CHAPTER V

RESULTS AND DISCUSSION

In this research, the properties of the blends of syndiotactic polystyrene (sPS) with several types of amorphous polymers, such as poly (α-methyl styrene), poly (ethyl methacrylate), poly(n-butyl methacrylate), poly(cyclohexyl methacrylate), poly(cis-isoprene) and poly(alpha-methyl styrene) were explored. This chapter also provides information about how to select polymer to dynamic mechanical properties tests and how to create master curve to find WLF constants.

5.1 Selecting Polymer to Blending

5.1.1 From Differential Scanning Calorimetry (DSC)

There are selected five systems of blends between syndiotactic polystyrene (SPS) and several polymers:

System 1: sPS and poly (cis-isoprene), (PIP)

System 2: sPS and poly (ethyl methacrylate), (PEMA)

System 3: sPS and poly (n-butyl methacrylate), (PBMA)

System 4: sPS and poly (cyclohexyl methacrylate), (PHMA)

System 5: sPS and poly (alpha-methyl styrene), (PaMS)

The miscibilities of binary blends are frequently ascertained by measurements of their T_g. In this work, the result from Differential Scanning Calorimetry (DSC) was found to conform with the previous work of P.Pahupongsub[25]. The glass transition temperatures (T_g), crystallization temperatures (T_c) and melting temperatures (T_m) of polymers were shown in Table 5.1.1 and 5.1.2.

Table 5.1.1 Glass transition temperatures (T_g), melting temperatures (T_m) and crystallization temperatures (T_c) of sPS1 blend system

System[a]	Heat up 1		Cool down	Heat up 2	
	$T_g(°C)$	$T_m(°C)$	$T_c(°C)$	$T_g(°C)$	$T_m(°C)$
sPS1	100.42	267.00	213.34	100.36	268.15
sPS1/PIP	88.58	268.74	220.26	74.88	268.75
sPS1/PBMA	85.85	268.81	220.59	88.03	265.59
sPS1/PEMA	75.13	268.33	214.88	83.50	263.52
sPS1/PHMA	70.75	265.45	222.06	75.54	263.26
sPS1/PaMS	88.74	266.84	221.12	93.33	265.37

[a]Conditions: Temperature 300 °C, MW of sPS 31.7×10^4 and composition sPS : another polymer
=80/20 (wt/wt) by melt mixing method

Table 5.1.2 Glass transition temperatures (T_g), melting temperatures (T_m) and crystallization temperatures (T_c) of sPS2 blend system

System[a]	Heat up 1		Cool down	Heat up 2	
	$T_g(°C)$	$T_m(°C)$	$T_c(°C)$	$T_g(°C)$	$T_m(°C)$
sPS2	97.47	267.52	234.70	100.25	265.73
sPS2/PIP	56.85	263.02	215.15	70.71	263.50
sPS2/PBMA	64.39	260.18	213.86	84.22	260.54
sPS2/PEMA	92.86	260.02	217.34	81.95	261.63
sPS2/PHMA	98.70	260.77	212.08	79.22	257.71
sPS2/PaMS	86.96	263.71	219.03	90.24	265.47

[a]Conditions: Temperature 300 °C, MW of sPS 13.0×10^4 and composition sPS : another polymer
=80/20 (wt/wt) by melt mixing method

In previous work, P.Pahupongsub [25] investigated miscibility of polymer blend of Syndiotactic Polystyrene (sPS) with those polymers.

The results of glass transition temperatures (T_g) of polymer blend are compared and given in Table 5.1.

Table 5.1.3 Glass transition temperature (T_g) of sPS polymer blend

Blending system[a]	T_g of Previous work(°C)		T_g of This work(°C)	
	Heat 1	Heat 2	Heat 1	Heat 2
sPS2/PIP	86.61	64.12	56.85	70.71
sPS2/PBMA	94.81	79.21	64.39	84.22
sPS2/PEMA	95.43	75.63	92.86	81.95
sPS2/PHMA	99.45	99.61	98.70	79.22
sPS2/PaMS	94.03	96.54	86.96	90.24

[a]Conditions: Temperature 300 °C, MW of sPS 13.0×10^4 for this work, MW of sPS 1.9×10^6 for previous work and composition sPS : another polymer =80/20 (wt/wt) by melt mixing method

From Table 5.1.2, Glass transition temperature (T_g) of sPS polymer blends have the same trend in both previous and this works. The T_g were lower than pure sPS ($T_g \sim 100$ °C) in all blending systems. The experiments were successful and useful to decrease the glass transition temperature from the pure components. Furthermore, they also showed the single T_g which were resulted from the partial miscibility of the two components in the blends, which can be miscible at some conditions, under the DSC condition. With DMA limitation, then miscibility was confirmed by DSC. Because of different source of sPS, T_g values of previous work were slightly different from this work.

From above, there are many results from DSC to support that four systems are suitable to study in this work.

5.1.2 From Thermal Gravity Analyzer (TGA)

Degradation of polymer blends was evaluated by Thermal Gravity Analyzer (TGA) between 50 °C to 400 °C at ramping rate of 20 °C/min and under 100 ml/min of nitrogen atmosphere. It was considered as rate of loss weight versus sample temperature. Table 5.1.3 shows the sample temperature at 5 % and 10 % weight loss in blend systems.

Table 5.1.3 Sample temperature at 5 % and 10 % weight loss[a]

Blending system	Temperature at 5% weight loss (°C)	Temperature at 10% weight loss (°C)
sPS2	345.94	377.48
sPS2/PIP	347.26	377.67
sPS2/PBMA	335.13	359.81
sPS2/PEMA	316.38	348.50
sPS2/PHMA	311.72	333.18
sPS2/PaMS	353.19	366.99

[a]Obtained from TGA
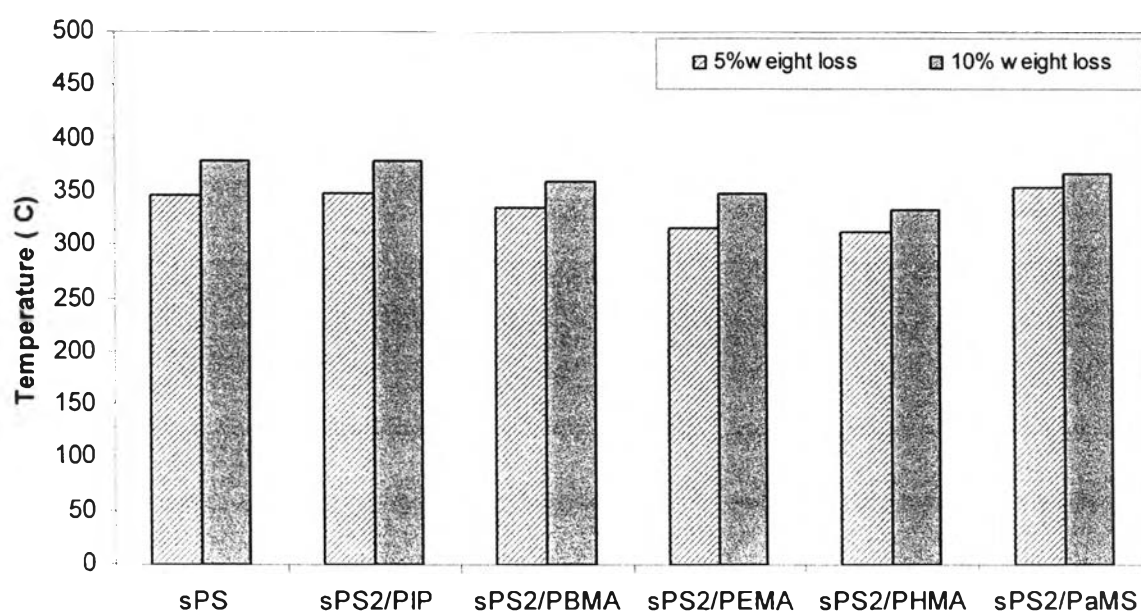
Figure 5.1.1 Temperature at 5% and 10% weight loss for blending system

As shown in Figure 5.1.1, sPS2/PaMS and sPS2/PIP blend systems were slow weight loss than pure sPS2 for 5 % weight loss because the sample temperatures of the 5% weight loss were higher than the temperatures of pure sPS2. The data were shown that their blend systems can develop thermal degradation property at 5 % weight loss. At 10 % weight loss, sPS2/PIP blend system has the highest resisted to thermal degradation. Sample temperature of sPS2/PHMA blend system was the lowest both in 5% and 10% weight loss. It can be explained that degradation of

sPS2/PHMA blending system was very fast when compared with other blending systems.

