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Physical aging in the mechanical properties of miscible polymer blends

Chang, Geng-Wen, Ph.D.

Case Western Reserve University, 1993

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**PHYSICAL AGING IN THE MECHANICAL PROPERTIES
OF MISCIBLE POLYMER BLENDS**

by

GENG-WEN CHANG

Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

Thesis Advisors: Dr. Alexander M. Jamieson

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January 1993

CASE WESTERN RESERVE UNIVERSITY

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PHYSICAL AGING IN THE MECHANICAL PROPERTIES OF MISCIBLE POLYMER BLENDS

Abstract

by

GENG-WEN CHANG

Changes in mechanical properties during isothermal physical aging were investigated for three miscible blends: polystyrene(PS)/poly(2,4-dimethyl 1,6-phenylene oxide)(PPO), PS/poly(vinyl methyl ether)(PVME), and poly(methyl methacrylate)(PMMA)/poly(ethylene oxide)(PEO). The aim was to compare the kinetics of the physical aging process between blends and pure components, using tensile stress relaxation and dynamic mechanical measurements. Positron annihilation lifetime(PAL) spectroscopy was used as a probe for structural disorder (free volume) to aid interpretation of the physical aging studies. Analysis of the aging stress relaxation data by generation of a stretched exponential master function, as proposed by Struik, was possible for both blends and homopolymers.

Discrepancies in the scaling of the characteristic stress relaxation time τ with respect to the temperature distance $T_g - T$ between PS/PPO, PS/PVME and the PS homopolymer were resolved by invoking the presence of concentration fluctua-

tions in the blends. By selecting the onset glass transition temperature (T_{gi}) as a reference point, the relaxation times for PS/PPO and PS/PVME glasses can be scaling to those of pure PS. This indicates that the initial stress decay is determined by the more mobile regions in the blends. However, this temperature scaling does not apply to the PMMA/PEO blend for which the τ values at fixed $T_{gi}-T$ are larger than for pure PMMA, suggesting that, in this system, the interaction between the blend components produces a more dense matrix.

Using the coupling theory of Ngai as a guide, we infer that the width of the spectrum of stress relaxation times in the blend may be increased by the presence of concentration fluctuations, or by an increase in matrix density (lower free volume). Thus, the increase observed in the spectral widths for both blends and homopolymers at lower temperatures indicates that the relaxing elements become more strongly coupled to the surrounding matrix. For the PS/PPO blend, the spectral width is narrower than for pure PS suggesting that increased free volume from dissolved PPO dominates over the effect of concentration fluctuations. By contrast, since the width for the PS/PVME blend is larger, the prime factor appears to be concentration fluctuations. In the PMMA/PEO blend, where, again, as increase in the spectral width is found, there may be contributions from both concentration fluctuations and a lower free volume.

Orthopositronium(o-Ps) lifetime and intensity values for the three blends and the constituent homopolymers, measured by PAL spectroscopy, are qualitatively

consistent with the behavior of the stress relaxation spectra, using arguments based on free volume concepts.

ACKNOWLEDGEMENTS

The author wishes to express sincere gratitude to Dr. Alexander M. Jamieson for his patience and guidance during the course of this study.

The author is also thankful to Servaas Vleeshouwers for his insightful discussion of this research and Zinbin Yu for helping me in conducting positron lifetime spectroscopy. Also, the appreciation of instrumental supports from Dr. Hatsuo Ishida, Dr. John D. McGervey, Dr. Joseph Mansour, and Mr. Alex Schnittlinger.

Special thanks to Adeyinka Adedeji for his useful suggestion during the preparation of this manuscript.

Finally, the author's thanks to the Chung Shan Institute of Science and Technology (CSIST, Taiwan) providing the scholarship.

DEDICATION

To my family

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Chapter 1: Introduction

1-1 The nature of physical aging.

In the last two decades, there has been increased interest in the structural and property changes that occur in glassy and partly glassy polymers upon annealing below the glass transition temperature(T_g). This time-dependent aging behavior is often a direct result of the non-equilibrium nature of the glassy state and has been observed to happen in many types of polymer systems containing glassy regions: purely glassy polymers, semicrystalline polymers and polymeric network glasses. The importance of this phenomenon in practical applications arises from the simple fact that polymer performance must necessarily be predictable to ensure compliance with design requirement throughout the anticipated service life of the polymer products. In the evaluation of polymers, the aging time is just as important as other factors such as temperature, pressure and humidity etc. A knowledge of the aging behavior of a polymer is indispensable to the prediction of its long term properties from short term tests.

Physical aging¹⁻⁴: this term refers to the non-equilibrium behavior, i.e. the enthalpy, volume and structure recovery(relaxation) which occurs as a result of long-lived non-equilibrium states which are produced during the cooling of glassy polymers from a temperature above their glass transition temperatures(T_g) to a temperature below their T_g . As a glassy polymer is cooled in a normal process

from the melt state through glass transition into the glassy state, there occurs a rapid decrease in molecular mobility which results in a sudden increase in viscosity and modulus as the transition temperature is approached. The polymer molecules are not able to reach their equilibrium conformation and packing with respect to the rate of temperature drop. As the temperature is further decreased the molecules are essentially "frozen" into a non-equilibrium state of high free energy. The specific volume, entropy and enthalpy in polymer glass are greater than they would be in the corresponding equilibrium state at the same temperature⁴. Although the molecular mobility is greatly reduced in the glassy state compared to the situation in the melt, there remains some finite motion which allows the molecules to move toward the equilibrium configuration. Therefore, a thermodynamic driving force for molecular rearrangement and continued densification of the packing polymer chains exists. The drive toward further densification of the system is commonly referred to as physical aging, and it is distinguished from chemical aging in which chemical transformation, in addition to molecular rearrangement, occurs. This gradual approach to equilibrium affects many properties of the materials. Two of the measurable thermodynamic state functions, enthalpy and volume, have been found to decrease with sub-T_g isothermal physical aging. Associated with these changes are certain variations in the physical and mechanical properties of polymer with time^{3,4}: increases in density, tensile and yield stresses, and elastic modulus; decreases in impact

strength, fracture energy, ultimate elongation, and creep rate; and a transition from ductile behavior to brittle fracture. Such changes in material properties could be vital in any long term applications.

Physical aging is also a very significant phenomenon⁴ in polymer and composite processing because this usually involves a rapid change from melt to glass. For example, the solidification time for polystyrene(PS) melt in a metal mold occurs only in a few seconds during the injection molding process.

In Fig.1-1 a specific volume versus temperature diagram⁴⁻⁶ is shown to illustrate the aging range and non-equilibrium state observed in a polymer glass. If the polymer could be cooled infinitely slowly through T_g , the dotted line would be followed as enough time was allowed for all modes of molecular relaxation to occur. In practice, however, finite cooling rate will induce a non-equilibrium condition (i.e., the solid line) and T_g will be evident. Volume relaxation, in Fig.1-1, towards the equilibrium line follows the direction indicated by the arrow. Experimentally, physical aging is most prominent within a temperature zone define by the T_g and T_{β} . Below T_{β} , only very localized molecular motion exists, and volume relaxation is very small. However, physical aging still proceeds in the sub- T_{β} region, but is difficult to monitor with conventional methods.

A simple but useful "free volume" concept⁴⁻⁶ has been extensively used to interpret the polymer glass behavior above and below T_g . Once a polymer is quenched from above to below T_g , the rate of approach to equilibrium is

Fig.1-1 Specific volume versus temperature for an amorphous polymer. Physical aging occurs via densification toward the equilibrium line.

governed by molecular mobility, M , of the polymer. The mobility in turn depends upon the degree of packing or inversely on the "free volume" available as shown in Fig.1-2. With decreasing free volume(increasing degree of packing) the mobility decreases at first slowly, but, later on, at an ever increasing rate until, at a critical value of free volume, the mobility steeply falls to zero. A simplified description of free volume treats segments of a polymer chain as spherical units, having a specified volume V_o (occupied volume), and the free volume as the "holes" created intermolecularly as a results of packing requirements. Thus, we can define the free volume as follows:

$$V_f = V - V_o \quad (1-1)$$

where V is the macroscopic volume of the polymer.

The changes in free volume may occur as a result of a redistribution of the "holes"⁷. The rate of this process determines the molecular mobility, M , giving the following closed loop scheme: V_f determines M which determines the rate of change of V_f , dV_f/dt , which in turn determines V_f

$$V_f \Rightarrow M \Rightarrow dV_f/dt \quad (1-2)$$

```

graph LR
    Vf[Vf] --> M[M]
    M --> dVf["dVf/dt"]
    dVf --> Vf
  
```

Fig.1-2 The reduction of molecular mobility with increasing degree of packing and decreasing free volume. Arrow represents the direction of free volume increase.

This scheme explains the essential features of both physical aging and the existence of a glass transition. It implies that, during the cooling process V_f can not decrease indefinitely. Below a certain temperature, M becomes so small that V_f essentially cease to decrease with temperature. The polymer glass then passes through its T_g . Upon further cooling, V_f can only change slightly, and slowly. Likewise, M no longer changes rapidly with temperature, though it continues to decrease slightly because some limited motion in glassy state decreases as temperature decreases. If we stop the cooling process, and keep it at a constant temperature (T_a), then the physical aging process begins. During isothermal physical aging at T_a , M is still small but not zero, therefore, allowing the gradual volume contraction as V_f seeks its equilibrium value. Note that, this closed loop scheme (Eq.1-2) indicates that volume relaxation is a non-linear and self-retarding process.

As discussed above, the basic property change during aging in the glassy state is the molecular mobility, M , which is limited only to local segmental motion in glassy state. Therefore, since the relaxation times in the glassy polymer are directly related to M , the mechanical properties of polymer glasses will be influenced by the physical aging process because of the changes in the relaxation times. A comprehensive investigation of the effects of aging on small-strain creep was carried out by Struik⁴. From this work⁴, a clear illustration of the aging effect is shown in Fig.1-3, which is taken from a study of the isothermal physical

Fig.1-3 Small strain creep curves of rigid poly(vinyl chloride)(PVC) quenched from 90°C (i.e., about 10°C above T_g) to 20°C and further kept at 20°C for a period of 4 years. The different curves were measured for various values of the time t_e , in days, elapsed after the quench⁴. The master curve at $t_e=1000$ days gives the result of a superposition by shifts which were almost horizontal; the shifting direction is indicated by the arrow.

aging of the tensile creep function of an amorphous polymer: poly(vinyl chloride) (PVC) at 40°C after being quenched from 90°C. It shows that for a change in aging time from 0.03 to 1000 days, creep is retarded by a factor of 10^4 - 10^5 . All individual creep curves could be superimposed to form a single master curve at an aging time 1000 days. The necessary shifts, as shown in Fig.1-3, are almost horizontal which indicates that indeed physical aging primarily affects the creep property by changing the relaxation times⁴.

In general, the shifts between successive creep(or stress relaxation) curves are specified in terms of aging shift factor, a_t , defined as⁴⁻⁶:

$$a_t = \tau / \tau_r \quad (1-3)$$

where τ and τ_r are characteristic times in a particular state of aging and at a reference state, respectively. In addition, a "shift rate" may be defined as follows

$$\mu = d\log(a_t) / d\log(ta) \quad (14)$$

where μ is the shift rate and ta is the aging time. Experimental data indicate the μ decreases as $T \rightarrow T_g$ and $T \rightarrow T_\beta$, respectively. Above T_g , the system is at equilibrium and there is no physical aging; and below the β transition, molecular segmental mobility is severely reduced and the aging effect is again reduced.

Besides the shifts which are observed in creep and stress relaxation curves, the existence of an overshooting peak, near the glass transition temperature in Differential Scanning Calorimetry (DSC) experiments, is another well known manifestation of physical aging. A polymer glass, quenched from the equilibrium melt has excess enthalpy, H , because of the "frozen-in" non-equilibrium state. During sub- T_g isothermal annealing for a period of time, the excess enthalpy is reduced by the process of physical aging. During a heating scan at constant heating rate one observes an overshoot peak at T_g which reflects the enthalpy reduction. The size of the peak is proportional to the quantity of enthalpy reduction during sub- T_g aging.

Follow that, the amount of the excess enthalpy decrease during isothermal physical aging process and the enthalpy recovered during heating scan increase with increase in aging time. Thus, the overshoot peaks become correspondingly larger. This phenomenon is commonly known as enthalpy relaxation^{1,3,4}.

1-2 Theoretical aspects of physical aging.

Research efforts¹⁻⁴ on physical aging of polymer glasses are currently being directed in two general directions:

1. To explore the aging phenomenon in various glassy polymers by novel experimental methods.

2. To develop a quantitative theory capable of satisfactorily predicting aging behavior for a variety of polymers under different conditions.

Several theoretical approaches are available to describe the changes that occur during physical aging in polymer glass, and the degree of success in quantitatively describing the related phenomena varies greatly. Three basic approaches⁷ are the free volume, thermodynamic, and kinetic theories. We will briefly review the free volume and thermodynamic theories which we shall refer to our present work.

Free volume theory

The concept of free volume⁴⁻⁷ first found utility in describing the transport properties of viscosity and diffusion in liquids. It is necessary to first look at the successes of free volume descriptions of viscosity for polymer melts, and then consider the applicability of such efforts to glassy state.

The starting point for the present study is the semi-empirical Doolittle equation⁸ for viscosity of a liquid.

$$\ln \eta = \ln A + B(V_0/V_f) \quad (1-5)$$

where η is the viscosity, V_0 is the occupied volume which includes both the volume within the Van der Waals radii and that which is associated with the molecular vibration; V_f is the free volume which refers to the difference between

the total macroscopic volume (V) and the occupied volume(Eq.1-1). A and B are constants. The interpretation of Eq.1-5 is that viscosity is intimately connected with mobility which, in turn, is closely related to free volume. As the free volume increases, the viscosity rapidly decreases. Eq.1-5 has been found to describe the viscosity dependence of simple liquids to a high degree of accuracy. Rearrangement of Eq.1-5 gives

$$\ln \eta = \ln A + B(1/f - 1) \quad (16)$$

where f is the fractional free volume V_f/V .

The empirical function of Williams, Landel and Ferry (WLF)⁹, which was originally developed empirically to describe the change in viscoelastic properties of polymers above T_g , describes the temperature dependence of viscosity and of mechanical relaxation phenomena in the region $T_g < T < T_g + 100^\circ\text{C}$. A shift factor a_t is defined which represents the temperature variation of the segmental friction coefficient or mobility for any mechanical relaxation process and is found to be represented by the following equation^{5,6}:

$$\ln(a_t) = -C_1(T - T_g)/(C_2 + T - T_g) \quad (1-7)$$

where the shift factor $a_t = \eta_T / \eta_{T_g}$ or τ_T / τ_{T_g} (τ is the relaxation time). It was originally thought that the coefficients C_1 and C_2 were universal, but they have been shown to vary from polymer to polymer. It is very interesting to note the variable $T_g - T$ in the right side of Eq.1-7 corresponds to the temperature distance above T_g . This implied that $T_g - T$ serves as a reference scale for the polymer melt behavior. Referring to the Doolittle equation (Eq.1-6), if it is assumed that, above T_g , the fraction free volume increases linearly with temperature, that is:

$$f = f_g + \alpha_f(T - T_g) \quad (18)$$

where f is the fractional free volume at T , any temperature above T_g , f_g is the fractional free volume at T_g , and α_f is the coefficient of thermal expansion of fraction free volume above T_g . We obtain

$$\ln \eta_T = \ln A + B(1/(f_g + \alpha_f(T - T_g)) - 1) \quad \text{at } T > T_g \quad (19)$$

$$\ln \eta_{T_g} = \ln A + B(1/f_g - 1) \quad \text{at } T = T_g \quad (110)$$

Subtraction yields

$$\ln(\eta_T / \eta_{T_g}) = \ln(a_t) = B(1/(f_g + \alpha_f(T - T_g)) - 1/f_g) \quad (111)$$

From above, the following expression is derived:

$$\text{Log}(a_t) = -(B/2.303f_g)(T-T_g)/((f_g/\alpha_f) + T-T_g) \quad (12)$$

which is identical to the WLF equation when we equate C_1 to $(B/2.303f_g)$ and C_2 to f_g/α_f . The WLF treatment of viscoelastic behavior of glassy polymers enjoys great success in the temperature range above T_g but is questionable in the non-equilibrium polymer glass.

Starting with on the free volume concept, Kovacs^{3,11,12} proposed a single parameter model for the description of volume relaxation in polymer glasses during aging. In general, the properties of a pure material in its equilibrium state can be completely determined by specifying its temperature and pressure. However, in a non-equilibrium glassy state, additional parameters are required to specify the state of the system. In the single parameter model, with a single parameter (i.e. free volume), in addition to temperature and pressure are used to describe the non-equilibrium state of polymer glass. For isobaric volume recovery, it is further presumed that the instantaneous rate of change in specific volume is proportional to the deviation from the equilibrium value V_∞ . Thus, Kovacs proposed the equation:

$$dV/dt = [\alpha_g V^\infty dT/dt] - (V - V^\infty)/\tau \quad (13)$$

where V^∞ is the equilibrium volume, $\alpha_g = V^\infty^{-1}(\partial V/\partial T)_p$ is the thermal expansion in the glassy state, dT/dt is the rate of cooling.

Defining a new variable:

$$\delta = (V - V^\infty)/V^\infty \quad (14)$$

which measures the deviation of the fractional free volume from its value at equilibrium, Eq.1-13 can be rewritten as

$$-d\delta/dt = \Delta\alpha dT/dt + \delta/\tau \quad (15)$$

in which $\Delta\alpha = \alpha_l - \alpha_g$ is the difference in the expansion coefficients of the melt and glassy state. Utilizing the Doolittle viscosity equation in a form analogous to Eq.1-5 and 1-11:

$$\ln \tau = \ln \tau_g + B(1/f - 1/f_g) \quad (1-16)$$

where τ is the volume relaxation time and τ_g is the volume relaxation time in equilibrium at a reference temperature T_g , f is fractional free volume, and f_g is the fractional free volume in equilibrium at T_g . Combining Eq.1-14 and 1-15 leads to:

$$-d\delta/dt = \Delta\alpha \, dT/dt + \delta \exp(B/f_g)/\tau_g \exp(B/f) \quad (17)$$

Although, it is expected that any single parameter model will have certain limitations in describing the non-thermodynamic state of glassy polymer, this model enables us to describe qualitatively the volume relaxation behavior of polymer glass after a single temperature jump and under constant rate of heating or cooling^{11,12}. Nevertheless, the difficulty of a single parameter model to describe the thermodynamic or mechanical state of a polymer glass has been recognized, especially with regard to the "memory effect" in volume recovery.

To overcome this, the multi parameter model^{3,11,12} introduces a distribution of relaxation times τ to model the complex behavior in the process. Eq.1-14 can be expressed in the following form:

$$-d\delta_i/dt = \Delta\alpha_i \, dT/dt + \delta_i/\tau_i \quad i = 1, 2, \dots, N \quad (18)$$

Each parameter i contributes an amount δ_i to the deviation of fractional free volume from equilibrium which is directly coupled with its corresponding relaxation time τ_i . The total deviation from equilibrium is defined by the sum of all parts δ_i

$$\delta_i = \sum_{i=1, N} \delta_i \quad (19)$$

$\Delta\alpha_i$ is the contribution of the i th parameter to the expansion coefficient, and therefore

$$\alpha_l - \alpha_g = \sum_{i=1, N} \Delta\alpha_i \quad (20)$$

This refinement enables description of the complex phenomena such as the effect of memory effect, non-linearity, etc.

Note that, as mentioned earlier, the molecular segmental mobility, M , increases with the elevating of temperature (see Fig.1-1) in the glassy state. When the temperature is near the glass transition zone, M increases very rapidly. Therefore, a comparison at the same temperature (T) may not accurately represent the difference among polymeric glasses since they have different T_g s. A more appropriate comparison might be possible at equal distances below a

given reference temperature, usually T_g . This temperature scale T_g-T is based on the presumption of "iso-free volume" at T_g ⁴².

In summary, free volume theory has proven itself extremely useful in qualitatively, and, in some cases quantitatively, describing the aging behavior observed in glassy polymer. This model introduces free volume in the form of segment-sized voids as a requirement for the onset of coordinated molecular motion, and provides a relationship between the coefficient of thermal expansion below and above T_g . It also yields equations relating viscoelastic motion to the variables of temperature and time. Nevertheless, the intrinsic disadvantage of a phenomenological free volume concept approach is that it does not provide insight into molecular processes associated with physical aging as well as poorly defining actual molecular motion¹³. For a more in-depth look into the free volume concept in the polymer glasses, the reader is referred to the literature^{5,6}.

Simha-Somcynsky statistical thermodynamic theory

Simha and Somcynsky¹⁴ have developed a theoretical equation of state for polymer liquids based on a lattice model with additional disorder introduced by vacancies or holes, and the other sites occupied by chain segments. The mathematical details of this model will not be presented here; however, the results of the extension of this theory to the polymer glass will be discussed.

The fraction h of such vacancies may be regarded as an excess free volume function over that existing in the completely filled lattice. A configurational partition function is evaluated for the Helmholtz free energy. In the liquid state, the free volume function h is determined by minimization of the configurational free energy which yields the average free volume at a specified temperature and pressure, as well as the mean square thermal fluctuation and size distribution of the free volume. Experimental data in the polymer melt state have verified the quantitative success of this theory^{15,16}.

Since the glassy state is non-equilibrium, minimization of free energy will no longer be applicable in defining the free volume function. In the isothermal physical aging glass, h will be a function of formation history in addition to the specified temperature and pressure $h(P,T,t_a)$. Thus, above T_g , $h(P,T)$ can be computed numerically from pressure-volume-temperature (PVT) data; below T_g , $h(P,T,t_a)$ can be computed from volume recovery data¹⁷. Robertson et al¹⁸⁻²⁰ have concluded that it is possible to establish quantitatively a connection between isothermal volume recovery data in polymer glasses and corresponding change in viscoelastic shift parameter for stress relaxation through the Doolittle type expression²⁰ coupled with Simha-Somcynsky theory. This approach has been successfully employed in the analysis of experimental data on volume and stress relaxation of poly(methyl methacrylate) and poly(vinyl acetate) during physical aging.

1-3 Methods to monitor the change of free volume during physical aging

Several spectroscopic techniques have been used to monitor the change in free volume during isothermal physical aging. In principle such measurements can yield numerical values for the average free volume, as well as quantify the free volume distribution. Such data could then be compared with theoretical models. In this section, we will briefly review these methods.

Sung et al²¹ first utilized Cis to Trans conversion of substituted stilbenes as photoisomerizable probes to study the changes of free volume in polymers. When irradiated with UV radiation of specified wavelengths, these probes undergo a Cis to Trans isomerization, and the kinetics of this process are found to depend on free volume. The percentage of Cis to Trans conversion is found to decrease during isothermal physical aging as the free volume in the local environment of the probe decreases. Also, it was found that the probe size has some influence on the results. By covalently attaching photoisomerizable probes to the polymer at different positions, it was further shown that the free volume at chain end is greater than that in the interior of chain²². Therefore, it is evident that a distribution of free volume must be considered. Also, Victor et al²³ employed photoisomerizable probes of varying molecular sizes to attempt conclusions regarding variations in size distribution of free volume during annealing in polystyrene of different molecular weights. They showed that the free volume

distribution changes during physical aging with the larger free volume portion of the distribution relaxing more rapidly.

Several results^{10, 24, 25,26} were reported from our laboratory work employing two approaches to monitor the variations of free volume during physical aging by fluorescence probe spectroscopy. First, the fluorescence emission intensity F shows a substantial increase during isothermal physical aging following a quench from melt. This intensity increases during aging, consistent with a decrease in radiationless de-excitation of the probe as the free volume of the polymer matrix decrease. With this fluorescence intensity technique, aging behavior of Auramine O dispersed in poly(vinyl acetate)(PVAc) has been investigated^{24,25}. A time dependent increase in emission intensity F with increasing aging time is observed, which could be interpreted as the relaxation of the matrix free volume. Similar observations, in other probe-polymer combinations, were also reported. Second, the fluorescence anisotropy which is a criterion of the rotational diffusive motion of the probe was found to be strongly dependent on the molecular mobility of polymer matrix in which it is located. The anisotropy increased with aging time, showing consistence with an increases in probe rotational correlation time, due to the collapse of free volume. The variations of anisotropy during isothermal aging time were investigated with a diphenylanthracene probe dispersed in PVAc combination²⁴.

Electron Spin Resonance(ESR) radicals have been widely used in the polymer science²⁷⁻²⁸ field to characterize relaxational transitions and the molecular mobility in polymers. Nitroxide spin probes or labels are incorporated into the polymer matrix as probes and a characteristic three line ESR spectrum is measured. As the mobility of the radicals decreases, so do the rotational correlation time and the spectrum become broad and asymmetric. Such spectra can be resolved using numerical analysis and it is found that the ratio of mobile and immobile component intensities reflect the changes in free volume as associated with physical aging.

The results of the above probe techniques indicate that fluorescence and ESR probes are indeed sensitive to free volume effects in glassy polymer during physical aging. However, a molecular probe must be dispersed in the polymer matrix and this generates some problem. In particular, there are uncertainties regarding the potential perturbation of the polymer matrix by the probe, which will increase with probe size and may make it difficult for such methods to quantitatively relate to the bulk properties of polymer. The positron annihilation lifetimes(PAL) method offers some possibility of avoiding this problem since the positron is the smallest physical probe. The detailed description of the PAL method is given in chapter 2.

