

CHAPTER III

RESULTS AND DISCUSSION

3.1 Effect of composition on T_g

PMMA/SAN blends are the completely miscible blends, which are identified by the formation of a single T_g which is blend ratio dependent. Glass transition temperature as a function of composition for a series of PMMA/SAN blends is shown in fig. 3.1.

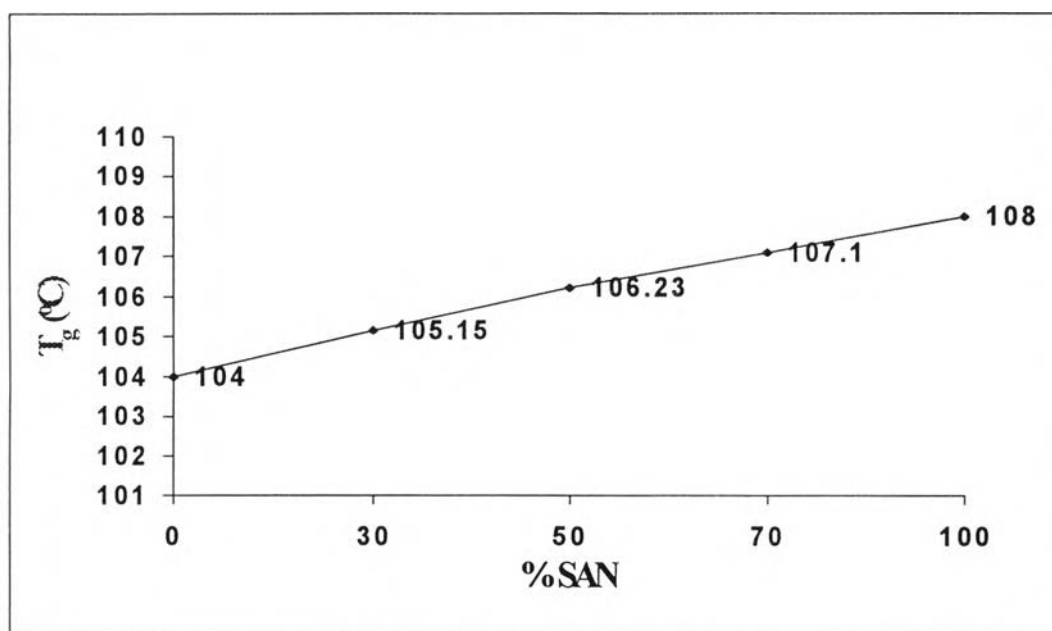


Figure 3.1 Effect of Composition on T_g

3.2 Stress scan experiment

At any given experimental time, the modulus increases with the aging time. Because during physical aging, the molecular mobility decreases, and hence, the relaxation and retardation times characteristic of the material increase. At the same time, the material typically becomes stiffer (higher modulus, lower creep compliance) and more brittle. By the comparing plots of different blend compositions, we see that the modulus of the sample generally

increases as the weight percentage of SAN increases, because the exothermic energy increases with the weight percentage of SAN. This plot is shown in fig. 3.2.

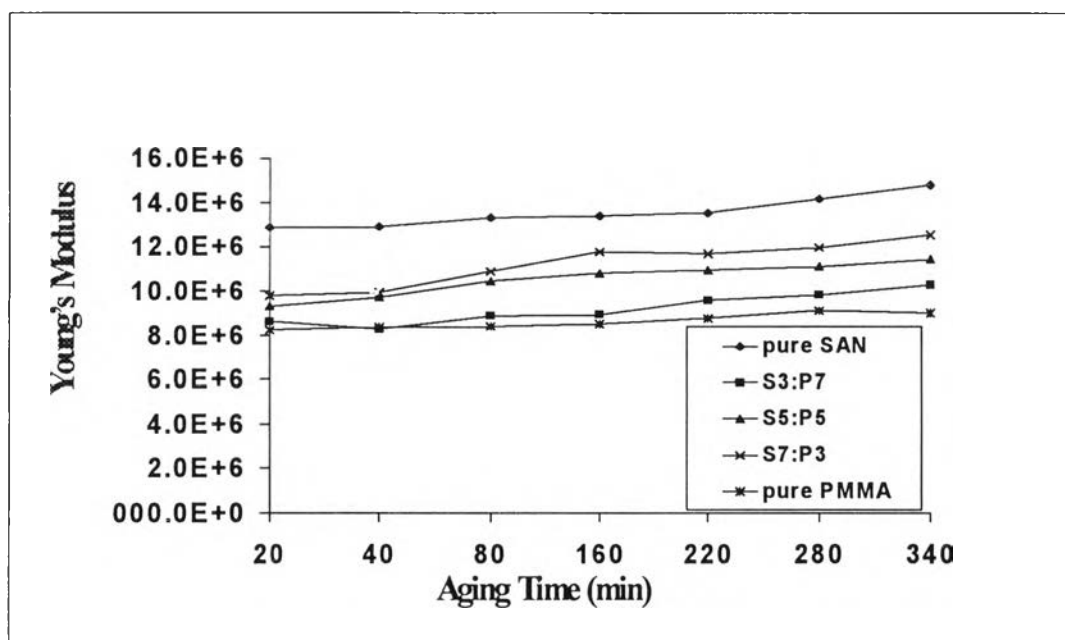


Figure 3.2 Effect of aging time on Young's Modulus at various blend compositions

3.3 Aging of components

The tensile creep response of the pure component and PMMA/SAN blends undergoing physical aging below the glass transition temperature are shown in figs. 3.3 - 3.9. The shape of the individual tensile-creep curve, expressed in term of normalized creep curve for different aging times and plotted against time on a logarithmic scale, does not change with composition, aging time or cooling rate. This resemblance in behavior is just what we would expect since above T_g , only temperature affects the time scale of creep curve because the equilibrium free volume is temperature-dependent but not time-dependent. Below T_g , the free volume becomes time-dependent, thus causing change in the creep curve with aging. Above T_g , temperature and therefore free volume has no effect on the shape of the creep curve, there should be no such effect below T_g either. We find that time-dependent change in free volume

during aging will only affect the position of the creep curve on log-time scale, and not its shape.

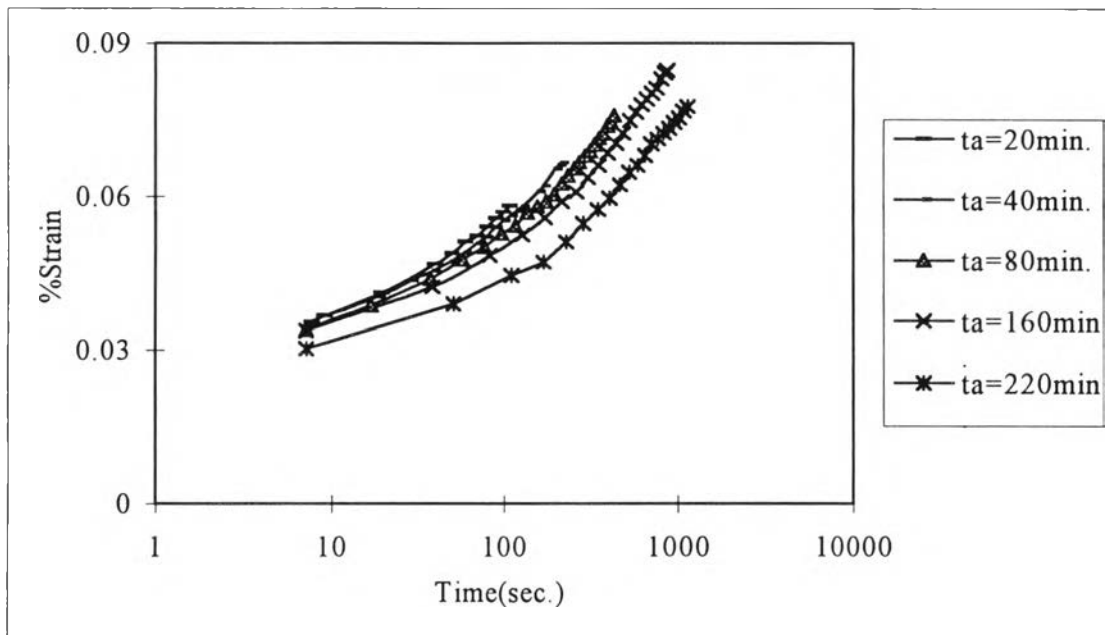


Figure 3.3 Isothermal tensile creep curves during isothermal annealing, $T_a = 59^\circ\text{C}$ of 100 % PMMA. Curves are shown for different aging times, t_a .