5.2 Mechanical Properties

5.2.1 Effect of time and temperature

For isothermal DMA data, E' curves were created with varying time at different temperatures. Figure 5.2.1-5.2.12 shown E' as the function of time at different temperatures for pure sPS and all the blend systems. It is observed that pure sPS and all the blends with different polymers exhibit the decreasing of E' with increasing time. The E' defined as storage modulus, which was the energy recovered per unit volume, decreased when polymer chains were more freely and separately moving by applying force at long time. At low temperatures, below glass transition temperature (T_g), storage modulus (E') slowly decreased because polymer chains were difficult to move. In the T_g temperature ranges, storage modulus (E') rapidly decreased with time because polymer chains were freely more separated at that temperature. At high temperature, the polymer chains required small energy or force to move the molecules from each other, then storage modulus (E') slowly decreased again. Furthermore, storage modulus was decrease with increasing temperature at the same time ranges. Because intermolecular forces of polymer chains decreased with increasing temperature, required energy to stretch was low.
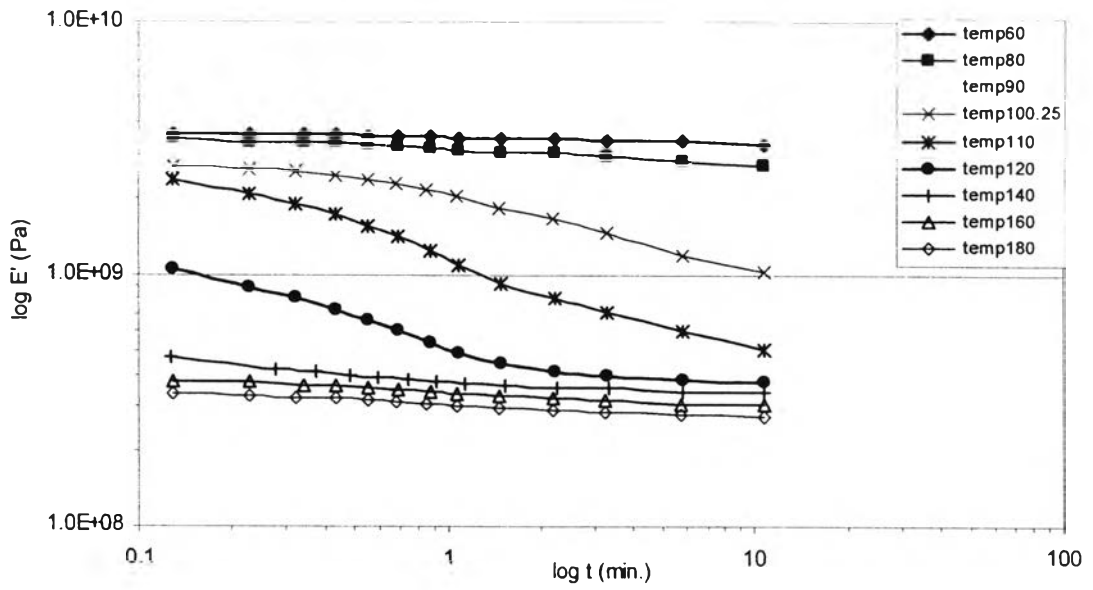
Figure 5.2.1 E' curve as time function for sPS1
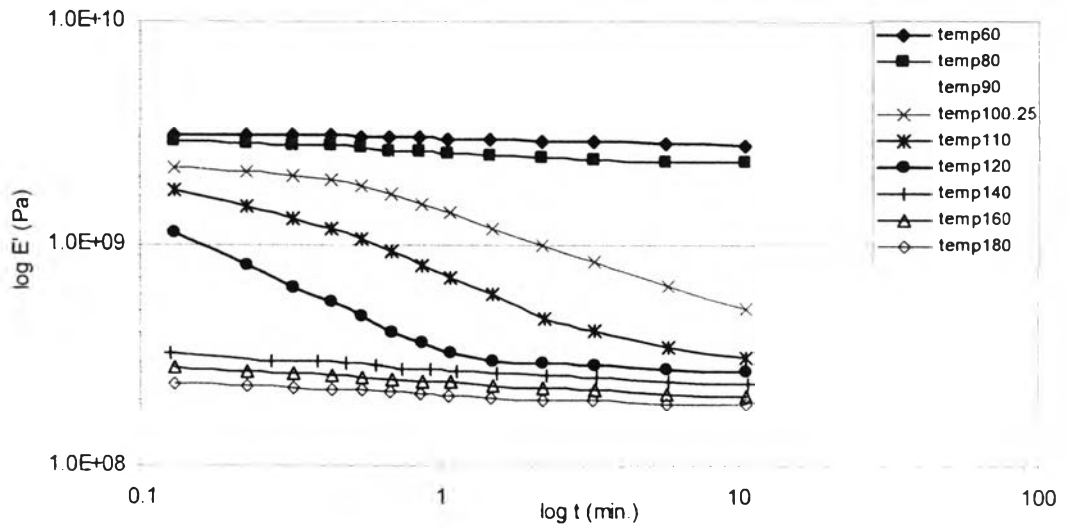
Figure 5.2.2 E' curve as time function for sPS2
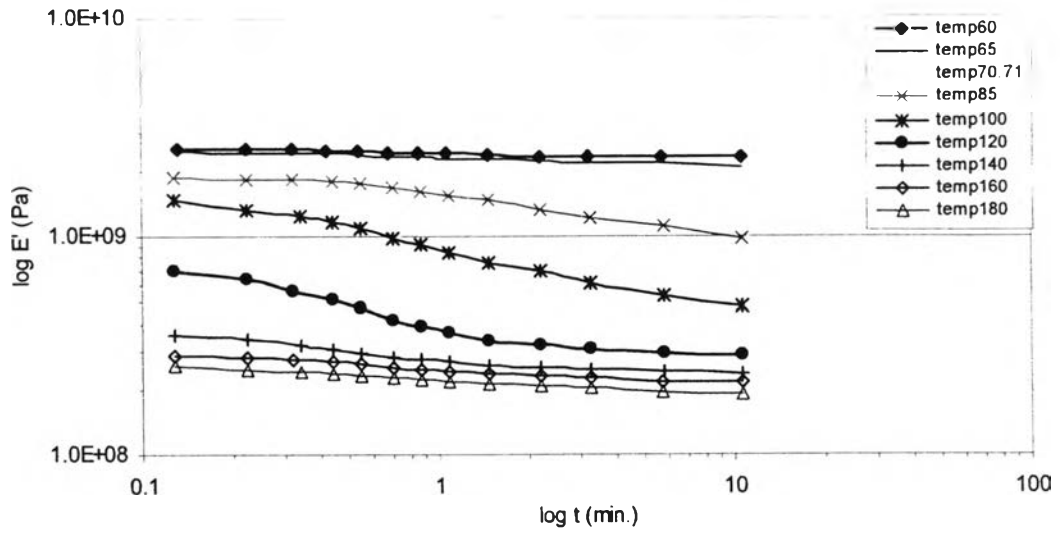
Figure 5.2.3 E' curve as time function for sPS1/PIP blend
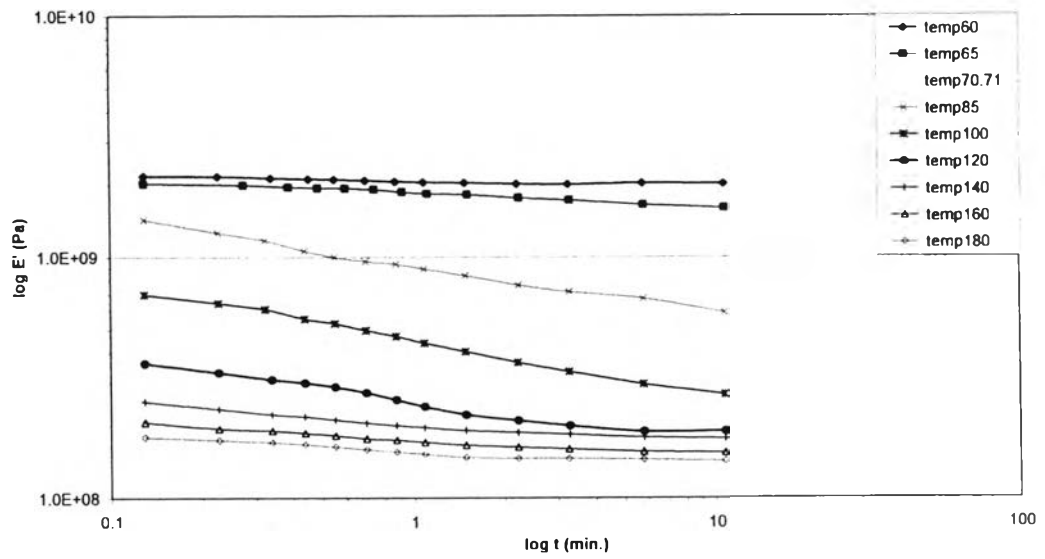
Figure 5.2.4 E' curve as time function for sPS2/PIP blend
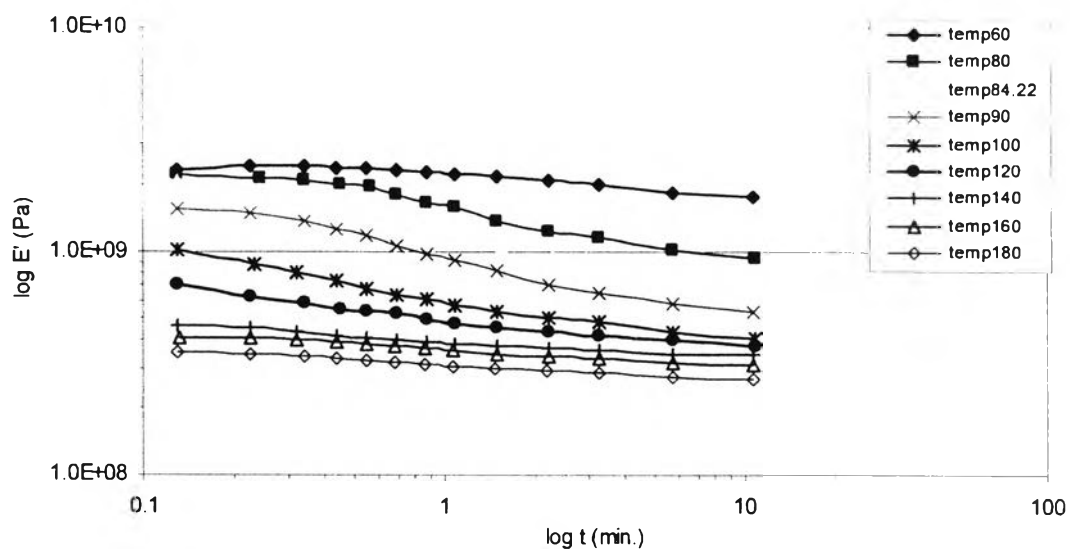
Figure 5.2.5 E' curve as time function for sPS1/PBMA blend
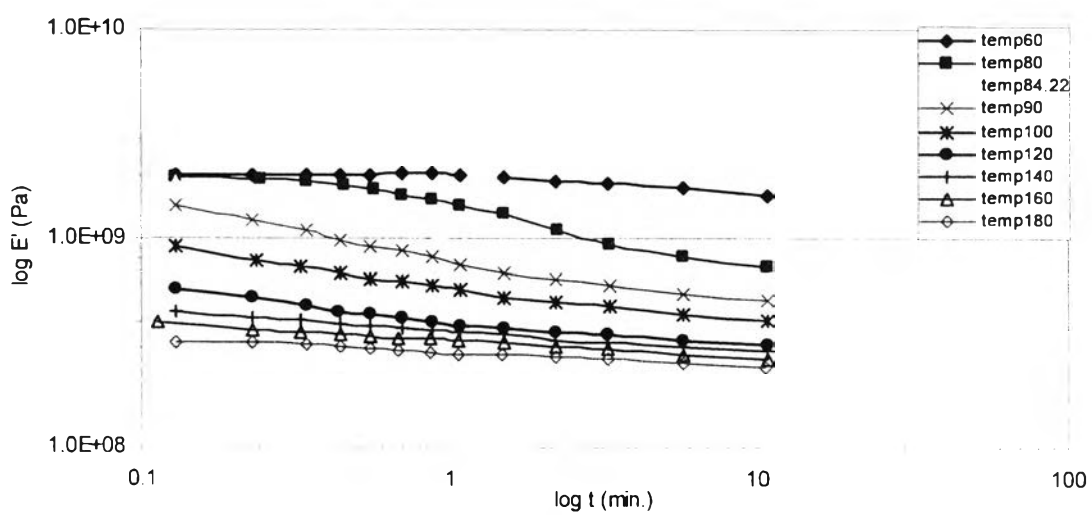
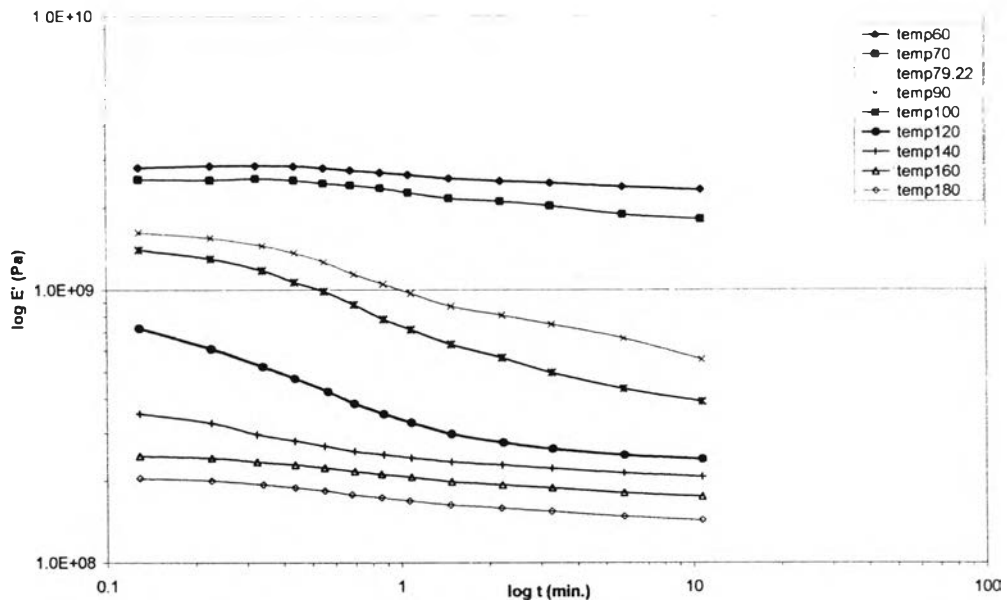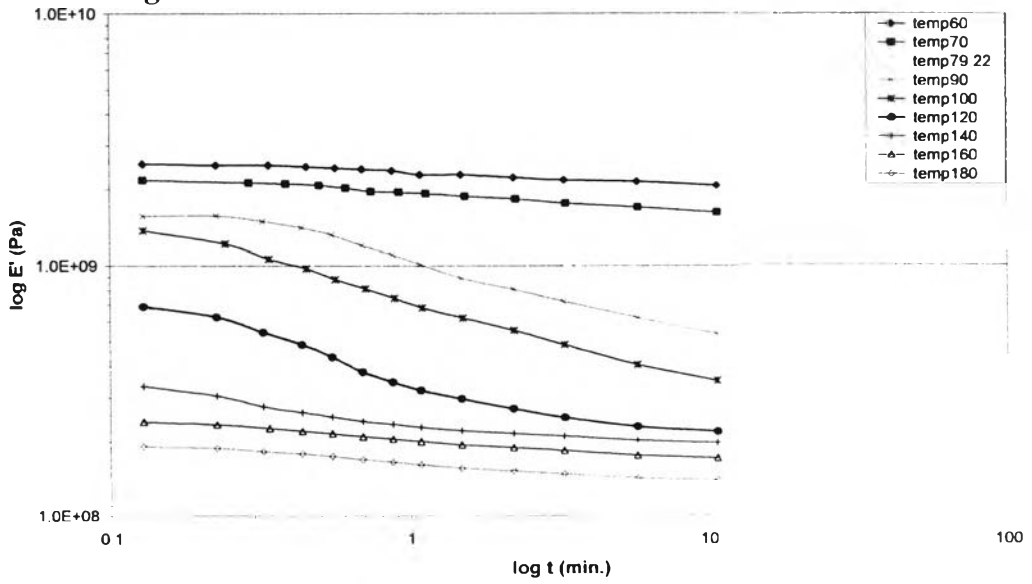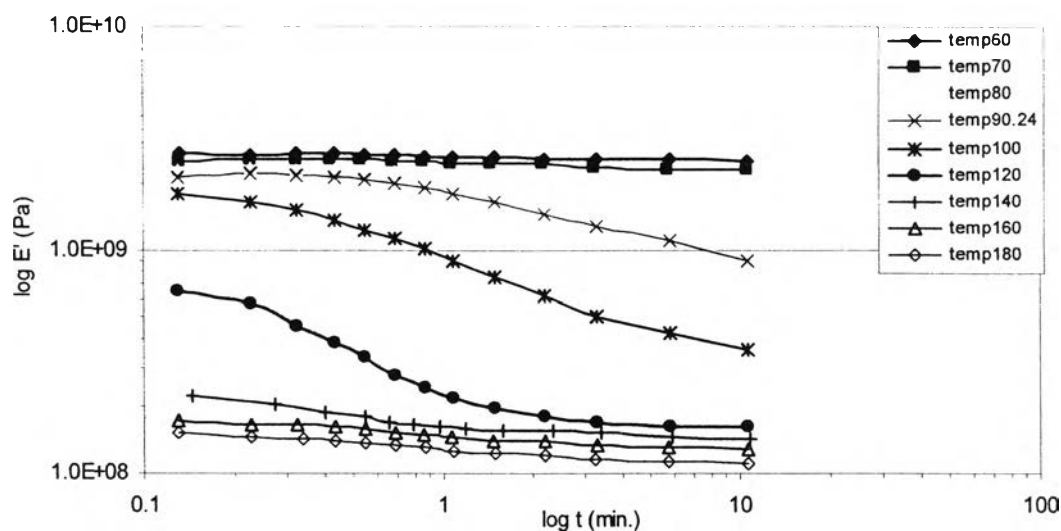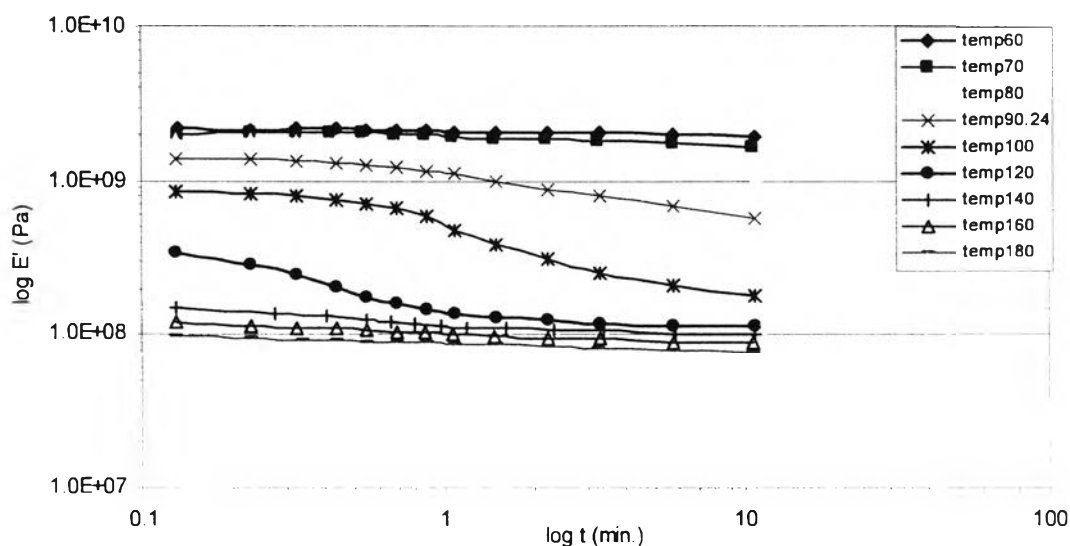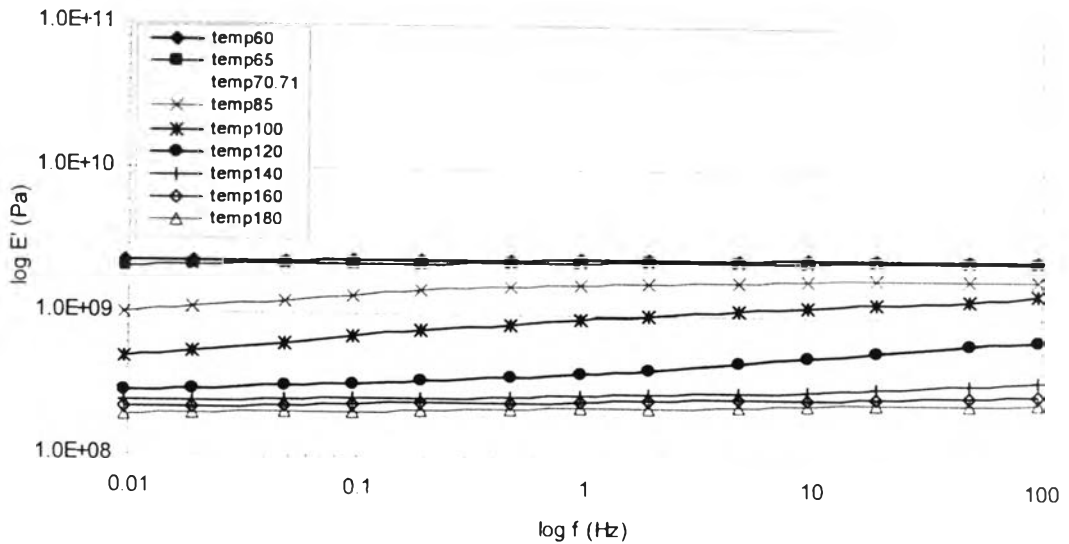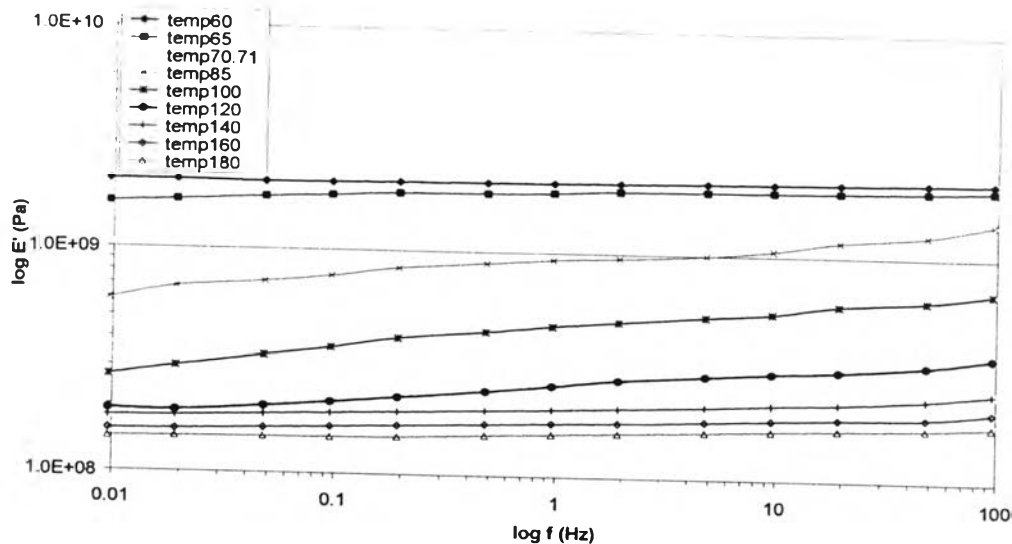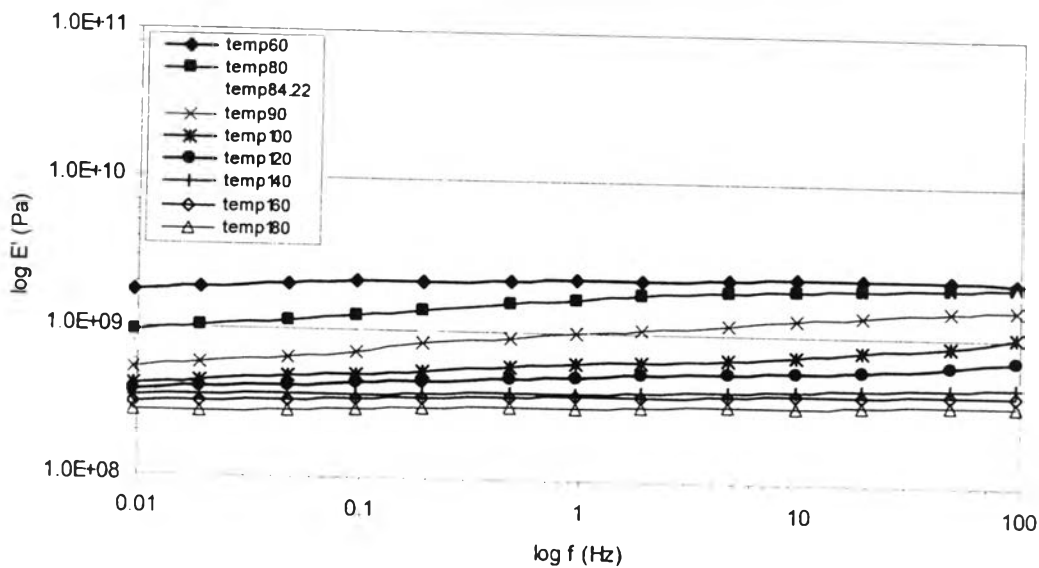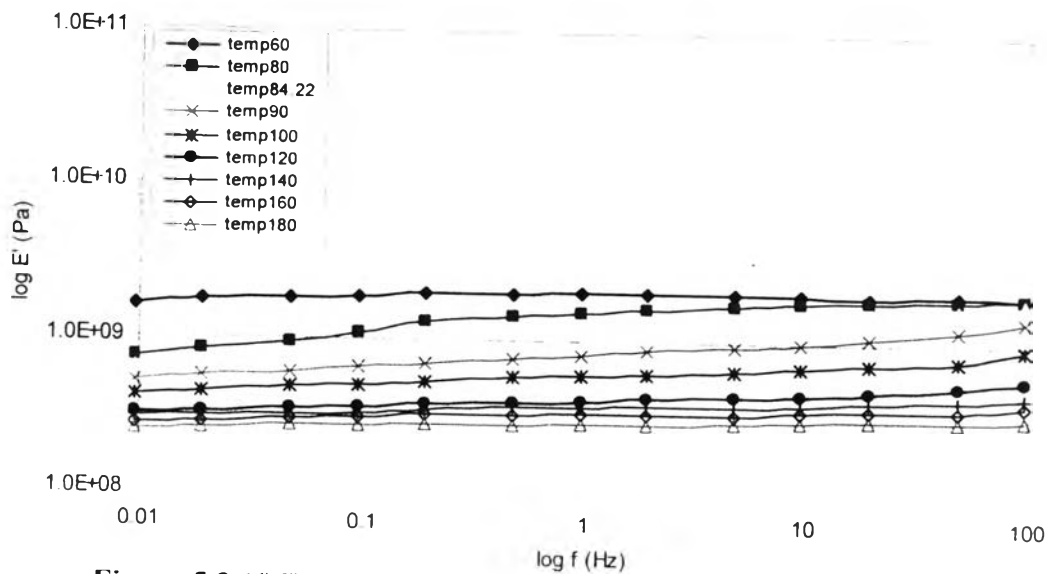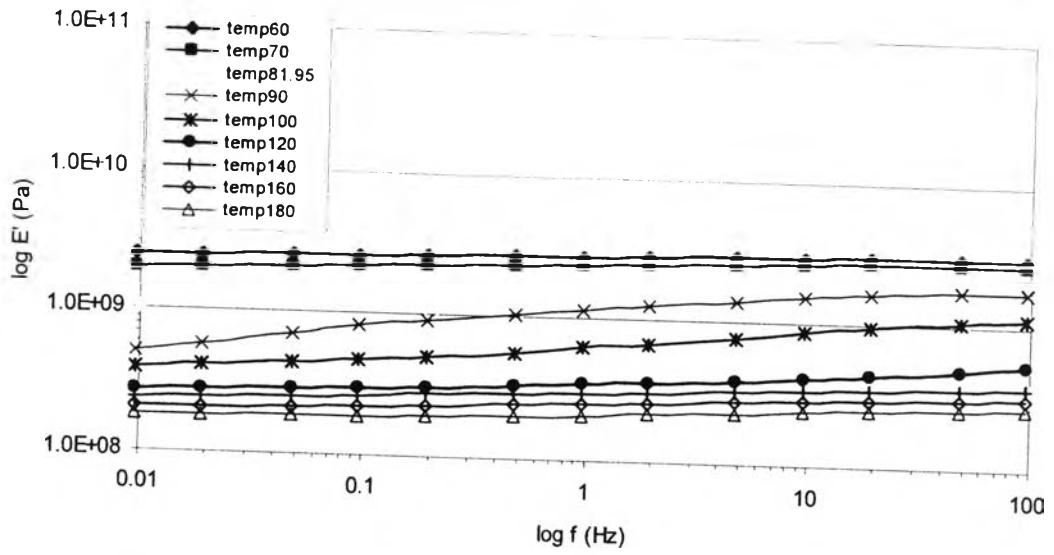**Figure 5.2.6** E' curve as time function for sPS2/PBMA blend
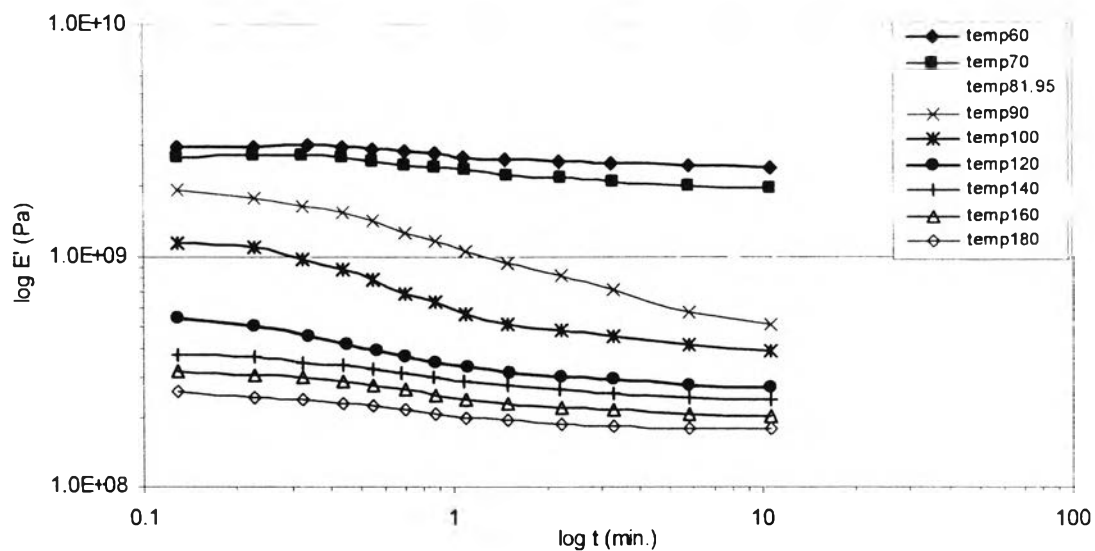
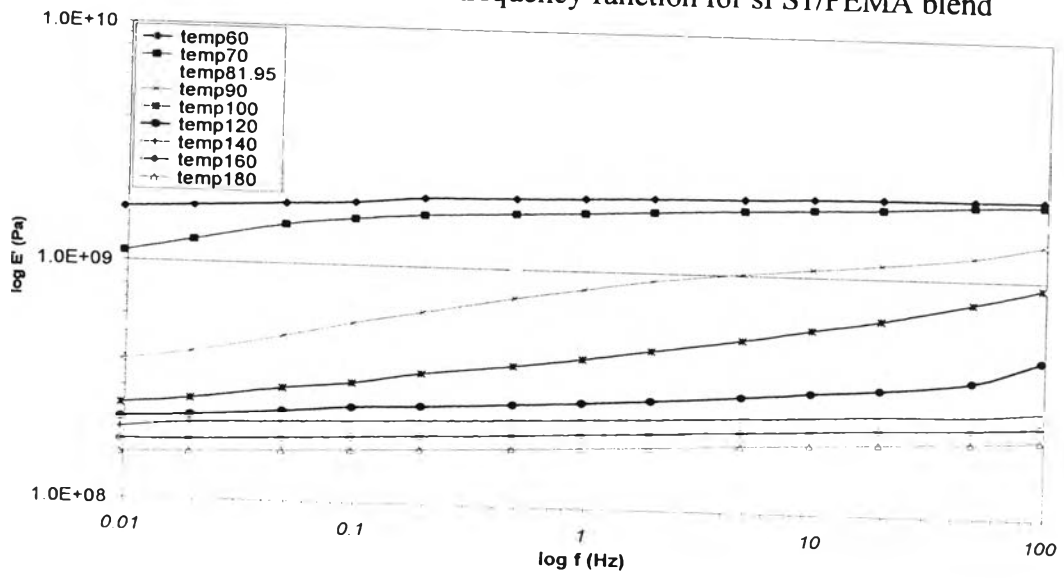**Figure 5.2.7** E' curve as time function for sPS1/PEMA blend
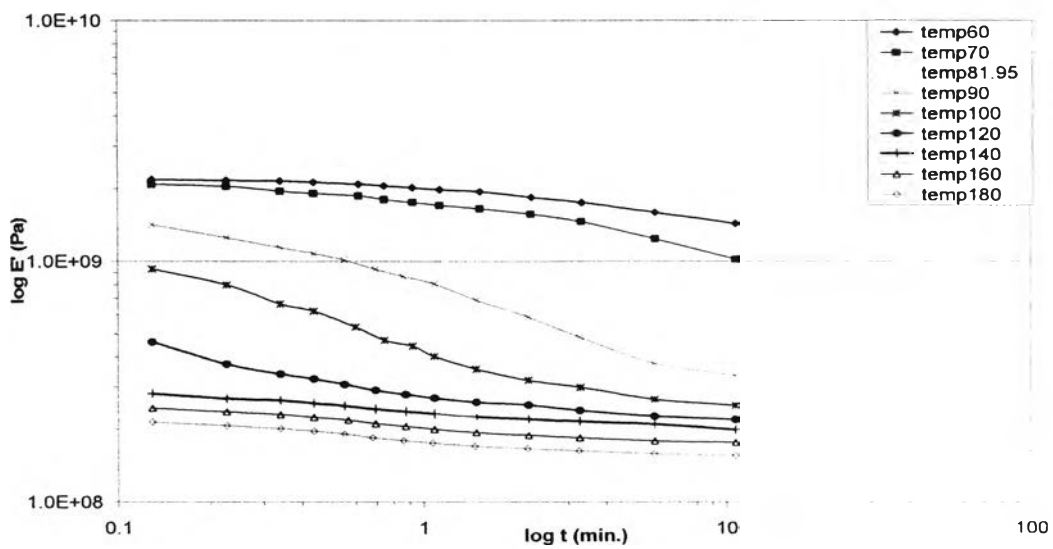
Figure 5.2.8 E' curve as time function for sPS2/PEMA blend