1-4 Summary of the literature on physical aging of multicomponent polymer systems

Currently, only a few physical aging studies on multicomponent polymer systems have been reported in the literature. The earlier studies were mainly concerned with changes in the mechanical properties with aging time and temperature in immiscible polymer blends. ABS (rubber modified styrene-acrylonitrile) immiscible blend was analyzed for the shear stress relaxation behavior as a function of aging time in sub- T_g condition by Booij et al³⁰. A stretched exponential function was used to describe the physical aging relaxation behavior of ABS in different thermal history, and it was found that the shear stress relaxation curves can be fitted to a universal master equation. The existence of a universal shape function implies that all relaxation times are identically shifted by temperature or thermal history. A similar experiment on PC/ABS immiscible blends was reported later by Maurer et al³¹ from the same laboratory (DSM, The Netherlands). During isothermal physical aging, the stress relaxation data of the constituent components ABS and PC also can be superimposed into master curves by horizontal shifting. At temperatures well below T_g , the aging rate is 0.9 for both ABS and PC independent of temperature; at temperatures near T_g the aging rate decreases to zero. Consequently, time-temperature superposition for the ABS/PC blend can be expected only within the low temperature regime below $T_g(\text{ABS}) < T_g(\text{PC})$. At high temperatures, the

shear stress relaxation moduli can be calculated from the properties of the immiscible blend components and their concentrations using a suitable morphological model. Recently, Ho et al³² investigated the effect of physical aging on tensile stress relaxation of poly(methyl methacrylate)(PMMA)/poly(styrene-co-acrylonitrile)(SAN), polystyrene/poly(2,6 dimethyl 1,4-phenylene oxide)(PPO), and poly(methyl methacrylate)/poly(vinylidene fluoride) miscible blends in the glassy state. Again, a stretched exponential master curve could be generated with a global value of 0.41 for the spectral parameter β for all three miscible blends 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 also been studied by Cavaille et al^{33,34} and Pathmanathan et al³⁵. 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 there blend.

In addition, the enthalpy relaxation during the physical aging process can be used to investigate the phase separation behavior of polymer blends. If a binary polymer blend system is phase separated, this will result into two distinct enthalpy recovery peaks, provided that the T_g s of the constituent polymers are sufficiently different. Several multicomponent polymer systems have been investigated^{36,37}; including immiscible blends, poly(vinyl chloride)/poly(isopropyl methacrylate),

polystyrene/poly(2-vinylpyridine) and the miscible blend poly(vinyl chloride)/poly(methyl methacrylate). Cowie et al^{38,39} have investigated enthalpy relaxations in the miscible blend, polystyrene /poly(vinyl methyl ether)(PVME). The initial departure of the enthalpy from the final equilibrium value was found to be much lower for the blend, than for the constituent polymers. They concluded that the relaxation process during aging arises primary from the contribution of PVME component. Finally, Ho et al^{40,41} used the four-parameter Moynihan model to simulate the enthalpy relaxation of a series of blends of PMMA with SAN. They showed that the calculated values for the isothermal enthalpy relaxation agree with their previously reported experimental data within the margins of experimental uncertainty.

1-5 Objectives of this study

This investigation described in this thesis represent an experimental contribution towards understanding the isothermal physical aging behavior in the mechanical properties of three miscible polymer blends and that of their constituent components. Static stress relaxation mechanical, dynamical mechanical spectroscopy and positron annihilation lifetime(PAL) spectroscopy were used as tools to investigate the changes at different aging temperatures following a quench from the equilibrium melt state. In this investigation, the positron lifetime

technique provides a view of how molecular behavior (free volume change) relates to viscoelastic properties (macroscopic change) in the polymer glass.

The miscible blends studied were polystyrene(PS)/poly(vinyl methyl ether)(PVME), polystyrene/poly(2,4 dimethyl 1,6 phenylene oxide) (PPO), poly(methyl methacrylate)(PMMA)/poly(ethylene oxide)(PEO). Both PS/PPO and PS/PVME blends have been subjected to extensive earlier studies and are classified as "miscible blends". Also, PMMA/PEO blends are miscible in the melt and in the solid at low PEO composition (lower than 20% PEO by weight). The choice of these three blend systems was based on three important features:

1. The glass transition temperatures and experimental conditions in physical aging experiments are in an easily accessible temperature range for blends and homopolymers.
2. Compatibility of the homopolymer components at convenient blend ratios.
3. Ease of preparation of the polymer glasses for blends and homopolymers.

In studying these blends, we selected compositions in which one component was highly dilute, specifically the systems PS/PPO(90/10), PS/PVME(90/10) and PMMA/PEO(85/15). Several related questions were explored:

1. Does mechanical relaxation time-aging time superposition work for the blend, as it does for homopolymers, and is there a change in the width of the relaxation time spectrum of the blend relative to the homopolymer ?

2. Does a molecular probe for free volume, i.e. positron annihilation lifetime spectroscopy, detect changes in molecule packing of the blend which are consistent with the effect of the polymeric additive on the mechanical relaxation spectrum ?
3. Can the addition of the minor component be describe by a simple effect of change of free volume by using the glass transition temperature as a reducing variable ?

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Chapter 1

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Chapter 2: Positron annihilation lifetime(τ) (PAL) studies of polymers

2-1 Positron, Positronium, and lifetime(τ)

The positron¹⁻³ is unlike some other well-known elementary particles such as electron, proton, and neutron, in that it does not exist naturally in our world except for a very short time. The positron is a positively charged particle (e^+) and an antiparticle to the electron (e^-). Thus, the positron and the electron have identical intrinsic physical properties such as mass, charge, magnetic moment and gyromagnetic ratio. Positrons can only be generated by certain nuclear reactions that follow a nuclear decay, or high energy irradiation. Several β emitting radioisotopes are commercially available as sources of positrons. One such isotope, ^{22}Na , simultaneously emits both positron and two gamma-rays each with a characteristic energy 1.21 Mev¹⁻³.

When a positron is injected into a polymer, it interacts with the molecules of the material through an elastic collision process, i.e. ionization and excitation. The time required for a positron to reach a thermalized state is only 10^{-12} seconds. During the "slowing down" process, and at a nearly thermalized stage, a positron may pick up an electron from the matrix molecules and form a bound state-- the so-called "positronium atom (Ps)"⁴⁻⁵. Therefore, between the times of thermalization and annihilation, the positron may exist in the polymer as either

a positron or Ps in the polymer and may suffer several possible fates:

- 1: annihilation as free positron, ($e^+ + e^- \rightarrow h\nu$).
- 2: bonding of an electron of opposite spin to form a para-positronium(p-Ps) and subsequent self annihilation, ($e^+ + e^- \rightarrow p\text{-Ps} \rightarrow 2\gamma$).
- 3: bonding of an electron of parallel spin to form ortho-positronium(o-Ps) and annihilation by "pick off" an electron with anti-parallel spin, ($e^+ + e^- \rightarrow o\text{-Ps}; o\text{-Ps} + e^- \rightarrow 2\gamma$).

Positronium is a dynamically stable state of e^+e^- bound by coulombic interaction, just as the proton and electron are bound in hydrogen. The electrical force between the electron and positron is dependent on their charges, and not their masses and is 10^{42} times the gravitational force. Since the charge of a positron is the same as charge of a proton, the radius of the electron's orbit is the same in positronium as it is in hydrogen, which is 0.528 Å. A simple schematic illustration of the difference between positronium and hydrogen is shown in Fig. 2-1.

From quantum statistical mechanical reasons, the ratio of p-Ps to o-Ps formation equals 1/3 in the polymer¹⁻³. o-Ps and p-Ps behave differently under vacuum due to conservation of the spin angular momentum during annihilation. Therefore, o-Ps (spin = 1) must produce three gamma-rays upon self annihilation; while p-Ps (spin = 0) only produces two^{1-3, 6-8}.

The lifetime of these bound states (o,p-Ps) in vacuum can be calculated

Fig.2-1 The ground state of the hydrogen and the positronium atom.

theoretically^{1-3, 6-8}. The positron annihilation rate λ is the product of positron velocity v , the available electron density ρ , and the relevant cross section. Thus for the p-Ps state with two gamma-rays annihilation; the annihilation rate is:

$$\lambda = \sigma_{2\gamma} \rho v \quad (2-1)$$

where $\sigma_{2\gamma}$ is the annihilation cross section for the two-gamma ray process. When a low-velocity free positron interacts with a free electron:

$$\sigma_{2\gamma} = 4\pi r^2 c/v \quad (2-2)$$

r is the classical radius of the electron, and c is speed of light in a vacuum. Combining Eq.2-1 and Eq.2-2, we obtained the positron annihilation rate in two-gamma rays as:

$$\lambda = 4\pi \rho r^2 c \quad (2-3)$$

These two gamma rays share an energy of 1.02 Mev (the rest mass energy of the positron added into the rest mass energy of electron). If the center of mass of annihilation pair is at rest, the two gamma-rays share the energy equal and emerge in opposite directions. This means that each gamma-ray photon has an

energy of 0.51 Mev.

By analogy to the hydrogen atom in the ground state, the electron density of p-Ps in vacuum is known, thus we can obtain λ directly from a combination of Eq.2-3 with

$$\rho(0) = 1/8\pi a^3 \quad (24)$$

where $\rho(0)$ is the electron density of hydrogen in ground state and a is the first Bohr radius. Combining Eq.2-3, 2-4, we obtain

$$\lambda = r^2 c / 2a^3 \quad (25)$$

The mean lifetime(τ_1) of p-Ps in vacuum is given by the inverse of the decay rate:

$$\tau_1 = 1/\lambda = 0.125 \text{ nanoseconds}$$

For three gamma-ray annihilation, the cross section is a constant fraction of

$$\sigma_{2\gamma}$$

$$\sigma_{3\gamma} = K \sigma_{2\gamma} \quad (26)$$

where K is a constant.

A similar calculation by combining Eq.2-5, 2-6 and $K=8hc/2\pi e^2$, leads to the o-Ps annihilation mean lifetime(τ_3) in a vacuum with three gamma rays emitted, which is due to the conservation of angular momentum:

$$\tau_3 = 1/\lambda = 142.1 \text{ nanoseconds}$$

Here, three gamma rays will share the 1.02 Mev available energy of 1.02 Mev with the rest masses of annihilation pair.

As mentioned above, positrons in a polymer may be annihilated by three major mechanisms: pickoff of o-Ps, p-Ps, or as free self annihilation of "positron". In a well annealed crystal, nearly all of the positrons will annihilate as free positrons¹⁻³. However if the material is porous, most of the positrons will annihilate through positronium^{1-3, 6-8} (o-Ps or p-Ps). p-Ps usually exhibits self annihilation, i.e. the electron and positron in the positronium annihilate each other. Therefore, its mean lifetime(τ_1) is approximately the same in the materials as it is in a vacuum. On the other hand, o-Ps usually annihilates by interacting with an external electron which has an anti-parallel spin. This annihilation mechanism is referred to as "pick off ", and results into two gamma-rays, being emitted. Each gamma-ray also possesses 0.51 Mev energy , which usually serves as the "stop" signal of annihilation. The pick up annihilation event causes the

lifetime of o-Ps to decrease from 142 ns in vacuum to 1 to 5 ns in the polymers. The magnitude of the o-Ps lifetime(τ_3) is strongly dependent on the electron density in the surrounding media. However, this lifetime(τ_3) is still considerably longer than that of a free positron(τ_3) and p-Ps (τ_1) in the same polymer, because the electron in o-Ps partially shields its positron from those electrons with anti-parallel spin, which would have annihilated it more rapidly. The lifetimes of free positron, o-Ps and P-ps in a vacuum and in a typical polymeric substrate (e.g.; polyvinyl acetate (PVAc)⁹) are shown in Fig.2-2. Because of the relatively long lifetime of o-Ps, its component is well resolved in a lifetime spectrum. Consequently, it is possible to make a precise determination of o-Ps lifetime(τ_3), and the fraction of positrons that annihilate as o-Ps.

The most important feature of o-Ps annihilation in polymers is that this species is preferentially trapped or formed in regions of low electron density or "holes"^{1-3, 6-10}. A distinction between the concept of a "hole" and free volume in the present work is that "hole" refers to a sites in the polymers in which o-Ps is localized, whereas the term free volume as used throughout to polymer literature, is related to macroscopic specific volume measurements which may include unoccupied sites unavailable for o-Ps localization.

Since the annihilation rate of o-Ps is proportional to the overlap of the positron and pick off electron wave functions, it is expected that the o-Ps lifetime will strongly depend on the size of the holes. Once formed, o-Ps diffuses through

	Para-Ps	Positron	Ortho-Ps
lifetimes	τ_1	τ_2	τ_3
in Vacuum	0.124 ns	∞	142 ns
in PVAc	0.11-12 ns	0.34 ns	1-3 ns

Fig.2-2 The spin configurations and lifetimes of ortho-positronium (o-Ps), para positronium (p-Ps), and free positron in a vacuum and in poly(vinyl acetate).

the materials and tends to localize in regions of reduced electron density, where it encounters fewer annihilating electrons, and thus has a longer mean lifetime(τ_3). This means that the lifetime of o-Ps provides information about these mean size of the localized sites. In addition, the corresponding intensity of the o-Ps pick off component is indicative of both the o-Ps formation probability and the density of localization. If a polymer has large holes, the chance of trapping an o-Ps increases. Thus, the intensity(I_3) is expected to be related to the number density of the holes. The sensitivity of lifetime(τ_3) and intensity(I_3) of the o-Ps pick off component to small hole and defects makes PAL spectroscopy a unique technique to probe free volume in polymers.

There is no doubt that o-Ps truly samples " holes " in the molecular substrate, but the precise behavior is still unclear. In polymers containing a distribution of hole sizes, we might expect to find a distribution of o-Ps lifetimes(τ_3). However, the results of previous studies in PVAc⁹ and polycarbonate(PC)^{8,10} show that apparently only a single lifetime component can be clearly identified as o-Ps. Thus, in previous analysis, it was assumed that an o-Ps, after being formed, samples a number of holes during its lifetime, so that all o-Ps have approximately the same lifetime, even though the holes are of different sizes. Thus o-Ps annihilation yields a measurement of the average hole volume $\langle V_f \rangle$. Recently, however, Kluin et al¹⁰ have proposed that certain anomalies in the free positron and p-Ps annihilation parameters are in fact artifacts of the spectrum fitting

procedure it originate from the existence of a distribution of τ_3 . Although we note that this situation is being actively explored, the immediate implications appear to be that the major τ_3 yield an accurate estimate of the true average hole size and volume, but that I_3 may underestimate the true number of "holes" to a degree which depend on the width of the distribution. A quite recent study by Kluin et al²⁶ through computer simulations, which were based on Monte Carlo studies of free volume, of positronium decay in PC show that the fitting results in I_3 significantly departs from the input values. The presence of a τ_3 distribution results in artifacts of the fitting procedure, which influence I_3 ²⁶.

2-2 Theoretical aspects of hole size and apparent free volume fraction(h/c)

We adopt the analysis previously used in our studies of o-Ps annihilation in PVAc⁹. The o-Ps annihilation lifetime(τ_3) and intensity(I_3) contain information on the mean size and density of "holes" in polymers. The relationship between average hole size and volume $\langle Vf \rangle$ and positron lifetime(τ_3) was quantified in a model proposed by Nakanishi et al¹¹ which was based on a model developed by Tao¹² for molecular liquids. It was assumed that an o-Ps in a hole of a polymer may be approximately pictured as a particle in a spherical potential well of radius R_0 . The potential is infinite when $r > R_0$ and constant when $r < R_0$. There is postulated to be an electron layer in the region $R < r < R_0$, where $R = R_0 - \delta R$, and δR is an adjustable parameter. Then, one can obtain a

relationship between R , the radius of hole, and o-Ps lifetime(τ_3) as follows:

The radial part of the Schrodinger equation for the center-of-mass motion of Ps is written as:

$$\{-(\hbar^2/2m_e)[d^2/dr^2 - l(l+1)/r^2] + V(r)\}\phi_{ps}(r) = E_n \phi_{ps}(r) \quad (2-7)$$

where

$$V(r)=0 \text{ at } 0 < r < R_0$$

$$V(r)=\infty \text{ elsewhere}$$

The wave function of Ps, $\phi(r)$, in its ground state, is non zero when only in the well:

$$\phi_{ps}(r) = (2\pi R_0)^{-1/2} \sin(\pi r/R_0)/r \quad 0 \leq r \leq R_0 \quad (2-8)$$

A homogeneous electron layer with thickness δR is assumed to surround the hole. By fitting experimental τ_3 -values against the data from molecular solids with known hole sizes¹³, it was determined that:

$$\delta R = R_0 - R = 1.656 \text{ \AA} \quad (2-9)$$

Consequently, the probability of a Ps in the ground state to penetrate through the electron layer is the integral of the square of the Ps wave function in the layer:

$$P = 4\pi \int_0^R |\phi|^2 r^2 dr = 1 - R/R_0 + 1/2\pi \sin(2\pi R/R_0) \quad (29)$$

It is now assumed that the annihilation rate of o-Ps inside the electron layer is 2 ns, which is the spin average annihilation rate of p-Ps and o-Ps, and which is also very close to annihilation rate of Ps. The o-Ps lifetime(τ_3) is the reciprocal of its annihilation rate, which is the product of the total rate and the probability of "pick off":

$$\tau_3^{-1} = 2[1 - R/R_0 + 1/2\pi \sin(2\pi R/R_0)] \quad (30)$$

From this relationship, R, the average hole radius, can be determined when τ_3 is known, and the mean hole volume is:

$$\langle V_f \rangle = 4/3\pi R^3 \quad (31)$$

The free volume fraction h^{6-8} can be written as

$$h = \int N(V_f) V_f dV_f = \langle V_f \rangle N \quad (22)$$

where $n(V_f)dV_f$ is the number density of holes whose volumes lie between V_f and $V_f + dV_f$, $N = \int n(V_f)dV_f$ is the number of holes per unit volume, and $\langle V_f \rangle$ is the average hole volume. The o-Ps lifetime (τ_3) can be related to the average hole volume through Eq.2-10 and 2-11. Assuming that the o-Ps intensity (I_3) is directly proportional to the total number of holes per unit volume, N , a simple relationship between I_3 and N is obtained:

$$N = CI_3 \quad (23)$$

Combining Eq.2-12 with 2-13, we derive an equation relating the positron results to the free volume fraction:

$$h^{ps} = CI_3 \langle V_f \rangle = CI_3^{3/4} \pi (R^3) \quad (24)$$

where the constant C relating the o-Ps intensity to the total number of holes depends on the rate of formation of o-Ps in holes; and $\langle V_f \rangle$, the average hole volume, is computed from τ_3 via Eq.2-10 and 2-11. The constant C can be determined by comparing the o-Ps parameter with $h(P,T)$ which is determined

from experimental P-V-T (pressure-volume-temperature) data at $T = T_g$ via the statistical mechanical theory of Simha-Somcynsky theory¹⁴⁻¹⁸. At this point, it is not known whether C is a universal constant or is dependent on the polymer chemistry.

2-3 Previous PAL spectroscopy studies in polymers

Positron annihilation has been successfully applied in materials research since its discovery in the late 1960s. The positron's lifetime in a variety of materials is extremely sensitive to phase transitions and the presence of defects as well as other inhomogeneities. The advantages of PAL spectroscopy include: it is nondestructive, no special sample preparation is required, a wide range of temperature is accessible, and, most important of all, is its small probe size. Small angle x-ray diffraction analysis becomes very difficult for measurement of the hole sizes below 10 Å; whereas photochromic and fluorescent methods incorporate a comparatively large probe into the materials. Thus, the extracted information about the hole sizes can be considered only as a rough estimate. However, PAL spectroscopy provides an effective nanometer scale probe for collecting structural information on solid and liquid polymers at the molecular, and even atom level.

The sensitivity of the o-Ps pick off component to the low electron density "hole" volume as related to the physical properties of polymers has been

demonstrated in several studies. In this section, we shall review some of the PAL literatures focusing on the studies of polymer behavior in the glassy and liquid states.

We can classify the previous studies of o-Ps annihilation characteristics in polymers into two major topics:

1. the temperature dependence of the o-Ps annihilation component behavior in polymers through glass transition zone and
2. the sensitivity of the o-Ps annihilation component to changes in free volume during isothermal physical aging of polymer glasses.

The variation of o-Ps lifetime (τ_3) with temperature has been studied for several polymers. Reports on poly(vinyl acetate)(PVAc)⁹, polystyrene¹⁹, polycarbonate(PC)^{6,8,10,20-23}, poly(methyl methacrylate)(PMMA)²⁴, and other Poly(alkyl methacrylate) show an increase in τ_3 with temperature, and an abrupt change in the slope of the τ_3 versus temperature plot at the T_g . The increase in τ_3 is an indication of the thermal expansion of the hole volume. The polymers become rubbery above T_g and the fractional free volume content move rapidly with temperature, which is consistent with the increase in the slope of τ_3 with temperature. The o-Ps intensity (I_3) which is considered as the density of holes also increases with temperature up to T_g . Quantitative correlation between the temperature dependent variation of the o-Ps pick off component and the Simha-Somcynsky free volume function (h) has also been reported. In PVAc, at

temperature $T > T_g$, Kobayashi et al⁹ found an excellent numerical correlation between h and the product $I_3 \langle V_f \rangle$ where $\langle V_f \rangle$ is calculated from Eq.2-11. Below T_g , quantitative interpretation of the positron data is more difficult due to the sensitivity to variations in thermal history.

Transitions at T_g and T_β in the polymer which result in a change in the electron density around an o-Ps trapping site may also affect the o-Ps pick off rate. As mentioned earlier, the lifetime is inversely proportional to the pick off rate and thus may reflect a change in electron density. The detection of T_g and T_β through PAL has been reported for several polymers. In a study of PC, Hill et al²⁰⁻²³ found a change in the temperature dependence of τ_3 and I_3 near the T_β (80°C) of PC. A similar effect at the β transition temperature in PC was also observed in our laboratory in Yu et al's work^{6,8}.

The sub- T_g molecular relaxation process and corresponding free volume changes which occur during isothermal physical aging in polymer glasses can not be easily measured using conventional methods. The capability of the lifetime technique to monitor the variation of hole size and density in glassy state can improve on current understanding of such phenomena. The effect of isothermal physical aging on τ_3 and I_3 in polymer glasses has been studied by several research groups. From our research group, Kobayashi et al⁹ investigated isothermal physical aging effect with aging time in PVAc and found that intensity of o-Ps annihilation exhibits a significant decrease, whereas the lifetime(τ_3)

demonstrates only a very weak dependence on aging time. Similarly, Kasbekar et al¹⁹ found that τ_3 remained nearly constant, and I_3 decrease during physical aging process using two different molecular weight of polystyrene at four different isothermal aging temperatures. Hill et al²⁰⁻²³ carried out a series of PAL studies on glassy polycarbonates, and also found that there is no systematic variation of τ_3 with aging time at three different aging temperatures (-10, 0, 30°C), however I_3 decreased with aging time. Recently, Liu²⁵ reported a 1.2% τ_3 drop in glassy PC after 50 hours isothermal physical aging at 120°C. A small decrease in I_3 was also found. In our laboratory, Kluin et al¹⁰ also made similar observation on PC at aging temperature 30 and 90 °C. Jean et al³ studied isothermal physical aging on two epoxy samples with compositions of DGEBA/DAB/DDH (5:0:5), and (5:5:0) with $T_g=28$ and 125 °C, respectively. The PAL experiments were performed for different aging times at temperatures $T_g-25^\circ\text{K}$ and $T_g-100^\circ\text{K}$. The o-Ps lifetimes(τ_3) decreased approximately linearly with the logarithm of aging time (1000 hours) at $T_g-25^\circ\text{K}$, but the change on τ_3 is negligible at $T_g-100^\circ\text{K}$. These authors did not report any data on I_3 versus aging time. In general, the above results from physical aging experiments in polymers can be interpreted as a minor change in average hole size, and a significant decrease in hole density with an elapsed aging time. However, as a cautious note, recent studies indicate that apparent change in I_3 and τ_3 may occur on long term exposure of polymer glasses to positrons due to chemical damage²⁶. Experiments demonstrate that

such effect are negligible as a prerequisite to studies relating o-Ps annihilation parameters of the polymer aging phenomena.

Finally, up to the present time, PAL studies on polymers have been limited to homopolymers. To our knowledge, no PAL study on polymer blends has yet been reported.

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Chapter 2

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Chapter 3: Physical aging of polystyrene/poly(2,6 dimethyl 1,4 phenylene oxide) blends

3-1 Background

Miscible and immiscible polymer blends¹⁻⁴

Polymer blends may be defined as physical mixtures of two or more structurally different polymers. Such materials have received rapidly growing interest in the last several decades. From a practical point of view, the interest in polymer blends arises from cost effectiveness and their relative ease to be tailored so as to fulfill the new application requirements. As a result, nowadays, a significant number of commercial blends have become available, and continuous efforts are expected to further explore and create more desirable material properties.

Broadly classified, there are two types of polymer blends: (1) miscible blends in which individual components are mutually soluble in one another and give rise to a single phase; (2) immiscible blends in which molecules are not intimately mixed, exhibiting heterogenous phases. When two polymers are blended, the most likely result is a two phase material. The reason that two polymers are not usually miscible becomes apparent from thermodynamic considerations¹⁻⁴. A necessary (but not sufficient) criterion for miscibility is that the free energy of mixing ΔG_m be negative. This is given by

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (3-1)$$

where ΔH_m is the enthalpy of mixing, ΔS_m is the entropy of mixing and T the absolute temperature. For the mixtures of small molecules, the gain in entropy is large, therefore, the free energy of mixing is often favorable, i.e. negative. However, this favorable entropic contribution does not exist when molecules of long chains are mixed. The ΔH_m and ΔS_m of mixing are generally both positive for pairs of polymers so that only if

$$\Delta H_m < T\Delta S_m \quad (3-2)$$

will the two polymers mix to form a single phase. Eq.(3-2) defines a lower limit for ΔH_m above which two polymer are not miscible. An additional, necessary and sufficient condition for the miscibility is given by:

$$[\partial^2 \Delta G_m / \partial \phi_i^2]_{T,P} > 0 \quad (3-3)$$

where ϕ_i is the volume fraction of the i th component. As a result, a mixture of polymers is miscible only to occur under three circumstances:(1) if the polymers are not of very high molecular weight then the entropy will not be negligible, and it may outweigh an unfavorable enthalpy of mixing, e.g. oligomer mixture. (2) If

the enthalpy of mixing is positive but very small, then a small entropy of mixing may be sufficient, i.e. mixtures of two polymer which are very similar in physical and chemical such as copolymers. (3) if the enthalpy of mixing is negative then two polymer would be expected to be miscible, i.e. favorable interaction such as hydrogen bond between the polymers. The miscible polymer blend was once considered to be rare occurrence, but over the last twenty years the number of miscible polymer pairs known has increased, and many of them have found practical applications. An example is the blend with the trademark "Noryl" which is a mixture of polystyrene and poly(2,6 dimethyl 1,4 phenylene oxide), though this commercial blend may also contain a rubbery second phase. A survey of miscible polymers can be found in several books¹⁻⁴.