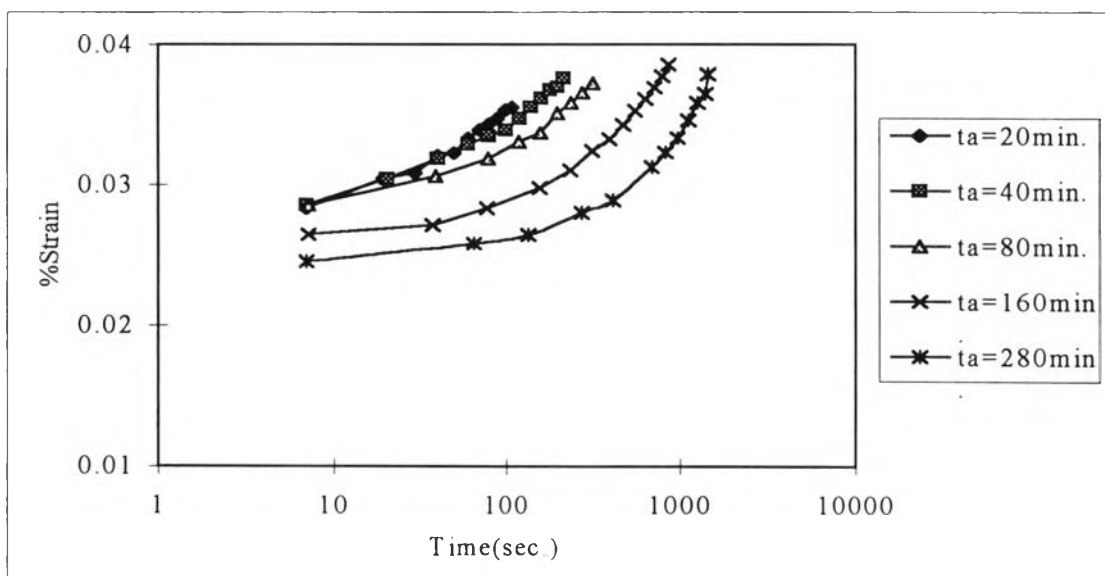


Figure 3.4 Isothermal tensile creep curves during isothermal annealing, $T_a = 63^\circ\text{C}$ of 100 % SAN. Curves are shown for different aging times, t_a .

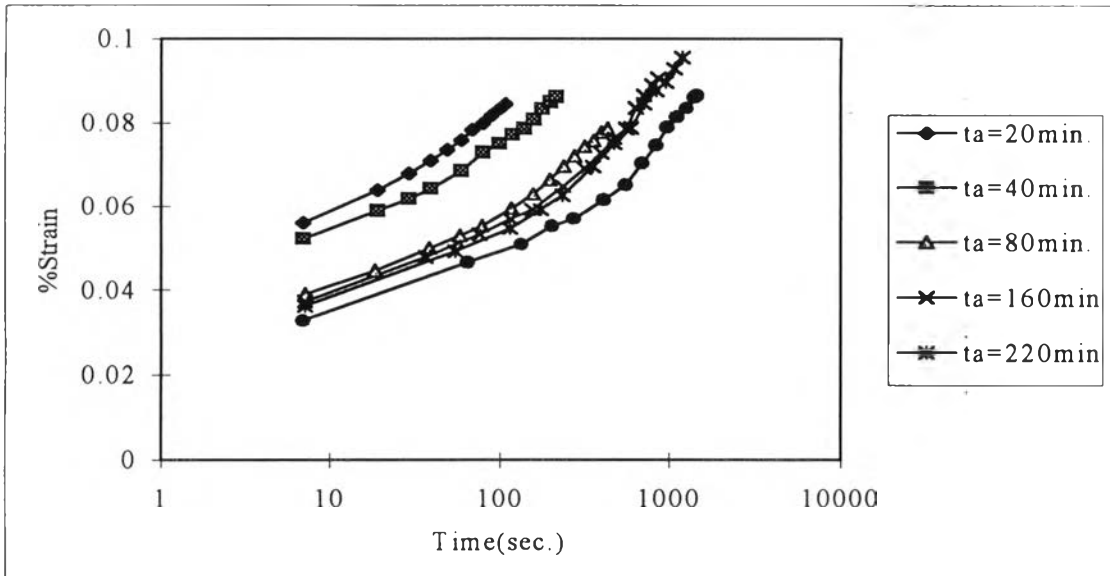


Figure 3.5 Isothermal tensile creep curves during isothermal annealing, $T_a = 60\text{ }^\circ\text{C}$ of PMMA/SAN blend (70:30). Curves are shown for different aging times, t_a .

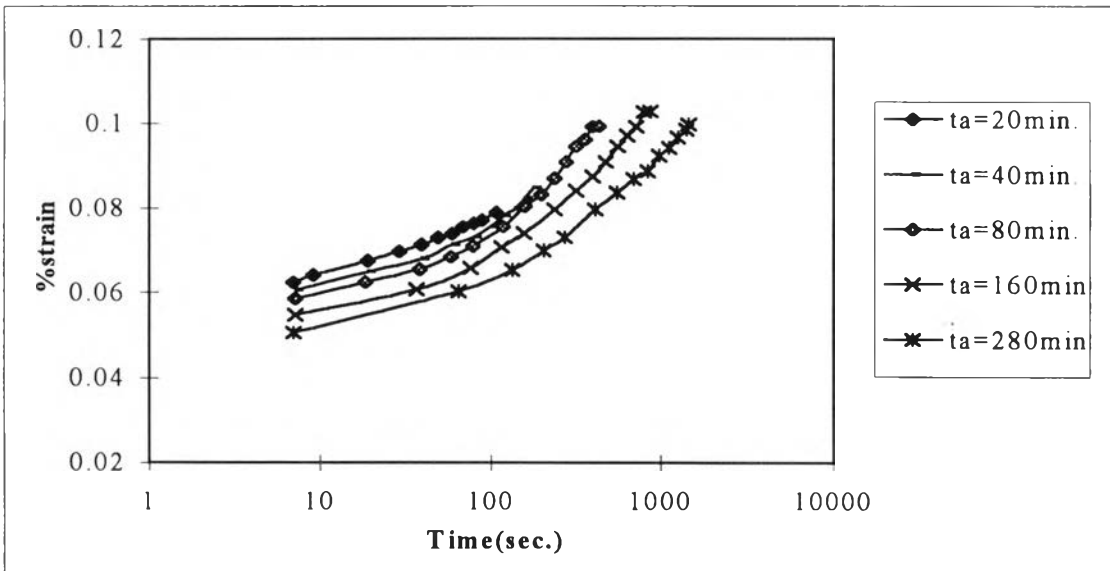


Figure 3.6 Isothermal tensile creep curves during isothermal annealing, $T_a = 61\text{ }^\circ\text{C}$ of PMMA/SAN blend (50:50). Curves are shown for different aging times, t_a .

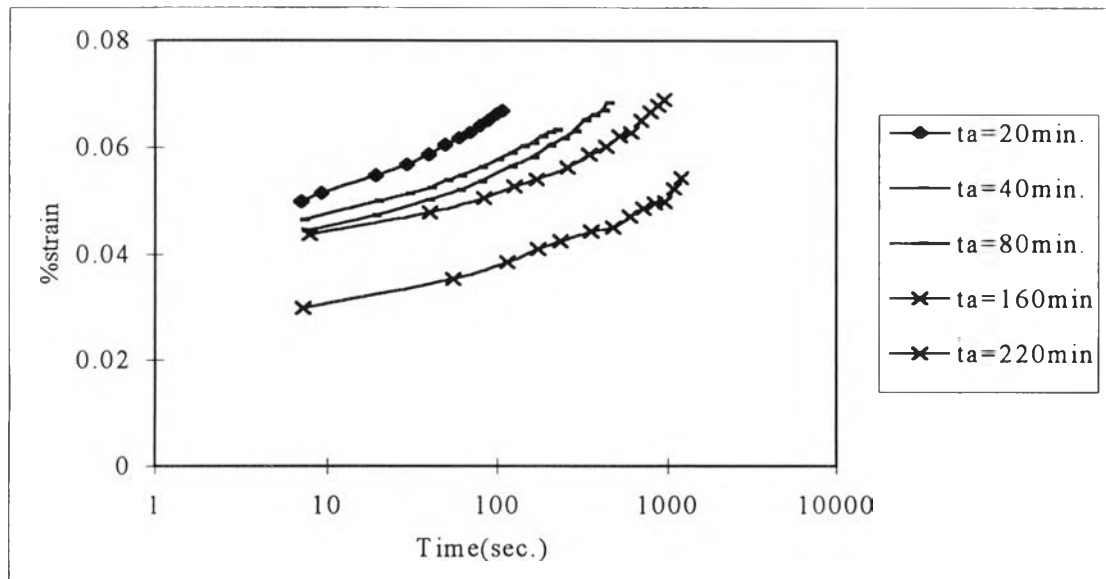


Figure 3.7 Isothermal tensile creep curves during isothermal annealing, $T_a = 62\text{ }^\circ\text{C}$ of PMMA/SAN blend (30:70). Curves are shown for different aging times, t_a .