log E' (Pa)

1 0E+10

1.0E+09

1.0E+08

0.1   1   10   100

log t (min.)

temp60
temp70
temp79.22
temp90
temp100
temp120
temp140
temp160
temp180

Figure 5.2.9 E' curve as time function for sPS1/PHMA blend

log E' (Pa)

1.0E+10

1.0E+09

1.0E+08

0 1   1   10   100

log t (min.)

temp60
temp70
temp79 22
temp90
temp100
temp120
temp140
temp160
temp180

Figure 5.2.10 E' curve as time function for sPS2/PHMA blend

Figure 5.2.11 E' curve as time function for sPS1/PaMS blend

Figure 5.2.12 E' curve of time as time function for sPS2/PaMS blend

5.2.2 Effect of frequency

Figure 5.2.13-5.2.24 shown storage modulus (E') as a function of frequency at different temperatures. Because of the sinusoidal oscillating force, the frequency can be varied from 0.01 to 100 Hz. (sec^{-1}) for pure sPS and all the blend systems. It is observed that pure sPS and all the blends with different polymers exhibit the increasing of storage modulus (E') with increasing of frequency. At high frequency, it meant that the samples were applied by force with small durations per unit time. Then, energy for high frequency was recovered much more than for low frequency. Storage modulus (E') at high frequency was so more than that at low frequency.
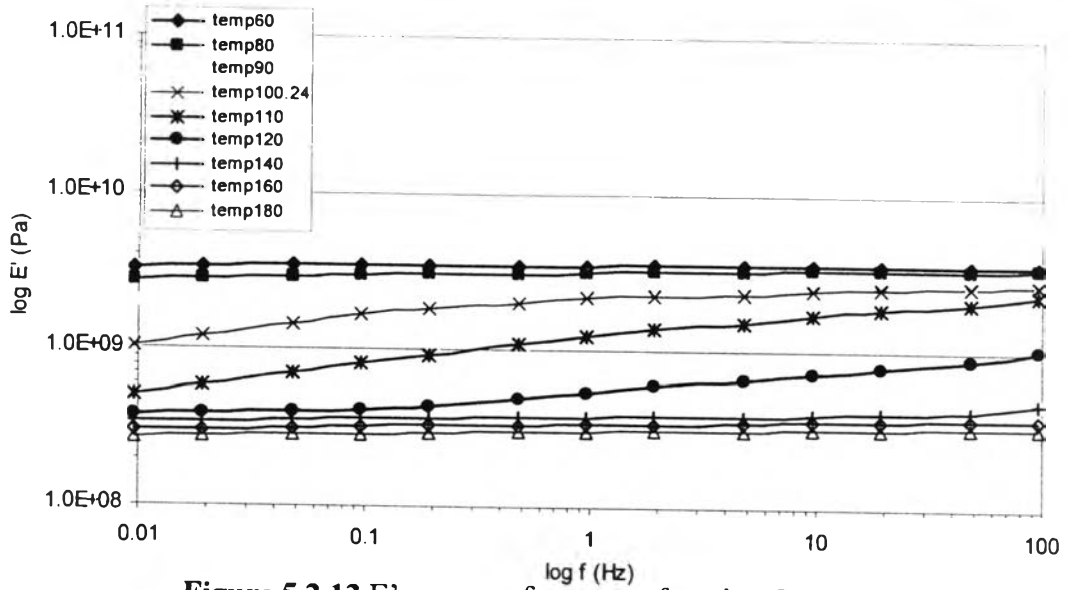
Figure 5.2.13 E' curve as frequency function for sPS1
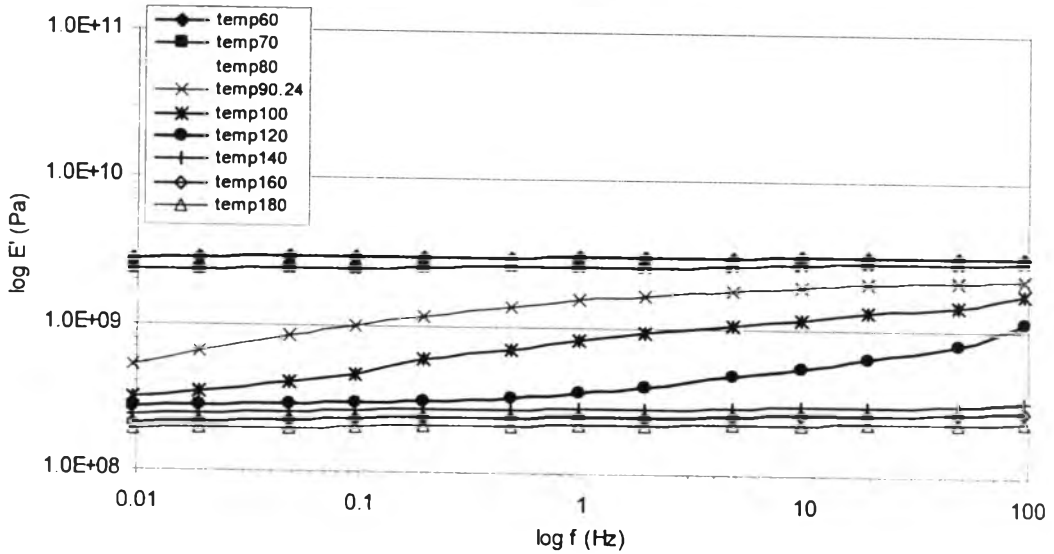
Figure 5.2.14 E' curve as frequency function for sPS2

Figure 5.2.15 E' curve as frequency function for sPS1/PIP blend

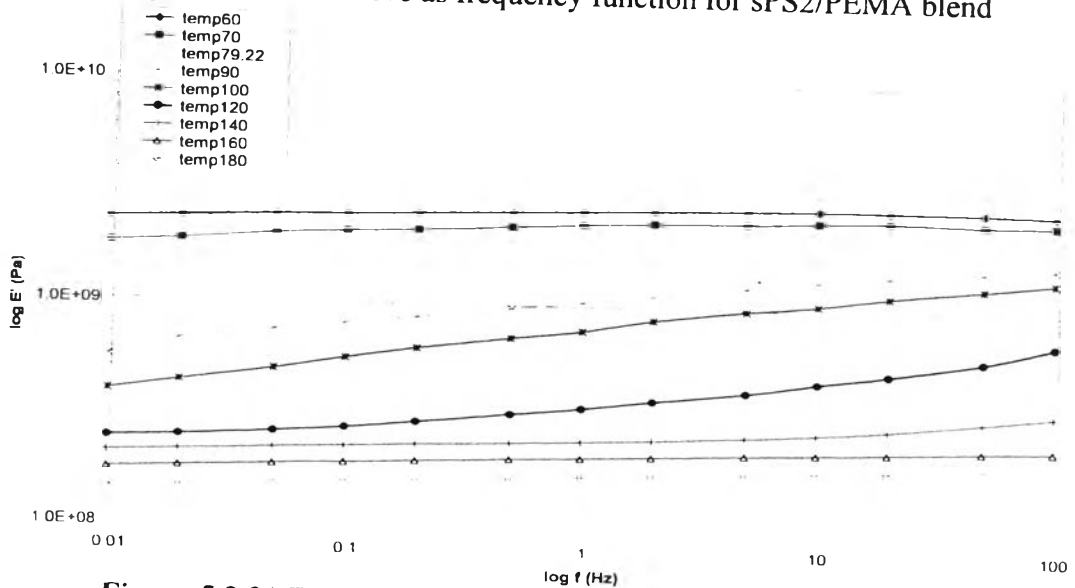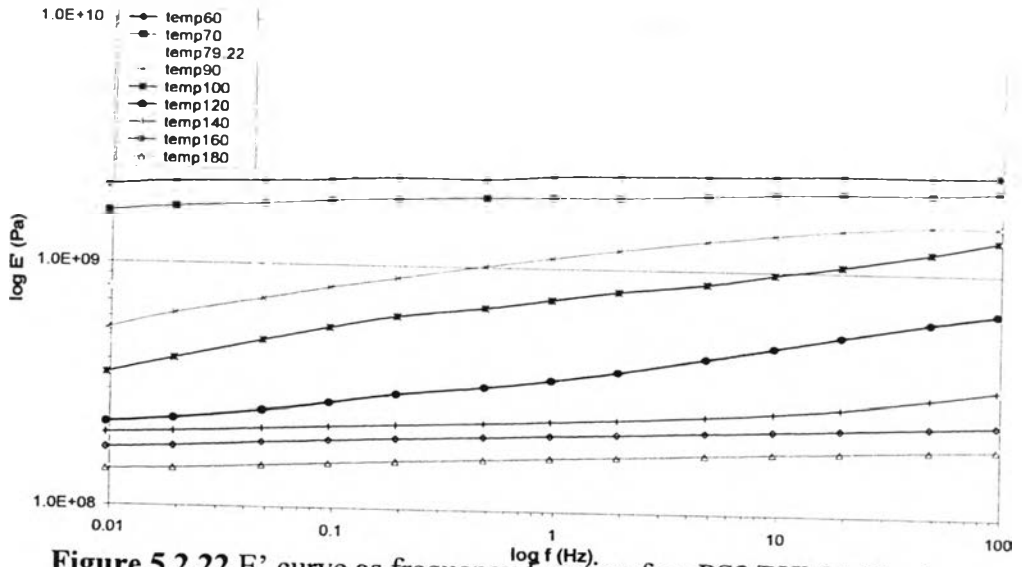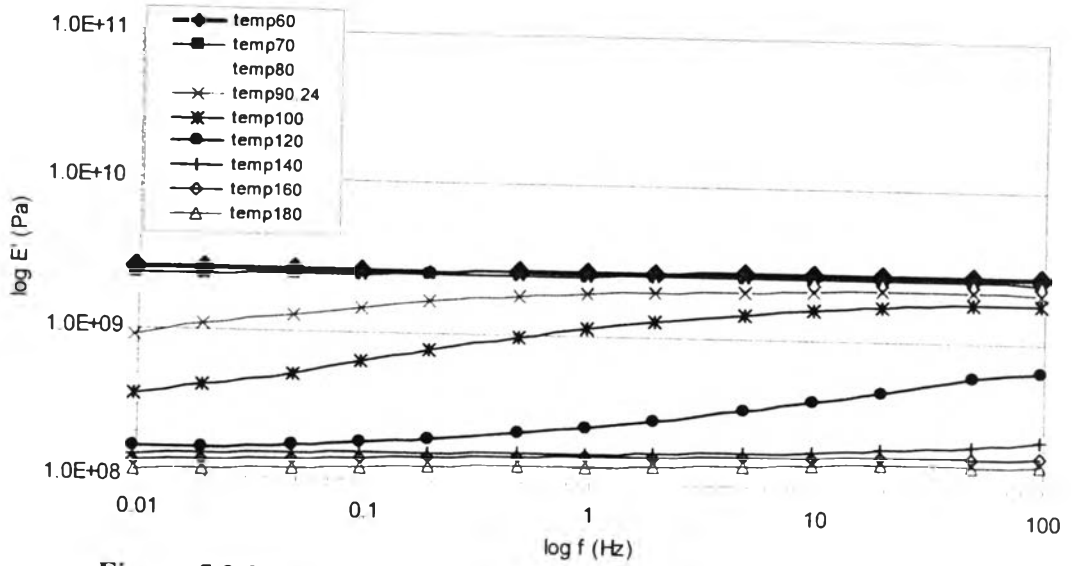**Figure 5.2.16** E' curve as frequency function for sPS2/PIP blend