Experimentally, the T_g has long been used as a criterion for determining the miscibility of polymer blends¹⁻⁴. It has been established that an immiscible blend will exhibit two T_g 's corresponding to those of pure polymeric components. Conversely, in a miscible blend, one T_g (often somewhat broadened) is observed, which occurs at a temperature intermediate between the individual T_g 's of the pure components. A number of experimental techniques of measuring T_g has been used to determine the miscibility. These include calorimetric, dynamic mechanical, dilatometric, and dielectric methods.

For the preparation of polymer blends, the most common commercial method for producing polymer blends is mechanical mixing, due to its simplicity and low

cost. In the laboratory examinations of the properties of blends are often conducted using methods that involve a third component (solvent), such as casting or freeze drying from a common solvent. Such methods require small quantities of materials, and less complicated equipment. In addition, polymer blends can also be prepared by in-situ polymerization, where a blend is prepared by polymerization of one component in the presence of the other. This method often produces an interpenetrating network(IPN) or simultaneous interpenetrating networks. Techniques for preparation of blends have been reviewed in the literature. Each method has its own advantages and disadvantages¹⁻⁴.

Polystyrene(PS)/Poly(2,6-dimethyl 1,4-phenylene oxide)(PPO) blends

The combination of polystyrene(PS) and Poly(2,6-dimethyl 1,4-phenylene oxide)(PPO) is the most investigated miscible polymer blend system. PS and PPO are thermodynamically compatible over entire the composition range. Their blends do not phase-separate even when heated up to 350°C⁵. The addition of PPO to PS causes a transition in mechanical behavior from a brittle material to a ductile glass⁶. The resulting blend is a tough material with good processability.

There have been many studies using various methods to investigate the PPO/PS blends. Differential scanning calorimetry, thermal-optical, dielectrical relaxation, and dynamic mechanical analysis of PS/PPO blends⁶⁻¹³ found a single T_g transition. Small angle neutron scattering(SANS)¹⁴ measurement yield a large

and positive second virial coefficient (A_2), indicating that PS is a good solvent for PPO.

Calorimetry has also shown a negative heat of mixing across the entire composition range. Some investigations¹⁵ indicate that the negative ΔH_m is attributable to phenyl-phenylene group coupling. Furthermore, PS/PPO blends have a negative excess volume of mixing, that is, the density of blend compositions is greater than the weighted average of the densities of the component homopolymers. This is believed to be the result of a contraction of free volume, or densification, on mixing which is an expected consequence of the energetic interaction between PS and PPO. The Flory-Huggins interaction parameter χ_{12} is around -0.06, as obtained from SANS¹⁴.

Mixtures of PPO and PS are of particular interest in our study for the following reasons:

1. The compatible blends of PS/PPO are amorphous in the solid state over the entire range of compositions. One of the constituent homopolymers, PS, is a typical polymer glass. Bulk PPO can not be thermally crystallized, thus glassy PPO can be easily made by simple compression molding¹.
2. The difference between the Tg's of PS and PPO is quite substantial. The Tg's of PS and PPO are around 100°C and 220°C, respectively.
3. PPO is highly ductile, whereas PS is highly brittle. The blends thus have interesting intermediate properties.

Recently, a preliminary investigation was carried out by Ho et al¹⁶ on the effect of physical aging on short-term static stress relaxation behaviors of PS/PPO. They reported a global spectral parameter β of 0.41 for the stretched exponential function analysis with respect to different aging temperatures and times. We shall reexamine their data, and further compare their results with ours. Furthermore, the physical aging phenomena of PS/PPO blends and their constituent homopolymers will be further explored through positron lifetime spectral analysis.

3-2 Experimental

Materials

Commercial polymer specimens were used in this study. Polystyrene(PS) and poly(2,6 dimethyl 1,4 phenylene oxide)(PPO) were purchased from Scientific Polymer Products, Inc. and Polyscience, respectively. The polymer samples had average molecular weights $M_n = 160,000$, $M_w = 280,000$ for PS; and $M_n = 21,000$, $M_w = 41,000$ for PPO. These polymers were directly used without further purification. The molecular structures of the two polymers are shown in the Fig.3-1.

Blends of 90/10 PS/PPO (by weight) were prepared by dissolving the two polymers in chloroform which has a boiling point of 61°C. The 5% (W/V) solution was cast into films on glass plates and dried in a hood at room

Polystyrene (PS)

Poly(2,4 dimethyl 1,6 phenylene oxide) (PPO)

Fig.3-1 Molecular structures of polystyrene and poly(2,4 dimethyl 1,6 phenylene oxide).

temperature. The solvent cast films, which were usually to be homogeneous, were treated under a vacuum oven at room temperature for 24 hours, followed by 72 hours at around 65°C to remove all the solvent. Then, these films were molded at $T_g + 40^\circ\text{C}$ to obtain a square sheet with thickness around 1 mm.

For the purpose of comparison, the same PS shall be used in the preparation of PS/PPO(90/10) blend and PS/PVME(90/10) blend in the next chapter. The pellet form of PS and powder form of PPO were also directly molded at $T_g + 40^\circ\text{C}$. The thickness of the homopolymer films is around 0.8-1 mm.

Standard ASTM D 1708-84 dog-bone shaped specimens and small disks with radius around 8 mm were cut from the molded sheets of the blends, and from the homopolymers by blade die. These specimens were kept in a sealed desiccator to prevent any moisture uptake before the static stress relaxation, dynamic mechanical, and PAL experiments were performed.

Differential scanning calorimetry

The glass transition temperature (T_g) of blend and PS samples were determined by Perkin-Elmer differential scanning calorimetry 7 at a heating rate of 20°C/min. Each DSC testing cycle consisted of heating up, cooling, and then repeat heating scans. The first heating scan gave a rough estimate of T_g ; the highest temperature in the transition region was then chosen as the annealing temperature, and the specimens annealed at this temperature for three minutes

to eliminate the previous thermal and mechanical history. The final heating scan was performed immediately after cooling (at $100^{\circ}\text{C}/\text{min}$) the sample from its annealing state, and the T_g was subsequently determined. The point of equal distance to the baseline, above and below the transition zone was chosen as T_g . This T_g value was used as the reference temperature in choosing the aging temperature. The above thermal history for DSC measurement was designed in order to facilitate the comparison of T_g 's of the blends and the homopolymers. The DSC curves for the PS/PPO blend, PS and PPO homopolymers are displayed in the Fig.3-2.

Static stress relaxation mechanical spectroscopy

The variation of static mechanical spectra during isothermal aging was probed using the small strain stress relaxation technique under simple tensile extension within the linear viscoelastic region. The static mechanical experiments were performed using a microprocessor controlled Rheometric Solids Analyzer II(RSA II)¹⁷ equipped with a temperature controlled testing chamber. The operation of the RSAII is just like that of a small Instron, except that it possesses two air-bearing transducers which make the response time of stress and strain less than 5 milliseconds. The chamber temperature stability was as good as $\pm 0.5^{\circ}\text{C}$ for the duration of measurements (max. 9 hours). The uniform temperature is maintained

Fig.3-2 DSC curves of PS/PPO(90/10) blend , PPO, and PS homopolymers at a heating rate of 20°C/min.

by positioning a thermocouple just at the center of the sample so as to monitor the variation of temperature.

The testing sequence of stress relaxation behavior during isothermal physical aging was chosen to conform with the schedule suggested by Struik¹⁸, which consisted of alternating aging and measuring periods. The dog-bone shaped samples were first annealed at $T_g + 10^{\circ}\text{C}$ for one hour in the testing chamber to eliminate their previous thermal history and to reach their thermodynamic equilibrium state. This was followed by quenching to the selected aging temperature (T_a) by blowing dry, cool air into the chamber, and maintaining isothermal conditions at T_a throughout the entire experimental period. The time required to cool the specimen from $T_g + 10^{\circ}\text{C}$ to T_a was only two minutes. The alternative of quenching in liquid nitrogen was rejected because a high cooling rate will produce some internal stress in these samples. These residual stresses may modify their mechanical properties. Also the measurement accuracy may be decreased due to the dimensional and shape changes which will occur at long aging times.

The time required for the temperature of the testing chamber's temperature to reach T_a was set as the initial aging time $t_a = 0$. Successive tensile stress relaxation tests were carried out at different aging times (t_a). During each test, the sample was strained, kept at a constant strain of 0.2%, and the stress was monitored until the testing time approached 10% of the aging time (t_a). This

ensured that the aging effects during individual tests were negligible. We define the tensile stress relaxation modulus (in units N/m^2):

$$E(t) = \sigma(t)/\epsilon \quad (34)$$

where $\sigma(t)$ is the stress recorded by RSAII, and the strain ϵ is 0.2%.

At the end of each measurement, the strain was released while the sample was still kept at isothermal condition in the chamber, at the aging temperature T_a , waiting for the next test. It is important to note the difference between the two time scales; t_a is the aging time, beginning at the moment of the chamber temperature attains T_a after a rapid quench, whereas t is the stress relaxation measurement time, which begins at the moment the 0.2% strain is applied.

All the data were collected and stored in the IBM PS2 mode 50 computer, and later converted to ASCII files for storage in floppy disks for further analysis. Each blend and the homopolymers were subjected to four different aging temperature tests.

Positron annihilation lifetime(PAL) spectroscopy¹⁹⁻²¹

The basic function of a positron annihilation lifetime spectrometer is to measure the time interval between the 1.28 Mev gamma-ray from the source due to the nuclear decay from source and one of the 0.511 Mev annihilation gamma-

rays. The positron annihilation lifetime spectrometer used in this work consists of a vacuum sample chamber, Barium Fluoride(BaF_2) and Cesium Fluoride(CsF) gamma-ray detectors, and a fast-fast coincidence detection system which is based on EG&G Ortec MIN modules(model 583 constant-fraction discriminators(CFD) and a model 566 time-to-amplitude converter(TAC)). The schematic diagram of this positron lifetime spectrometer is shown in Fig.3-3. Positron lifetime spectra were collected on a PCA multichannel analyzer (Nucleus Inc.). To optimize the time resolution function as well as the efficiency of the spectrometer, a cylindrical CsF 1.5" length and 1.5" diameter, coupled by glycerol to a photomultiplier tube (type H2431, Hamamatsu) was used as a scintillator to detect the 1.28 Mev gamma-ray which indicates the "birth" of a positron. In order to detect the 0.511 Mev annihilation gamma-ray, which serves as the "death" signal, a conical BaF_2 -crystal of 0.8" and 1.0" diameter and 1.0" length likewise mounted to a photomultiplier tube (type H2431Q, Hamamatsu) was employed.

Disk shaped polymer film samples with radius around 8 mm and thickness around 1 mm were stacked to 2 mm thickness. The radiation source ^{22}Na was sandwiched between the two 2 mm stacked disks. This three layer sandwich was completely enclosed in a copper sample holder. Heating wires were mounted at the two opposites sides of the sample holder, so that a good thermal contact to the sample can be achieved, and to prevent the possibility of any thermal gradient. The entire assembly was then installed inside a vacuum chamber which

Fig.3-3 A block diagram of PAL spectrometer²⁰

is connected to a vacuum pump and a meter. Each selected measuring temperature was kept constant within $\pm 0.2^{\circ}\text{C}$ during the entire period of PAL spectra collection by means of two diode sensors, which are connected to a temperature controller (Lake Shore Cryogenics, model 805). Uniformity and stability are maintained by using two sensors to monitor the temperature because they cover two different surface areas and control temperature fluctuations during the data collection.

The source, $^{22}\text{NaCl}$, was deposited on a thin aluminum foil (1.7 mg/cm^2) within an area of diameter 2.5 mm. The foil was then folded up into a 7 mm square shape to prevent any loss of the source. The source packet was sandwiched between two samples as mentioned earlier. A proton in the ^{22}Na nucleus decays to a neutron and a positron. The gamma-decay of the intermediate state of ^{22}Na is employed as the "birth" signal of the positrons. The relatively slow decay rate of ^{22}Na makes it a practical isotope for lifetime spectroscopy. ^{22}Na has a long half-life 2.6 years, and in small quantities the isotope emits positron at a sufficiently low rate so as not to saturate the sample with positron. Ideally, only a single positron should be present in the sample at any time. The nuclear decay scheme of ^{22}Na is shown in Fig.3-4.

The windows of the constant fraction differential discriminators used to select the energy range of the gamma ray were set using a ^{22}Na positron source with

Fig.3-4 The nuclear decay scheme²⁰ of a positron source ^{22}Na .

a polycarbonate sample. Spectra which contained about 1.2 million counts were collected within 30 minutes (at a count rate of 670 cps).

The time resolution function in each measurement was determined in the process of computer fitting of the data, and was compared with independent measurements using the prompt gamma ray of ^{60}Co . For ^{60}Co the full width at half maximum(fwhm) was consistently less than 230 cps.

Two kinds of experiment which were performed with the PAL spectrometer: isothermal physical aging and temperature dependence experiments. Since the goal of the PAL investigation is to probe the change in free volume in the blend and homopolymer at comparable temperatures T_g-T during isothermal physical aging, the thermal and mechanical history of the samples must be precisely controlled.

For each physical aging experiment, the annealing temperature was held at $T_g+10^\circ\text{C}$ for one hour to erase the prior thermal history, and to attain an equilibrium state. After quenching to the selected aging temperature (T_a) at approximately $5^\circ\text{C}/\text{min}$. followed by a thermal equilibration period of 10 minutes followed, the temperature of the entire sample was uniform and stable. Data were then collected over 18 to 37 hours of isothermal physical aging. The accumulation time for each datum was set at 60 minutes for the entire aging test period.

For the study of the temperature dependence of PAL spectra, the temperature was also raised from ambient temperature to $T_g + 10^{\circ}\text{C}$ and held for one hour to erase prior thermal history of the sample, and to reach thermodynamic equilibrium. The sample was cooled to the selected temperature at a cooling rate of around $5^{\circ}\text{C}/\text{min}$ and held for 10 minutes to reach thermal equilibrium, and spectra were recorded for 45 minutes at this temperature. Subsequently, the sample was heated to $T_g + 10^{\circ}\text{C}$ for 25 minutes to create a new annealing period followed by cooling to the next selected temperature then recorded spectra for 45 minutes after 10 minutes for thermal equilibrium. Spectra were recorded as above in the temperature range near T_g to ambient.

All the specimens for PAL spectroscopy were cut from the same sample sheet for the mechanical studies. Separate samples were used for temperature dependence and isothermal physical aging studies.

2-3 Data analysis

Static stress relaxation mechanical spectra

The simplest definition of "relaxation" is the time-dependent return to equilibrium of a system which has experienced a change in the constraints acting on it. The constraints may be pressure, temperature, volume, or may involve an applied field such as mechanical stress and magnetic field. The relaxation

behavior of the system is observed by monitoring the way some property changes with time. For small perturbation, the rate at which a perturbed system returns to equilibrium is proportional to the distance from equilibrium. If we assign the parameter, $\phi(t)$, to the difference between the value of an observed property at time, t , and the equilibrium value reached at an infinite time after a step function change in constraint then

$$- d\phi(t)/dt \propto \phi(t) \quad (3-5)$$

which has the simple exponential solution with a single time constant τ ,

$$\phi(t) = \exp(-(t/\tau)) \quad (3-6)$$

The constant τ , is called the characteristic relaxation time. Most previous studies of relaxation phenomenon of polymer glasses have reported that Eq.(3-6) does not describe well. Instead, a Kohlrausch-Williams-Watts (K-W-W)^{22,23} stretched exponential function of the form:

$$\phi(t) = \exp(-(t/\tau)^{\beta}) \quad (3-7)$$

where τ is a characteristic relaxation time and β is a spectral width parameter, $0 < \beta < 1$, is generally found to yield an excellent fit to experimental data compared to Eq.3-6. Of course, one reason for the good fit is the introduction of an adjustable parameter, β , in Eq.3-7 in contrast with Eq.3-6. The β parameter may be interpreted as a measurement of the width of the relaxation spectrum. The distribution of relaxation times becomes broader as β becomes smaller. (Fig.3-5).

From the relaxation function of Eq.3-7, the mean relaxation time $\langle \tau \rangle$ is found to be²³:

$$\langle \tau \rangle = \int \phi(t)dt = \int \exp(-(t/\tau)^\beta) dt = (\tau/\beta)\Gamma(1/\beta) \quad (3-8)$$

where Γ is the gamma function. Extraction of parameters for a stretched exponential function is usually accomplished by using a non-linear least square fit for the experimental data. In this study, a nonlinear least square-Marquadt-Levenberg algorithm was used for analysis of the relaxation phenomena during isothermal aging.

Most relaxation phenomena which occur in polymers can be understood in terms of a summation of many different elementary processes, each of which is governed by a single exponential decay with characteristic relaxation time τ . It is

Fig.3-5 Plot of stretched exponential function, $\phi(t) = \exp(-(t/\tau)^\beta)$, showing the effect of the spectral parameter β : (a) β covering nearly the full range of possible values, (b) an expanded view showing the effect of small changes in β .

theoretically appealing to express the relaxation spectrum as an integral sum of exponential decays:

$$\begin{aligned}
 \phi(t) &= \sum \exp(-t/\tau) \\
 &= \int \exp(-t/\tau) d\tau \\
 &= \int \tau \exp(-t/\tau) d\ln\tau \\
 &= \int \rho(\tau) \exp(-t/\tau) d\ln\tau
 \end{aligned} \tag{3-9}$$

where $\rho(\tau)$ is the distribution function of relaxation times. The $\rho(\tau)$ can be calculated from $\phi(t)$ by using the Alfrey's approximation method²⁴.

$$\rho(\tau) = -[d\phi(t)/d\ln\tau]_{t=\tau} \tag{3-10}$$

Substituting Eq.(3-7) into Eq.(3-10) we obtain

$$\rho(\tau) = \beta(t/\tau)^\beta \exp(-(t/\tau)^\beta) \tag{3-11}$$

Once the parameter β and τ were extracted by nonlinear least square-Marquadt-Levenberg fits, the distribution function of relaxation times $\rho(\tau)$ can be computed via Eq.3-11.

In this work, we monitored the tensile stress relaxation curves at different aging times at the same aging temperature. A typical stress relaxation curve of a polystyrene after two hours of isothermal physical aging at $T_g-15^{\circ}\text{C}$ after a quenched from the melt state is exhibited in Fig.3-6. Combining Eq.3-4 and 3-7, we have

$$\phi(t) = E(t)/E_0 = \exp(-(t/\tau)^{\beta}) \quad (3D)$$

$$E(t) = \sigma(t)/\epsilon = E_0 \exp(-(t/\tau)^{\beta}) \quad (3E)$$

where $E(t)$ is the relaxation modulus collected at time t and E_0 is the initial value of the relaxation modulus at testing time $t=0$. The steps for the analysis of stress relaxation curves during isothermal physical aging through the stretched exponential function fitting are shown as follows:

1. A initial value E_0 was obtained from the first data point of experimental results for the tensile stress relaxation curves. This datum was usually recorded at 0.29 sec after applied strain(0.2%).
2. This initial value of E_0 , determined for each measurement, was used to calculate β and τ by fitting each stress relaxation curves to Eq.3-13 using a nonlinear least square-Marquadt-Levenberg algorithm with two unknowns (β

Fig.3-6 Typical stress relaxation curve of a polystyrene specimen after two hours of physical aging at $T_g - 15^\circ\text{C}$ when quenched from the melt state.

and τ). This is a subroutine function from the Mathview ProfessionalTM software package²⁵. We had success in converting the original data file created by the Rheometric RSAII to ASCII files. Therefore, we can transfer the data files within the PC, VAX, and MAC.

3. The resulting spectral parameter β for all the tested data were found to lie within a narrow range. Then, an average β was obtained.
4. We then proceeded to recalculate E_0 and τ based on the average value of β again using the nonlinear least squares-Marquadt-Levenberg algorithm with two unknown parameters (E_0 and τ).
5. The average β and the final computed values of E_0 and τ were taken as stretched exponential fits (Eq.3-12) to the tensile stress relaxation curves.

From the above data fitting sequence, it follows that an average β value at different aging times during the isothermal physical aging process is adequate to represent the short term stress relaxation changes.

Positron lifetime spectra^{20,21,25}

Fig.3-7 shows a typical PAL spectrum which include the lifetimes of each positron annihilating in the polymer, in the ²²Na source and in the aluminum foil^{20,21}. Positron lifetime spectra can normally be resolved into a number of exponential, each representing an annihilation process with a mean lifetime (τ) and a relative intensity (I). In our case, each spectrum was fitted to a sum of four

exponentially decaying functions convoluted with a resolution function, by means of the program PATFIT-88²⁶. The resolution function was approximated as a sum of three Gaussians whose statistical weights and full widths at half maximum (FWHM) are determined by the fitting program. The resolution function consistently had FWHM of about 230 ps equal to that found from the ⁶⁰Co source.

After the resolution function is found from analysis of the initial run on a sample, the parameters to be determined in each subsequent analysis are the position t_0 for the starting point of each exponential decay and four intensities (I_s, I_1, I_2, I_3) and four decay constants (reciprocals of the mean lifetimes τ_s, τ_1, τ_2 , and τ_3) for the exponential functions. From the known foil thickness, the number of positrons annihilating in the aluminum foil was calculated to be about 7%, i.e., I_s . In addition, the positron lifetime in aluminum is known to be $\tau_s = 180$ ps¹⁹⁻²¹; therefore, the values of I_3 and τ_3 can be fixed in the curve fitting procedure.

The PATFIT-88 program has the flexibility to permit constraints in some parameters. There are seven parameters which need to be determined through PATFIT-88 fitting after subtracting the known source component. They are the starting time t_0 , the three lifetimes and the three intensities. As mentioned in chapter 2, theoretically, the shortest lifetime component results from annihilation of Para-PS, whose mean lifetime is known to be approximately 125 ps. Therefore,

Fig.3-7 A typical PAL spectrum of polycarbonate²⁰.

here was a constraint, τ_1 fixed at 120 ps, applied for PAL data analysis. However, we tabulate the constrained and unconstrained fitting results of PAL data in the appendix A.

The experimental work of PAL spectroscopy has been performed in collaboration with Dr. John McGervey of the department of Physics and Mr. Zinbin Yu who carried out most of the PAL data analysis presented in this thesis.

3-4 Results and discussion

Differential scanning calorimetry(DSC) thermogram

Fig.3-2 depicts the DSC traces obtained for quenched PS/PPO(90/10) blend, PS and PPO homopolymers at a heating rate of 20⁰C/min. The point of equidistance to the base line above and below glass transition zone, was taken as the glass transition temperature. **The symbol " Tg " will be used to represent the equidistance glass transition temperature obtained from the DSC thermogram.** The same definition shall be maintained throughout this work except when otherwise stated.

Miscibility was evidenced in the blend of PS/PPO(90/10) by the exhibition of a single Tg at 116⁰C which falls between the Tgs of the constituent homopolymers. A single Tg in the PS/PPO blend implies miscibility¹⁻⁴. The Tgs for the PS and PPO homopolymer are 105 and 212⁰C, respectively. The Tg values of blend and homopolymer are in agreement with the literature values^{1,5,6,11,27}. Thus, these Tg values were used as the reference temperatures in choosing the annealing temperatures for isothermal physical aging experiments.

A broadening of the glass transition zone was observed in the PS/PPO blend compared with those of pure homopolymers. The width of the transition zone, which has been defined as the horizontal distance between the onset and the final temperatures of transition zone, was 18⁰C for the blend compared with

9⁰C and 8⁰C for PS and PPO, respectively.

Schneider et al²⁸⁻³⁰ have already made an extensive and systematic analysis of the broadening of the glass transition zone in compatible polymer blends. They concluded that this broadening can generally be attributed to the distribution of molecular segmental environments generated by local concentration fluctuations³¹⁻³³. In the latter part of this section, we shall employ this concept in the interpretation of discrepancies between the mechanical behavior of the blend and constituent homopolymers during physical aging experiments.

Static stress relaxation mechanical spectra

Momentary tensile stress relaxation $E(t)$ at different aging times (t_a) during isothermal physical aging of a PS/PPO(90/10) blend quenched from the equilibrium melt ($T_g + 10^0\text{C}$) to the selected aging temperature, $T_a = 96^0\text{C}$ ($T_g - 20^0\text{C}$), is shown in Fig.3-8. Tensile stress relaxation mechanical spectra were obtained with increasing aging time(t_a) following the experimental sequence suggested by Struik¹⁸. Fig.3-8 shows that the shape of the relaxation curves is not affected by the aging times(t_a) during the isothermal physical aging, but the position of the curves on the logarithmic testing time scale shifts to longer times with increasing aging time. This indicates that the characteristic relaxation time(τ) of the stress relaxation curves become longer with increasing aging time. Using Eq.3-13 and the nonlinear least square Marquardt-Levenberg fitting

Fig.3-8 Stress relaxation curves for PS/PPO(90/10) blend during isothermal aging at $T_g - 20^\circ\text{C}$ ($T_a = 96^\circ\text{C}$) after a quench from equilibrium melt above T_g . Symbols correspond to different aging times(t_a) as indicated; solid lines are fits to stretched exponential function with $\beta = 0.48$.

procedures²⁵ described in Section 3-3, each tensile stress relaxation curve can be represented by a stretched exponential function with spectral parameter $\beta = 0.48$. The solid curves in Fig.3-8 are the best-fit results. From such fits, the instantaneous modulus E_0 , characteristic relaxation times τ were determined and presented in Table 3-1, together with the values of the mean relaxation times, $\langle \tau \rangle$, which were calculated via Eq.3-8. E_0 shows only very slight variation which is a reflection of the densification of blend specimens during isothermal physical aging^{34, 35}. Such densification has also been observed earlier³⁶. The increase of τ and $\langle \tau \rangle$ with aging times(t_a) confirms the early statement (see section 1-1) that physical aging primarily affects the magnitude of the relaxation times¹⁸.

