

CHAPTER I

INTRODUCTION

1.1 Introduction

Products of glassy polymer are usually made by processing them in the melt state, followed by a fixation of the shape by cooling below the glass transition temperature, T_g . During the cooling, the material solidifies and stiffens, but the period is too short for this process to reach a stable equilibrium state. So during the service lifetime of the product, configurational adjustments occur that result in a slow change toward equilibrium. This process is called physical aging. During physical aging, the molecular mobility decreases, and hence, the relaxation and retardation times, characteristics of the viscoelastic behavior, increase. Thus, significant changes in mechanical properties occur.

Struik and el al.(1978) investigated the effect of physical aging on creep compliance of many amorphous polymers and other materials. They found that over a broad temperature range below the glass-transition temperature, T_g , the momentary creep curve (i.e. measured on a short time scale, t , relative to the aging time, t_a), exhibits a universal shape independent of chemical structure, thermal history or test temperature.(Struik et al., 1978) From measurement of the creep retardation times, t_0 one can determine a viscoelastic shift parameter $a = t_0(t_a)/t_0(t_{a, ref})$.

A theoretical analysis of the time evolution of the viscoelastic shift parameter, a , during isothermal physical aging of glassy polymer provides a relation between the shift parameter and the free volume parameter $f(T, t_a)$ via the Doolittle equation:

$$\log a(T, t_a) = A - B / f(T, t_a), \quad (1.1)$$

where f is the free volume and A, B are constants.

A quantitative correlation was found (Simha et al., 1984) between experimental data on $a(T, t_a)$ for several polymers and $f(T, t_a)$ values calculated from volume relaxation data $V(T, t_a)$ using a statistical mechanical equation of state (Simha et al., 1969).

Interestingly, the free volume distribution function obtained from the experimental data showed a small decrease in width during isothermal physical aging from which one might anticipate a similar decrease in the width of the viscoelastic relaxation spectrum. However, it is possible that the universal master function which fits creep and stress relaxation data during physical aging which is of the stretched exponential form, may not be sensitive to small changes in the shape of the relaxation spectrum.

1.2 Viscoelastic Theory of Physical Aging

Changes in viscoelastic properties can be interpreted as changes in relaxation and retardation times, which in turn are due to change in the free volume. It is found experimentally that the time dependence of viscoelastic response curves can be scaled on a logarithmic time scale. The distance on the time axis over which a creep curve has to be displaced to be superimposed on a reference creep curve defines the shift factor, a . This shift factor is equal to the ratio of the specific retardation times scale for the two curves. Using the Doolittle equation Eq.(1.1), the shift factor can be related to a free volume quantity : that is

$$\ln a(T, t_a) = B \left[\frac{1}{f(T, t_a)} - \frac{1}{f(T_{ref}, t_{a, ref})} \right], \quad (1.2)$$

where $a(T, t_a)$ is the shift factor calculated for aging time t_a and aging temperature T , B is a constant, and $f(T, t_a)$, $f(T_{ref}, t_{a, ref})$ are fractional free volumes at aging times t_a and $t_{a, ref}$ and at aging temperatures T and T_{ref} , respectively.

Because the reference state is not an equilibrium state, an aging reference time must be chosen to define this state. As pointed out earlier, the shift factor can be found experimentally by superimposing creep or stress relaxation curves relative to a master equation.

In this study, shift factors were calculated from retardation times, deduced by superposition on a master curve of the stretched exponential form, and investigated as a function of aging time and cooling rate.

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

$$D(t) = \frac{\varepsilon(t)}{\sigma} \quad (1.3)$$

Physical aging results in a shift in the retardation spectrum. An empirical description of the dependence of $D(t)$ on t in the temperature region below T_g , where physical aging occurs, is as follows:

$$D(t) = D(0) \exp[-(t/t_0)^\beta], \quad (1.4)$$

where $D(0)$ is the compliance immediately after applying the stress; t_0 is characteristic time or retardation time, dependent on aging time and aging temperature, and β is a constant.

The shift factor a for t_0 at t_a , is defined with respect t_0 at $t_{a, ref}$ as

$$a = \frac{t_0(t_a)}{t_0(t_{a, ref})} \quad (1.5)$$

The dependence of $D(0)$ on t_a results in a vertical shift. Struik(1978) reported a small dependence of $D(0)$ on t_a , in some cases positive and in some negative.