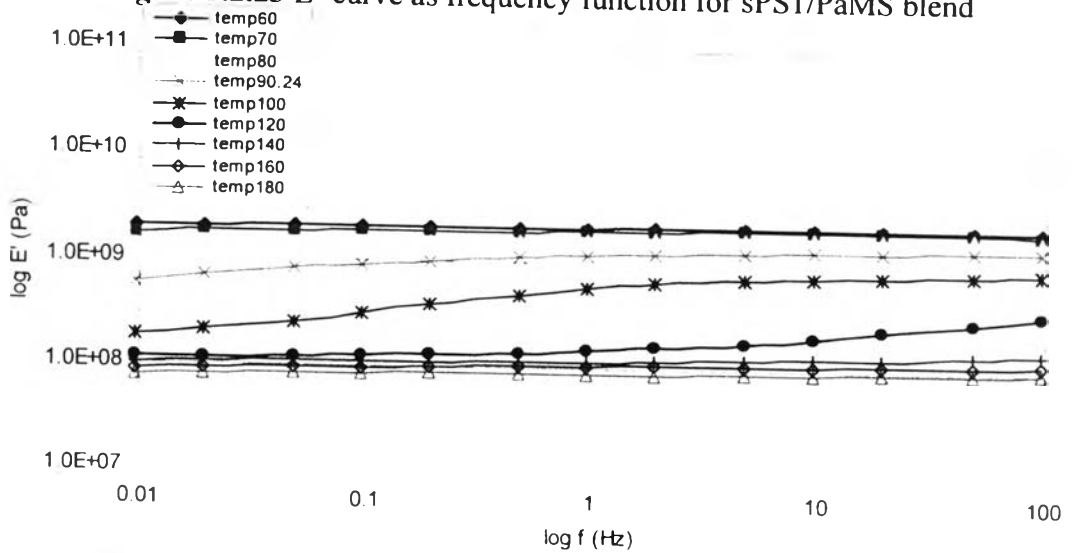**Figure 5.2.17** E' curve as frequency function for sPS1/PBMA blend

Figure 5.2.18 E' curve as frequency function for sPS2/PBMA blend

Figure 5.2.19 E' curve as frequency function for sPS1/PEMA blend

Figure 5.2.20 E' curve as frequency function for sPS2/PEMA blend

Figure 5.2.21 E' curve as frequency function for sPS1/PHMA blend

Figure 5.2.22 E' curve as frequency function for sPS2/PHMA blend

Figure 5.2.23 E' curve as frequency function for sPS1/PaMS blend

Figure 5.2.24 E' curve as frequency function for sPS2/PaMS blend

5.2.3 Creating master curve by using Time-Temperature Superposition (TTS)

From E' curves above, then the master curves of DMA can be created by Time-Temperature Superposition (TTS). In each blends, glass transition temperature (T_g) was chose as reference temperature (T_r) because T_g was considered as processing temperature. The T_gs from DSC data were reported as in Part 5.1.1 of this work. In Time-Temperature Superposition (TTS) method, the shift factors (a_T), as calculating graphically, were used to create master curve. Figure 5.2.25-5.36 show the master curves of pure sPS and all the blends systems as a function of time after shifting curve.
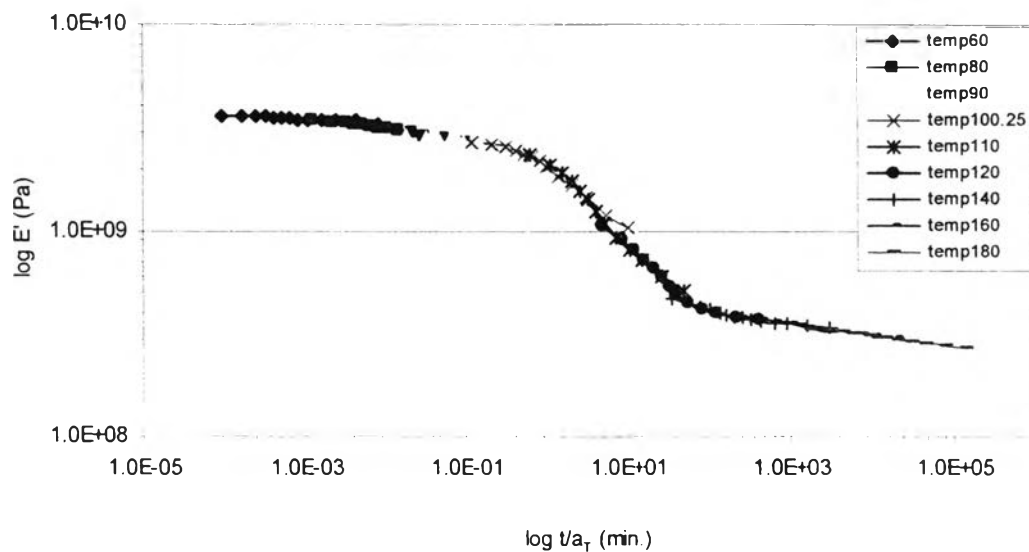
Figure 5.2.25 Master curve for sPS1 as time function with T_r 100.25 °C
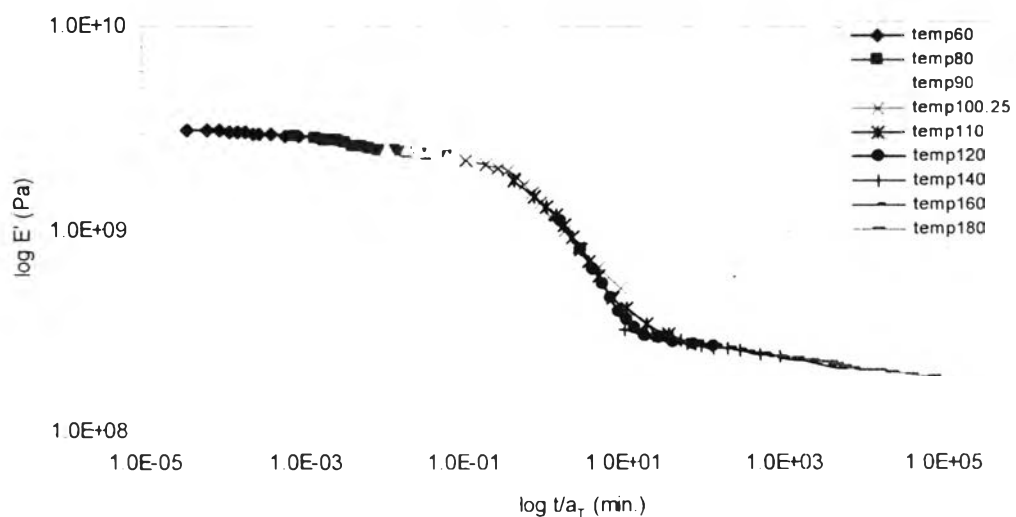
Figure 5.2.26 Master curve for sPS2 as time function with T_r 100.25 °C
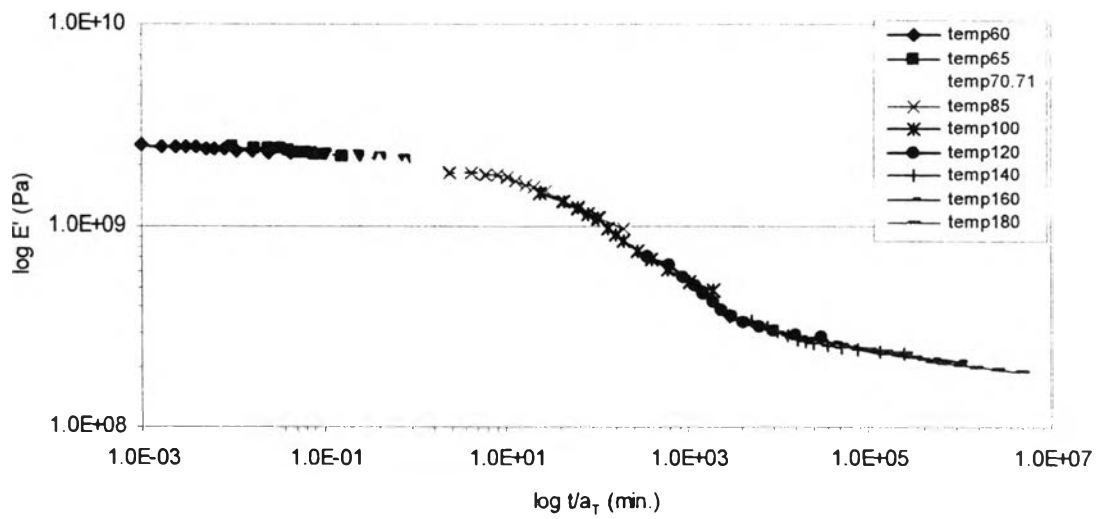
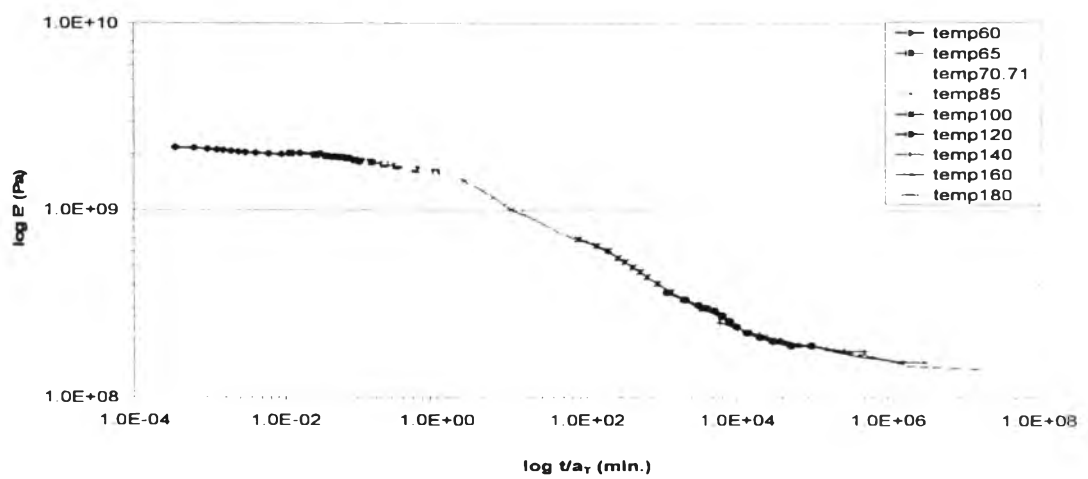**Figure 5.2.27** Master curve for sPS2 as time function with T_r 100.25 °C