It is well known that the molecular segmental mobility, M , increases with the elevation of temperature (see Fig.1-1) in the glassy state. When the temperature is near the glass transition zone, M increases very rapidly. Therefore, a comparison at the same temperature(T) may not accurately represent the difference between the blend and the homopolymers since they have different T_g s. A more appropriate comparison might be possible at equal distances below a given reference temperature, usually T_g . This temperature scale $T_g - T$ is based on the presumption of "iso-free volume" at T_g ³⁷. **Thus, the comparable temperature distance, $T_g - T$, shall be used as a reference scale in our studies.**

The results of physical aging experiments on the PS/PPO blend at other aging temperatures, $T_a = T_g - 15, 25, 30^\circ\text{C}$, exhibit the same general features: a

Ta °C	ta min.	Eo x10 ⁹ Pa	τ sec	β	$\langle \tau \rangle$ sec
Tg-15	30	4.89	368.1	0.47	831.0
	60	4.92	548.4	0.47	1238.0
	120	4.97	775.8	0.47	1751.3
	240	4.93	1581.3	0.47	3569.7
Tg-20	30	5.03	463.7	0.48	978.9
	60	5.07	692.8	0.48	1462.6
	120	5.07	1035.9	0.48	2186.9
	240	5.06	2282.3	0.48	4818.2
Tg-25	30	5.16	889.4	0.45	2173.4
	60	5.19	1353.7	0.45	3308.0
	120	5.27	1994.7	0.45	4847.5
	240	5.17	4337.7	0.45	10600.3
Tg-30	30	5.12	1801.7	0.43	4908.8
	60	5.17	2149.2	0.43	5855.6
	120	5.24	3451.2	0.43	9402.9
	240	5.23	5459.2	0.43	14873.8

Table 3-1 Stretched exponential curves fitting results for PS/PPO(90/10) blend.

systematic shift of the stress relaxation curves to longer relaxation times. The same data analysis using the stretched exponential function fitting was carried out for these stress relaxation spectra at different T_g - T . The relaxation parameters, E_0 , τ , β , and $\langle \tau \rangle$, were determined from these data and also are summarized in Table 3-1. The isothermal physical aging behavior of the PS/PPO blend as probed by the momentary tensile stress relaxation tests is quite similar to the aging phenomenon which Struik reported from momentary creep measurements on homopolymers¹⁸. This implies that qualitatively the behavior of the PS/PPO miscible blend with respect to stress relaxation mechanical spectra is similar to that of the pure components.

Analogous isothermal physical aging measurements were made with the PPO and PS homopolymers at the aging temperature distances T_g -15, 20, 25, 30°C. Fig.3-9 and 3-10 show, respectively, the stress relaxation curves of PPO and PS homopolymers at aging temperature T_g -20°C with four different aging times (t_a from 30 to 240 minutes). The solid curves in Fig.3-9 and Fig.3-10 are the stretched exponential function fits with the spectral parameter $\beta = 0.56$ for PPO and $\beta = 0.45$ for PS. The relaxation parameters (E_0 , β , τ , and $\langle \tau \rangle$) resulting from the stretched exponential function fits for the stress relaxation spectra of the PPO and PS homopolymers at different aging times and temperature distances are summarized in Table 3-2 and 3-3, respectively.

As we observed, the physical aging behavior for PS and PPO homopolymer

Fig.3-9 Stress relaxation curves for PPO homopolymer during isothermal aging at $T_g - 20^\circ\text{C}$ ($T_a = 192^\circ\text{C}$) after a quench from equilibrium melt above T_g . Symbols correspond to different aging times (t_a) as indicated; solid lines are fits to stretched exponential function with $\beta = 0.56$.

Fig.3-10 Stress relaxation curves for PS homopolymer during isothermal aging at $T_g - 20^\circ\text{C}$ ($T_a = 85^\circ\text{C}$) after a quench from equilibrium melt above T_g . Symbols correspond to different aging times (t_a) as indicated; solid lines are fits to stretched exponential function with $\beta = 0.45$.

Ta °C	ta min.	Eo x10 ⁹ Pa	τ sec	β	$\langle \tau \rangle$ sec
Tg-15	30	3.47	214.1	0.58	337.0
	60	3.57	302.8	0.58	476.6
	120	3.72	428.2	0.58	674.0
	240	3.85	605.5	0.58	953.2
Tg-20	30	3.58	372.4	0.56	617.0
	60	3.69	563.6	0.56	903.6
	120	3.79	798.3	0.56	1322.9
	240	3.92	1168.8	0.56	1936.9
Tg-25	30	3.70	448.9	0.50	897.8
	60	3.74	680.3	0.50	1360.8
	120	3.92	1031.3	0.50	2062.6
	240	4.04	1563.1	0.50	3126.2
Tg-30	30	3.87	598.9	0.46	1415.2
	60	3.93	790.2	0.46	2190.1
	120	4.10	1222.8	0.46	3389.3
	240	4.21	1892.4	0.46	5245.2

Table 3-2 Stretched exponential curves fitting results for PPO.

Ta °C	ta min.	Eo x10 ⁹ Pa	τ sec	β	$\langle \tau \rangle$ sec
Tg-15	30	2.88	511.9	0.47	1166.0
	60	2.88	816.3	0.47	1859.0
	120	2.91	1276.9	0.47	2908.5
	240	2.90	2234.0	0.47	5088.6
Tg-20	30	2.91	1186.2	0.45	2985.4
	60	2.93	1783.8	0.45	4489.4
	120	2.95	3150.0	0.45	7927.9
	240	2.96	5645.0	0.45	14207.2
Tg-25	30	2.97	2507.7	0.41	7748.9
	60	2.97	4322.9	0.41	13357.9
	120	3.98	8116.8	0.41	25081.1
	240	3.02	14386.4	0.41	44454.3
Tg-30	30	2.94	5730.4	0.40	19442.9
	60	2.96	8313.0	0.40	28205.6
	120	2.99	12610.9	0.40	42788.1
	240	2.99	25248.2	0.40	85665.8

Table 3-3 Stretched exponential curves fitting results for PS.

also similar to that described by Struik¹⁸. Furthermore, we observed that the relaxation time-aging time superposition¹⁸ was valid for both our blend and the constituent homopolymers.

Clearly, from Fig.3-8, 3-9, and 3-10, these stress relaxation curves can be superimposed by simple horizontal shifting along the logarithmic time axis (X-axis) to form a master curve. To perform this superposition for the construction of a master curve, the β at the various aging times must be the same, i.e., the shape of these relaxation curves must be invariant. The characteristic relaxation times τ control the shifting in this time domain relaxation experiment. Therefore, we calculated the shift factors using Eq.1-3. Besides, the shift procedure can also be carried out manually using a light box^{34,38}. Within the experimental error, the shift factors obtained from Eq.1-3 and manual shifting are essentially the same. We will demonstrate this point in the later section 4-4. The master curves for PPO, PS, and the blend at the same aging temperature distance, $T_g - 20^\circ\text{C}$, were constructed as shown in Fig.3-11; where aging time $t_a = 4$ hours was taken as the reference time. It is clearly seen from Fig.3-11 that the stress relaxation process proceeds much faster in the PPO homopolymer than in the blend and PS. In Fig.3-11, to reach 80% extent of relaxation, it takes 40 seconds for PPO, 90 seconds for blend and 180 seconds for PS during stress relaxation test at $t_a = 4$ hours and $T_a = T_g - 20^\circ\text{C}$. This implies that the increase of relaxation rates ($\Gamma = \tau^{-1}$) is in the order of $\Gamma_{\text{PPO}} > \Gamma_{\text{blend}} > \Gamma_{\text{PS}}$ with decreasing T_g at the

Fig.3-11 Superposition of stress relaxation curves of PS/PPO blend, PS, and PPO homopolymers at different aging times(t_a) and the reference time was selected at $t_a = 4$ hours; aging temperature $T_a = T_g - 20^\circ\text{C}$. The master curves from left to right are PPO, blend, and PS respectively. Comparisons are made with stretched exponential function with respective, $\beta = 0.56, 0.48, 0.45$.

comparable aging temperature distance $T_g - 20^\circ\text{C}$.

The relaxation curve of the PPO homopolymer shows a narrower relaxation spectrum as is manifested by a smaller β value (see Fig.3-11). There is a close similarity in the relaxation curve of PS/PPO blend and PS homopolymer, as expected since PS is the major component (90% by weight) in the blend. The PS "matrix" in the blend has the dominant influence on the overall relaxation behavior of this binary miscible mixture. This also gives an implication that PS-rich regions, which are generated by concentration fluctuations, may have an important role in stress relaxation experiment.

In contrast to chemical aging or degradation, physical aging is a thermoreversible process^{18,39}. This means that the original state of thermodynamic equilibrium can be recovered by reheating the aging polymer above T_g and the previous aging history will be erased or "forgotten"^{18,39}. Re-cooling to the same aging temperature should introduce the same aging effect as before. The thermoreversibility of PS/PPO blend is depicted in Fig.3-12 which presents the physical aging behavior of PS/PPO blend at $T_g - 20^\circ\text{C}$ upon being quenched from the equilibrium melt. The stress relaxation spectra data were collected at aging times 60 and 120 minutes. The relaxation spectra for the first run are displayed as solid curves in Fig.3-12. In the repeated experiments, the blend specimen was reheated to $T_g + 10^\circ\text{C}$ and held at this equilibrium melt state for one hour, and again quenched to $T_g - 20^\circ\text{C}$. The relaxation spectra were

Fig.3-12 Stress relaxation curves(solid curves) for PS/PPO(90/10) blend during isothermal aging at $T_a = T_g - 20^\circ\text{C}$ and $t_a = 1, 2$ hours following a quench from equilibrium melt above T_g . Symbols on the curves represent the repeat experimental tests for thermoreversibility.

obtained at the same aging times as the first run; i.e., $t_a=60$ and 120 minutes. The reaging results are presented symbolically in Fig.3-12. Data from the second quench (symbols) essentially coincide with the curves of first quench. This confirms that the PS/PPO blend does not degrade chemically during the physical aging process and that we indeed observed the pure thermoreversible physical aging effect in the PS/PPO blend.

The calculated mean relaxation times $\langle \tau \rangle$, using Eq.3-8, are displayed in Tables 3-1, 3-2, and 3-3 for the PS/PPO blend, and PPO, and PS homopolymers, respectively. A plot of $\langle \tau \rangle$ versus aging temperature distance, T_g-T , for homopolymers and blend at a constant aging time ($t_a=4$ hours) is shown in Fig.3-13. The mean relaxation times of the blend falls between the respective times of the constituent components. Thus, blending 10% PPO homopolymer into the PS matrix results in a decreased mean relaxation time. From Table 3-1, 3-2, and 3-3, the values of $\langle \tau \rangle$ at other aging times, when plotted at comparable aging temperature distances T_g-T , show a similar discrepancy as Fig.3-13.

It is interesting to compare our $\langle \tau \rangle$ data with those reported by Ho et al¹⁶. These literature values are also exhibited in Fig.3-13. The $\langle \tau \rangle$ values at comparable temperature differences $T_g-20, 35, 50^\circ\text{C}$ for the PS/PPO blend and PS homopolymers calculated via Eq.3-8 using the data (τ and β) from Ho et al¹⁶ are numerically comparable, but not identical to our values. Except for the $\langle \tau \rangle$ values of Ho et al for the blend at $T_g-35^\circ\text{C}$, all data from our work and that of

Fig.3-13 Mean relaxation time $\langle \tau \rangle$ versus the comparable aging temperature distance, $T_g - T$, for PS/PPO (90/10), PPO, and PS homopolymers at constant aging time $t_a = 4$ hours. Second Y axis(right side) is the reduced mean relaxation time $\langle \tau \rangle / t_a$. Comparisons are made with the $\langle \tau \rangle$ data taken from Ho et al¹⁶.

Ho et al fall within the two fitted lines for the PS/PPO blend and the PS homopolymer. Note that the $\langle \tau \rangle$ values for the PPO homopolymer in the work of Ho et al show a large scatter compared with ours. However, their data are consistent with our observation that at fixed Tg-T, PPO homopolymer has the shortest mean relaxation time $\langle \tau \rangle$ among three materials. Furthermore, a global spectral parameter $\beta = 0.41$, which is smaller than ours, was found by Ho et al¹⁶. Note, however, these discrepancies are probably due to the following reasons:

1. There is a difference in the blend composition between the work of Ho et al and us. In Ho's work, a PS/PPO(80/20) (by weight) blend is only composition near our experiments. Thus, the $\langle \tau \rangle$ values of Ho et al in Fig.3-13 were taken from results of the stress relaxation experiments in a PS/PPO(80/20) blend.
2. In Ho's work, a strain rate of 0.01 min^{-1} was applied for 30 seconds to impose a 0.5% strain using an Instron Tensile Tester. However, note that, in the first few seconds during which the specimen is being strained, there must already occur stress relaxation³⁸. By contrast, in our work, the Rheometric Solid Analyzer RSAII can achieve the preset strain within 0.2-0.3 second.
3. The stress relaxation spectra used for the stretched exponential function fitting in the experiments of Ho et al were collected after 5 minutes from the onset of the test. The different time sectors employed to conduct the master decay function curve is another potential source of discrepancy between our results and those of Ho et al.

In Fig.3-13, the mean relaxation time $\langle \tau \rangle$ increases as the $T_g - T$ increases for all three materials which implies that the rate of relaxation (Γ) slows down (longer relaxation time) when polymer is in deeper in the glassy state. This, of course, is consistent with the physical picture that the molecular mobility decreases as the temperature is reduce.

It is customary to attempt treating $\langle \tau \rangle$ data with a pseudo-WLF type empirical expression^{40,41} of the form:

$$\ln \langle \tau \rangle = C_0 + C_1(T_g - T)/(C_2 + T_g - T) \quad (34)$$

where C_0 , C_1 and C_2 are adjustable parameters related to reference temperature; usually T_g . These parameters are usually obtained using a nonlinear least square fitting. Since the $\langle \tau \rangle$ becomes longer with the increasing aging time (t_a) at comparable aging temperature distances $T_g - T$, an extra term which represents the aging time parameter, must be added to Eq.3-14. This makes Eq.3-14 not practical because four parameters in an equation usually have a non-unique solution during nonlinear fitting, particularly, if only four comparable aging temperature distances verse mean relaxation time $\langle \tau \rangle$ data set available. Therefore, a reduced mean relaxation time $\langle \tau \rangle / t_a$ is introduced and exhibited in the second Y-axis of Fig.3-13. Empirically, an expression of the form:

$$\text{Log}(\tau/t_a) = K(T_g - T) \quad (35)$$

with K as adjustable constant is found to fit our experimental data and values

taken from Ho et al¹⁶, as shown in Fig.3-13.

With the observation of a broad glass transition zone in the DSC trace of the PS/PPO blend, the concept of "local concentration fluctuations"^{28, 31-33}, which we mentioned earlier, will be used to evaluate the observed discrepancy between the blend and homopolymers. This concept was employed used by Ngai et al³² and Wetton et al³¹ to interpret the dielectric and dynamic mechanical spectra at glass transition zone in the miscible blends.

As presented earlier, the width of temperature for the transition zone in the DSC traces of the PS/PPO blend is 18°C which is broader than those of PS (9°C) and PPO (8°C) (see Fig.3-2). This broader glass transition zone originates from the concentration fluctuations of miscible blends. Modifying the model which Struik developed to interpret the aging phenomena of semicrystalline polymers¹⁸, we assume as a simple approximation that the dynamics of the PS/PPO(90/10) blend in the glassy state can be classified as PS-rich regions and PPO-rich regions. Of course, the PS-rich regions will in fact compose the major volume in the PS/PPO(90/10) glass. However, we modelled the glass transition zone of PS/PPO blend with an assumption that there is a simple division of the temperature scale within the transition zone into two characteristic regions:

1. region 1 ($T_{g_i} < T < T_g$) with PS rich compositions.
2. region 2 ($T_g < T < T_{g_f}$) with PPO rich compositions.

The T_{g_i} and T_{g_f} can be treated as the apparent glass transition temperatures of PS-rich and PPO-rich regions, respectively. A simple schematic illustration of this

model is displayed in Fig.3-14. In addition, the width of the glass transition region for component homopolymers will be broadened by density fluctuations and we again can define the T_{g_i} and T_{g_f} for the PS. Using an expression similar to that proposed by Struik¹⁸, we assume the total relaxation modulus $E(t)$ is simply the sum of a contribution $E_i(t)$ from region 1 (PS rich) and a contribution $E_f(t)$ from region 2 (PPO rich). Thus, we have:

$$E(t) = E_i(t) + E_f(t) \quad (36)$$

As mentioned earlier, the equidistance point used in defining the glass transition temperature of the PS/PPO blend in the DSC curve refers to T_g . Therefore, at a specified value of aging temperature distance $T_g - T = T_a$, the actual aging temperature (T_a) of the PS/PPO blend is located closer to T_{g_i} for the blend than that for component homopolymers due to the broader transition zone. As discussed in chapter 1, the chain mobility and free volume increases as the absolute temperature approaches the glass transition zone. Therefore, at fixed $T_g - T$, the PS rich regions of the blend have higher chain mobilities than for the pure PS homopolymer since the distance between T_a and T_{g_i} is shorter for the blend than that for the PS homopolymer. In contrast, the contributions from PPO rich regions should have lower mobility because their effective T_g is at a larger temperature distance from T_a . Therefore, Eq.3-16 suggests that the decay of $E(t)$ in the PS/PPO(90/10) blend will be determined by the regions of higher mobility,

Fig.3-14 Schematic illustration showing the concept of "concentration fluctuation" within the glass transition zone of PS/PPO blend in the DSC trace.

i.e. by $E_i(t)$. This is consistent with our observations exhibited in Fig.3-13 that the mean relaxation times $\langle \tau \rangle$ of PS/PPO are shorter than those of the PS homopolymer at constant $T_g - T$. Thus, the contributions from the PS-rich regions dominate the initial decay of the stress relaxation function. We therefore propose that the discrepancy between the $T_g - T$ scaling of the PS/PPO blend and PS, at least in part results from the neglect of the more mobile PS rich regions.

When we select the onset glass transition temperature, T_{gi} , of the PS-rich regions as the reference temperature in the PS/PPO blend, this corresponds to a 9°C shift to the left. In a similar way, the onset glass transition temperature T_{gi} of PS homopolymer was chosen as reference temperature and this corresponds to a 4.5°C shift to the low temperature side of the transition zone in Fig.3-2 and 3-14. This rescaling result is shown in Fig.3-15 and produces a closer superposition of PS/PPO blend and PS data as compared to in Fig.3-13. This superposition of blend and PS indicates a state of "equivalent" mean relaxation time over the entire range of $T_{gi} - T$ for these two materials, and may be viewed as a manifestation of the contribution of the more mobile region 1 (PS rich domain) to the initial stress relaxation of the blend. In summary, by using the respective T_{gi} as the point of reference, a comparison of the physical aging dynamics in glasses of PS and PS/PPO detects no significant differences. This further supports the concept that the discrepancy between the $T_g - T$ scaling of the PS/PPO(90/10) blend and PS homopolymer originates from the local

Fig.3-15 Superposition of $\langle \tau \rangle / t_a$ is obtained for PS/PPO blend and PS by using $T_{gi} - T$ as scaling variable rather than $T_g - T$.

concentration fluctuations.

Note that, according to Eg.3-8, the mean relaxation time $\langle \tau \rangle$ is a function of the spectral parameter β and of the characteristic relaxation time τ . From Table 3-1, 3-2 and 3-3, it is clear that the spectral parameter β is not in fact a universal constant, but changes for different materials as well as for different aging temperatures. To assess the influence of β , we plot the reduced characteristic relaxation times τ/τ_a versus $Tg_i - T$ for blend and PS as exhibited in Fig.3-16. The closer superposition of two data sets relative to Fig.3-13 confirms our interpretation that the effect of physical aging in the PS/PPO blend is influenced by concentration fluctuations at $Tg - T$ scale.

We conclude that physical aging behavior monitored by the stress relaxation spectra for the PS/PPO blend is influenced considerably by the existence of concentration fluctuations. These give rise to a range of local Tg values, or equivalently a broad glass transition region which constitutes to a discrepancy in the $Tg - T$ scaling between blend and homopolymers. In Fig.3-15 and Fig.3-16, we note that there is evidence for a residual smaller discrepancy, i.e. that $\langle \tau \rangle$ or τ of blend at fixed $Tg_i - T$ is smaller than for the PS homopolymer, particularly at larger $Tg_i - T$. This remaining small discrepancy could arise from the presence of extra free volume introduced by the added PPO to the PS matrix. As evident in Fig.3-13, for pure PPO, at fixed $Tg - T$, the relaxation times are shorter than for pure PS. This reflects greater molecular mobility, i.e. higher free volume, in PPO which does not conform to $Tg - T$ scaling and which is consistent with the greater

Fig.3-16 Superposition of τ/τ_a is obtained for PS/PVME blend and PS by using $T_{g_i} - T$ as scaling variable rather than $T_g - T$.

ductility of PPO^{6,66,78} compared with PS in the glassy state. In summary, the behavior of the blend with respect to stress relaxation spectra resembles that of the pure components except that the presence of concentration fluctuations leads to a distribution of effective relaxation times which span a range of apparent T_g values. The initial part of the stress relaxation function is determined by the more mobile PS-rich domains.

Fig.3-17 exhibits the normalized distribution function of relaxation times $\rho(\tau)$ for the PS/PPO blend obtained using Eq.3-11 at aging temperature distance $T_g-20^\circ\text{C}$. The four curves shown are the distribution functions at different aging times, progressing from the initial spectrum ($t_a=30$ min.) to the final spectrum ($t_a=4$ hours). The maximum of the function corresponds to the characteristic relaxation time τ and the mean relaxation time $\langle \tau \rangle$ is located to the right of the maximum; as exhibited in the $\rho(\tau)$ curve at $t_a=4$ hours in Fig.3-17. The width of the distribution function is determined by the spectral parameter β and an average value $\beta=0.48$, which was extracted from earlier non-linear fits of stress relaxation spectra (see Fig.3-8), was used. Since β is assumed constant, the width and shape of the $\rho(\tau)$ function does not change during physical aging. Fig.3-16 shows that the peak maximum moves toward longer relaxation times during physical aging. From this figure, it can be seen that the intensity of molecular segmental motion associated with the particular logarithmic relaxation time value $\log(\tau)=2.67$ decrease from a maximum intensity 0.18 at aging time $t_a=30$ minutes to 0.14 at $t_a=240$ minutes. Thus, it is clearly evident in Fig.3-17 that the

Fig.3-17 Normalized distribution function of relaxation times $\rho(\tau)$ of PS/PPO(90/10) blend at different aging times and a constant aging temperature $T_a = T_g - 20^\circ\text{C}$.

intensities of shorter relaxation time elements (left side of $\rho(\tau)$) decrease, and longer relaxation elements (right side of $\rho(\tau)$) increase during physical aging. The molecular segmental motions with shorter relaxation times (i.e., relaxing elements with higher mobility and higher free volume) disappear due to more effective chain packing and associated densification during physical aging process. A similar shift in $\rho(\tau)$ can be observed in the PPO and PS homopolymers during isothermal physical aging, except that the width of the distribution function is different because of the different β derived from the fitting process.

The concept of a constant spectra parameter β during isothermal physical aging was also used by Matsuoka et al.⁴⁴. His argument was based on the assumption that all the relaxing elements in a polymer glass are aging at different rates but the distribution for such rates remains constant. On the other hand, Ngai et al.^{33,45-47} and Yee et al.⁴⁸ introduced the idea of a variable β during physical aging and proposed that the value usually decreases with the aging time; that is the width of the distribution function becomes wider. From their argument⁴⁵, the broadening of the distribution function at longer aging time could be attributed to a higher degree of cooperative motion or, in other words, an increase in the coupling strength between the relaxing elements and surrounding matrix in the polymer⁴⁵⁻⁴⁸. During physical aging, the molecules undergo an increase in chain packing effectiveness and the relaxing elements become more coupled to their surroundings with the continuous reduction of free volume. Therefore, the mobility of these relaxing elements must occur through

the cooperative motion. On the other hand, theoretical analysis by Simha et al⁴⁹ reached a conflicting conclusion about variation in β during physical aging process. From their model, they deduce a very small increase of the β parameter with increasing aging time⁴⁹. This corresponds to a narrowing of the relaxation spectrum during aging which is physically due to the fact that larger free volume elements (shorter relaxation times) change more rapidly. Such wide and even opposite arguments about β are difficult to evaluate due to the fact that the stretched exponential function is a very versatile curve fitting equation. If we reexamine the initial fitting results in Fig.3-8, the average value $\beta = 0.48$, in fact, was an average of value 0.51, 0.50, 0.48 and 0.45 obtained from individual fits for the aging times $t_a = 30, 60, 120$, and 240 minutes, respectively. This behavior is consistent with Ngai and Yee's claim, i.e., β decreases as the elapsed aging time t_a increases.

Our approach has been to present the data reduction which involves fewest floating parameters (i.e. constant β) but which is consistent with the results within experimental error. We note, however, that, release of the constraint of constant β does not alter the principal conclusions of our experiments in term of the Tg-T scaling of the relaxation time distribution.

Fig.3-18 contrasts the normalized distribution functions of the relaxation times at a comparable aging temperature distance Tg-20°C and aging time $t_a = 4$ hours for the PS/PPO blend and homopolymer components. The following features may be noted:

Fig.3-18 Comparison of normalized distribution function of relaxation times $\rho(\tau)$ for PS/PPO(90/10) blend, PPO, and PS homopolymers at $T_a = T_g - 20^\circ\text{C}$ and $t_a = 240$ min.

