

CHAPTER IV

DISCUSSION

4.1 Young's Modulus, E

Because of nonuniform material properties for different samples, the effect of composition on E cannot be perceived clearly. From the previous work [E.P. Cizek, 1978], it was found that the relationship between E and % PPO is non-linear. When PS is the major component, the relationship is linear; E increases linearly with % PPO, when % PS is in the range of 65-100. The critical point, which gives the highest E, is around at 65-70 % PPO.

For a particular composition, and at the highest temperature or lowest ΔT , the lowest values E was found. As mentioned in the introduction section, even below T_g molecular mobility, M, is not quite zero; where M is proportional to the inverse of the free volume which is proportional to temperature. When a certain force is applied, the sample will respond with a higher strain at the higher temperature. The higher strain results in a lower E.

4.2 Isothermal Tensile Creep

All components show similar behavior on the creep results. Creep curves are shifted along the logarithmic time scale, the more so the longer the aging time. These changes can be attributed to changes in the relaxation times which are directly related to the segmental mobility, M, which evolves during aging. So the shift is influenced by aging.

The superimposability of the creep curves proves that aging does not influence the shape of the creep curve. It follows that an increase in aging time changes all relaxation times by exactly the same factor and the changes in V_f during aging will only affect the position of the creep curve on log-time scale, and not its shape. This fact is well known for pure polymers. Our results show that it is approximately true for miscible blends of PS/PPO as well.

4.3 Retardation Time, t_0

As shown in fig.1.1b, the mobility, M , depends on the degree of packing, or in other words, on the free volume, V_f .

On the effect of compositions from these experiments, PPO has a chemical structure with a higher degree of packing than PS. With a lower free volume and a lower mobility, the materials with high % PPO will have a higher retardation time, t_0 , a characteristic time corresponding to an external mechanical force.

The stress relaxation times at $T_g - T_a = 12^\circ\text{C}$ are larger for the higher % PPO suggesting decreased mobility in PPO. This is in contrast to the recent work on stress relaxation [Geng-Wen Chang, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1993]. The difference may be because of different grades of materials which were used in the experiments. The commercial grade of PS containing additives, which was used in our experiment, could cause the worst packing of PS chains, causing a higher free volume and a higher mobility as well. Another possibility is that the creep studies were done close to T_g ($\Delta T = 12^\circ\text{C}$) than those of Chang ($\Delta T = 15^\circ\text{C}$). Further work may be necessary to clarify the nature of this discrepancy.

We calculated the mean retardation time $\langle \tau \rangle$, to minimize error on β and t_0 , using the formula [Chang, 1993]

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

where τ , or t_0 , is the retardation time. The calculated $\langle \tau \rangle$ values are shown in Table 4.1 and 4.2.

Table 4.1 The mean retardation time $\langle \tau \rangle$ of all compositions at fixed $\Delta T = 12^\circ\text{C}$.

t_a (min)	100% PS		70:30 / PS:PPO		50:50/ PS:PPO		100% PPO	
	t_0 (sec)	$\langle \tau \rangle$	t_0 (sec)	$\langle \tau \rangle$	t_0 (sec)	$\langle \tau \rangle$	t_0 (sec)	$\langle \tau \rangle$
80	1484	1933	-	-	-	-	-	-
160	2249	2503	2553	2775	-	-	8283	11319
210	-	-	-	-	8647	10662	-	-
260	2606	4438	3121	4264	10919	18109	-	-
320	-	-	4032	6501	13097	24401	20333	50335
400	3173	6588	4727	7437	-	-	26317	87464
480	-	-	-	-	13608	28260	-	-

Table 4.2 The mean retardation time $\langle\tau\rangle$ of 50:50/PS:PPO blend varied temperature, $\Delta T = 7, 12$ and 17°C .

Aging time (min)	50:50 / PS:PPO					
	$\Delta T = 7^\circ\text{C}$		$\Delta T = 12^\circ\text{C}$		$\Delta T = 17^\circ\text{C}$	
	t_0 (sec)	$\langle\tau\rangle$ sec	t_0 (sec)	$\langle\tau\rangle$ sec	t_0 (sec)	$\langle\tau\rangle$ sec
160	-	-	-	-	27575	49863
210	19330	24468	8647	10662	52514	82626
260	24692	27495	10919	18109	52998	90274
320	33609	48498	13097	24401	61247	72956
480	-	-	13608	28260	-	-

From the tables, it can be observed that the mean retardation times $\langle\tau\rangle$ shows the same trend as the stress relaxation times (t_0).

On the effect of compositions, the materials with higher %PPO have a higher $\langle\tau\rangle$, because of the higher degree of packing.

For the effect of temperature, V_f decreases with the temperature. At a lower temperature, system would take a longer time for mechanical response. So it should have the higher t_0 and $\langle\tau\rangle$. In our studies, the effect of temperature could not be seen so clear as in the normal way. The possibility is that the testing temperatures, which were chosen in our experiments, are too close together. They are not different enough to be used to investigate the effect of temperature.

Volume-relaxation undergoes a slow process which attempts to establish an equilibrium. This indicates that during aging the system tends to go to an equilibrium state. When the system is close to an equilibrium, the ability for responding to a mechanical force decreases. So t_0 increases with the aging time.

4.4 Aging Rate, μ

The aging can be characterized by the double-logarithmic shift rate μ , defined as: $\mu = -d \log a / d \log t_a$ [Struik, 1978]. $\log a$ varies linearly with $\log t_a$, as shown in figs.3.2c and 3.2f, where the slope is μ .

Because of the chemical structure, PS shows very poor crystallization tendencies. PS is more rigid than PPO which is the more flexible plastic possessing a higher free volume. But the PS used in this study is the commercial grade with additives, so it could have a higher free volume than pure PPO. The smaller μ -value for PS indicates molecular motion is less self retarding, i.e. there is a lesser degree of cooperativity. At a certain time, PPO properties can be changed faster than PS, indicating a higher aging rate. For the effect of compositions, μ increases with % PPO.

We observed creeps for the certain blend system, 50:50 / PS:PPO, where the aging temperature was varied. We found that, in the range of $\Delta T = 7-17$, μ remains at about unity. Struik [1] investigated μ as a function of temperature for various polymers. It appeared that, just below T_g , μ rapidly increases to about unity, remaining unity over a more or less wide temperature range below T_g . At low temperatures, finally, the aging begins to cease, and μ decreases.

When the equilibrium state is approached, μ will begin to decrease, and at equilibrium, aging ceases and μ is zero. Such an approach to equilibrium is possible at temperatures close to or below T_g . This explains why the shift rate, μ , decreases to zero near T_g .

Struik [1978] had explained the aging process stops at low temperature from the free-volume theory as followed :

The temperature range of aging is bounded by T_g as the upper bound and by the highest secondary transition temperature T_β as the lower bound. When a polymer is cooled through the T_β range, the polymer segments will (partially) lose their flexibility because side-group motion becomes frozen.

Below T_g , and during aging, the free volume, V_f , will diminish to a value at which segmental motion is strongly hindered, although they are still internally flexible [Struik, 1978]. Segmental motion will therefore be much more hindered at temperature below T_β . Here, segmental motion, and therefore aging also, will practically disappear.