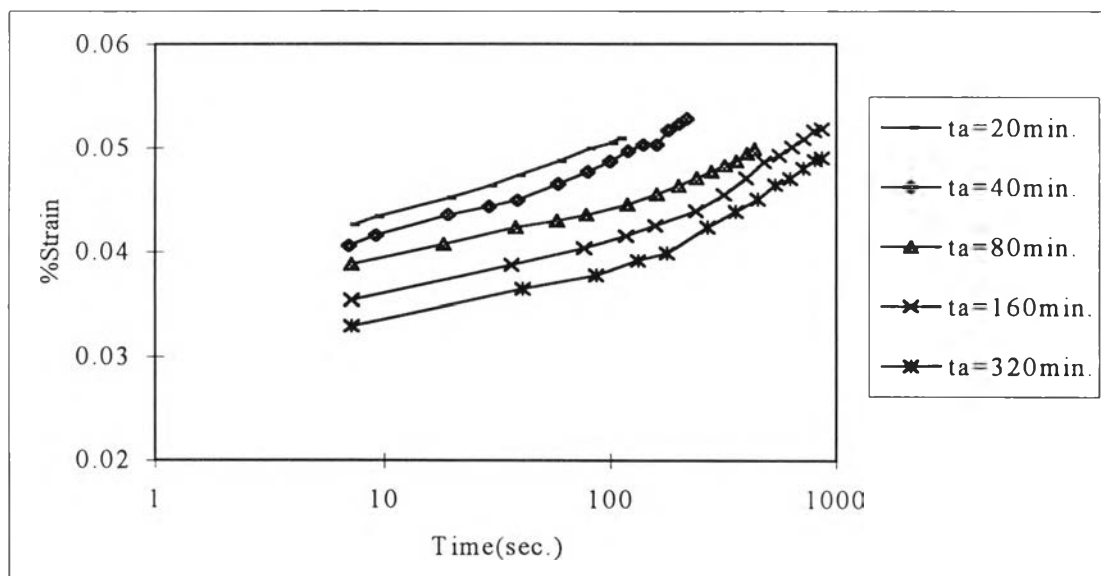


Figure 3.8 Isothermal tensile creep curves during isothermal annealing, $T_a = 61\text{ }^\circ\text{C}$ of PMMA/SAN blend (50:50). Curves are shown for different aging times, t_a , with a cooling rate equal to $5\text{ }^\circ\text{C}/\text{min}$.

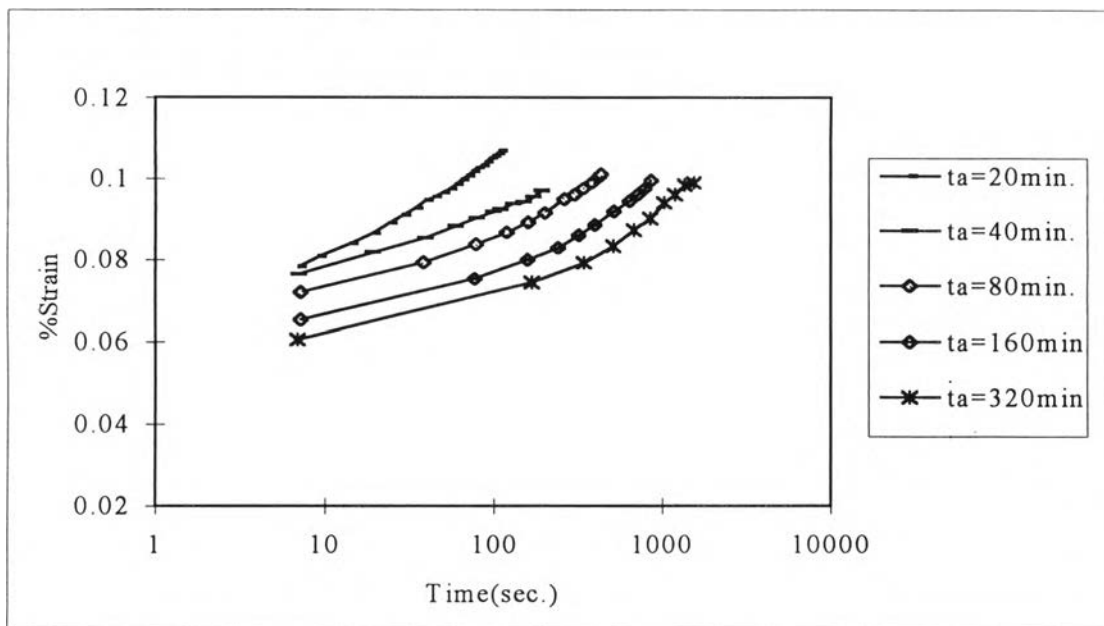


Figure 3.9 Isothermal tensile creep curves during isothermal annealing, $T_a = 61\text{ }^\circ\text{C}$ of PMMA/SAN blend (50:50). Curves are shown for different aging times, t_a , with a cooling rate equal to $20\text{ }^\circ\text{C}/\text{min}$.

All of the curves in Figs. 3.3-3.9 were separately fitted to Eq.(1.4) to find individual values of β . An average value for β was calculated for each composition. All curves of each composition were fitted to Eq.(1.4) with the average value β to obtain values for t_0 . The superposition of the curves are shown in Figs. 3.11-3.17.

For pure PMMA, pure SAN and any ratio of PMMA/SAN blends we calculated the average β and obtained values for t_0 which are tabulated in Table 1 and Table 2.

Table 2 lists the corresponding values of t_0 of the above mentioned value for β in Table 1. Using a reference aging time $t_{a,\text{ref}} = 80\text{ min.}$, shift factor, a , was calculated. The superposition of curves of any compositions of PMMA/SAN blends are shown in Figs. 3.12-3.17.

3.4 Retardation time

Table 1 Show The Individual Values of β and The Average β for any Composition of PMMA/SAN Blends

Material	Individual β of each aging time								Average β
	ta=20min	ta=40min	ta=80min	ta=160min	ta=220min	ta=280min	ta=320min	ta=340min	
1.pure PMMA	0.479	0.425	0.395	0.364	0.351	0.221	-	0.232	0.400
2.pure SAN	0.451	0.38	0.312	0.416	0.251	0.223	-	-	0.390
3.PMMA/SAN(70:30)	0.299	0.357	0.489	0.386	0.265	0.222	0.293	-	0.320
4.PMMA/SAN(50:50)	0.253	0.243	0.192	0.231	0.185	0.157	-	0.165	0.210
5.PMMA/SAN(30:70)	0.219	0.196	0.196	0.175	0.266	0.166	0.134	-	0.200
6.PMMA/SAN(50:50)	0.154	0.164	0.164	0.194	-	-	0.194	-	0.173
7.PMMA/SAN(50:50)	0.172	0.138	0.153	0.162	-	-	0.225	-	0.178

Note : Material 1-5 with a cooling rate equal 10 °C/min, material 6 and 7 with cooling rate equal 5,20 °C/min, respectively

Table 2 Values for t_0 Obtained by Computer Fitting of Tensile Creep Data

Aging time, t_a (min.)	Materials						
	PMMA	PMMA/SAN	PMMA/SAN	PMMA/SAN	PMMA/SAN	PMMA/SAN	SAN
	100%	(30:70)	(50:50)	(70:30)	(50:50)*	(50:50)**	100%
20	369.68	299.24	514.00	862.20	673.67	335.91	1274.80
40	462.46	706.93	1614.08	1426.90	826.90	1036.72	2060.26
80	555.46	1593.31	2593.75	1021.93	1892.22	1197.75	4287.10
160	714.76	1773.35	3025.07	1586.30	980.22	1797.91	6339.60
220	598.94	-	3740.39	9792.37	-	-	21591.41
280	-	2292.73	-	-	-	-	22427.42
320	-	-	6870.18	-	3985.73	5106.16	-