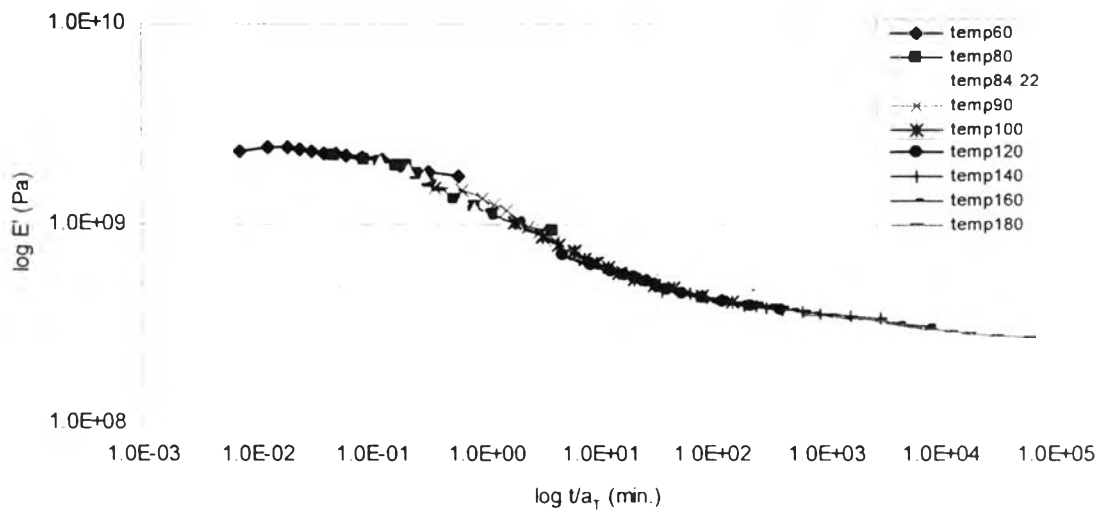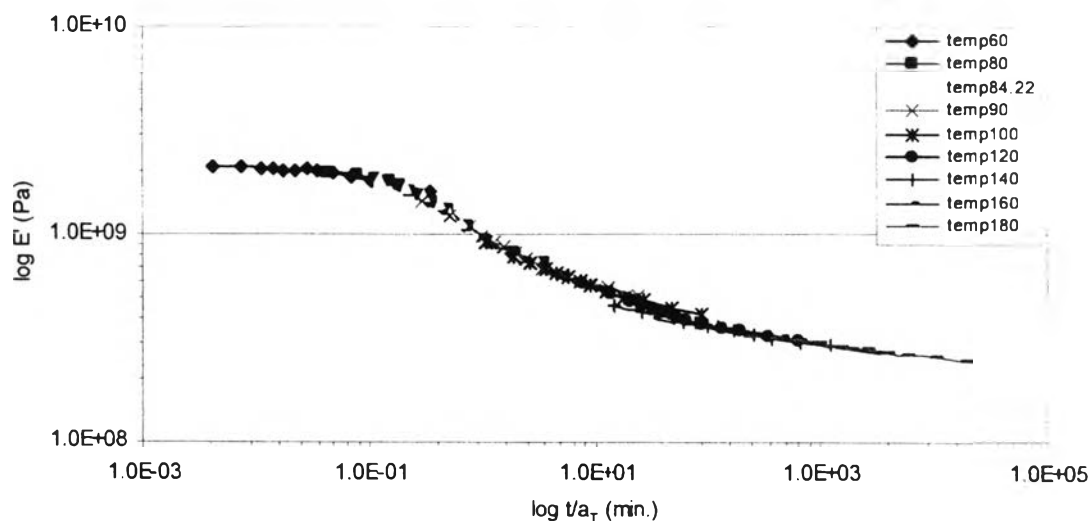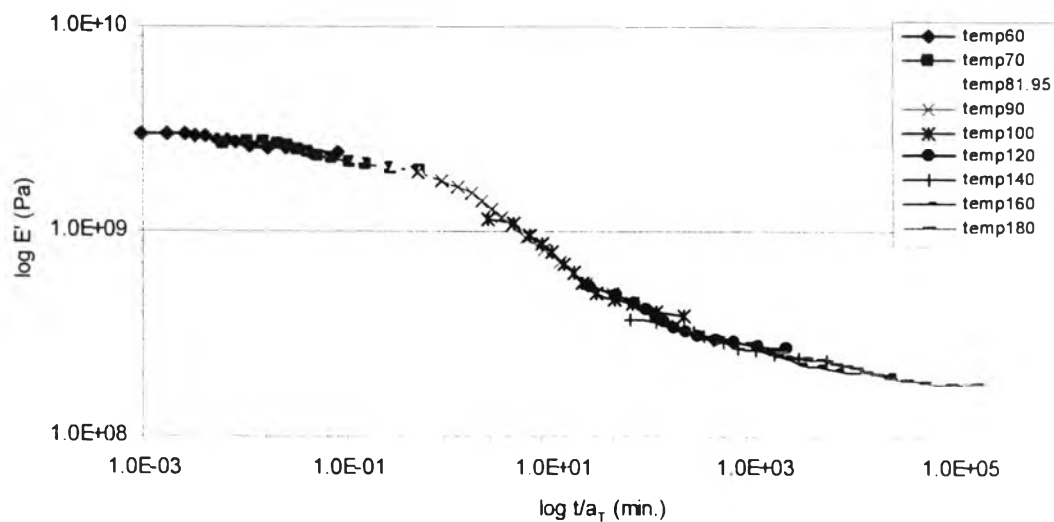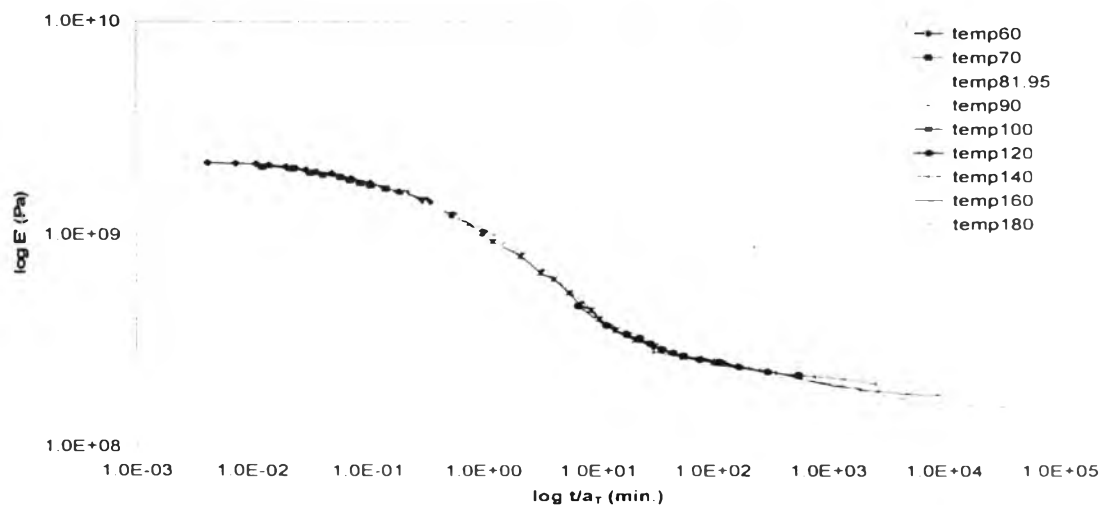**Figure 5.2.28** Master curve for sPS2/PIP blend as time function with T_r 70.71 °C

Figure 5.2.29 Master curve for sPS1/PBMA blend as time function with T_r 84.22 °C

Figure 5.2.30 Master curve for sPS2/PBMA blend as time function with T_r 84.22 °C

Figure 5.2.31 Master curve for sPS1/PEMA blend as time function with T_r 81.95 °C

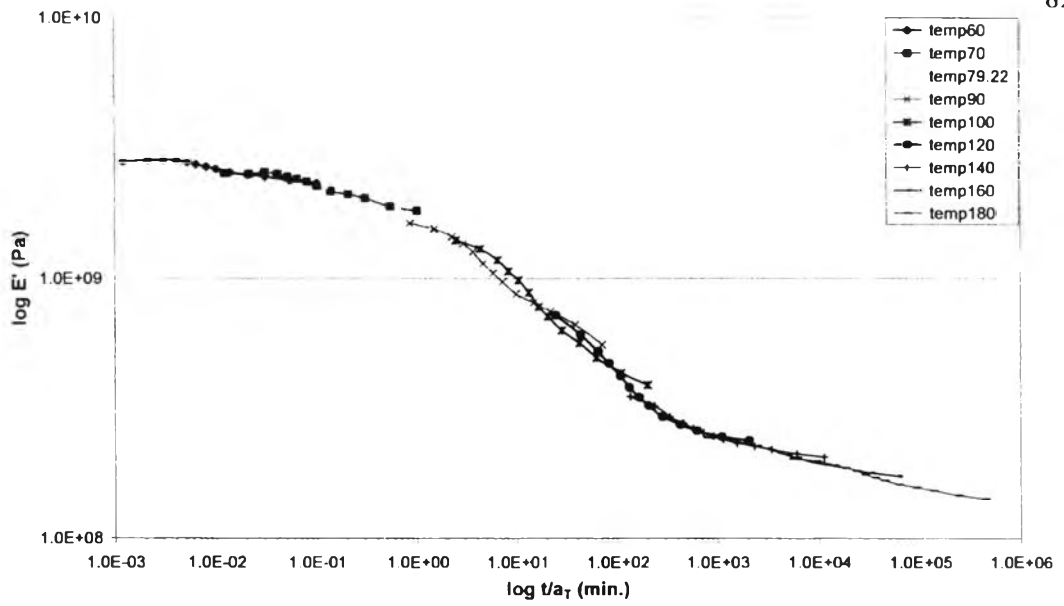**Figure 5.2.32** Master curve for sPS2/PEMA blend as time function with T_r 81.95 °C

Figure 5.2.33 Master curve for sPS1/PHMA blend as time function with T_r 79.22 °C
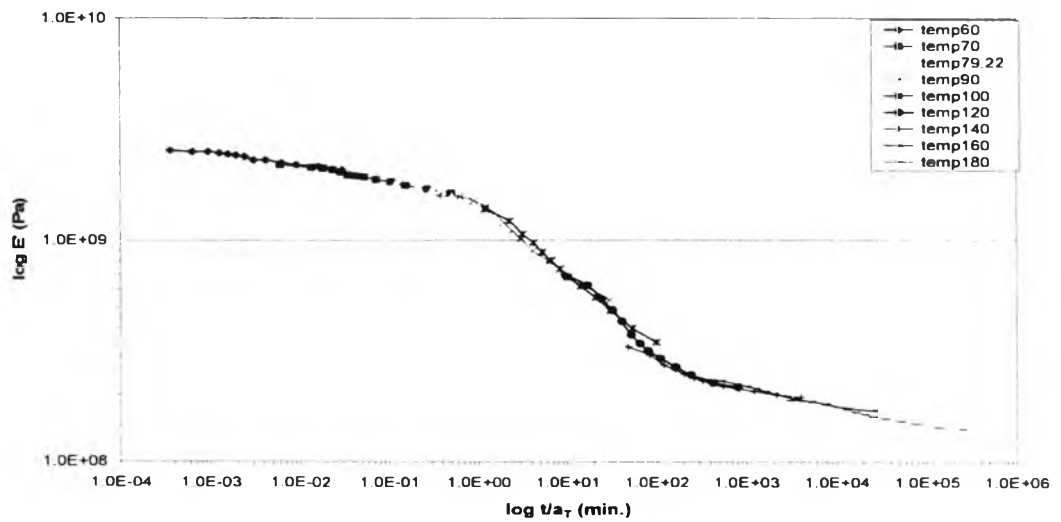

Figure 5.2.34 Master curve for sPS2/PHMA blend as time function with T_r 79.22 °C
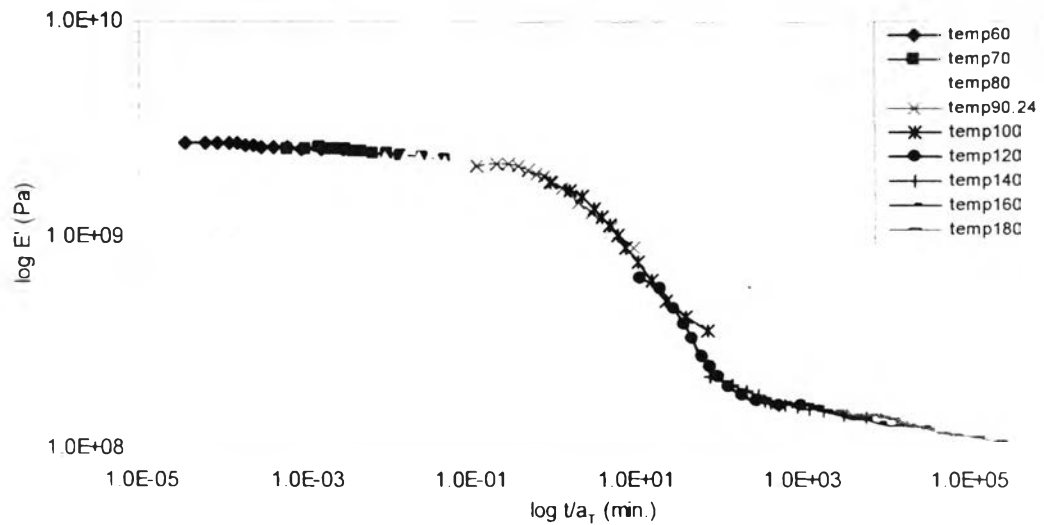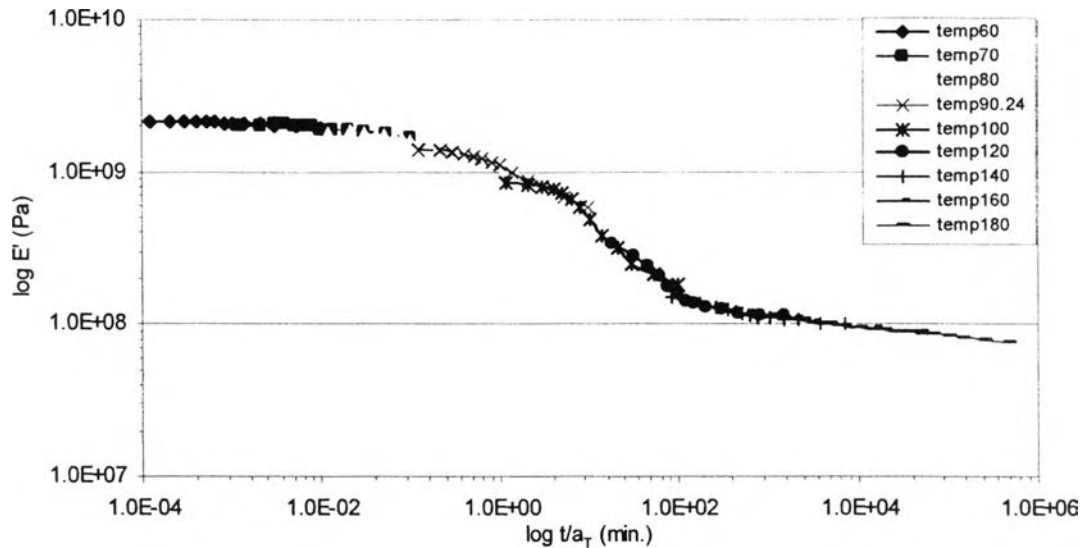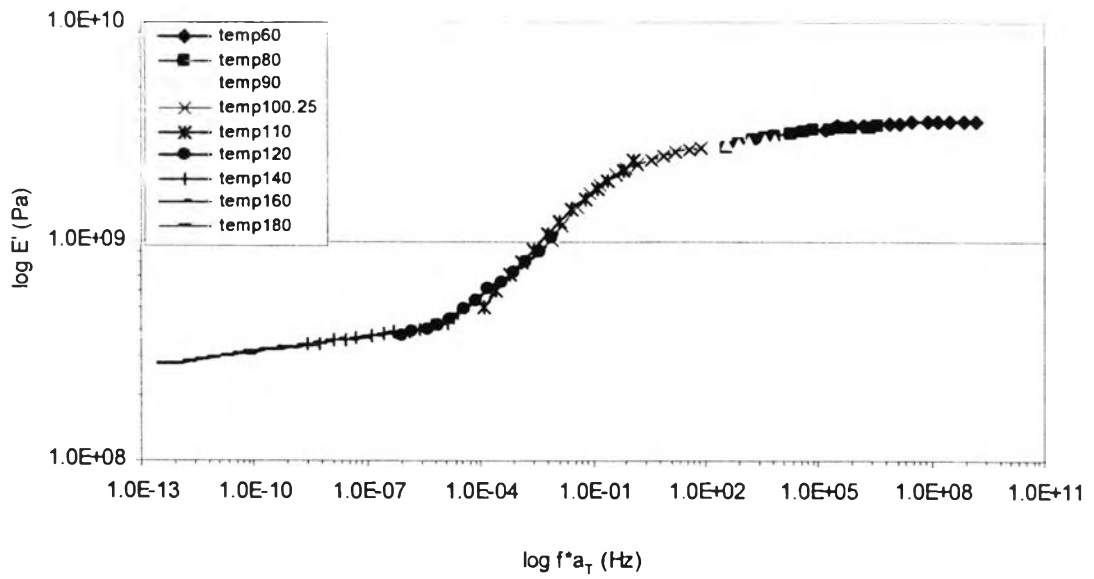