1. The width of the PS/PPO blend spectrum is intermediate between that of PS and PPO in Fig.3-18. This is consistent with the expectation that the $\rho(\tau)$ function of PS/PPO is a composite of contribution from the two constituent homopolymers.
2. The PPO homopolymer affiliated with the shortest mean relaxation time $\langle \tau \rangle$ also has the narrowest width among the three material. This is consistent with the fact that, even PPO though has the highest T_g , it is also more ductile in the solid state than PS^{1,6}. It is further evident from Fig.3-18 that the addition of PPO to PS partial confers a more ductile property (i.e. enhanced mobility) in the glass. Also, this observation is consistent with the coupling model of Ngai^{33,45-47}, i.e. higher mobility means smaller coupling and hence larger β .
3. Fig.3-18 usually illustrates the effective mixing of PPO with PS in that no portion of the relaxation spectrum of the blend extends to the longer relaxation times characteristic of pure PS. Also, a different perspective on the role of concentration fluctuations is given in that the region of higher local PPO concentration (shorter relaxation time) will not exhibit temperature scaling consistent with PS (shaded region) while these rich in PS will not scale with the PPO temperature (cross hatched area).

As mentioned earlier, the spectral parameter β is not a universal constant, but changes with the materials as well as the aging temperature. In Fig.3-19, we present the dependence of the spectral parameter β on the temperature distance $T_g - T$ for PS/PPO blend and homopolymers. Our experimental values encompass

Fig.3-19 The dependence of spectral parameter β on the comparable aging temperature distance $T_g - T$.

typical selected literature values. The range of β in our experimental studies is from 0.4 (PS at $T_g-30^\circ\text{C}$) to 0.56 (PPO at $T_g-10^\circ\text{C}$). From stress relaxation spectra of inorganic glasses, a $\beta=0.5$ was reported by Rekshon et al⁵¹, whereas $\beta=0.33$ was found from creep compliance in polymer glasses of various chemical structures by Struik¹⁸. From the work of Ho et al¹⁶, stress relaxation spectra of blends and homopolymers yield a global β which is equal to 0.41.

Form Fig.3-19, we finds that β systematically decreases with increase of T_g-T ; i.e., as one goes deeper into glassy state. This suggests that the distribution function $\rho(\tau)$ becomes broader at lower temperatures in the polymer glasses. As discussed earlier, a broadening of $\rho(\tau)$ means that the relaxing elements in the polymer glass have higher degree of cooperative motions with their surrounding matrix⁴⁴. This observation is again consistent with the coupling model of Ngai⁴⁵⁻⁴⁸ since at lower temperature one expects more densification and hence a stronger coupling between the relaxing elements with the surrounding matrix. In other words, the molecularly segmental mobility decreases due to the restricted cooperative motions and generates a broader distribution function at lower temperature, i.e smaller β value. The study on the tensile stress relaxation behavior of PC glass by Yee et al⁵¹ provides the experimental observations that the increase of breadth in the distribution of relaxation times as the temperature decreases. It is a common phenomenon in enthalpy relaxation experiments to observe variations of β with temperature^{40,41}. The variation of β with temperature also has been taken to indicate a failure of time-temperature

superposition²⁴ for polymer glasses in the thermodynamic nonequilibrium state.

Recently, an extensive and systematic dynamic mechanical and dielectric analysis of the PS/PPO blends in the glassy state by K. Pathmanathan, G.P. Johari, L. Monnerie, and J.Y. Cavaille⁵²⁻⁵⁴ showed that, on addition of up to 30% (by weight) PPO homopolymer in a PS glass, a β relaxation peak is observed in the dielectric loss spectrum of the PS/PPO blends which reflects motion of the ether linkage and occurs at a value near that of T_{β} in pure PS glass. The location of this transition does not change with PPO concentration despite a large increase in T_g of blend. This led to the suggestion that cooperativity among segmental motions of the polystyrene chains is required in allowing a change in the matrix, necessary to facilitate the dipolar orientations of the polar segments of the PPO⁵⁴. This intermolecular cooperation is consistent with the views of Wellingshoff et al¹⁵ that the reasons for the compatibility of the blends are the strong interactions which modify the molecular environment of polymer chains. In PS/PPO blend, the interaction was suggested to be between the phenyl ring of PS and the phenylene ring in PPO¹⁵.

An interesting feature of Fig.3-19, is that the β value of PS/PPO blend is larger than PS glass in the entire range of T_g - T . Two major factors control the β value at T_g - T scale. The first factor is the effect of concentration fluctuations which is expected to widen the relaxation spectrum in the blends, i.e. to decrease β ; The second factor is the effect of any large change in structure (free volume). This may be increase or decrease β depending on whether the minor blend

component causes an increase or decrease in free volume. For the PS/PPO blend, since β is larger than pure PS, we expect, following Ngai's coupling theory, there is slightly weaker coupling of the relaxing elements with the surrounding matrix, i.e. in the PS/PPO blend the effect of increased free volume (smaller $\langle \tau \rangle$) dominates over the effect of concentration fluctuations.

The blending of PPO chains in PS matrix has the ability to introduce a different environment with extra free volume for the PS chains during the cooperative motions in the glassy state. In Fig.3-13, the PS/PPO blend apparently has shorter $\langle \tau \rangle$ than those of pure PS homopolymer. At the same T_g - T scale, the blend exhibits more segmental mobility than the PS homopolymer.

In Fig.3-20 we show a double logarithmic plot of the mean relaxation time $\langle \tau \rangle$ against aging time (t_a) for thermally quenched PS/PPO(90/10) blend at various comparable aging temperature distances T_g - $T=30, 25, 20, 15^\circ\text{C}$. Consistent with previous observations^{34,38,39}, $\log \langle \tau \rangle$ increases proportional to $\log t_a$. The slope of this relationship is referred to as the shift rate ($\mu = d\log \langle \tau \rangle / d\log t_a$). Analogous double logarithmic plots of the $\langle \tau \rangle$ versus t_a for the respective PPO and PS homopolymers are shown in Fig.3-21 and 3-22.

The dependence of shift rate μ against the aging temperature distance T_g - T for PS/PPO blend, PPO, and PS homopolymers is shown in Fig.3-23. The shift rates of the three materials decrease on approaching T_g . This is consistent with the observation reported by Struik¹⁸.

As discussed in the Eq.1-2, the physical aging phenomenon is a nonlinear and

Fig.3-20 Double logarithmic plot of mean relaxation time $\langle \tau \rangle$ against aging time (t_a) for a thermally quenched PS/PPO(90/10) blend at various aging temperatures $T_a = T_g - 30, 25, 20, 15^\circ\text{C}$.

Fig.3-21 Double logarithmic plot of mean relaxation time $\langle \tau \rangle$ against aging time (t_a) for a thermally quenched PPO homopolymer at various aging temperatures $T_a = T_g - 30, 25, 20, 15^\circ\text{C}$.

Fig.3-22 Double logarithmic plot of mean relaxation time $\langle \tau \rangle$ against aging time (t_a) for a thermally quenched PS homopolymer at various aging temperatures $T_a = T_g - 30, 25, 20, 15^\circ\text{C}$.

Fig.3-23 Comparable aging Temperature distance, $T_g - T$, dependence of shift rate μ for PS/PPO blend, PPO, and PS homopolymers.

self-retarding process. Struik¹⁸ described the mobility M as inversely proportional to the aging time t_a ,

$$M = K/t_a \quad (3-17)$$

where K is a constant.

The conditions¹⁸ on which Eq.3-17 is based are:

- (a) The process must be strongly self-retarding.
- (b) The system must be far enough from the initial melt state.
- (c) The system must be far enough from equilibrium in the glass.

Since the mechanical relaxation times are inversely proportional to M , Eq.3-17 implies that they increase proportionally to aging time.

$$\tau = K_i t_a \quad (3-18)$$

where K_i is a constant.

The horizontal shift is proportional to the magnitude of change in the relaxation times, Therefore, using Eq.3-18 and Eq.1-4, we have:

$$\mu = d\log(a_t)/d\log(t_a) = 1$$

The validity of $\mu = 1$ derives from the condition (a)-(c). The failure of one of these

conditions will give in general¹⁸

$$0 < \mu < 1$$

The absent of strong aging effects at temperatures lower than T_g or higher than T_g can be attributed to the failure of the conditions (b) and (c), respectively. Therefore, in Fig.3-23, the similarity in the μ values in the blend compared with PS may be attributed to the dominant role of the major PS component in the blend in controlling the kinetics of the aging process and a similar coupling strength within the relatively large uncertainty introduced by the presence of local concentration fluctuations. This causes the failure of condition (c) and reduces the μ . The substantially lower value of μ in PPO homopolymer indicates that this material is less self-retarding.

As discussed earlier, the relaxation dynamics of PS/PPO(90/10) and PS detects no major difference when using the T_{g_i} -T scale (see Fig.3-15 and 3-16). Thus, a superposition curve can be roughly constructed by the horizontal shifts and using T_{g_i} -T scale as exhibited in Fig.3-24. This curve is similar to the aging rate curves in homopolymers reported by Struik¹⁰ which exhibit a level region and rapidly decrease in μ as near the glass transition temperature. This again verified our argument that the discrepancy in the Tg-T scaling is due to the concentration fluctuations in the blend.

Fig.3-24 Superposition of shift rate μ versus $T_{g_i} - T$ of the PS/PPO blend to PS by shifting leftward from the midpoint T_g of the blend.

Positron annihilation lifetime(PAL) spectra

PAL spectra of polymers are ordinarily resolved into three components^{56,57}. The third and the most significant constituent is the longest-live component indicative of the ortho-positronium(o-Ps) decay. The lifetime(τ_3) of o-Ps pick off component can be related to the size of the "hole", and the intensity I_3 can be correlated with the relative number of holes in an unit volume of a polymer, i.e., hole density. As mentioned earlier, the hole size and density are related to the free volume available in the polymers. Therefore, τ_3 and I_3 are sensitive to the polymer properties that affect or are affected by the free volume, including molecular weight^{58,59}, degree of crosslinking⁶⁰, and pressure⁶¹ and external stress^{62,63}.

The observed variations of o-Ps lifetime(τ_3) with the normal linear temperature scale for the PS/PPO(90/10) blend and the component homopolymers in the glassy state exhibit an approximately linear increase, as shown in Fig.3-25. The increase in τ_3 with temperature implies an increase in the hole size sampled by the o-Ps. Note that the thermal expansion of the hole size shown a discrete increase in the PS/PPO blend at T_g , as expected, and that within experimental errors, the τ_3 values of the PS homopolymer in Fig.3-25 are in a good agreement with the published data⁶⁵. Also, the magnitude of τ_3 for the PPO homopolymer is considerably larger than for either PS homopolymer or the PS/PPO blend in Fig.3-25. To estimate the average hole volume $\langle v_f \rangle$, we can use Eq.2-10 and 2-11 to calculate the hole volume from τ_3 for these three

Fig.3-25 Temperature dependence of ortho-positronium (o-Ps) lifetime τ_3 in PS/PPO blend, PPO, and PS homopolymers. Second Y axis represents the average hole volume calculated from Eq.2-10 and 2-11.

materials and the results are exhibited as the same curves in Fig.3-25 referred to the right side Y-axis. Qualitatively, the larger hole size in PPO is consistent with the shorter mechanical relaxation time $\langle \tau \rangle$ in this polymer. For the blend with rich PS composition (90 % by weight), the hole size shows almost no difference compared with the PS homopolymer, as the curves of PS and blend are close to each other in Fig.3-25. The variations of the intensity I_3 , corresponding to the longest lifetime component τ_3 , are presented in Fig.3-26. It is also observed that I_3 increases with increasing temperature for the three materials. The PPO homopolymer with highest τ_3 in Fig.3-25 and I_3 in Fig.3-26 has the highest free volume.

These results are in qualitative agreement with results of the recent work of de Araujo et al⁶⁶, who incorporated the free volume concept of Frenkel⁷⁶, together with an equation relating blend composition developed by Kanig⁷⁷, to calculate the ratio of the specific volumes of repeating unit and the "hole". From the composition-dependence of T_g , they found in qualitative agreement with our results that the free volume in PPO is larger than that in PS at T_g . From the above observation, the ductile behavior⁶ of PPO may be attributed to the higher free volume. Also, the theoretical work from Tonelli⁷⁸ showed that the greater freedom of rotation in the PPO chain may be the explanation for its high impact strength which is greater than that of polycarbonate over the temperature range - 200 to 100°C⁷⁹⁻⁸². This idea again is consistent with our PAL observations since the greater freedom of the bulky phenylene ring should need considerable free

Fig.3-26 Temperature dependence of orthopositronium (o-Ps) intensity I_3 in PS/PPO blend, PPO, and PS homopolymers.

volume.

The response of I_3 in the blend is more sensitive to the presence of PPO than τ_3 ; thus 10% PPO in the PS matrix results in a substantial increase in o-Ps intensity (see Fig.3-26). This implies that blending 10% PPO homopolymer with PS glass generates extra free volume in the blend, and is consistent with the idea that the PPO homopolymer has a effect of increase free volume in the PS glassy matrix, even though its T_g is higher. All these temperature dependent phenomena discussed above are consistent with earlier investigations^{20,21,67,68} on PC and PVAC, and with the above interpretation of I_3 and τ_3 in terms of relative variations in the free volume of polymers.

In order to compare the PAL spectra with static relaxation mechanical spectra we need to reexamine the PAL results at a comparable temperature distance scale, $T_g - T$. Fig.3-27 and 3-28 shows this comparison using T_g as the scaling variable (i.e. $T_g - T$). For the three materials, I_3 and τ_3 each decrease as temperature decrease in the glassy state (as $T_g - T$ becomes larger). This is again consistent with free volume argument^{24,42} and physical intuition.

Fig.3-29 displays the apparent free volume fraction, $h/c = I_3 / \langle V_h \rangle$, for PS/PPO blend, PPO and PS homopolymers. The h/c curves, which are proportional to the fractional free volume, are expected to behavior in a similar fashion to $\langle V_f \rangle$ in Fig.3-27. We can therefore attempt to interpret the changes in h/c in terms of relative variations in free volume with the changing $T_g - T$.

A caution must be noted here in qualitatively correlating I_3 with the number

Fig.3-27 Comparisons of the comparable temperature distance T_g-T dependence of orthopositronium (o-Ps) lifetime τ_3 in PS/PPO blend, PPO and PS homopolymer. Second Y axis represents the average hole volume calculated from Eq.2-10 and 2-11.

Fig.3-28 Comparisons of the comparable temperature distance $T_g - T$ dependence of ortho-positronium (o-Ps) intensity I_3 in PS/PPO blend, PPO, and PS homopolymers.

Fig.3-29 Comparisons of the temperature distance T_g-T dependence of apparent free volume fraction, $h/c=I_3<V_h>$, for PS/PPO blend, PPO and PS homopolymers.

of holes. As mentioned in chapter 2-1, a quite recent study by Kluin et al⁸² through computer simulations, which were based on Monte Carlo studies of free volume, of positronium decay in PC show that the fitting results in intensities significantly departs from the input values. The presence of a τ_3 distribution results in artifacts of the fitting procedure, which influence I_3 ⁸².

Again, Tg_i -T scale was used to check the idea of the discrepancy in Tg-T scale is mainly due to concentration fluctuations. Fig.3-30 and 3-31 depict the τ_3 and I_3 versus Tg_i -T scale, respectively, for PS/PPO blend and PS homopolymer. The good superposition of τ_3 data versus Tg_i -T plot can be understood by using Tg_i as the reference temperature consistent with the discussion regarding Fig.3-15 and 3-16. This again confirms the concept of equivalent glass dynamics at Tg_i -T scale and support the idea that the discrepancy at Tg-T scaling is due to concentration fluctuations in the blend. However, poor superposition is found, as shown in Fig.3-31, where the intensity(I_3) of o-Ps pickoff component is plotted versus Tg_i -T. We note that the I_3 can not be quantitatively related to the hole density following the discussion of Kluin et al⁸², since some portion of the o-Ps intensities at short times is obscured by the p-Ps and e^+ decay components⁸². We point out that the discrepancy is in the direction of larger free volume in the blend which is consistent with the evidence in Fig.3-15 and 3-16 that the mechanical relaxation times are slightly smaller at fixed Tg_i -T and also that the β parameter is larger for the blend, as compared to pure PS.

Fig.3-32 displays the apparent fraction of free volume (h/c), which is the

Fig.3-30 Comparisons of the comparable temperature distance $T_{g_i} - T$ dependence of orthopositronium (o-Ps) lifetime τ_3 in PS/PPO blend and PS homopolymer.

Fig.3-31 Comparisons of the comparable temperature distance $T_{gi}-T$ dependence of ortho-positronium (o-Ps) intensity I_3 in PS/PPO blend and PPO homopolymers.

Fig.3-32 Comparisons of the temperature distance $T_{gi}-T$ dependence of apparent free volume fraction, $h/c=I_3 \langle V_h \rangle$, for PS/PPO blend and PS homopolymers.

combining contributions from τ_3 and I_3 through Eq.2-14, versus T_g-T for PS/PPO blend and PS. Again, we achieve better superposition compared with Fig.3-31 and the differences are in the direction of larger free volume in the blend.

A comparison of the plots of Fig.3-13, 3-27, and 3-28 reveals that, at a comparable aging temperature distance T_g-T , a material with large $\langle \tau \rangle$ is associated with short τ_3 and I_3 and h/c. For example, the PS homopolymer has the smallest τ_3 , I_3 , and h/c and the longest $\langle \tau \rangle$ among the three materials. The behavior of the PS/PPO blend in Fig.3-13, 3-27 and 3-28 is observed to fall in between that of its constituent homopolymers. Those observations provide evidence to support the idea that the mean stress relaxation time is associated with the free volume decrease^{24,42}.

In summary, the results from PAL experiments are qualitatively consistent with that of stress relaxation spectra in blends and homopolymers at T_g-T scale. The concept of free volume is adequate to interpret the observations in our works.

In situ monitoring of the physical aging process by PAL spectroscopy

Fig.3-33 and 3-34 show, respectively, the changes of o-Ps lifetime(τ_3) and intensity(I_3) for the blend and homopolymers during isothermal physical aging at $T_g-75^\circ\text{C}$ following a quench from equilibrium melt. For these three materials, the lifetime(τ_3) showed no systematic variation with aging time t_a . Within deviation of experimental error, τ_3 may be considered constant through experimental

Fig.3-33 Variations of the orthopositronium (o-Ps) lifetime(τ_3) in PS/PPO blend, PPO, and PS homopolymers during isothermal physical aging at comparable temperature $T_g-75^\circ\text{C}$ after a quench from a temperature above T_g .

Fig.3-34 Variations of ortho-positronium (o-Ps) intensity I_3 in PS/PPO blend, PPO, and PS homopolymers during isothermal physical aging at comparable temperature $T_g-75^\circ\text{C}$ after a quench from a temperature above T_g .

duration. The τ_3 values for these three materials during aging at Tg-75°C are quite close to the results from temperature dependence measurements (see Fig.3-27) since both measurements have similar initial sample thermal history: annealing and quenching. In Fig.3-33, the τ_3 of the blend is also close to that of the PS homopolymer during the aging process, c.f. Fig.3-27. PPO homopolymer still possesses the highest τ_3 . The constancy of τ_3 is consistent with the previous positron study of the PVAC⁶⁷ and PC^{20,21,68} during physical aging. In addition, it is in agreement with previous literature in polymer glasses⁶⁸⁻⁷³ probed by PAL spectroscopy during physical aging. Recently, Kluin et al⁶⁸ have proposed that certain artifacts of the spectrum analysis fitting procedure originate from the existence of a distribution of τ_3 values, and that consequently the variations of τ_3 are too small to be detected during data analysis. However, this postulate needs further verification.

In Fig.3-34, the intensity(I_3) of the PS homopolymer exhibits a significant decrease with aging time during aging at Tg-75°C. The aging temperature for the PS homopolymer corresponding to 30°C, i.e. below Tg, but quite close to the T_β ⁵²⁻⁵⁵. On the contrary, there are no changes in I_3 for PPO homopolymer, and only a small decrease for the PS/PPO blend as displayed in Fig.3-34. The initial values of I_3 for the three materials are slightly lower than the values obtained in the temperature dependence experiment (see Fig.3-26). From the thermal history point of view, the data from the temperature dependence measurements may be considered as the initial aging values of the sample.

Clearly, there is a large variation in the intensity than in the lifetime of the o-Ps annihilation component during physical aging. The τ_3 values remain approximately constant as a function of time during isothermal physical aging, and the I_3 values decrease in a manner similar to that observed during volume recovery⁷⁴. In our previous study of physical aging of PVAC⁶⁷, the I_3 shows substantial decrease during aging at low temperature, and from moderate to a very slight decrease at high temperature, specifically, there is no significant variation when the aging temperature is near T_g . Because o-Ps is thought to localize in the regions of reduced electron density such as free volume sites in polymers, a decrease in the I_3 indicates a decrease of the concentration of free volume sites available for localization. This suggests that physical aging only reduces the number of holes, while the mean hole size $\langle V_f \rangle$ from τ_3 does not change. This decrease in number of holes must be results in, or be the result of, a decrease in molecular mobility of the polymer chains. This decrease in I_3 is consistent with the concept of closer packing of polymer chain and reduction of free volume due to aging. However, the recent work of Kluin et al⁶⁸ suggests that the decrease in I_3 in a material is the consequence of the existence of a hole size distribution.

A comparison of the results from Fig.3-33 and 3-34 indicates that the decrease of free volume during isothermal physical aging for the blend and PS is mainly due to the loss of the holes rather than a shrinkage of holes and this is consistent with the conclusions from the previous positron spectra studies of our group⁶⁷.

Fig.3-35 displays the plot of the apparent free volume fraction h/c , calculated using Eq.2-14 against aging time, the PS homopolymer exhibits a decrease with aging time, and the other two materials show almost constancy. We could note that previous PAL observations of the changes in free volume of polymers during physical aging are usually limited to the temperature below T_g , i.e., deep in the glassy state. The reason has yet to be established. Unfortunately, it is difficult to observe the changes of I_3 in polymers aging within the temperature range $T_g < T < T_g$ where the stress relaxation studies were performed.

The comparatively low sensitivity of the free volume parameters (τ_3 and I_3) from o-Ps sampling during physical aging process in PPO homopolymer compared with PS homopolymer is another evidence of high mobility of PPO.

We must address an additional issue concerning the possibility of radiation damage from positron exposure, i.e., the decrease in I_3 during physical aging experiment may be the combination of effects from physical aging and radiation damage. First, our results are in agreement with recent measurements from Welander et al⁸¹ and Kluin et al⁸² on homopolymers that no effect of irradiation time on τ_3 was occurred. However, the magnitude of radiation effect can be significant and is dependent on the particular material⁸². If the radiation effect exists, the I_3 always decrease with the time of exposure to positron radiation. Therefore, no conclusions regarding the contribution of physical aging to the decrease in I_3 at $T_g-75^\circ\text{C}$ in Fig.3-34 can be made without further evidence of the radiation damage.

Fig.3-35 Variations of apparent free volume fraction, $h/c = I_3 < V_h >$, in PS/PPO blend, PPO and PS homopolymers during isothermal physical aging at comparable temperature $T_g-75^\circ\text{C}$ after a quench from a temperature above T_g .

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Chapter 3

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Chapter 4: Physical aging of polystyrene/poly(vinyl methyl ether) blends

4-1 Background

Blends of polystyrene(PS) and poly(vinyl methyl ether)(PVME) have been investigated rigorously in fundamental studies of polymer-polymer miscibility¹⁻⁴. PS/PVME blends are compatible over a wide range of composition. However, phase separation can be induced by heating above the lower critical solution temperature(LCST) or by casting films from suitable solvents¹⁻³. Two-phase behavior was reported for blends cast from trichloroethylene or chloroform, whereas single phase behavior was exhibited by films cast from toluene or xylene¹⁻³. Further investigations indicated the initially single phase film cast from the appropriate solvent exhibited phase separation when heated above their LCST which occurs around 125°C¹⁻³.

At a temperature below LCST, a homogeneous mixture of PS and PVME, cast from toluene, was suggested by the observations from differential scanning calorimetry (DSC) which showed a single composition-dependent T_g which occurs at a temperature between the two T_gs of the respective homopolymer components (T_g of PVME around 244°K, and T_g of PS around 375°K)⁵. Although the observed glass transition is broad, there appear no DSC peaks at the respective transition temperatures of 244 and 375°K, indicating that the mixture is homoge-

neous. A negative value of the interaction parameter χ has been measured in concentrated PS/PVME blends by small angle x-ray diffraction and vapor sorption methods.²⁻³

Phase separation phenomena of PS/PVME blends induced by change of temperature or solvent have also been extensively studied¹⁻⁴. Since we are interested only in the miscible blend, there will be no literature review on this topic.

The only literature concerning physical aging behavior of PS/PVME blends was described by Cowie et al⁷. The results from their enthalpy relaxation experiments were reviewed in section 1-4.

In the present work, isothermal physical aging effects on dynamic, static mechanical and PAL spectra were investigated for the miscible PS/PVME blends and compared with that of pure PS homopolymer. To our knowledge, no literature can be found on this topic for PS/PVME blend.

PVME is a glass-forming material with a T_g around 250^oK⁸. With PVME composition up to 20%(by weight) in the blend, a glassy miscible blend can be prepared at ambient temperature through a solution casting process. Therefore, a weight ratio of 90/10 PS/PVME blend was chosen for this study.

4-2 Experimental

Materials

The polymers used in this part of study were polystyrene (PS) and poly(vinyl methyl ether)(PVME). All the polymers were purchased from Scientific Polymer Products. The polymer specimens had average molecular weights $M_n = 160,000$ $M_w = 280,000$ for PS; and $M_n = 47,500$, $M_w = 98,500$ for PVME. The purchased samples were used without further purification. The molecular structures of these two polymers are shown in the Fig.4-1.