Note : * The cooling rate was 5°C/min

** The cooling rate was 20 °C/min.

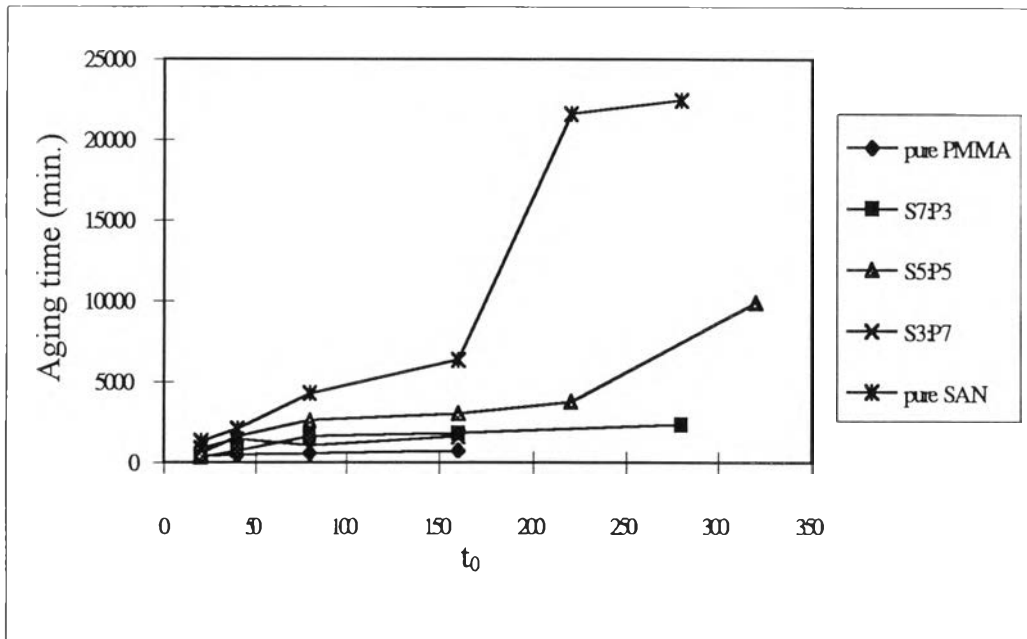


Figure 3.10 Effect of Composition on T_0

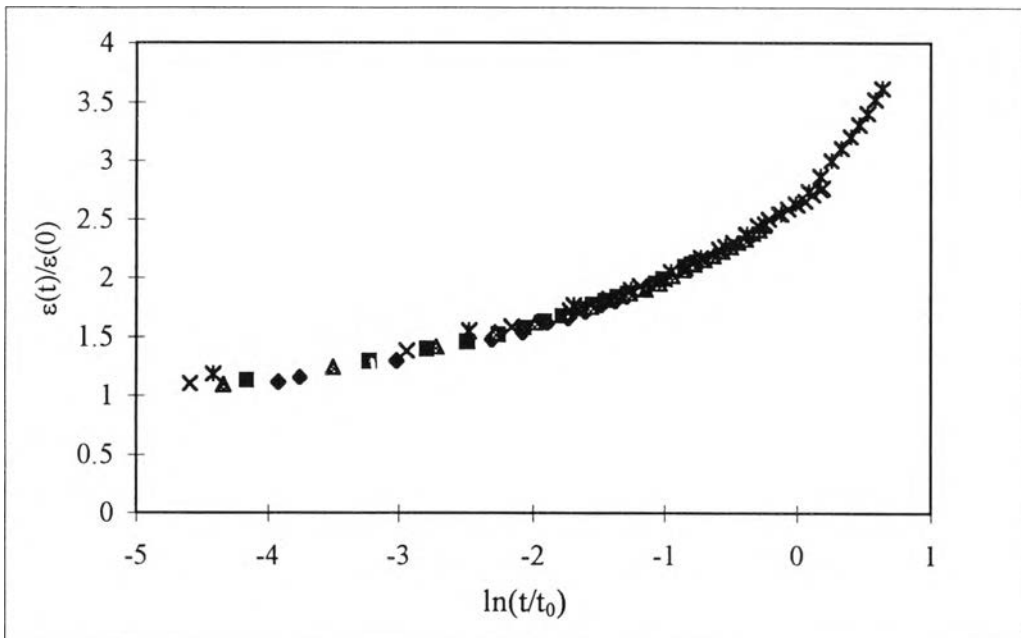


Figure 3.11 Superposition of creep curves for 100%PMMA .

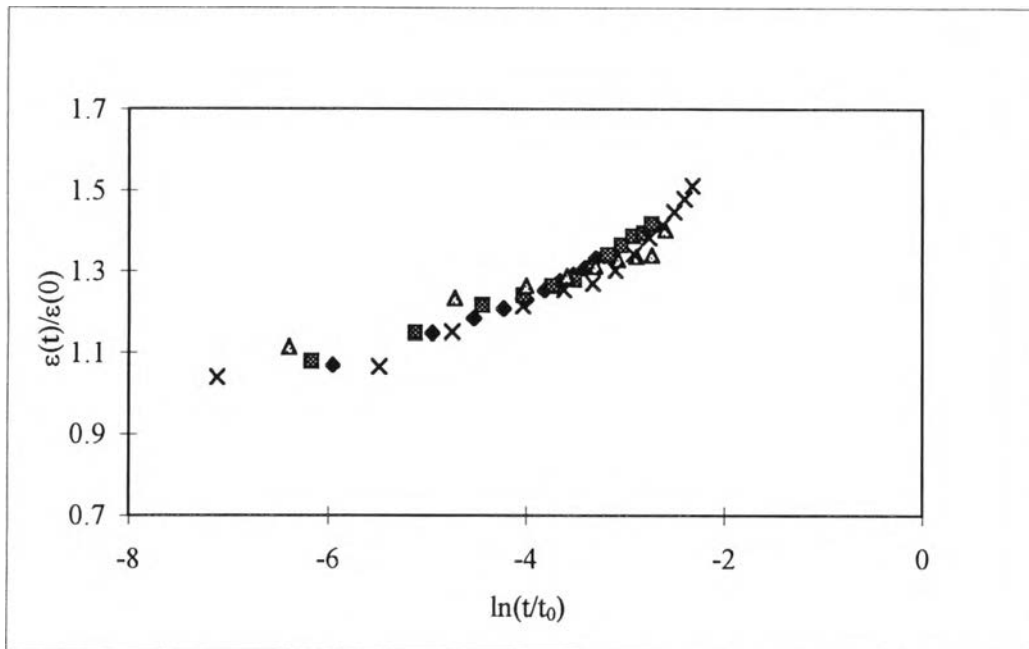


Figure 3.12 Superposition of creep curves for 100%SAN.

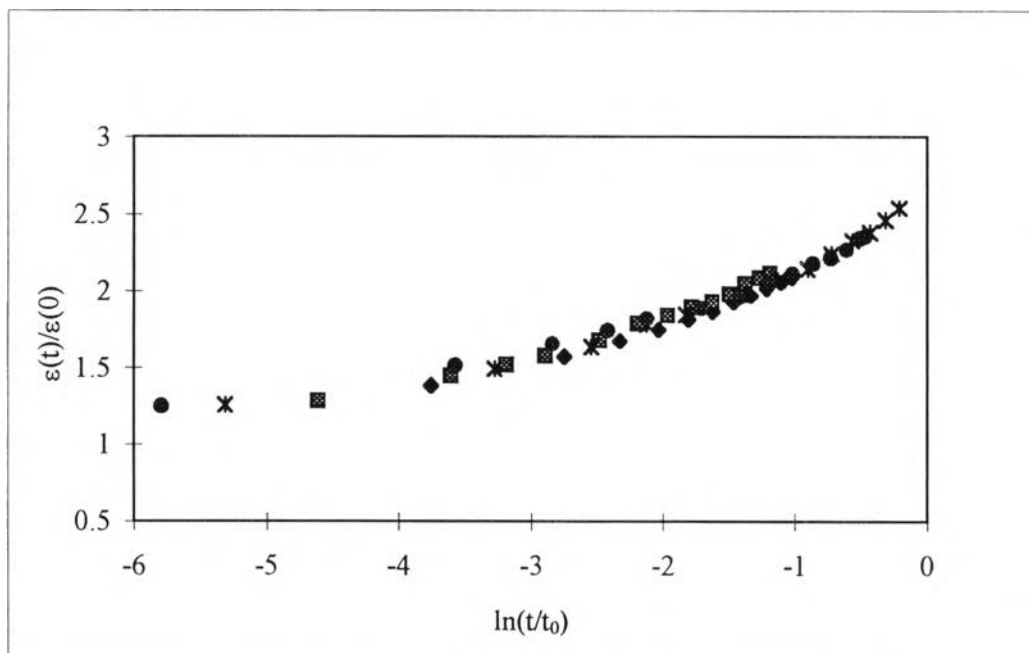


Figure 3.13 Superposition of creep curves for PMMA/SAN (70:30) Blend.

