are obtained, and the dependence of  $t_0$  on the aging time can be determined.

The shift factor  $a$  for a curve at  $t_a$  is related to a reference curve at  $t_a = t_{a,ref}$  as

$$a = t_0(t_a) / t_0(t_{a,ref}). \quad (1.6)$$

Since in creep experiments the stress,  $\sigma$ , is constant, Eq (1.5) can also be written as

$$\varepsilon(t) = \varepsilon(0) \exp [(t/t_0)^\beta]. \quad (1.7)$$

Because experiments are done at a very small tensile strain, the sample cross section and the stress can be considered to be constant during an experiment [S. Vleeshouwers, A.M. Jamieson, and R. Simha; 1989].

#### 1.4 Previous Studies

Many properties of thermoplastic compositions provided by the mixture of polyphenylene ether and styrene resin were investigated by E.P.Cizek [1978]. It was found that blend properties, such as flexural strength, compressive strength, and tensile strength, improved over those of the polyphenylene ether or styrene resin individually. Compositions containing from 40 to 85 percent polyphenylene ether and from 60 to 15 percent styrene resin exhibit the best overall combination of properties.

For physical aging of PS/PPO blends, there is only a few studies have been currently reported in the literature. Ho et al. [1991] investigated the effect of physical aging on tensile stress relaxation of PS/PPO blends. A stretched exponential function was used to describe the physical aging relaxation behavior. It was found that the stress relaxation curves can be fitted



to a universal master equation. The stretched exponential master curve could be generated with a global value of 0.41 for the spectral parameter  $\beta$  at different aging temperatures. The characteristic relaxation time showed an empirical power law correlation with aging temperature and time. Dynamic mechanical and dielectric behavior during isothermal physical aging in PS/PPO blends have been studied by Cavaille et al. [1990, 1992] and Pathmanathan et al. [1985]. A monotonic decrease in loss factor  $\tan \delta$  from dielectric spectra, and in loss modulus ( $G''$ ) from dynamic mechanical spectra with aging time at sub- $T_g$  temperatures confirm substantial mobility within glassy state of these blends.

The kinetics of stress relaxation during isothermal physical aging of PS/PPO blends were investigated by G.W.Chang [1993]. The behavior of the blends, dilute in one component, was compared with that of the neat major component at equal temperature distances,  $T-T_g$ , from the mid-point glass transition temperature. It was found that the stress relaxation rate do not scale with  $T-T_g$  and the addition of the second component produces a change in the packing density of the blend. Moreover, it is expected that the initial stress decay is determined by regions enriched in the more mobile component because of the presence of concentration fluctuations in the blend.

## 1.5 Research Objectives

To study the effect of the physical aging of PS and PPO blends on tensile creep as a function of *aging time, composition and aging temperature.*