Figure 5.2.35 Master curve for sPS1/PaMS blend as time function with T_r 90.24 °C
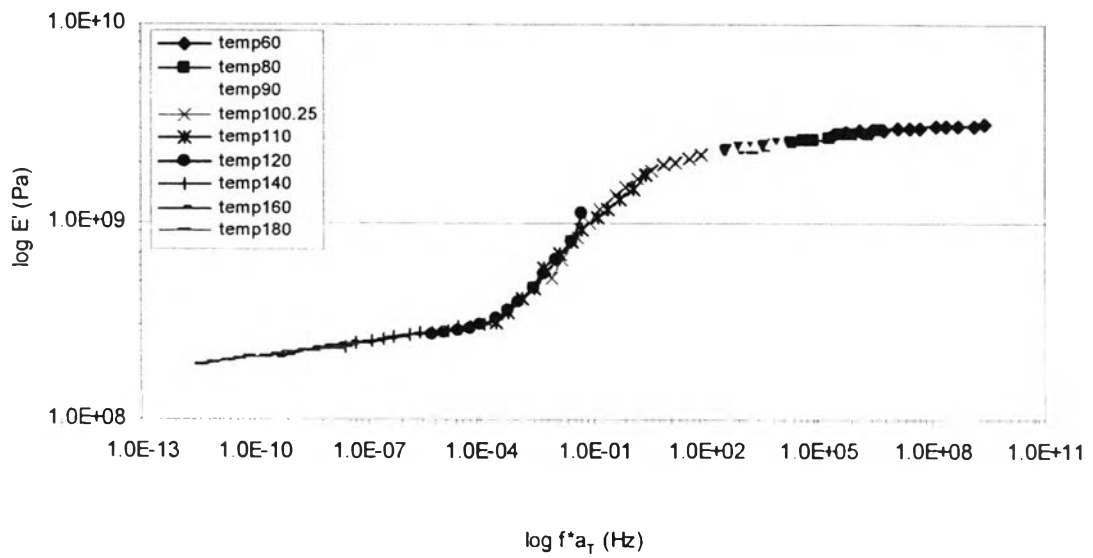
Figure 5.2.36 Master curve for sPS2/PaMS blend as time function with T_r 90.24 °C

As in the above master curves, they can be created as function of time. In addition, the master curves were created on the basis of real life usages. Polymers properties (storage modulus (E')) can be predicted at desired temperature for various time of the bearing loads because storage modulus of time scans was equivalent that of temperature scans. Storage modulus at low time was equivalent with that at low temperature. The desired temperature can be called reference temperature (T_r), as, in the above figures, the reference temperatures were chosen at the glass transition temperature (T_g). Moreover, storage modulus (E') can still be predicted in the function of frequency. Because it is hard to report the usage of polymer in frequency domain (0.01-100 Hz). But for the ease of calculation the ranges of master curve can be also created as function of frequency. Figure 5.2.37-5.2.48 show the master curves as function of frequency for pure sPS and all the blend systems.
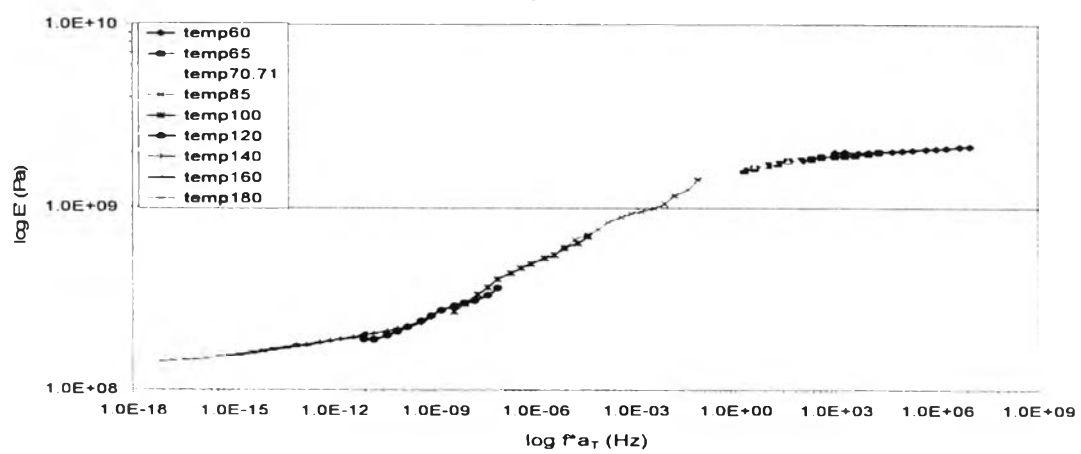
Figure 5.2.37 Master curve for sPS1 as frequency function with T_r 100.25 °C
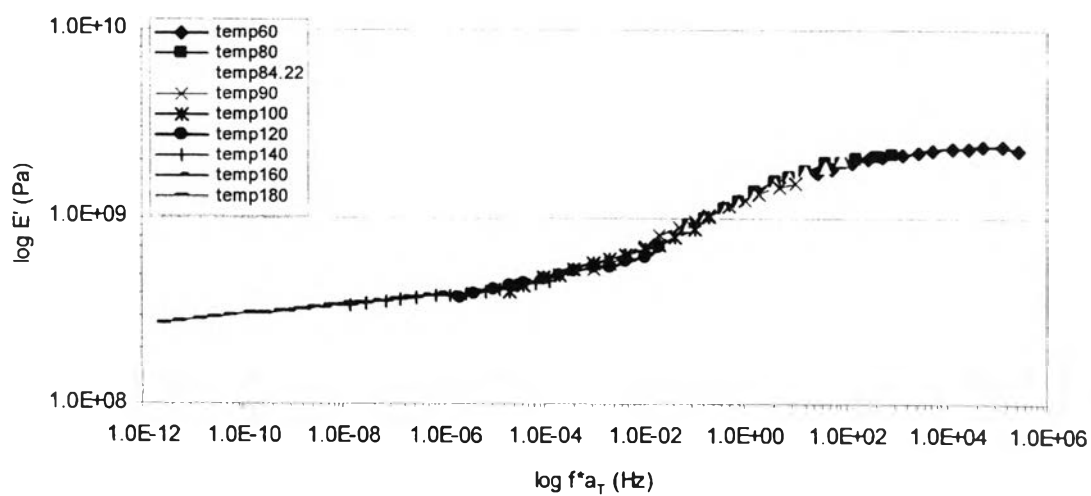

Figure 5.2.38 Master curve for sPS2 as frequency function with T_r 100.25 °C
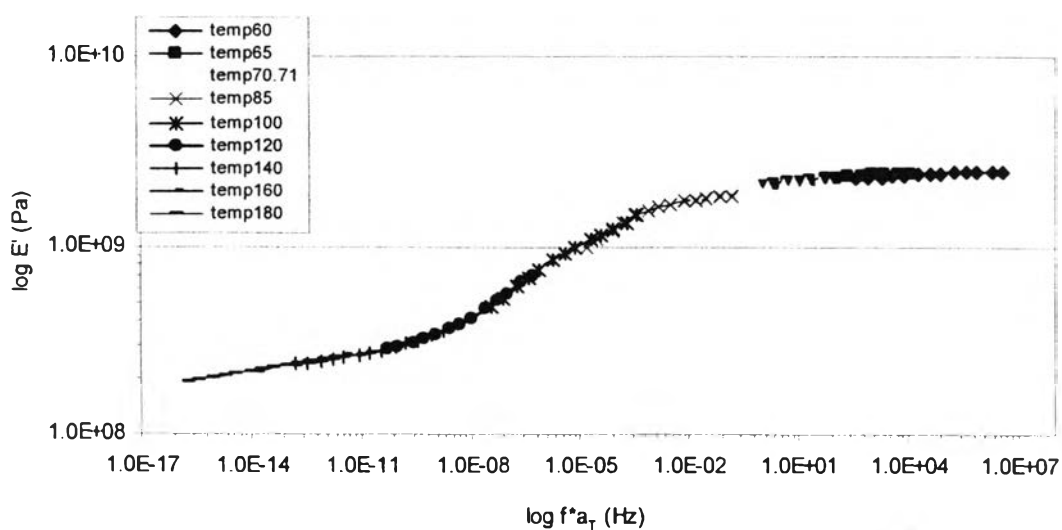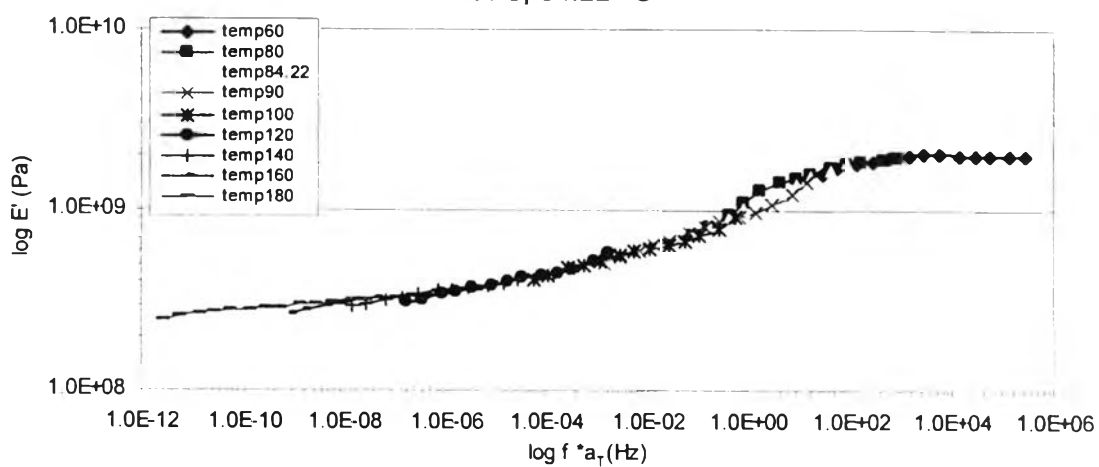
Figure 5.2.39 Master curve for sPS1/PIP blend as frequency function
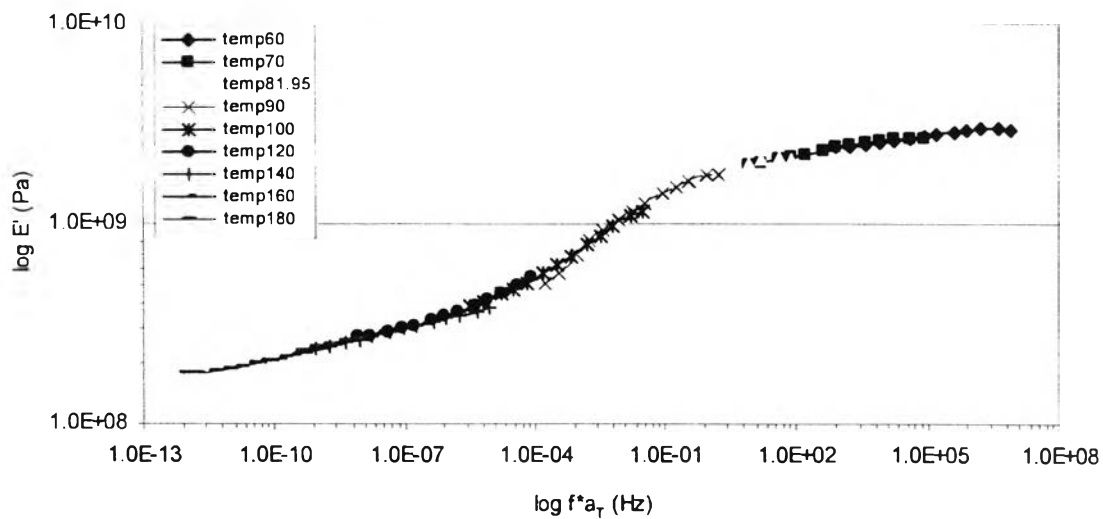
with T_r 70.71 °C