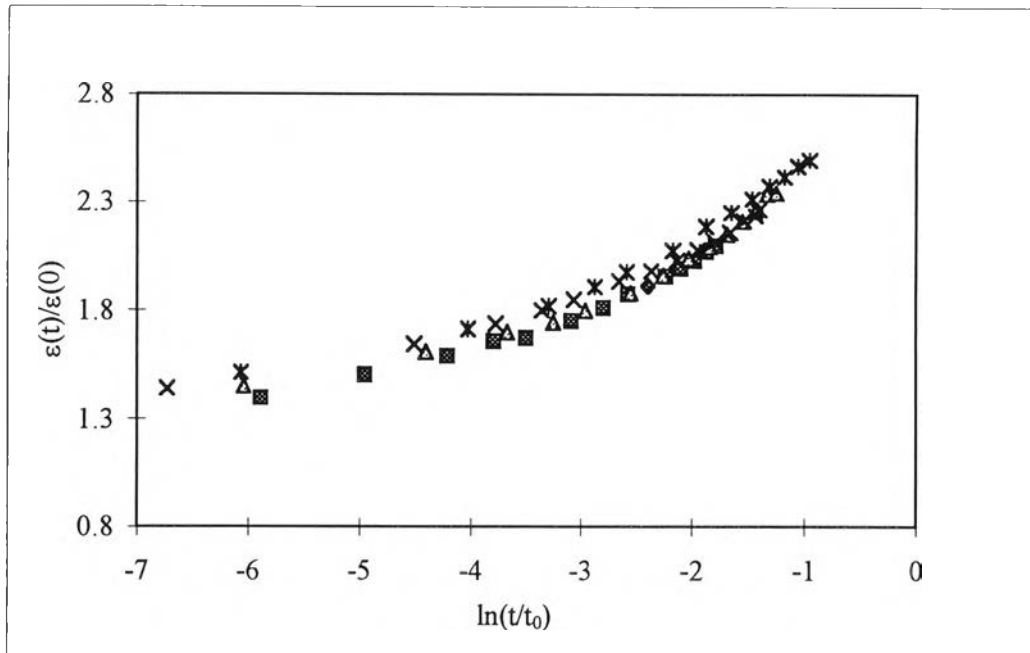


Figure 3.14 Superposition of creep curves for PMMA/SAN (50:50) Blend.

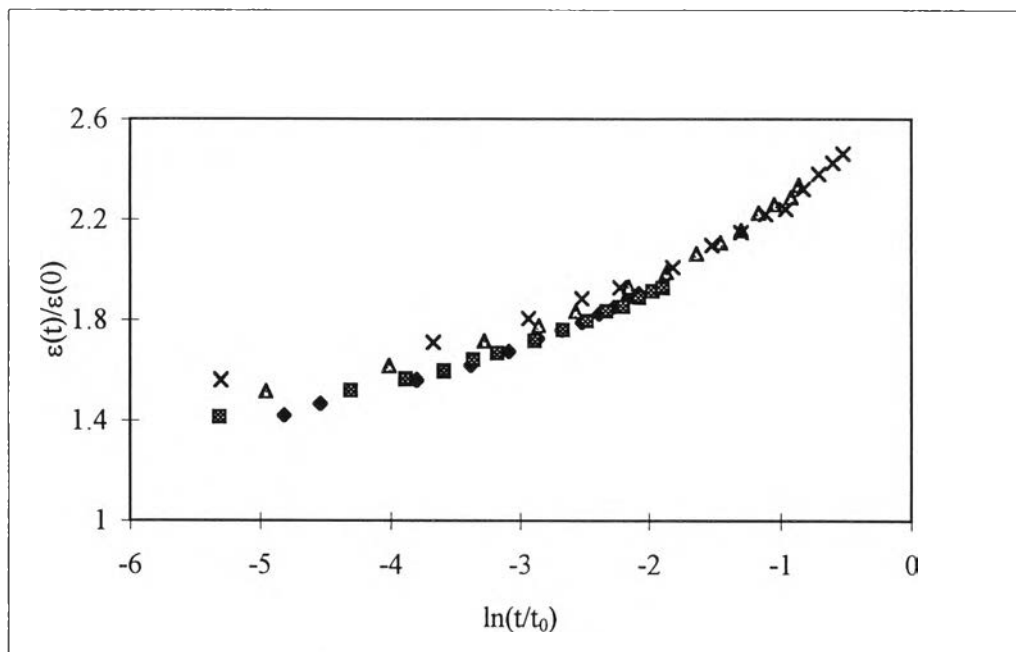


Figure 3.15 Superposition of creep curves for PMMA/SAN (30:70) Blend.

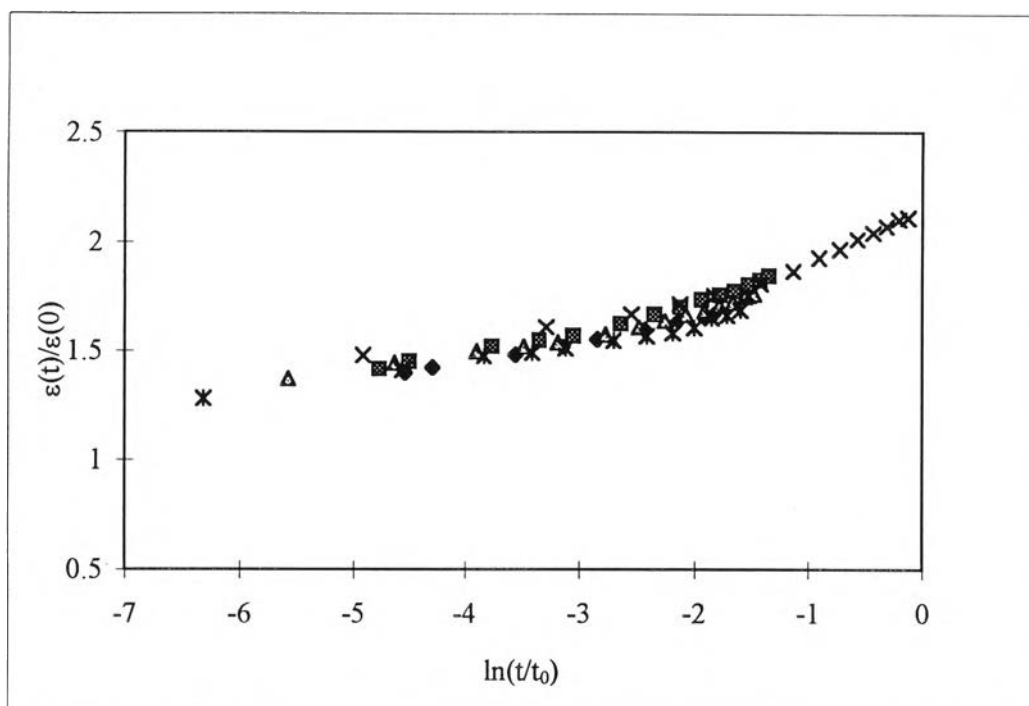


Figure 3.16 Superposition of creep curves for PMMA/SAN (50:50) Blend, with a cooling rate = 5°C/min.