The binary mixture of 90/10 (by weight) PS/PVME was prepared by dissolving at a composition of 5% (w/v) solution in toluene. The polymer mixture was kept in solution for two days with continuous stirring to assure homogeneity. Then, this 5% (W/V) polymer mixture solution was cast into film on a glass plate. The toluene was removed by evaporation at ambient temperature in a hood for two days. These films were then subjected to further drying under vacuum at 60°C for 48 hours. Finally, the vacuum dried samples were compression molded at 110°C to remove any residual solvent, and a clear specimen sheet with thickness around 0.6-0.8 mm was obtained.

It is impossible to prepare a polymer glass from pure PVME homopolymer at ambient temperature because of its low T_g ⁸. The dried pellets of pure PS were directly molded into a sheet at temperature 150°C. The PS homopolymer used

polystyrene(PS)

poly(vinyl methyl ether)(PVME)

Fig.4-1 Molecular structures of polystyrene(PS) and poly(vinyl methyl ether)(PVME).

in this work is the same as the previous PS/PPO blends (Chapter 3). The thickness of the PS sample is around 0.8-1 mm. ASTM D 1708-84 dog-bone shaped specimens and disk shaped specimens with radius 8 mm were cut from the molded sheets of the blend and homopolymer using a blade die. The specimens were kept in a sealed desiccator to prevent any moisture uptake before the static, dynamic mechanical, PAL experiments were performed.

Differential scanning calorimetry

The DSC curves for the PS/PVME blend and PS homopolymer are shown in Fig.4-2. The detail procedures for DSC experiment has been reported in the section 3-2.

Static stress relaxation mechanical and PAL spectroscopy

The static stress relaxation mechanical and PAL spectroscopy procedures used in this part of experiment have been described in the section 3-2.

Dynamic mechanical spectroscopy

The changes in the damping factor $\tan\delta$ in dynamic viscoelastic experiment during isothermal physical aging were monitored using the RSAII in the "dynamic mode-- frequency scanning." The sample dimensions were the same as those used in the static stress relaxation mechanical measurements.

Fig.4-2 DSC curves of PS/PVME(90/10) blend and PS homopolymer at a heating rate of 20°C/min.

The samples were again annealed at $T_g + 10^{\circ}\text{C}$ for one hour to attain the equilibrium state, then quenched to the aging temperature (T_a), as rapid as possible, by directly blowing dry cold air into the testing chamber. The temperature was maintained at T_a for the entire period of the aging test. With a similar time sequence to that applied in the static stress relaxation measurement, $\tan\delta$ was recorded in a frequency domain during the physical aging process. The start of aging (aging time $t_a = 0$) was set to be the moment that the chamber temperature reached T_a .

4-3 Data analysis

The data analysis procedures for stress relaxation and PAL spectra described in section 3-3 were also applied in the study of PS/PVME blends.

4-4 Results and discussion

Differential scanning calorimetry(DSC) thermogram

The DSC curves of PS homopolymer and PS/PVME(90/10) blend obtained at a heating rate of 20°C/min. after quenching from melt are shown in Fig.4-2. The glass transition temperatures(T_g) for PS/PVME blend and PS homopolymer are 72°C and 105°C, respectively. These T_g values are consistent with literature data⁹. A single T_g in the PS/PVME blend indicates the compatibility of PVME and PS homopolymers¹⁻⁵. A much broader glass transition zone than that of PS homopolymer was found in the PS/PVME blend. The breadth of the transition zone turns out to be 35°C compared to 9°C for the PS homopolymer and 18°C for the PS/PPO blend in the previous experiments. A similar observation was reported by Cowie et al⁶⁻⁷. In their work⁶⁻⁷, the breadth of the glass transition $\Delta T = 38^\circ\text{C}$ for a PS/PVME(50/50) blend; whereas PS homopolymer has $\Delta T = 6.8^\circ\text{C}$. This implies that a wider range of local dynamical fluctuations is present in this blend system.

Static stress relaxation mechanical spectra

Fig.4-3 exhibits the momentary tensile stress relaxation modulus $E(t)$ for different aging times(t_a) during isothermal physical aging at a comparable aging temperature distance $T_g - 20^\circ\text{C}$ for a PS/PVME(90/10) blend after quenching

Fig.4-3 Stress relaxation curves for PS/PVME(90/10) blend during isothermal aging at $T_g - 20^\circ\text{C}$ ($T_a = 52^\circ\text{C}$) after a quench from equilibrium melt above T_g . Symbols correspond to different aging times(t_a) as indicated; solid lines are fits to stretched exponential function with $\beta = 0.38$.

from equilibrium melt ($T_g + 10^\circ\text{C}$). The principle of relaxation time-aging time superposition from Struik¹⁰ was valid in Fig.4-3¹⁰. With increasing aging time, the stress relaxation spectra in Fig.4-3 shift to longer time scale, but the shape of the curves does not change. It is clearly by inspection that, within experimental error, these relaxation spectra can be well represented by the stretched exponential functions with $\beta = 0.38$, as the solid curves shown in Fig.4-3. The relaxation parameter β , τ , E_0 , and $\langle \tau \rangle$ extracted from these spectra in Fig.4-3 as well as stress relaxation spectra at comparable aging temperature distances $T_g - 15$, 25 , 30 are summarized in Table 4-1. The slight variations of E_0 and substantial longer τ with increasing aging time are due to the densification and chain packing during the isothermal physical aging. These results are qualitatively similar between PS/PVME(90/10) and PS/PPO(90/10) polymer glasses.

Analogous isothermal physical aging for the PS homopolymer was carried out at $T_g - T = 15, 20, 25, 30^\circ\text{C}$ after quenching from the melt state ($T_g + 10^\circ\text{C}$). Fig.4-4 displays the stress relaxation spectra of PS at $T_g - 20^\circ\text{C}$ with four different aging times. Through non-linear least square fits, an average $\beta = 0.45$ was obtained. The solid curves in Fig.4-4 are the results of stretched exponential function fits. The relaxation parameters for PS homopolymer at comparable aging temperature distance $T_g - T = 15, 20, 25$, and 30 are given in Table 4-2. There PS data reproduce those contained in chapter 3.

Ta °C	ta min.	Eo x10 ⁹ Pa	τ sec.	β	$\langle \tau \rangle$ sec
Tg-15	30	3.00	66.5	0.39	237.4
	60	2.96	86.6	0.39	309.1
	120	2.77	125.2	0.39	446.9
	240	2.85	149.0	0.39	531.8
Tg-20	30	3.26	225.4	0.38	850.9
	60	3.29	322.5	0.38	1217.4
	120	3.31	435.8	0.38	1645.1
	240	3.28	637.8	0.38	2407.6
Tg-25	30	3.40	564.8	0.38	2230.7
	60	3.57	822.4	0.38	3248.2
	120	3.62	1095.6	0.38	4327.2
	240	3.64	1620.2	0.38	6399.1
Tg-30	60	3.67	1656.5	0.37	6926.0
	120	3.73	2362.3	0.37	9877.0
	240	3.74	3625.5	0.37	15158.5

Table 4-1 Stretched exponential curves fitting results for PS/PVME (90/10) blend.

Fig.4-4 Stress relaxation curves for PS homopolymer during isothermal aging at $T_g - 20^\circ\text{C}$ ($T_a = 85^\circ\text{C}$) after a quench from equilibrium melt above T_g . Symbols correspond to different aging times (t_a) as indicated; solid lines are fits to stretched exponential function with $\beta = 0.45$.

Ta °C	ta min.	Eo x10 ⁹ Pa	τ sec	β	< τ > sec
Tg-15	30	2.88	511.9	0.47	1166.0
	60	2.88	816.3	0.47	1859.0
	120	2.91	1276.9	0.47	2908.5
	240	2.90	2234.0	0.47	5088.6
Tg-20	30	2.91	1186.2	0.45	2985.4
	60	2.93	1783.8	0.45	4489.4
	120	2.95	3150.0	0.45	7927.9
	240	2.96	5645.0	0.45	14207.2
Tg-25	30	2.97	2507.7	0.41	7748.9
	60	2.97	4322.9	0.41	13357.9
	120	3.98	8116.8	0.41	25081.1
	240	3.02	14386.4	0.41	44454.3
Tg-30	30	2.94	5730.4	0.40	19442.9
	60	2.96	8313.0	0.40	28205.6
	120	2.99	12610.9	0.40	42788.1
	240	2.99	25248.2	0.40	85665.8

Table 4-2 Stretched exponential curves fitting results for PS.

Again, we note that the physical aging phenomena with respect to static stress relaxation spectra for PS homopolymer and PS/PVME blend as again similar to that observed by Struik¹⁰ in creep tests of homopolymers under similar isothermal physical aging condition.

Master curves of blend and PS homopolymer at comparable aging temperature distance $T_g - 20^{\circ}\text{C}$ were constructed and exhibited in Fig.4-5. It is clearly demonstrated in Fig.4-5 that the PS/PVME blend has a faster rate of relaxation ($\Gamma = \tau^{-1}$) than that of the PS homopolymer. This means that the relative magnitude of Γ falls opposite to that of T_g (i.e., $T_{g\text{blend}} < T_{g\text{PS}}$). This contrasts with the observations in chapter 3 for the PS/PPO blends where the relative magnitude of Γ is parallel to that of the T_g s.

To verify the aging thermoreversibility of PS/PVME blends, the same thermal history for annealing at a temperature of $T_g + 10^{\circ}\text{C}$ was repeated on a single specimen, and the results are given in Fig.4-6. The deviation between the solid curves (first run) and symbols (second run) is only 1.5%. The short heating to a temperature above T_g at the beginning of second quench run completely erased all the thermal history. It shows that the effects from thermal history in the PS/PVME glass can be performed with excellent reproducibility on the same specimen in this work. Thermoreversibility is a typical feature of physical aging process¹⁰.

Fig.4-5 Superposition of stress relaxation curves of PS/PVME blend and PS homopolymers at different aging times(t_a) and the reference time was selected at $t_a = 4$ hours; aging temperature $T_a = T_g - 20^\circ\text{C}$. Comparisons are made with stretched exponential function with respective, $\beta = 0.38$ and 0.45 .

Fig.4-6 Stress relaxation curves(solid curves) for PS/PVME(90/10) blend during isothermal aging at $T_a = T_g - 20^\circ\text{C}$ and $t_a = 1, 2$ hours following a quench from equilibrium melt above T_g . Symbols on the curves represent the repeat experimental tests for thermoreversibility.

The mean relaxation time $\langle \tau \rangle$, which was calculated via Eq.3-8, versus comparable aging temperature distance $T_g - T$ for the blend and PS at aging time $t_a = 4$ hours is presented in Fig.4-7. The scale of reduced mean relaxation time, $\langle \tau \rangle / t_a$, shows at the right side Y-axis in Fig.4-7. In comparison with the pure PS homopolymer, blending of 10% PVME homopolymer into PS matrix results in a shorter mean relaxation time $\langle \tau \rangle$ over the entire $T_g - T$ range. From Table 4-1 and 4-2, values of $\langle \tau \rangle$ versus $T_g - T$ at other aging times show a similar discrepancy to that occurs in Fig.4-7.

Furthermore, the slopes of these data in Fig.4-7 are positive. That corresponds to the concept that the $\langle \tau \rangle$ becomes longer when aging temperatures approach the deeper glassy state. It is consistent with the concept that molecular mobility decrease and $\langle \tau \rangle$ becomes longer with reducing temperature¹⁰.

Linear equation fits were carried out for these data as shown in Fig.4-7. The fitting results again lead to the similarly empirical expression as in chapter 3, i.e., $\text{Log}(\tau/t_a) = K(T_g - T)$.

The concept utilized for PS/PPO blends that the breakdown in $T_g - T$ scaling originates at least partly in the broader transition zone due to local concentration fluctuation will be applied here, and the data treatment similar to that for the PS/PPO blend in chapter 3 will again be used. As presented in Fig.4-2, the breadth of transition zone in the blend is 35°C which is broader than that of PS homopolymer, i.e.; 9°C. At equal $T_g - T$, the actual aging temperature (T_a) in the

Fig.4-7 Mean relaxation time $\langle \tau \rangle$ versus the comparable aging temperature distance, $T_g - T$, for PS/PVME (90/10) and PS homopolymers at constant aging time $t_a = 4$ hours. Second Y axis (right side) is the reduced mean relaxation time $\langle \tau \rangle / t_a$.

PS/PVME blend is closer to T_{g_i} (PVME rich regions) and further from T_{g_f} (PS rich regions) than for the pure PS homopolymer. Comparison between pure PS homopolymer and the PS/PVME blend as exhibited in Fig.4-7 shows that the mean relaxation times $\langle \tau \rangle$ of PS/PVME are shorter than for PS homopolymer at fixed $T_g - T$. This indicates that the contributions from the more mobile PVME-rich regions outweigh these from the PS-rich regions. This supports the concept that the discrepancy between the $T_g - T$ scaling of the PS/PVME blend and PS partly results from the PVME rich regions which are generated by the local concentration fluctuations of the blend, again suggest the use of $T_{g_i} - T$ as a scaling variable. Thus, we shift the T_g of PS/PVME blend by 17.5°C (due to the concentration fluctuations) and that of PS homopolymer by 4.5°C (due to the density fluctuations) to the left in Fig.4-7. We obtain an approximate superposition of blend and PS data as shown in Fig.4-8(a). As for the PS/PPO study, we can remove the effect of β on mean relaxation time $\langle \tau \rangle$ and plot the reduced characteristic relaxation time τ/τ_a versus $T_{g_i} - T$ of PS/PVME blend and PS as exhibited in Fig.4-8(b). An even better superposition is obtained consistent with our interpretation that the effect of physical aging in the PS/PVME blend is influenced by a range of microheterogeneous environment due to concentration fluctuations. We conclude that physical aging behavior monitored by the static stress relaxation mechanical spectra for the PS/PVME blend also can be substantially influenced by the presence of concentration fluctuations as in the

Fig.4-8 (a) Superposition of $\langle \tau \rangle / \tau_a$ is obtained for PS/PVME blend and PS by using $T_{gi} - T$ as scaling variable rather than $T_g - T$.

Fig.4-8 (b) Superposition of τ/τ_a is obtained for PS/PVME blend and PS by using $T_{gi}-T$ as scaling variable rather than T_g-T .

PS/PPO blend. The PS/PVME blend behaviors, with respect to stress relaxation spectra, are the same as observed a pure component except that concentration fluctuations lead to a distribution of relaxation times reflecting a range of local T_g values. In the blend, the initial decay of the stress relaxation function during physical aging is determined by the most mobile PVME-rich region.

Fig.4-9 exhibits the normalized distribution function of relaxation times $\rho(\tau)$ for the PS/PVME blend calculated via Eq.3-11 at the comparable aging temperature distance $T_g-20^\circ\text{C}$. These distribution functions progress from the initial spectrum ($t_a=30$ min.) to the final spectrum ($t_a=4$ hours). The width of distribution spectrum is determined by the spectral parameter β with an average value $\beta=0.38$, which was extracted from non-linear fits of static stress relaxation spectra (see Fig.4-3). Fig.4-9 shows that the peak maximum moves toward longer relaxation times during physical aging. This is the similar behavior to that of the PS/PPO blend in chapter 3. The variations of $\rho(\tau)$ function can be interpreted using the free volume concept; that is, the molecular segmental motions with shorter relaxation times (i.e., relaxing elements with higher mobility) are reduced as a result of with the decrease of free volume due to enhanced chain packing and densification during physical aging process.

In Fig.4-10 we display the normalized distribution function of relaxation times $\rho(\tau)$ for the PS/PVME blend and PS homopolymer at $T_a=T_g-20^\circ\text{C}$ and $t_a=4$ hours. A clear difference between blend and homopolymer can be observed on

Fig.4-9 Normalized distribution function of relaxation times $\rho(\tau)$ of PS/PVME(90/10) blend at different aging times and a constant aging temperature $T_a = T_g - 20^\circ\text{C}$.

Fig.4-10 Comparison of normalized distribution function of relaxation times $\rho(\tau)$ for PS/PVME(90/10) blend PS homopolymers at $T_a = T_g - 20^\circ\text{C}$ and $T_a = 240^\circ\text{C}$.

both sides of $\rho(\tau)$. For example, the blend possesses a larger contribution at short relaxation times (left side) and smaller at longer relaxation times (right side) than seen in PS. Also, the width of the relaxation spectrum of the PS/PVME blend is wider than that of the PS homopolymer. This reflects the variations in the β values for blend and PS. As mentioned in chapter 3, the width of the $\rho(\tau)$ can be treated as a criterion for degree of cooperatively molecular motions in polymer glasses¹¹, and is quite sensitive to the variations in temperature. The broader distribution function of relaxation times (smaller β) reflects enhanced coupling of segmental motions with the surrounding matrix in the PS/PVME blend.

In Fig.4-11, we present the dependence of spectral parameter β on the comparable temperatures distance T_g-T for blend and homopolymer. The range of the β in our studies is from 0.47 (PS at $T_g-15^\circ\text{C}$) to 0.37 (blend at $T_g-30^\circ\text{C}$) which is comparable to the selected literature values^{10,12}. It appears that β decreases with the increasing of T_g-T ; i.e., approaching the deeper glass state. This is the same indication that the distribution function $\rho(\tau)$ becomes broader as temperature advances into the deeper glass state. As discussed earlier, a broadening of $\rho(\tau)$ means that the relaxing elements in the polymer glasses have higher degree of cooperative motions with their surrounding matrix¹¹.

Fig.4-11 The dependence of spectral parameter β on the comparable aging temperature distance $T_g - T$; T is the aging temperature.

For the PS/PVME blend, β is smaller than pure PS, this means that the dispersion in relaxation spectrum due to a range microheterogeneous environments is the dominant effect. The contributions from PVME to increase the free volume play a less important role in determining the width of distribution function. This dominant effect of concentration fluctuations is evident by the extra broader glass transition zone (35°C, see Fig.4-2) in the PS/PVME blend.

In Fig.4-12 we show a double logarithmic plot of mean relaxation time $\langle \tau \rangle$ against aging time (t_a) for a thermally quenched PS/PVME(90/10) blend at various aging comparable aging temperature distances $T_g - T = 30, 25, 20, 15^\circ\text{C}$. This shows, consistent with the previous observations in our laboratory^{18,19}, and in the literatures²⁰, that $\text{Log} \langle \tau \rangle$ is proportional to $\text{Log}(t_a)$. The slope of lines is referred to as the shift rate $\mu = (d\text{log} \langle \tau \rangle / d\text{log} t_a)$ which is approximately constant at each aging temperature.

Analogous data treatment with respect to the $\langle \tau \rangle$ versus t_a on the double logarithmic plot for PS homopolymer is shown in Fig.4-13, and the shift rates again can be obtained from the slopes.

At comparable aging temperature distances $T_g - T$, the dependence of the shift rate μ for the PS/PVME blend and PS homopolymers is shown in Fig.4-14. The shift rates of each material decreases on approaching T_g . This is consistent with the general conclusions of Struik¹⁰. That physical aging is a nonlinear and self-retarding process¹⁰. Thus, in Fig.4-14, the lower μ values in the blend compared

Fig.4-12 Double logarithmic plot of mean relaxation time $\langle \tau \rangle$ against aging time (t_a) for a thermally quenched PS/PVME(90/10) blend at various aging temperatures $T_a = T_g - 30, 25, 20, 15^\circ\text{C}$.

Fig.4-13 Double logarithmic plot of mean relaxation time $\langle \tau \rangle$ against aging time (t_a) for a thermally quenched PS homopolymer at various aging temperatures $T_a = T_g - 30, 25, 20, 15^\circ\text{C}$.

Fig.4-14 Comparable aging Temperature distance, $T_g - T$, dependence of shift rate μ for PS/PVME blend PS homopolymers.

with PS may reflect the broadening of the transition zone which effectively brings the blend closer to the equilibrium melt.

To check the idea of equivalent relaxation dynamics of PS/PVME blend and PS under T_{g_i} -T scale (see Fig.4-8). A superposition curve can be roughly made by the horizontal shifts and using T_{g_i} -T scale as x-axis as exhibited in Fig.4-15. This again curve is similar to the aging rate curves in homopolymers reported by Struik¹⁰ that shows a level region and rapidly decrease in μ as near the glass transition temperature. Here, it again verified our argument that the discrepancy in the Tg-T scaling is due to the concentration fluctuations in the blend.

Dynamic mechanical spectra

The effect of physical aging on dynamic mechanical properties of PS/PVME blend was measured by recording dynamic spectra $\tan\delta(\omega)$ with increasing aging time (t_a) at a constant comparable aging temperature distance $T_g - 20^\circ\text{C}$. The plot of $\tan\delta$ versus frequency (ω), which ranges from 1 to 100 rad/sec, is shown in Fig.4-16. With increasing aging time, the $\tan\delta$ shifts to the left, i.e; to the low frequency side. This effect can be interpreted as a decrease in $\tan\delta$ value (at a constant ω) with increasing aging time. The $\tan\delta$ is a measure of the ratio of energy loss to the energy stored in a cyclic deformation²¹. Therefore, the decreasing $\tan\delta(\omega)$ implies that the damping characteristic of PS/PVME glass deteriorates with increasing aging time and polymer glass becomes more rigid.

Fig.4-15 Superposition of shift rate μ versus $T_{g_i} - T$ of the PS/PVME blend to PS by shifting leftward from the midpoint T_g of the blend.

Fig.4-16 Evolution of damping factor $\tan\delta$ as a function of frequency(ω) for PS/PVME(90/10) blend at different aging times(t_a) and a constant aging temperature distance $T_g-20^\circ\text{C}$ after a quench from the melt state.

This is consistent with the physical intuition that the packing of the polymer chains becomes more compact which adopts more equilibrium conformation during physical aging process.

It is appeared that a good superposition can be obtained by a simple horizontal shift along the logarithmic frequency scale, as exhibited in Fig.4-17. Thus, the shift factor a_t and shift rate μ can be obtained.

In Fig.4-18, we show a double logarithmic plot of shift factor, which was obtained from Fig.4-16, versus aging time (t_a) for a thermally quenched PS/PVME(90/10) blend at comparable aging temperature distance $T_g - T = 20^\circ\text{C}$. The shift factors from static stress relaxation spectra in Fig.4-3 calculated via Eq.1-3 as well as light box manual matching method are also plotted in Fig.4-18. These shift factors lie on a straight line on the double logarithmic plot. The shift rate was found to be 0.5. It shows that the shift rate, obtained from dynamic and static mechanical experiment under tensile load, agree with one another and verify the equivalence of dynamic and static viscoelastic properties²¹.

Positron annihilation lifetime(PAL) spectra

The temperature dependence of τ_3 and I_3 in PS/PPO blend and PS homopolymer are shown in Fig.4-19 and 4-20. The variations of average hole volume $\langle V_f \rangle$ versus temperature is also exhibited in Fig.4-19 as referred to the right side Y-axis. The linear increase in τ_3 and $\langle V_f \rangle$ with temperature is

Fig.4-17 Superposition of damping factor ($\tan \delta$) data of PS/PVME blend at different aging times(t_a) and $t_a = 4$ hours was selected as the reference time ;aging temperature $T_a = T_g - 20^\circ \text{C}$.

Fig.4-18 Double logarithmic plot of shift factor a_t against aging times (t_a) for a thermally quenched PS/PVME blend PS homopolymer at aging temperature $T_a = T_g - 20^\circ\text{C}$.

Fig.4-19 Temperature dependence of ortho-positronium (o-Ps) lifetime τ_3 in PS/PVME blend and PS homopolymers. Second Y axis represents the average hole volume calculated from Eq.2-10 and 2-11.

Fig.4-20 Temperature dependence of orthopositronium (o-Ps) intensity I_3 in PS/PVME blend and PS homopolymer.

consistent with the idea that thermal expansion enlarges the holes which are sampled by o-Ps. At a particular temperature, the PS rich blend has a longer τ_3 and higher I_3 than that of pure PS due to the additional 10% PVME. This implies that as observed for PS/PPO blends, blending of PVME in PS glassy matrix has a effect of introducing extra free volume. The difference between blend and constituent homopolymers in I_3 and τ_3 is clearer in PS/PVME than in the PS/PPO system (see Fig.3-25 and 26). This may reflect differences in the intrinsic flexibility of the PPO chain relative to PVME chains²²⁻²⁴. Flexible chains are usually associated with a higher free volume. This is also consistent with our observation PVME has higher ability to offer free volume than PPO in the PS glass, as indicated by the results of stress relaxation experiments in Table 3-1 and 4-1; i.e. PS/PVME has shorter mean relaxation time $\langle \tau \rangle$ than that of PS/PPO blend. In general, the above observations of the temperature dependence of I_3 and τ_3 is again similar to our earlier reports on homopolymers²⁵⁻²⁹.

Fig.4-21 and 4-22 displays,respectively, the dependence of τ_3 and I_3 for PS/PVME blend and PS at comparable temperature distance T_g-T , again using midpoint T_g as the scaling temperature. Deeper in the glassy state (i.e. higher T_g-T), smaller values of τ_3 and lower I_3 indicate that lower free volume is available in polymer glasses and hence lower molecular segmental mobility. The PS/PVME blend possesses more numerous and larger holes than the PS glass at the same T_g-T .

Fig.4-21 Comparisons of the comparable temperature distance $T_g - T$ dependence of orthopositronium (o-Ps) lifetime τ_3 in PS/PVME blend and PS homopolymer. Second Y axis represents the average hole volume calculated from Eq.2-10 and 2-11.

Fig.4-22 Comparisons of the comparable temperature distance $T_g - T$ dependence of ortho-positronium (o-Ps) intensity I_3 in PS/PVME blend and PS homopolymer.

This is further illustrated in Fig.4-23 which displays the apparent free volume fraction, $h/c = I_3 / \langle V_h \rangle$, for the PS/PVME blend and the PS homopolymer. The h/c curves, which qualitatively correspond to the free volume fraction, parallel to the data results in Fig.4-21 and 22. The blend has higher h/c values than PS over the entire range of $T_g - T$ values.