Since in creep experimental the stress σ is constant, Eq.(1.4) can also be written as

$$\varepsilon(t) = \varepsilon(0) \exp[(t/ t_0)^\beta], \quad (1.6)$$

with $\Delta l(t) = L \varepsilon(t)$ and L is the initial length of the sample. Because experiments were done at very small tensile strains, the sample cross section and stress can be considered to be constant during an experiment.

The shifts between successive creep curves are nearly constant. The horizontal components of the shifts are denoted by $\log a$, which is taken positive for a shift to the left (a means the acceleration factor). The rate of physical aging can thus be characterized by the double logarithmic shift rate μ , defined as:

$$\mu = \frac{d \log a}{d \log t_a} \quad (1.7)$$

Apart from some deviation at short time, $\log a$ varies linearly with $\log t_a$, and the slope of the line is close to unity.

The shift rate, μ , was constant over wide range of t_a . Above T_g , μ is zero. Just below T_g , it rapidly increases to about unity, remaining unity over more or less a wide temperature range below T_g . At lower temperatures, finally, the aging rate begins to slow down, and μ decreases again (Struik, 1978). When the equilibrium state is approached, μ also begins to decrease, and at equilibrium, aging ceases, and μ is zero. Such an approach to equilibrium is possible at temperatures close to or above T_g . This explains why the shift rate, μ , decreases to zero near T_g . The theoretical discussion by Ngai et al. (1990) indicates that the magnitude of the exponent β is dependent on

the degree of cooperativity in the couplugg between the motions of the relaxation groups which enable densification of the surrounding matrix. As the cooperativity increases , β decrease.

1.3 Polymer Blends

Polymer blending is the way to find the new material that are required to meet needs and can usually be implemented far more rapidly and economically than 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 thermoplastic alloys and blends. Other 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 blend, making them more desirable than those of the individual polymers in the blend and (iii) to meet the market demand such as the plastic recycling process blending.

For polymers blends, a distinction must be made between miscible blends and immiscible blends. A necessary condition for miscibility is

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \leq 0 \quad (1.8)$$

A sufficient condition for miscibility in all proportions in then that

$$\left(\frac{\partial^2 \Delta G_{\text{mix}}}{\partial \phi_i^2} \right)_{T,P} > 0 \quad (1.9)$$

When the molecular weight of the polymers in the blend increases ΔS_{mix} become small or zero. Miscible polymer blends show flow behavior which is equivalent with homopolymer flow behavior. A blend which consists of two totally miscible polymers can usually be characterized by a single intermediate

glass transition temperature (T_g), although the width of the glass transition region may be broad.

In this study, a series of poly(methyl methacrylate) (PMMA) and poly(styrene-co-acrylonitrile) (SAN) were prepared and aged and their viscoelastic properties evaluated. The choice of the PMMA/SAN system was based on several important factors: availability of each component, PMMA is a high-performance polymer which has UV light stability and good thermal and weathering resistance. Disadvantages of PMMA are its lack of abrasion resistance, limited stress-crack resistance and flammability. While SAN has a good environmental stress-crack resistance, very low price but do not have such a high transparency or such good weathering properties as PMMA. Also we were interested in determining whether the strong intermolecular interaction between SANs and PMMA influence the physical aging behavior.

1.4 Previous Studies

J. Mijivic and coworkers[1989] studied the experimental results of isothermal enthalpy relaxation of a series PMMA/SAN blends which were blended with a twin-screw extruder. The enthalpy relaxation was monitored by differential scanning calorimetry (DSC). They found that: 1. the higher the aging temperature, the faster relaxation process; 2. under similar aging conditions SAN-rich blends relax slightly faster than PMMA-rich blends and 3. the effect of blending on relaxation is related to the aging temperature in a complex manner.

Tai Ho and coworkers[1990] used the Moynihan model to simulate enthalpy relaxation of a series of PMMA/SAN blends. They calculated specific heat function in the rate heating approach and calculated isothermal

enthalpy relaxation in the isothermal approach; they were found to be in good agreements with experimental data (T. Ho et al., 1990).

1.5 Objectives

To compare the time dependence of mechanical properties in glassy state of miscible polymer blends against those of the pure blend components at equal temperature distance $T_g - T$ with specific goal:

- To study blends of two polymers which are poly(methyl methacrylate) (PMMA) and poly(styrene-co-acrylonitile) (SAN).
- To study tensile creep test with different composition and cooling rates.
- To study how β , t_0 and μ depend on composition, aging time or cooling rate.