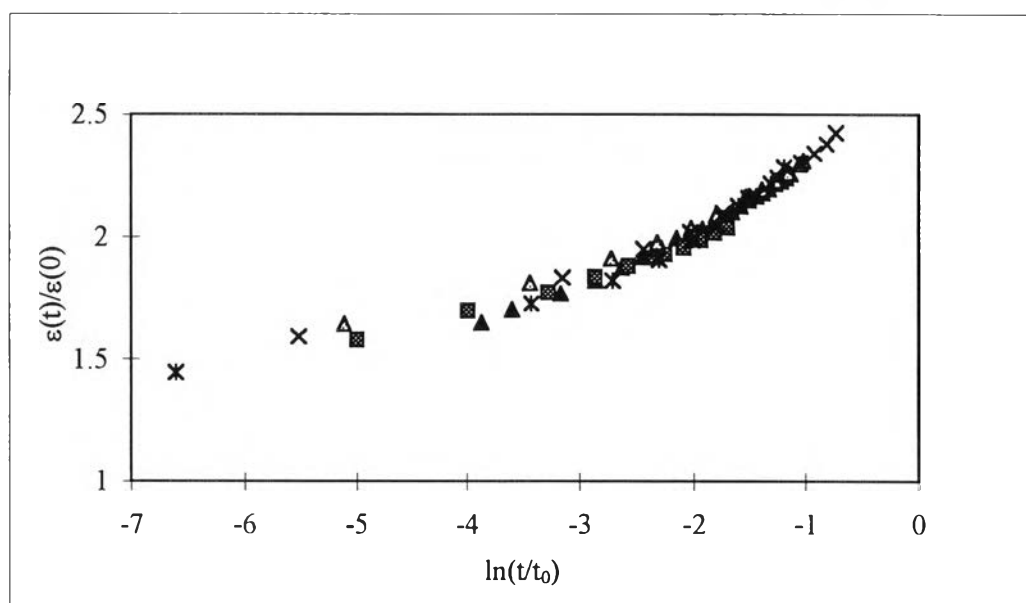


Figure 3.17 Superposition of creep curves for PMMA/SAN (50:50) Blend, with a cooling rate = 20°C/min.

Table 2 shows the values for t_0 which were obtained by computer fitting of tensile creep data. From this table, we can see that for various compositions, t_0 increases as the aging time, t_a increases. Because in this state below T_g , the configurational adjustments occur that result in a slow change toward equilibrium, the molecular mobility decreases, and hence, the retardation time increases. So, we can conclude that the retardation time is a measurement of the material's internal time scale to creep deformation which is proportional to the aging time. The aging process is of a self-delaying nature. The more free volume, v_f , decreases, the higher t_0 will be, and the process is slowed down. For such self-delaying processes a general law could be derived, stating that t_0 will increase proportionally with t_a . Thus, each tenfold increase in t_a will induce a tenfold increase in t_0 .

In Fig. 3.18 logarithm of the shift factor $a = t_{0(t_a)}/t_{0(t_a,ref)}$ for creep experiments are plotted against the logarithm of the aging time for pure PMMA.

All points lie approximately on a straight line with a slope μ which is the double-logarithmic shift rate which determines how fast the material approaches the equilibrium state. Figs. 3.19-3.22 show the plots of $\log a$ vs $\log(t_a)$ for pure SAN, for various compositions of the PMMA/SAN blends. The plots of $\log a$ vs $\log(t_a)$ for PMMA/SAN = 50:50 at various cooling rates are shown in Figs. 3.23-3.24.

Now, we can study the effect of composition on the aging rate from the plot of shift rate, μ vs the composition which is shown in Fig. 3.25. We can study the effect of the cooling rate on the aging rate from the plot of shift rate vs the cooling rate as shown in Fig. 3.26. We can see that from Fig. 3.25 that the shift rate increases almost linearly with the weight percentage of SAN. Fig. 3.26, the shift rate increases nonlinearly with the cooling rate.

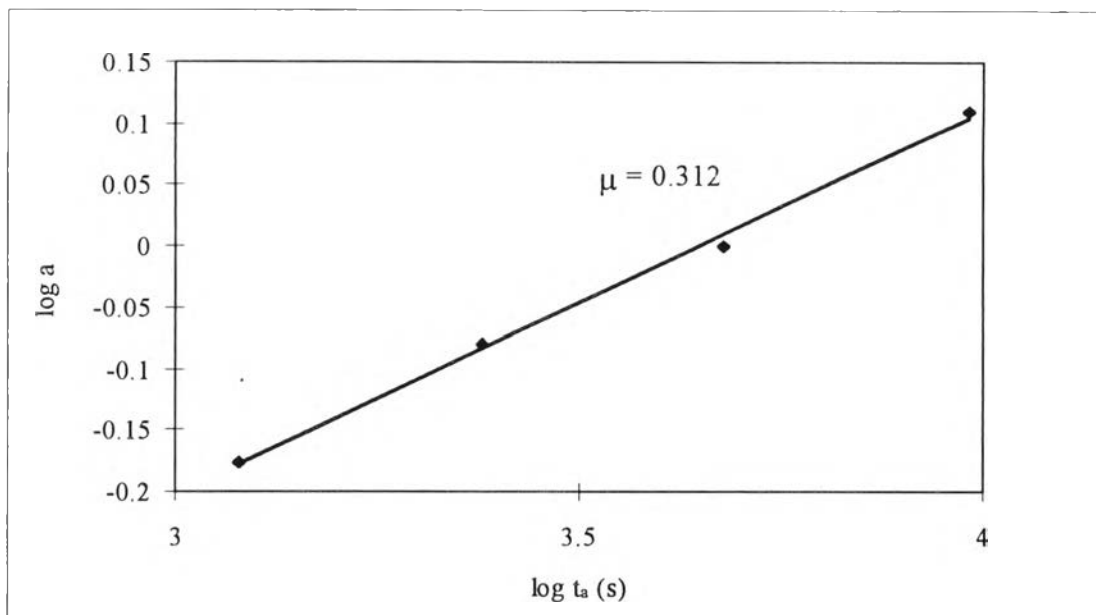


Figure 3.18 $\log a$ vs $\log(t_a)$ for 100 % PMMA , with a cooling rate equal to 10 °C/min.

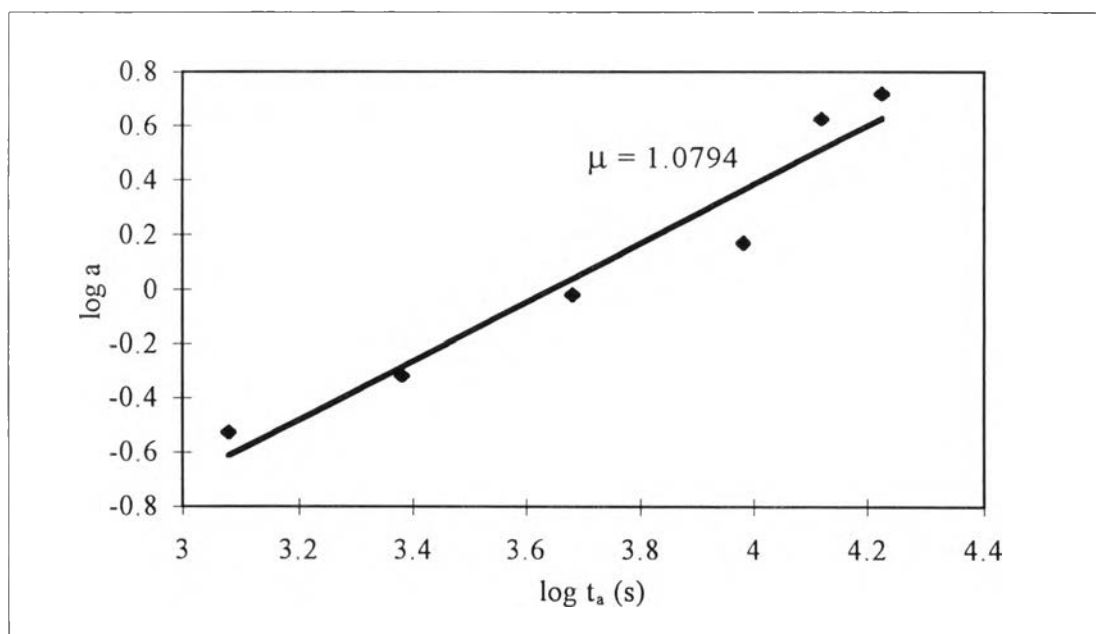


Figure 3.19 $\log a$ vs $\log(t_a)$ for 100 % SAN , with a cooling rate equal to 10 °C/min.