Fig.4-24 and 4-25 display the τ_3 and I_3 versus $T_{g_i} - T$ scale, respectively, for PS/PVME blend and PS homopolymer. Here, $T_{g_i} - T$ scale was used to check the idea that the discrepancy in $T_g - T$ scale is mainly due to neglect of concentration fluctuations. The superposition of the τ_3 versus $T_{g_i} - T$ can be obtained by using T_{g_i} as the reference temperature consistent with the discussion regarding Fig.4-8. This result again supports the concept of equivalent glass dynamics at fixed $T_{g_i} - T$ and supports the idea that the discrepancy at $T_g - T$ scaling is due to concentration fluctuations in the PVME blend. However, a rather poorer superposition is again found in for I_3 as shown Fig.4-25. Again, we note that I_3 can not serve as a quantitative measurement of the hole density following discussion of Kluin et al⁸². A better superposition compared with Fig.4-25 can be obtained as exhibited in Fig.4-26, which shows the apparent fraction of free volume (h/c) when plotted versus $T_{g_i} - T$ for PS/PVME blend and PS, as shown in Fig.4-26.

In summary, the results from PAL spectroscopy are qualitatively consistent with those from stress relaxation analysis in the PS/PVME (90/10) blend system. When compared at equal $T_g - T$, blending PVME or PPO into PS glassy matrix has

Fig.4-23 Comparisons of the temperature distance $T_g - T$ dependence of apparent free volume fraction, $h/c = I_3 \langle V_h \rangle$, for PS/PVME blend and PS homopolymer.

Fig.4-24 Comparisons of the comparable temperature distance $T_{g_i} - T$ dependence of orthopositronium (o -Ps) lifetime τ_3 in PS/PVME blend and PS homopolymer.

Fig.4-25 Comparisons of the comparable temperature distance $T_{gi}-T$ dependence of ortho-positronium (o-Ps) intensity I_3 in PS/PVME blend and PS homopolymer.

Fig.4-26 Comparisons of the temperature distance $T_{g_i} - T$ dependence of apparent free volume fraction, $h/c = I_3 \langle V_h \rangle$, for PS/PVME blend and PS homopolymer.

the similar effect, i.e. introduces extra free volume. Moreover, results from PAL and stress relaxation experiments are consistent in that they show PVME homopolymer offers more free volume than PPO homopolymer in PS glass.

In situ monitoring of the physical aging process by PAL spectroscopy

Finally, isothermal physical aging experiments were carried out on the PS/PVME blend and on the PS homopolymer which were probed by PAL spectroscopy at comparable aging temperatures $T_g-40^{\circ}\text{C}$.

Fig.4-27 and 4-28 show, respectively, the changes of o-Ps lifetime(τ_3) and intensity(I_3) during isothermal physical aging at $T_g-40^{\circ}\text{C}$ for the PS/PVME blend and PS. The lifetime(τ_3) remains almost constant with aging time t_a . These τ_3 values for blend and PS during aging are quite close to the values obtained in temperature dependence measurements (see Fig.4-21 and 4-22). This constant τ_3 behavior is consistent with the previous PAL studies on the PVAC^{25,28} and PC^{26,27,29} during physical aging experiments. It is also in agreement with the previous literature results on the physical aging behavior of polymer glasses³⁰⁻³⁴ probed by PAL spectroscopy. Also, consistent with earlier studies, the intensity I_3 of o-Ps component in PS/PVME blend and PS homopolymer at comparable aging temperature distance $T_g-40^{\circ}\text{C}$ decreases continuously with aging time.

Fig.4-29 displays the apparent free volume fraction, $h/c=I_3<V_h>$, for PS/PVME blend and PS homopolymer, shown behavior parallel to the data

Fig.4-27. Variations of orthopositronium (o-Ps) lifetime τ_3 in PS/PVME blend and PS homopolymer during isothermal physical aging at comparable temperature Tg-40°C following a quench above Tg.

Fig.4-28 Variations of orthopositronium (o-Ps) intensity I_3 in PS/PVME blend and PS homopolymer during isothermal physical aging at comparable temperature distance $T_g-40^\circ\text{C}$ following a quench above T_g .

Fig.4-29 Variations of apparent free volume fraction, $h/c = I_3 / V_h$, in PS/PVME blend and PS homopolymer during isothermal physical aging at comparable temperature distance $T_g-40^\circ\text{C}$ following a quench above T_g .

results in Fig.4-28. The blend has higher h/c values than PS over the entire T_g-T . A simple comparison of the rate of relaxation(Γ) of apparent free volume h/c for PS/PVME blend and PS homopolymer at $T_g-40^\circ\text{C}$ was carried out by normalizing against the initial value, taken as $(h/c)_0$ at $t_a=2$ hours, as exhibited in Fig. 4-30. No significant difference is evident between the rates of relaxation(Γ) of PS/PVME blend and PS homopolymer. However, the Γ obtained from PAL spectra is slower than that observed in stress relaxation spectra (see Fig.4-5), consistent with the fact that the former was performed at larger T_g-T . However, during physical aging experiments, different properties measured by different techniques, are likely to be sensitive to the segmental motions having relaxation times in different ranges of the total spectrum³⁵.

A quantitative interpretation of the PAL experiment is precluded by the problem discussed in chapter 3, i.e. the o-PS intensity (I_3) can not be exactly qualified³⁶, and some unknown contribution to the aging time dependence of I_3 may exist due to the positron irradiation damage³⁶.

Fig.4-30 Variations of normalized apparent free volume fraction, $(h/c) = (h/c)_0$, in PS/PVME blend and PS homopolymer during isothermal physical aging at comparable temperature distance $T_g-40^\circ\text{C}$ following a quench above T_g .

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Chapter 4

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Chapter 5. Physical aging of poly(methyl methacrylate)/poly(ethylene oxide) blends

5-1 Background

In this chapter we consider a special kind of miscible blend: i.e., binary-crystalline/amorphous blends¹⁻² which consist of mixtures of a crystallizable and an amorphous component which are miscible in the amorphous state. At temperatures above the melting temperature(T_m) of the crystallizable component, or in blends which are compositionally rich with the amorphous component, these blends may be one phase and miscible. However, in blends which are compositionally rich in the crystallizable component or at temperatures below T_m , a separate pure crystalline phase will be formed. The morphology of these blends may be considered as crystalline domains embedded in an amorphous matrix¹⁻², which is a compatible mixture of the two polymers in this phase separated blend³. Of course, the amorphous matrix will be richer in the non-crystallizable component than the overall blend composition.

One such blend, which has been studied extensively, is the polyethylene oxide (PEO)/atactic poly(methyl methacrylate) (a-PMMA) system. Most of earlier studies of PEO/PMMA blends have been carried out to better understand the miscibility⁴⁻⁶, crystallization kinetics⁷⁻¹², thermodynamic interaction parameter¹³⁻¹⁵, and microstructure¹⁶⁻¹⁸. Generally, X-ray and neutron scattering

techniques reveal a morphology consisting of the PEO crystallites coexisting with an amorphous PMMA/PEO^{3,9,13} mixture. At a given temperature, the dilution by non-crystalline PMMA causes a depression of the overall kinetic rate of crystallization of PEO in proportion to the amount of PMMA added^{11,12}. Miscibility of PMMA with PEO in the melt and solid amorphous states has been predicted theoretically and subsequently verified^{4,20}. Also, the influence of the tacticity of PMMA on blend structure and miscibility was evaluated by several research groups^{5,6,10,11,12,18}. At the present time, questions remain regarding degree of miscibility of isotactic and syndiotactic PMMA with PEO^{5,6,10,12,18}. Conflicting conclusions about the miscibility of i-PMMA and PEO have been reported^{5,6,8,12,18}. However, it appears to be generally recognized that atactic PMMA is miscible with PEO in the melt and amorphous states^{5,6,10,11,12,18}.

Calorimetric²¹ and spectroscopic¹⁶ investigations have focused on the crystallization behavior of PEO in PMMA/PEO blends. They reveal a totally amorphous character when the PEO content is below 20 weight percent in the PMMA/PEO blends^{21,26}. Up to 20% of PEO, blends are transparent and show a single T_g ¹⁶. At higher PEO content, crystallization takes place and blends become opaque. Accordingly we decided to investigate a 15% (by weight) PEO/PMMA blend in this study.

Currently, no literature can be found concerning the physical aging behavior of PMMA/PEO glassy polymer blends. In this investigation, we aim to compare

the isothermal physical aging behavior of a glassy a-PMMA/PEO (85/15) blend with that of pure a-PMMA homopolymer. Positron annihilation lifetime spectroscopy, static stress relaxation analysis, dynamic mechanical spectroscopy, and differential scanning calorimetry will be used as the tools for our exploration.

5-2 Experimental

Materials

The polymers used in study were atactic poly(methyl methacrylate) (a-PMMA) and poly(ethylene oxide) (PEO). All the polymers were purchased from Scientific Polymer Products, and were used without further purification. The a-PMMA has average molecular weight $M_n=280,000$ and $M_w=400,000$ obtained from GPC. The viscosity average molecular weight (M_v) of PEO is 180,000, determined by viscometry using the following equation⁶

$$[\eta]=3.97 \times 10^{-4} M^{0.69} \quad (5-1)$$

at 30°C for benzene as solvent. The molecular structures of these two polymers are shown in Fig.5-1.

The binary mixtures of 85/15 (by weight) PMMA/PEO were prepared by dissolving the two polymers in 5% (w/v) chloroform solution. The polymer mixture was kept in solution for two days with continuous stirring to assure homogeneity. Then, this 5% (W/V) polymer mixture solution was cast on a disposable aluminum pan which was covered with a perforated aluminum foil. The chloroform solvent was removed by evaporation at ambient temperature for two days. The solvent cast films were subjected to further drying under vacuum

Fig.5-1 Molecular structures of poly(methyl methacrylate)(PMMA) and poly(ethylene oxide)(PEO)

at 60°C for 48 hours. Finally, the vacuum dried sample was compression molded at 130°C to removed any residual solvent and a square sheet with thickness around 0.6-0.8 mm was obtained.

It is not possible to prepare a polymer glass from pure PEO homopolymer at ambient temperature because of its low T_g (around -50 to -67°C) and high crystallizability²²⁻²⁴. Dried powder of pure PMMA homopolymer was directly molded into a sheet at temperature 180°C. The thickness of PMMA specimen is around 0.8-1 mm. Standard ASTM D 1708-84 dog-bone shaped specimens and disk shaped specimens with radius around 8 mm were cut from the molded sheet of the blend and the homopolymer by a blade die. Since PEO is quite sensitive to moisture, the specimens were kept in a sealed desiccator to prevent any moisture uptake before static stress relaxation, dynamic mechanical, and PAL experiments were performed.

Differential scanning calorimetry

The DSC curves for the PMMA/PEO blend and PMMA homopolymer are shown in Fig.5-2. The detailed procedures for DSC have been reported in the section 3-2.

Fig.5-2 DSC curves of PMMA/PEO(85/15) blend and PMMA homo-polymer at a heating rate of 20°C/min.

Static stress relaxation mechanical and PAL spectroscopy

The static stress relaxation mechanical and PAL spectroscopy methodology used in this study are identical to those in section 3-2.

Dynamic mechanical spectroscopy

The changes in the storage modulus $E'(t)$ in dynamic viscoelastic experiment during physical aging were monitored using the Rheometric RSAII in the "dynamic mode-- time scanning." The sample dimensions were the same as the static relaxation mechanical experiments.

The specimens were annealed at $T_g + 10^\circ\text{C}$ for one hour to attain the equilibrium state, then quenched to the aging temperature (T_a), as quickly as possible, by directly blowing cold dry air into the testing chamber. The temperature was maintained at T_a over the entire period of the aging test. E' was recorded in the time domain at intervals of 15 minutes. The start of aging (aging time $t_a = 0$) was set to be the moment that the chamber temperature reached T_a .

5-3 Data analysis

The data analysis procedures for stress relaxation and PAL spectra described in section 3-3 were also applied in the study of PMMA/PEO blends.

5-4 Results and discussion

Differential scanning calorimetry(DSC) thermogram

Fig.5-2 shows the DSC traces obtained for the quenched PMMA/PEO(85/15) blend and PMMA homopolymer at a heating rate of $20^{\circ}\text{C}/\text{min}$. Note that the pure components have Tgs which differ by 160°C ²⁴. The presence of a single blend glass transition temperature at 67°C , which falls between the Tgs of the two pure constituent homopolymers, strongly indicates their miscibility²⁵. The Tg values of the blend and PMMA homopolymer are in consistent with the literature values^{13,16}. No evidence of an exotherm at the T_m of PEO homopolymer is observed.

A broadening of the glass transition zone was observed in the PMMA/PEO blend compared with that of PMMA homopolymer. The breadth of the transition zone was 35°C for the blend as against 15°C for PMMA. This implies that a range of local concentration fluctuation is presented in PMMA/PEO blends. In summary, the broader transition zones of these three miscible blends (PS/PPO, PS/PVME, and PMMA/PEO) compared to those of the component homopolymers are in agreement with the observations by Schneider et al²⁶⁻²⁸.

Static stress relaxation mechanical spectra

Fig.5-3 and 5-4 show, respectively, the momentary tensile stress relaxation moduli $E(t)$ for a PMMA/PEO(85/15) blend and a PMMA homopolymer at different aging times(t_a) during isothermal physical aging at an aging temperature distance $T_g-27^{\circ}\text{C}$, after quenching from equilibrium melt ($T_g+10^{\circ}\text{C}$). Struik's relaxation time-aging superposition concept is the reason in these figures²⁹. With increasing aging time, the stress relaxation spectra shift to longer time scale, but the shape of the curves remains approximately constant. Within the experimental error, the stress relaxation curves of the blend and PMMA may be represented by a single stretched exponential functions with $\beta=0.25$ and 0.32 , respectively, as the shown by solid curves exhibited in Fig.5-3 and 5-4. There is some deviation of the stress relaxation function in the blend from the master curve at longer aging time. There are in the direction of increase width of the relaxation spectrum at longer aging time. It is consistent with the prediction of the Ngai coupling theory³²⁻³⁷. To maintain consistency with analysis in earlier chapter, we will neglect these deviations which do not change the main conclusions of our experiments.

The relaxation parameters β , τ , E_0 , and $\langle\tau\rangle$ extracted from in Fig.5-3 and 5-4 as well as mechanical relaxation spectra at aging temperature distances T_g-7 , 17 , 27 37 are summarized in Table 5-1 and 5-2. For comparison, the results of the unconstrained fits, in which β is allowed to vary with aging time, for the

Fig.5-3 Stress relaxation curves for PMMA/PEO(85/15) blend during isothermal aging at $T_g-27^\circ\text{C}$ ($T_a=40^\circ\text{C}$) after a quench from equilibrium melt above T_g . Symbols correspond to different aging times(t_a) as indicated; solid lines are fits to stretched exponential function with $\beta=0.25$.

Fig.5-4 Stress relaxation curves for PMMA homopolymer during isothermal aging at $T_g - 27^\circ\text{C}$ ($T_a = 88^\circ\text{C}$) after a quench from equilibrium melt above T_g . Symbols correspond to different aging times(t_a) as indicated; solid lines are fits to stretched exponential function with $\beta = 0.32$.

Ta °C	ta min.	Eo x10 ⁸ Pa	τ sec	β	< τ > sec
Tg-7	60	7.06	85	0.32	576
	120	7.07	156	0.32	1060
	240	7.00	252	0.32	1720
	480	7.04	445	0.32	3030
Tg-17	60	9.06	414	0.29	4320
	120	9.19	671	0.29	7000
	240	9.26	1270	0.29	13300
	480	9.00	3470	0.29	36200
Tg-27	60	10.3	1180	0.25	29100
	120	10.3	2250	0.25	55600
	240	10.0	6350	0.25	157000
	480	10.1	9240	0.25	228000

Table 5-1 Stretched exponential curves fitting results for PMMA/PEO (85/15) blend.

Ta °C	ta min.	Eo x10 ⁸ Pa	τ sec	β	$\langle \tau \rangle$ sec
Tg-7	60	0.44	56	0.48	125
	120	0.44	90	0.48	199
	240	0.40	140	0.48	310
	480	0.44	192	0.48	423
Tg-17	60	3.25	74	0.48	160
	120	3.25	121	0.48	259
	240	3.00	277	0.48	485
	480	3.00	301	0.48	644
Tg-27	60	7.08	312	0.32	2270
	120	7.19	726	0.32	5290
	240	7.05	1770	0.32	12900
	480	7.37	2250	0.32	16400
Tg-37	60	10.3	1118	0.33	6887
	120	10.3	1898	0.33	11639
	240	10.0	4185	0.33	25780

Table 5-2 Stretched exponential curves fitting results for PMMA.

PMMA/PEO blend are tabulated in Appendix B. The substantial increases in τ as aging time elapses for the results from constrained fits (Table 5-1 and 5-2) and unconstrained fits (free β) are due to the densification and chain packing during the physical aging²⁹. However, the results from unconstrained fits are slightly but significantly better than the constrained fits due to the intuitively better result for E_0 , viz E_0 increases slightly with aging time. Also, the parameter β of PMMA/PEO(85/15) blend systemically decrease with aging time during unconstrained fits. This behavior is, in fact, observed for all three blends. These results are qualitatively similar to these described earlier chapter for PS/PVME(90/10) and PS/PPO(90/10) polymer glasses. Master curves of blend and PMMA homopolymer at comparable aging temperature distance $T_g-27^\circ\text{C}$ were constructed and exhibited in Fig.5-5. In direct contrast to the behavior of PS/PVME and PS/PPO, Fig.5-5 indicates that the blend has a slower rate of relaxation ($\Gamma=\tau^{-1}$) than PMMA homopolymer.

To verify the aging thermoreversibility of PMMA/PEO(85/15) blend, a single specimen was subjected to repeated thermal history of annealing at a temperature of $T_g+10^\circ\text{C}$. The result is given in Fig.5-6, and shows that the effects of thermal history on stress relaxation in PMMA/PEO blend glasses is reproducible on the same specimen. This is a major feature of physical aging behavior²⁹⁻³¹, in contrast to chemical aging phenomena.

Fig.5-5 Superposition of stress relaxation curves of PMMA/PEO blend and PMMA homopolymers at different aging times(t_a) and the reference time was selected at $t_a = 4$ hours; aging temperature $T_a = T_g - 27^\circ\text{C}$. Comparisons are made with stretched exponential function with respective, $\beta = 0.25$ and 0.32 .

Fig.5-6 Stress relaxation curves(solid curves) for PMMA/PEO blend during isothermal aging at $T_a = T_g - 27^\circ\text{C}$ and $t_a = 1, 2$ hours following a quench from equilibrium melt above T_g . Symbols on the curves represent the repeat experimental tests for thermoreversibility.

The mean relaxation time $\langle \tau \rangle$ plotted versus aging temperature distance $T_g - T$ is compared for the blend and PMMA at an aging time $t_a = 4$ hours in Fig.5-7. The scale of reduced mean relaxation time $\langle \tau \rangle / t_a$ is shown at the right side Y-axis in Fig.5-7. In comparison with the pure PMMA homopolymer, blending of 15% PEO homopolymer into the PMMA matrix results in a longer mean relaxation time $\langle \tau \rangle$ over the entire $T_g - T$ range. From Table 4-1 and 4-2, values of $\langle \tau \rangle$ versus $T_g - T$ at other aging times also show the same discrepancy as in Fig.5-7. Note that employment of $T_{g_i} - T$ as a reducing parameter could lead to ever larger discrepancies between blend and PMMA homopolymer. Thus, the evidence seems very clear that there is a larger reduction in mobility in the PMMA/PEO blend. This is quite different from our previous observations in PS/PPO and PS/PVME blends. Surprisingly, in contrast to PS/PPO and PS/PVME blends, PMMA/PEO blends are believed not to exhibit a strong enthalpic interaction^{13-15, 22-24}. From small angle neutron scattering of PMMA homopolymer, PMMA/PEO(95/5), (90/10), and (80/20) blends, it has been further concluded that within experimental error, the configuration of PMMA in the presence of PEO is equivalent to that of pure PMMA homopolymer in the bulk isotropic state¹³, i.e. there is no change in radius of gyration. However, unlike PVME and PPO, pure PEO is a highly crystallizable polymer³⁻²⁰ and adopts a helical structures in the pure state^{17,18}. FTIR experiments suggest that PEO prefers to adopt a trans planar structure when blended with PMMA,

Fig.5-7 Mean relaxation time $\langle \tau \rangle$ versus the comparable aging temperature distance, $T_g - T$, for PMMA/PEO (85/15) and PMMA homopolymers at constant aging time $t_a = 4$ hours. Second Y axis (right side) is the reduced mean relaxation time $\langle \tau \rangle / t_a$.

however, as opposed to the helical structure of pure PEO^{17,18}. The effect, if any, of this conformation change on molecular dynamics is not clear, but it is conceivable that it could cause a reduction in overall segmental mobility and hinder the relaxational behavior of PEO/PMMA blends²⁴. The above tentative explanation could explain the observation of a longer $\langle \tau \rangle$ in the glassy PMMA/PEO blend.

Recently, several studies involving rheological²²⁻²³ and rheol-optical²⁴ experiments on the relaxation dynamics of PMMA/PEO blends in the melt state reported an increase in the characteristic relaxation times of PMMA and PEO components in the blend melt which are interpreted due to the enhanced monomeric friction coefficients of the two polymer^{22,23}. However, the motions in the glasses involve segments much smaller than these which determine the melt rheology. The experimental results in the melt can not serve as direct evidence for the interpretation of the observations in the glassy state.

The positive slopes of these data in Fig.5-7 are consistent with the expectation that $\langle \tau \rangle$ becomes longer when aging temperatures are deeper in the glassy state. It is also consistent with the idea that molecular mobility decreases and $\langle \tau \rangle$ becomes longer with reduction of the temperature.

Linear equation fits were carried out for these data as shown in Fig.5-7. The fitting results again lead to the similarly empirical expression as in chapter 3 and 4, i.e., $\text{Log}(\tau/\tau_a) = K(T_g - T)$.

As mentioned earlier, the concept of reducing variable temperature distance from glass transition temperature, which we discussed in chapter 3 and 4, does not apply to this PMMA/PEO(85/15) blend system. If T_{g_i} is used as a scaling reference temperature, there is a large discrepancy in the scaling of $\langle \tau \rangle$ versus $T_{g_i} - T$. The longer $\langle \tau \rangle$ values at fixed $T_{g_i} - T$ in the PMMA/PEO blend indicates a structural change in the glassy state which results in an increase effective monomeric friction coefficient or a small free volume available. Thus, this system provides clear evidence of non-universality in the comparable temperature distance dependence of the mechanical relaxation times.

Fig.5-8 exhibits the normalized distribution function of relaxation times $\rho(\tau)$ for the PMMA/PEO blend calculated via Eq.3-11 at a comparable aging temperature distance $T_g - 7^\circ\text{C}$. These distribution functions progress from the initial spectrum ($t_a = 60$ min.) to the final spectrum ($t_a = 8$ hours). The width of distribution spectrum is determined by the spectral parameter β with an average $\beta = 0.32$, which was extracted from non-linear fits of stress relaxation spectra. Fig.5-8 shows that the peak maximum moves toward longer relaxation times during physical aging. This behavior is similar to the other miscible blends in our studies.

In Fig.5-9, we compare the normalized distribution function of relaxation times $\rho(\tau)$ for the PMMA/PEO blend with PMMA homopolymer at $T_a = T_g - 27^\circ\text{C}$ and $t_a = 4$ hours. It is observed that the distribution of relaxation times for the blend

Fig.5-8 Normalized distribution function of relaxation times $\rho(\tau)$ of PMMA/PEO(85/15) blend at different aging times and a constant aging temperature $T_a = T_g - 7^\circ\text{C}$.

Fig.5-9 Comparison of normalized distribution function of relaxation times $\rho(\tau)$ for PMMA/PEO(85/15) blend and PMMA homopolymer at $T_a = T_g - 27^\circ\text{C}$ and $T_a = 240$ min.

is broader than the homopolymer at equal T_g-T . Based on the coupling theory of Ngai³³⁻³⁷, this is a manifestation of more cooperatively of molecular motions, and a stronger coupling strength in the blend. We hypothesize that the molecular structure of PEO, originally helical, transforms into a trans planar conformation which makes the cooperative motions with PMMA homopolymer in the blend more restrained. Therefore, a longer mean relaxation time $\langle \tau \rangle$ of the blend compared with that of PMMA was observed at T_g-T scale.

The dependence of spectral parameter β on the comparable temperature distance T_g-T for the blend and homopolymer is displayed in Fig.5-10. It appears that β decrease with increasing T_g-T ; i.e., deeper in the glassy state. This again verifies the concept that the distribution function $\rho(\tau)$ becomes broader as temperature decreases deeper in the glass. As discussed earlier, a broader $\rho(\tau)$ function is consistent with the concept that the relaxing elements in the polymer glasses have a higher degree of cooperativity, and a stronger coupling with their surrounding matrix³²⁻³⁷. The smaller β values in the blend, compared to the PMMA homopolymer, may thus be interpreted as due to the stronger coupling between PMMA homopolymer and a "rigid" trans planar PEO structure in the blend. The evidences from extra broader transition zone (see Fig.5-2) and longer mean relaxation time $\langle \tau \rangle$ (i.e. smaller free volume available) imply that the smaller β value in the PMMA/PEO blend is a combination from concentration fluctuations and a small free volume (longer mean stress relaxation time).

Fig.5-10 The dependence of spectral parameter β on the comparable aging temperature distance $T_g - T$.

In Fig.5-11 and 5-12 we show a double logarithmic plot of mean relaxation time $\langle \tau \rangle$ against aging time (t_a) for a thermally quenched PMMA/PEO blend and the PMMA homopolymer, respectively, at various comparable aging temperature distances $T_g - T = 7, 17, 27^\circ\text{C}$. Consistent with the previous observations in our laboratory³⁸⁻³⁹ and in the literature^{31,40}, $\log \langle \tau \rangle$ increases proportionally to $\log t_a$. The slope of the lines are referred to as the shift rate $\mu = (d \log \langle \tau \rangle / d \log t_a)$.