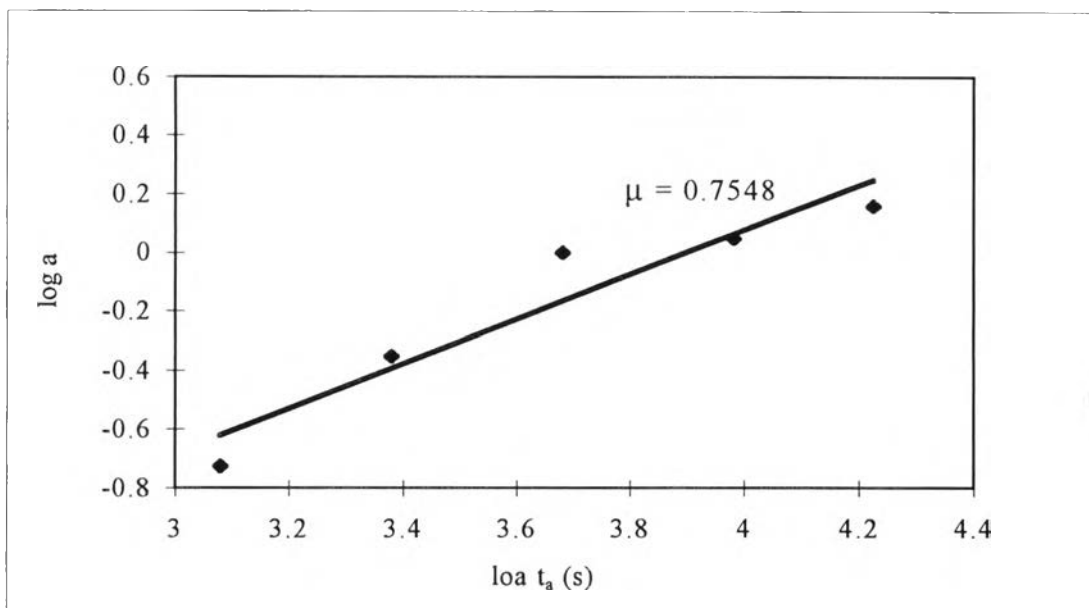


Figure 3.20 $\log a$ vs $\log(t_a)$ for PMMA/SAN (70:30), with a cooling rate equal to $10^\circ\text{C}/\text{min}$.

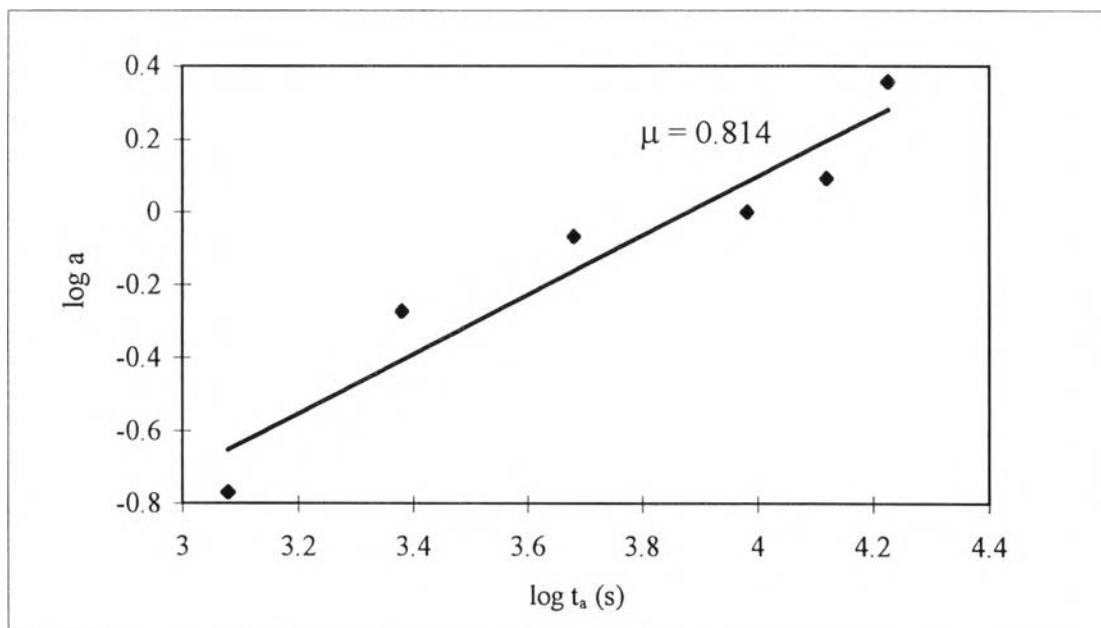


Figure 3.21 $\log a$ vs $\log(t_a)$ for PMMA/SAN (50:50), with a cooling rate equal to $10^\circ\text{C}/\text{min}$.

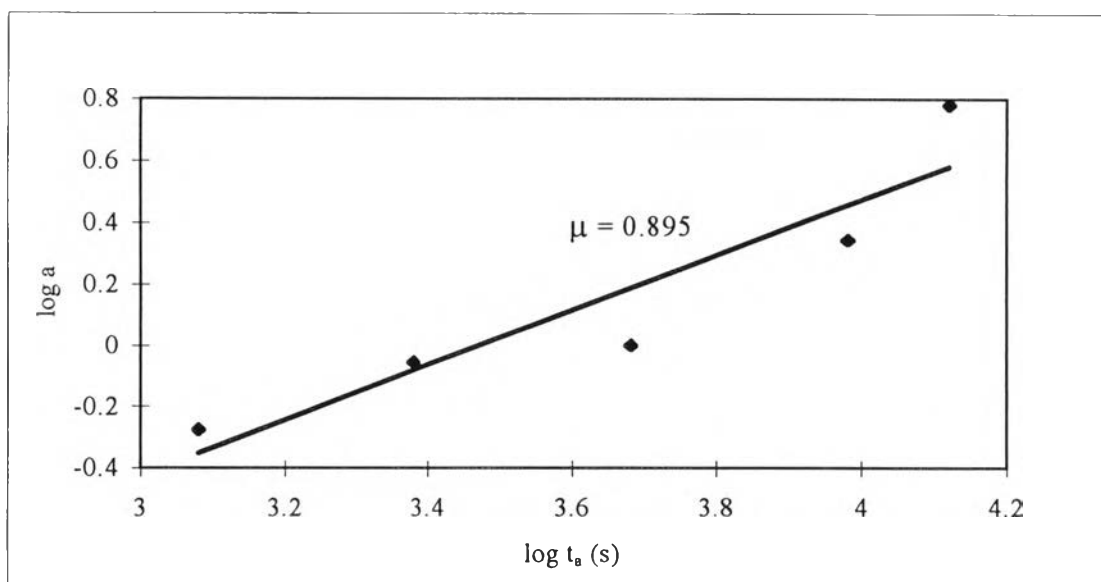


Figure 3.22 $\log a$ vs $\log(t_a)$ for PMMA/SAN (30:70), with a cooling rate equal to 10 °C/min.

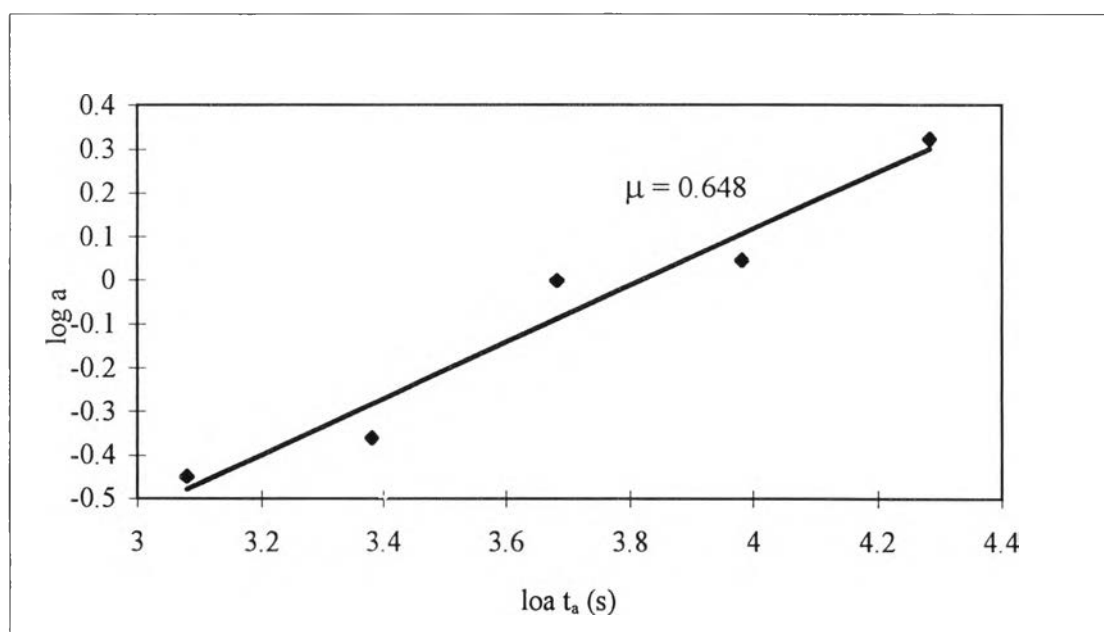


Figure 3.23 $\log a$ vs $\log(t_a)$ for PMMA/SAN (50:50), with a cooling rate equal to 5 °C/min.

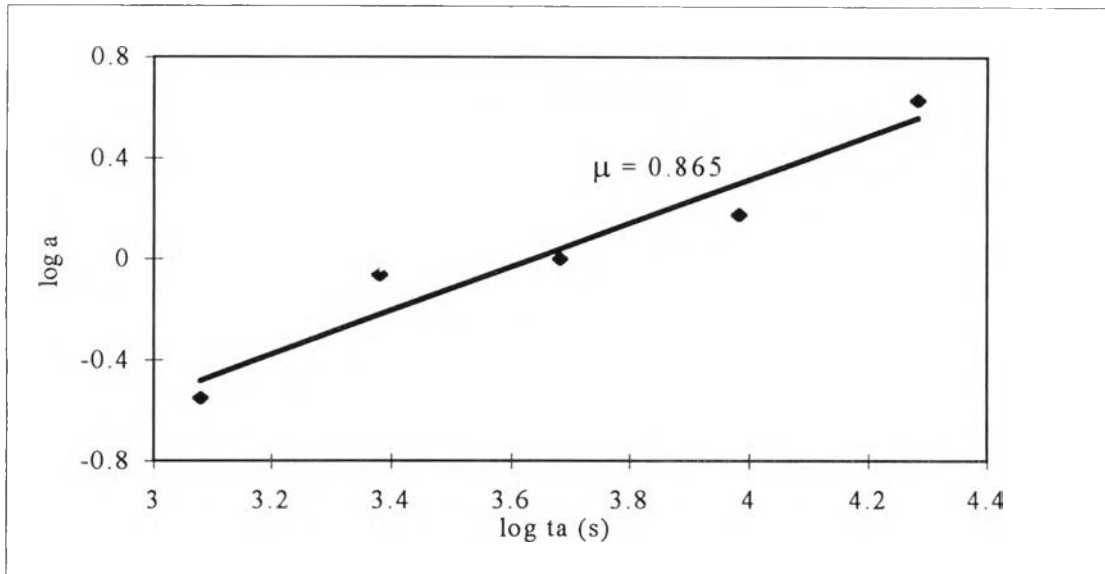


Figure 3.24 $\log a$ vs $\log(t_a)$ for PMMA/SAN (50:50), with a cooling rate equal to 20 °C/min.

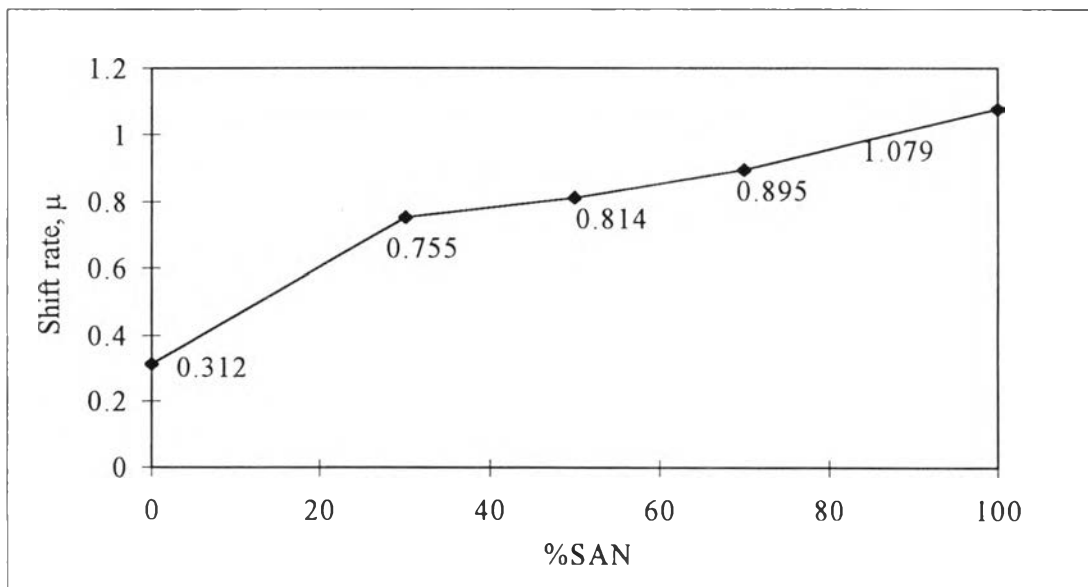


Figure 3.25 Effect of Composition on Aging Rate.

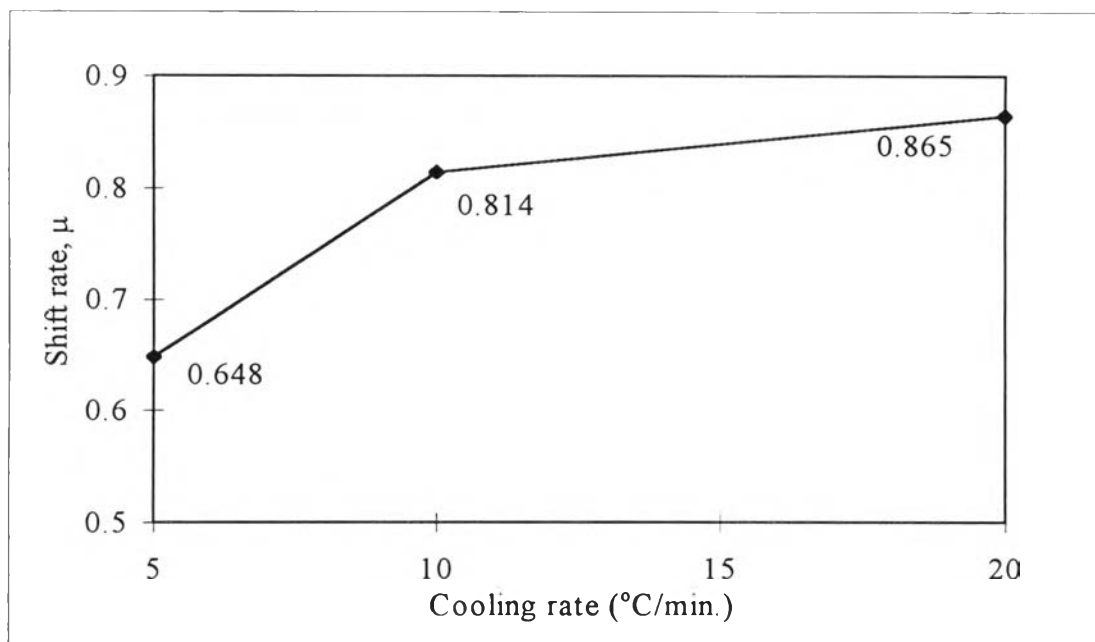


Figure 3.26 Effect of Cooling Rate on Aging Rate.

It is very interesting in Table 1 that the values of the β parameter describing the shape of the creep curve are smaller for the blend than for pure PMMA and SAN25. This means, according to the thesis of Ngai, that the motion of the relaxing elements is more strongly coupled to the matrix in the blend. Such an effect is consistent with the idea that specific interactions between the blend components lead to a strong cooperativity in molecular motion.

The aging rates of blend are intermediate between those of pure PMMA and SAN25 (Fig.3.25). However the value $\mu = 0.312$ for PMMA seems too small. Since $T_g - T = 45$ °C implies a large distance from T_g , the decrease of μ below unity in the blend may indicate a slowing down of aging because of the strong coupling between the blend components, the increase in μ in the 50/50 blend with quench rate (Fig.3.26) is consistent with the expectation that the blend which one is farther from equilibrium is the more rapidly quenched blend.