The dependence of shift rate μ on the aging temperature distance $T_g - T$ for the PMMA/PEO blend and PMMA homopolymer is shown in Fig.5-13. This is in agreement with the observations reported by Struik^{29,30} that shift rates of the two materials decrease on approaching T_g . The shift rate of the PMMA homopolymer decreases from a value close to unity at $T_g - 27^\circ\text{C}$, similar to the literature value^{29,30}, to around 0.5 at $T_g - 7^\circ\text{C}$ as the aging temperature moves into the transition zone. However, for the PMMA/PEO(85/15) blend with its broader transition zone, the shift rate shows a sharp reduction only when the temperature is very near the T_g , i.e. $T_g - 7^\circ\text{C}$.

Dynamic mechanical spectra

Fig.5-14 and 5-15 show, respectively, the double logarithmic plots of $E'(t)$ (storage modulus), determined at frequency = 0.16 Hz and 0.2% strain, against aging time (t_a) for a thermally quenched PMMA/PEO blend and PMMA

Fig.5-11 Double logarithmic plot of mean relaxation time $\langle \tau \rangle$ against aging time (t_a) for a thermally quenched PMMA/PEO(85/15) blend at various aging temperatures $T_a = T_g - 27, 17, 7^\circ\text{C}$.

Fig.5-12 Double logarithmic plot of mean relaxation time $\langle \tau \rangle$ against aging time (t_a) for a thermally quenched PMMA homopolymer at various aging temperatures $T_a = T_g - 37, 27, 17, 7^\circ\text{C}$.

Fig.5-13 Comparable aging Temperature distance, $T_g - T$, dependence of shift rate μ for PMMA/PEO blend and PMMA homopolymers.

Fig.5-14 Dependence of storage modulus $E'(t)$ at 0.16 Hz on aging times for PMMA/PEO blend at different $T_g - T$ during isothermal physical aging.

Fig.5-15 Dependence of storage modulus $E'(t)$ at 0.16 Hz on aging times for PMMA homopolymer at different aging temperature distances $T_g - T$ during isothermal physical aging.

homopolymer at comparable aging temperature distances $T_g - T = 7, 17, 27^\circ\text{C}$. The increase in E' with time in both figures results from a progressive decrease in segmental mobility. It is qualitatively consistent with the experimental results from stress relaxation spectra that the relaxation time becomes longer with increasing aging time.

The rates of aging for the blend and PMMA, derived from the slopes of the lines in Fig.5-14 and 5-15, are plotted against the aging temperature distance $T_g - T$ shown in Fig.5-16, where the rate of increase of E' is expressed as a percentage increase per decade of aging time at a frequency of 0.16 Hz^{42,43}. Specifically, an aging rate equals $(2.303)(100)(S)$, where S is the slope $d\text{Log}E'/d\text{Log}t_a$. Comparisons between Fig.5-16 and Fig.5-13 show that both figures are qualitatively consistent with each other. Specifically, we note the sharp decrease in aging rates between $T_g - 27^\circ\text{C}$ and $T_g - 7^\circ\text{C}$ in PMMA due to the approach toward the transition zone; and the more moderate decrease in shift rate in the PMMA/PEO blend because of the broader transition zone.

Positron annihilation lifetime(PAL) spectra

The temperature dependence of τ_3 and I_3 in the PMMA/PEO blend and PMMA homopolymer are shown in Fig.5-17 and 5-18, respectively. The corresponding variations of average hole volume ($\langle V_f \rangle$) are denoted on the right

Fig.5-16 Dependence of aging rate on aging temperature distance $T_g - T$ expressed as the percent increase of E' per decade aging time(t_a) of PMMA/PEO blend and PMMA homopolymer.

Fig.5-17 Temperature dependence of ortho-positronium (o-Ps) lifetime τ_3 in PMMA/PEO blend and PMMA homopolymers. Second Y axis represents the average hole volume calculated from Eq.2-10 and 2-11.

Fig5-18 Temperature dependence of orthopositronium (o-Ps) intensity I_3 in PMMA/PEO blend and PMMA homopolymer.

side ordinate in Fig.5-17. The linear increase in τ_3 and $\langle V_f \rangle$ with temperature is consistent with the expectation that thermal expansion enlarges the holes, as sampled by o-Ps. The τ_3 values of the PMMA homopolymer are in agreement with literature data⁴³. It is interesting to note that the PMMA rich blend composition has a longer τ_3 , but the I_3 is substantially lower than that of pure PMMA at the same temperature. The positronium quench effect of oxygen atoms in PEO chains could be the partial reason for the substantial lower intensity of o-Ps annihilation component. However, we did not see such effect in PS/PVME and PS/PPO blends since the PVME and PPO chains possess oxygen atoms. Qualitatively, the above observations of the temperature dependence of I_3 and τ_3 is quite similar with our earlier reports on homopolymers^{44,45}.

Fig.5-19 and 5-20 show, respectively, the dependence of τ_3 and I_3 for PMMA/PEO blend and PMMA at comparable temperature distance Tg-T. The PMMA/PEO blend has a shorter τ_3 and lower I_3 in the Tg-T scale indicating that the free volume available in PMMA/PEO blend is smaller than that of PMMA homopolymer. These results are in agreement with the evidence from stress relaxation spectra that the blend has a longer $\langle \tau \rangle$. This, in turn, indicates a lower molecular segmental mobility in the PMMA/PEO(85/15) blend and implies that blending PEO in PMMA glass results in smaller free volume. This role of the minor component PEO in a PMMA glass is quite opposite to that of PPO and PVME in a PS glass. The preference trans for a planar conformation

Fig.5-19 Comparison of the comparable temperature distance $T_g - T$ dependence of orthopositronium (o-Ps) lifetime τ_3 in PMMA/PEO blend and PMMA homopolymer. Second Y axis represents the average hole volume calculated from Eq.2-10 and 2-11.

Fig.5-20 Comparison of the comparable temperature distance $T_g - T$ dependence of ortho-positronium (o-Ps) intensity I_3 in PMMA/PEO blend and PMMA homopolymer.

and consequent intermolecular interactions of PEO apparently reduces the total free volume available in the blend.

Fig.5-21 displays the apparent free volume fraction, $h/c = I_3 < V_h >$, for the PMMA/PEO blend and PMMA homopolymer. The h/c curves, which qualitatively correspond to the fractional free volume fall parallel to the data results in Fig.5-19 and 5-20. The blend has lower h/c values than PMMA over the entire Tg-T.

In summary, the results from PAL spectra are again qualitatively consistent with that from stress relaxation spectra in PMMA/PEO (85/15) blend system. At the Tg-T scale, the blending of PEO in a PMMA glassy matrix has an effect of reducing free volume.

In situ monitoring of the physical aging process by PAL spectroscopy

Finally, we carried out isothermal physical aging experiments, which were monitored in suit by PAL spectroscopy, for the PMMA/PEO(85/15) blend and PMMA homopolymer at comparable aging temperature Tg-37°C.

Fig.5-22 and 5-23 show, respectively, the changes of o-Ps lifetime(τ_3) and intensity (I_3) for the PMMA/PEO(85/15) blend and PMMA homopolymer during isothermal physical aging at Tg-37°C. The lifetime(τ_3) remains almost constant with aging time t_a . These τ_3 values for blend and PMMA during aging are quite close to the results from the temperature dependence measurements

Fig.5-21 Comparison of the temperature distance $T_g - T$ dependence of apparent free volume fraction, $h/c = I_3 \langle V_h \rangle$, for PMMA/PEO blend and PMMA homopolymers.

Fig.5-22 Variations of orthopositronium (o-Ps) lifetime τ_3 in PMMA/PEO blend and PMMA homopolymer during isothermal physical aging at comparable temperature distance $T_g-37^\circ\text{C}$ following a quench above T_g .

Fig.5-23 Variations of orthopositronium (o-Ps) intensity I_3 in PMMA/PEO blend and PMMA homopolymer during isothermal physical aging at comparable temperature distance $T_g-37^\circ\text{C}$ following a quench above T_g .

(see Fig.4-19 and 4-20) because both measurements have similar thermal history: annealing then quenching. Constancy of τ_3 is consistent with our previous PAL study of the PVAC^{44,45} and PC⁴⁶⁻⁴⁸ during physical aging.

Fig.5-24 is a plot of the apparent free volume fraction h/c against aging time, the blend and PMMA homopolymer show almost constancy. The β transition temperature for PMMA homopolymer is around 50°C ⁴⁹, which is lower than T_g - 37°C , may be one reason for the displayed constancy in h/c , τ_3 and I_3 . Another reason may be that the long term decay behavior in o-Ps component for PMMA and blend was concealed at our short term physical aging experiments. However, the constancy in τ_3 and I_3 in PMMA and blend reflect that no radiation damage is caused by expose to the positron source over the 20 hours experimental duration. Again caution must be noted in qualitatively correlating I_3 with the number of holes⁵⁰.

Fig.5-24 Variations of apparent free volume fraction, $h/c=I_3/V_h$, in PMMA/PEO blend and PMMA homopolymer during isothermal physical aging at comparable temperature distance $T_g-37^\circ\text{C}$ following a quench above T_g .

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Chapter 5

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Chapter 6: Summary and conclusions

In summary, an investigation of the effect of physical aging on mechanical properties has been carried out for the miscible blends PS/PPO(90/10), PS/PVME(90/10) and PMMA/PEO(85/15) blends and their constituent homopolymers in the glassy state. Each material was tested via static stress relaxation, dynamic mechanical and positron annihilation lifetime spectroscopy during the isothermal physical aging process after a quench from the equilibrium melt state. Our goal was to compare the isothermal physical aging behavior of three miscible polymer blends with that of their constituent components. Besides, we attempted to determine whether in blends or homopolymers, a universal description of the kinetics of physical aging could be empirically defined using $\ln(a(T))$ as a reducing variable, the temperature distance from the glass transition temperature.

The experimental results obtained in this study have led to the following conclusions concerning the nature of physical aging in miscible binary polymer systems. Some of the conclusions were unidentified in the previous literature.

We observed that the concept of stress relaxation time-aging time superposition was approximately valid for both blends and homopolymers from

the static stress relaxation experiments. The results from stretched exponential function fits with constrained β value show that the physical aging affects stress relaxation spectra by shifting the characteristic relaxation time τ and mean relaxation time $\langle\tau\rangle$ toward longer time scale for these materials. These observations are consistent with the pioneer work of Struik. However, for the PMMA/PEO(85/15) blend, there is evidence that unconstrained fits, in which β is allowed to vary with aging time, are slightly but significantly better than the constrained fits and lead to an intuitively better result for E_0 , viz E_0 increases slightly with aging time. Also, the parameter β systemically decrease with aging time. This behavior is, in fact, observed for all three blend systems, when unconstrained fits are used to interpret the static stress relaxation data.

The thermoreversible nature of physical aging has been verified in PS/PVME(90/10), PS/PPO(90/10), and PMMA/PEO (85/15) blends through cyclic stress relaxation measurements.

An apparent discrepancy in the scaling of the mean stress relaxation times $\langle\tau\rangle$ with respect to T_g-T between PS/PPO, PS/PVME and the constituent PS homopolymer is resolved by invoking the presence of concentration fluctuations on the blends manifested by the broadening of the glass transition region in the DSC thermogram. By using the onset glass transition temperature (T_{g_i}) as a point

of reference, a comparison of the dynamics of PS/PPO and PS/PVME glasses with PS homopolymer detects no significant differences. This is consistent with the concept that the T_g - T scaling of the initial decay of stress relaxation function is determined by the more mobile regions of the glass which in the blends are influenced by the local concentration fluctuations. These low T_g , high mobility regions control the initial decay of the stress relaxation modulus ($E(t)$) in the blends. In the PS/PPO blend, the more mobile regions are PS-rich, in the PS/PVME blend, they are PVME-rich. We thus conclude that relaxation behavior in blend can be influenced considerably by the presence of concentration fluctuations.

However, this interpretation does not apply to the PMMA/PEO(85/15) blend system. Here, if T_{g_i} is used as a scaling reference temperature, there is a large discrepancy in the scaling of $\langle \tau \rangle$ versus T_{g_i} - T . Thus, this system provides clear evidence of non-universality in the dependence on temperature distances of the mechanical relaxation times. The longer $\langle \tau \rangle$ values at fixed T_g - T in the PMMA/PEO blend indicates a structural change in the glassy state which results in an increase in the effective monomeric friction coefficient, i.e. a smaller free volume available. Interestingly, for PMMA/PEO blend in the melt state, rheological evidence from the literature indicates an increased monomeric friction factor relative to the pure homopolymer. Also, we note that from the literature,

spectroscopic evidence indicates that PEO prefers to adopt a trans planar structure when in contact with PMMA in the blend, as opposed to the primary helical structure of PEO in the pure state. Note that another source of non-universality in the blend dynamics is that the β parameter is different from that of the constituent homopolymer component. Two effects contribute to this. One is the effect of concentration fluctuations; this is expected to widen the relaxation spectrum, i.e. to decrease β ; a second effect arises from any large change in structure (free volume). This may either increase or decrease β depending on whether the minor blend component causes an increase or decrease of free volume. For the PS/PPO blend, since β is slightly increased relative to pure PS, we infer, from Ngai's coupling theory a weaker coupling of the relaxing elements with surrounding matrix, i.e. the effect of an increased free volume from the dissolved PPO dominates over the effect of concentration fluctuations. For the PS/PVME blend, since β is decreased relative to pure PS, we deduce that the dominant effect is the dispersion in relaxation spectrum, due to a range of microheterogeneous environments. In PMMA/PEO, β is again decreased in the blend relative to pure PMMA. Here the effect is a combination from concentration fluctuations and a smaller free volume (longer mean stress relaxation time).

We also observe an increase in the breadth of the distribution function of

relaxation times $\rho(\tau)$ for the blends and homopolymers in the glassy state at lower temperatures indicating that the relaxing elements in the polymer glass have higher degree of cooperative motions with their surrounding matrix. This observation is again consistent with the coupling model of Ngai since at lower temperature one expects more densification and hence a stronger coupling between the relaxing elements with the surrounding matrix.

The increases in storage modulus and decreases in damping factor from the dynamic mechanical spectra in PS/PVME and PMMA/PEO blends, respectively, reflect the densification and chain packing during physical aging process.

We have attempted to discover whether the positron lifetime technique provides any molecular level support in terms of free volume changes as they relate to viscoelastic properties, for our above interpretation of changes during physical aging of polymer material. It is gratifying to discover that the results from PAL measurements are qualitatively consistent with those of stress relaxation spectra for the blends and homopolymers. In PAL spectroscopy, the o-Ps lifetime(τ_3) can be related to an average hole size, while the o-Ps intensity can be viewed (with caution) as a measurement of the average number of holes. For PS/PPO(90/10) and PS/PVME(90/10) blends at fixed T_g - T , we find a decrease in the mean stress relaxation time $\langle \tau \rangle$ and an increase of o-Ps lifetime(τ_3) and

intensity(I_3) compared with the PS homopolymer, All of these effects can be attributed to an increase of free volume on adding PPO and PVME to the PS glass. The scaling temperature T_g-T produces an approximate superposition of the blend and the PS data for τ_3 and h/c . In contrast, blending PEO with PMMA glass has the effect of decrease free volume as evidenced by a longer $\langle\tau\rangle$, a smaller τ_3 and I_3 in the PMMA/PEO blend than that of the PMMA homopolymer at the same T_g-T .

Finally we have also investigated changes in the o-Ps pickoff component lifetime(τ_3) and intensity(I_3) during isothermal physical aging. The results are similar to literature observations in that τ_3 remains approximate constant whereas I_3 systematically decreases with aging time. A quantitative interpretation of these data is precluded because we do not have data on possible chemical damage due to prolonged positron irradiation. Qualitatively, however, it is interesting that I_3 decreases rapidly in the systems which contain PS homopolymer, whereas very little physical aging effect is found in the PEO/PMMA system which has a smaller τ_3 and I_3 (i.e. smaller free volume).

Appendix A

Unconstrained and constrained fitting results of PAL data¹

Unconstrained fitting results of PMMA homopolymer at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.222	0.474	2.025	36.88	34.13	28.98	30
0.232	0.516	2.067	41.40	29.98	28.62	40
0.254	0.604	2.170	49.29	22.62	28.09	50
0.236	0.539	2.205	42.37	28.73	28.90	60
0.237	0.539	2.213	43.14	27.59	29.26	70
0.241	0.576	2.296	45.92	25.10	28.99	80
0.245	0.595	2.336	46.83	23.96	29.22	90
0.247	0.646	2.397	47.87	23.79	28.35	100
0.241	0.591	2.314	45.31	24.82	29.88	110
0.233	0.582	2.330	43.32	27.89	30.01	115
0.229	0.537	2.337	40.38	29.02	30.60	120

¹T1, T2 and T3 represent the three lifetime components of PAL spectra. I1, I2 and I3 are intensity.

Unconstrained fitting results of PMMA/PEO blend
at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.280	0.570	2.124	56.73	25.58	17.69	30
0.271	0.521	2.147	50.26	31.28	18.47	40
0.276	0.553	2.341	52.85	29.20	17.95	50
0.263	0.505	2.207	47.53	33.81	18.67	55
0.285	0.597	2.422	57.42	24.95	17.63	60
0.285	0.581	2.390	57.29	24.57	18.15	65
0.284	0.575	2.42	56.11	25.22	18.3	67
0.283	0.558	2.434	55.03	26.60	18.37	70

Unconstrained fitting results of PPO homopolymer
at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.204	0.635	2.623	36.61	22.18	41.21	30
0.193	0.566	2.611	33.53	23.83	42.64	50
0.192	0.534	2.624	32.30	24.21	43.49	70
0.203	0.624	2.720	36.01	21.74	42.25	90
0.199	0.609	2.743	34.84	22.63	42.53	100
0.185	0.555	2.709	31.81	24.57	43.63	110
0.184	0.554	2.744	31.41	24.51	44.08	130
0.192	0.617	2.829	33.78	22.59	43.63	150
0.189	0.585	2.808	32.74	22.91	44.34	170
0.191	0.611	2.821	33.50	22.87	44.02	182
0.196	0.625	2.852	34.03	22.07	43.90	190
0.197	0.628	2.880	34.87	23.01	44.51	192
0.199	0.623	2.871	35.01	22.90	44.42	197

Unconstrained fitting results of PS homopolymer
at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.222	0.568	2.096	41.77	19.85	32.90	40
0.220	0.576	2.148	41.46	21.22	32.89	50
0.223	0.562	2.155	41.50	21.55	32.85	60
0.219	0.557	2.187	40.49	22.31	33.29	70
0.232	0.645	2.203	44.97	18.94	33.68	75
0.224	0.550	2.178	41.11	22.14	34.26	80
0.207	0.500	2.189	35.87	27.21	34.18	85
0.221	0.567	2.231	40.70	23.28	35.34	90
0.213	0.513	2.251	37.37	25.81	35.35	100
0.222	0.567	2.34	38.90	24.34	36.19	105

Unconstrained fitting results of PS/PPO blend
at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.255	0.490	2.092	50.01	34.66	34.36	30
0.251	0.485	2.107	50.20	34.75	34.50	40
0.261	0.503	2.119	54.60	30.21	34.57	50
0.267	0.525	2.160	57.31	27.88	34.55	60
0.258	0.484	2.230	50.71	34.19	34.73	70
0.266	0.510	2.226	55.28	29.48	35.11	80
0.255	0.491	2.240	52.11	36.21	35.21	86
0.252	0.469	2.260	47.33	37.13	35.39	90
0.251	0.482	2.341	53.34	35.56	35.41	96
0.256	0.511	2.347	51.61	33.42	35.55	100
0.234	0.467	2.358	41.59	42.14	35.79	110
0.221	0.479	2.427	50.11	32.11	35.91	116
0.234	0.520	2.421	49.99	36.22	36.05	120

Unconstrained fitting results of PS/PVME blend
at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.223	0.644	2.134	45.42	18.98	35.60	30
0.216	0.591	2.138	42.94	21.05	36.01	35
0.222	0.642	2.179	45.16	19.50	36.04	40
0.215	0.580	2.178	42.80	21.09	36.11	45
0.218	0.614	2.234	43.32	21.24	36.23	50
0.231	0.715	2.309	46.99	18.90	36.35	55
0.208	0.562	2.280	40.62	22.94	36.44	60
0.221	0.630	2.348	44.08	20.29	36.50	65
0.216	0.599	2.353	42.92	20.41	36.67	70
0.223	0.645	2.36	43.66	21.45	37.09	72

Constrained fitting ($\tau_1 = 120$ ps) results of PMMA homopolymer at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.120	0.365	1.960	13.20	56.03	30.76	30
0.120	0.368	1.981	13.66	55.39	30.96	40
0.120	0.365	2.049	13.01	55.69	31.31	50
0.120	0.376	2.109	14.15	54.54	31.30	60
0.120	0.370	2.118	13.83	54.52	31.64	70
0.120	0.371	2.181	14.41	53.83	31.75	80
0.120	0.372	2.213	14.32	53.54	32.15	90
0.120	0.384	2.240	15.43	52.55	32.02	100
0.120	0.375	2.194	14.60	52.57	32.83	110
0.120	0.381	2.245	14.86	52.37	32.78	120

Constrained fitting ($\tau_1 = 120$ ps) results of PMMA/PEO blend at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.120	0.370	1.968	10.02	69.60	20.38	30
0.120	0.373	2.025	10.08	69.41	20.51	40
0.120	0.380	2.187	10.68	69.14	20.18	50
0.120	0.374	2.091	10.58	68.91	20.51	55
0.120	0.379	2.234	10.38	69.38	20.24	60
0.120	0.375	2.228	10.04	69.50	20.46	65
0.120	0.378	2.289	10.05	69.60	20.35	70

Constrained fitting ($\tau_1 = 120$ ps) results of PPO homopolymer at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.120	0.411	2.523	19.60	36.37	44.04	30
0.120	0.406	2.541	19.31	36.10	44.59	50
0.120	0.395	2.567	18.19	36.74	45.07	70
0.120	0.409	2.626	19.34	35.89	44.78	90
0.120	0.415	2.655	19.58	35.59	44.83	100
0.120	0.417	2.647	19.92	34.81	45.27	110
0.120	0.419	2.684	19.84	34.49	45.67	130
0.120	0.429	2.744	20.55	33.62	45.83	150
0.120	0.421	2.736	20.09	33.70	46.21	170
0.120	0.422	2.70	20.11	33.65	46.11	182
0.120	0.425	2.761	19.86	33.92	46.21	190
0.120	0.423	2.73	19.99	34.01	46.70	192
0.120	0.424	2.82	20.78	33.90	46.40	197

Constrained fitting ($\tau_1 = 120$ ps) results of PS homopolymer at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.120	0.351	2.023	15.92	43.15	36.52	40
0.120	0.362	2.067	16.86	43.12	36.56	50
0.12	0.362	2.101	16.69	43.55	36.51	60
0.120	0.364	2.111	16.58	43.85	36.57	70
0.120	0.358	2.094	16.02	44.33	37.01	75
0.120	0.360	2.106	15.66	45.33	37.65	80
0.120	0.371	2.133	16.84	44.59	37.57	85
0.120	0.372	2.148	16.76	44.74	38.00	90
0.120	0.369	2.190	16.39	45.04	38.02	100
0.120	0.371	2.210	16.50	45.11	38.92	105

Constrained fitting ($\tau_1 = 120$ ps) results of PS/PPO blend at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.120	0.354	1.933	11.08	71.11	38.18	30
0.120	0.359	2.007	12.06	71.10	38.34	40
0.120	0.356	2.018	11.12	71.76	38.41	50
0.120	0.359	2.057	11.20	71.93	38.39	60
0.120	0.360	2.118	11.05	72.20	38.17	70
0.120	0.358	2.110	10.58	72.31	38.59	80
0.120	0.356	2.120	12.34	72.21	38.66	86
0.120	0.362	2.138	11.32	71.72	39.07	90
0.120	0.370	2.225	12.71	70.48	39.77	100
0.120	0.375	2.235	13.70	68.78	39.90	110
0.120	0.373	2.350	13.50	71.45	39.80	116
0.120	0.375	2.378	12.44	72.13	40.06	120

Constrained fitting ($\tau_1 = 120$ ps) results of PS/PVME blend at different temperatures.

T1	T2	T3	I1	I2	I3	Temp.
0.120	0.355	2.094	17.90	42.74	39.36	30
0.120	0.362	2.117	18.53	42.46	39.01	35
0.120	0.359	2.137	18.18	42.79	39.04	40
0.120	0.360	2.163	18.28	42.86	38.86	45
0.120	0.370	2.204	18.97	42.37	38.66	50
0.120	0.366	2.235	18.15	43.19	38.66	55
0.120	0.373	2.273	19.51	41.66	38.83	60
0.120	0.370	2.317	18.80	42.39	38.81	65
0.120	0.367	2.337	18.98	41.67	39.35	70
0.120	0.369	2.380	19.03	41.55	40.03	72

Appendix B

Unconstrained stretched exponential curves fitting results for
for the stress relaxation spectra in the PMMA/PEO(85/15) blend

Ta °C	ta min.	Eo x10 ⁸ Pa	τ sec	β	<τ> sec
Tg-7	60	6.6	105	0.35	858
	120	6.9	169	0.33	1551.7
	240	7.1	235	0.31	2448.5
	480	7.5	367	0.30	4073.7
Tg-17	60	8.7	472	0.32	4616.8
	120	9.0	724	0.31	7543.6
	240	9.3	1263	0.29	15025.3
	480	9.2	3061	0.26	45326.3
Tg-27	60	9.8	1326	0.28	16906.5
	120	10	2422	0.27	33190.3
	240	10	6146	0.23	116239.5
	480	11	8879	0.22	183633.8

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