Figure 5.2.40 Master curve for sPS2/PIP blend as frequency function
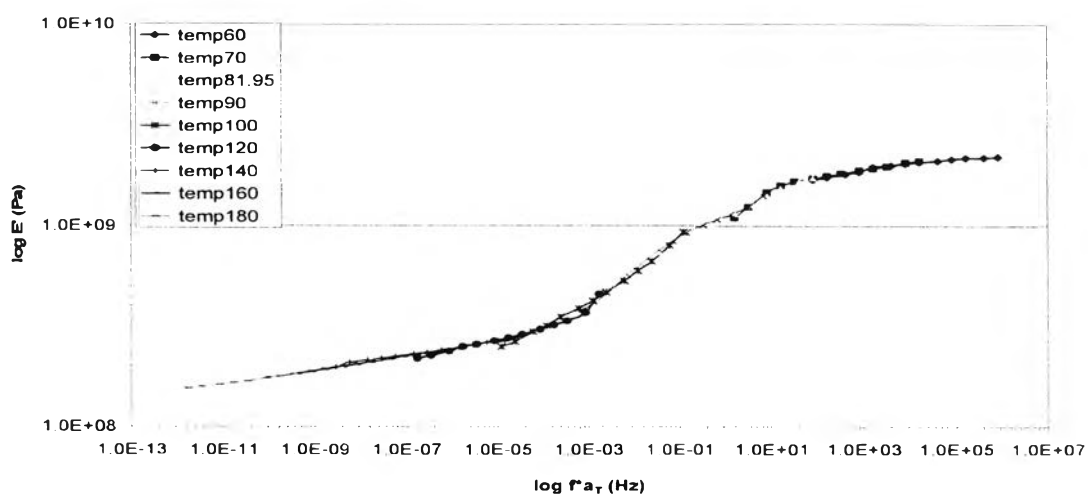
with T_r 70.71 °C

Figure 5.2.41 Master curve for sPS1/PBMA blend as frequency function with T_r 84.22 °C

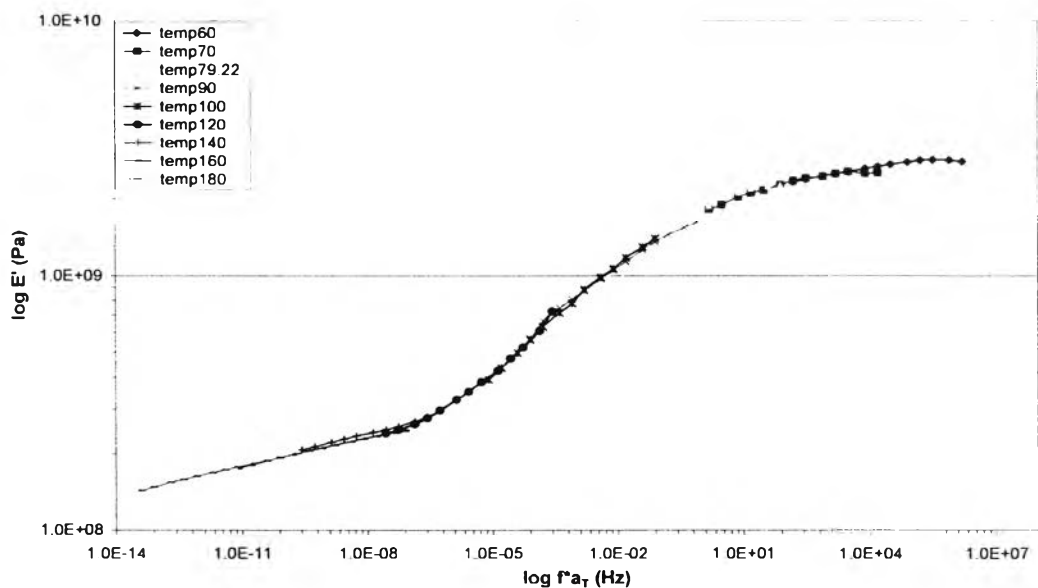**Figure 5.2.42** Master curve for sPS2/PBMA blend as frequency function with T_r 84.22 °C

Figure 5.2.43 Master curve for sPS1/PEMA blend as frequency function
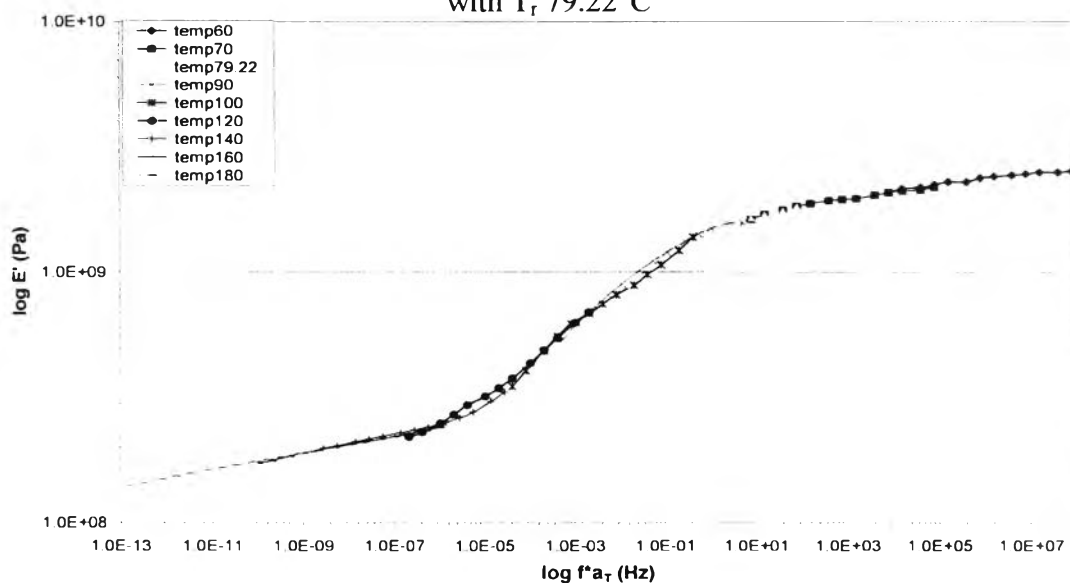
with T$_r$ 81.95 °C

Figure 5.2.44 Master curve for sPS2/PEMA blend as frequency function
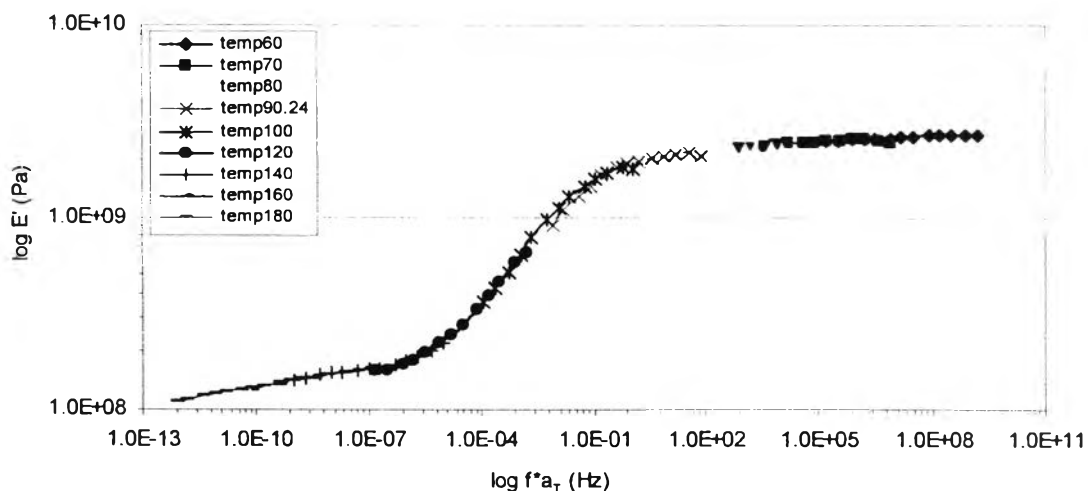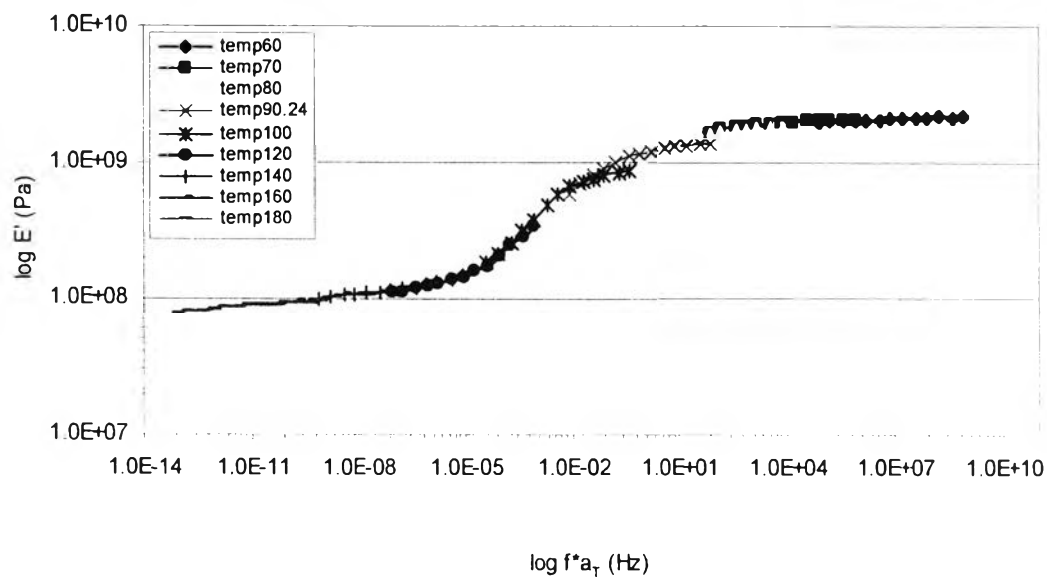
with T$_r$ 81.95°C

Figure 5.2.45 Master curve for sPS1/PHMA blend as frequency function with T_r 79.22°C

Figure 5.2.46 Master curve for sPS2/PHMA blend as frequency function with T_r 79.22°C

Figure 5.2.47 Master curve for sPS1/PaMSblend as frequency function

with T_r 90.24°C

Figure 5.2.48 Master curve for sPS2/PaMSblend as frequency function

with T_r 90.24°C

5.2.4 Effect of main component (sPS)

From these experiments, sPS were the main component for all the blend systems because the ratio of sPS to blended polymers in all the blend systems were 80:20 percent by weight. The master curves were created for comparing the deviation from the main component. Figure 5.2.49-5.2.54 show the effects of main components in each blend system. It was found that storage modulus (E') of sPS1 main component was higher than that of sPS2 main component in all blend systems. For pure sPS, storage modulus of sPS1 was still higher than that of sPS2 because molecular weight

of sPS1 was much higher than that of sPS2. Molecular weight can be related directly to polymer chain length. More molecular weight was more polymer chain length. Longer polymer chains required more energy, storage modulus (E'), to stretch the chains from each other. Moreover, the same trend can be found in all the blend systems.
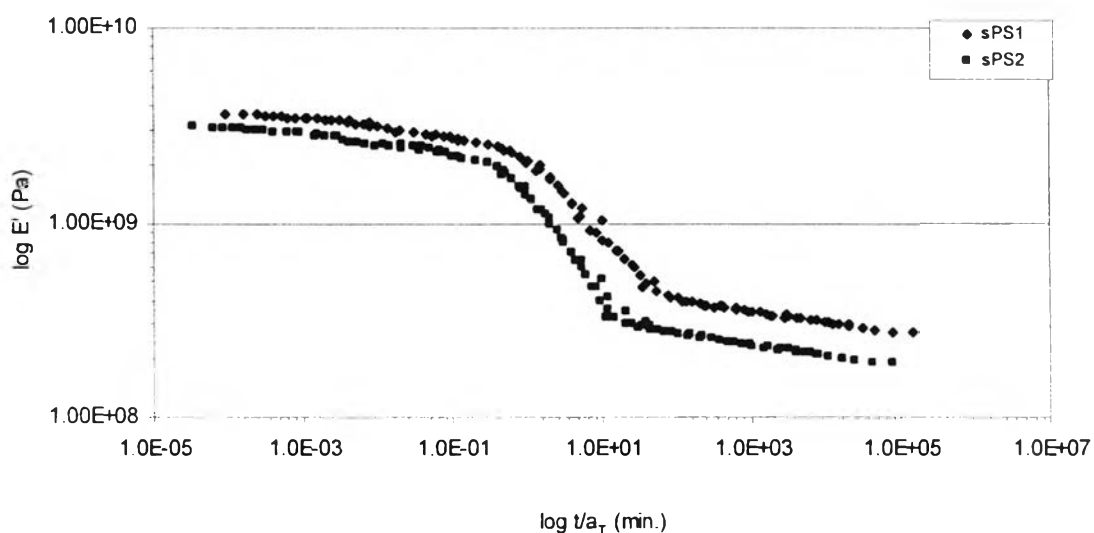
Figure 5.2.49 Master curve for sPS1 and sPS2
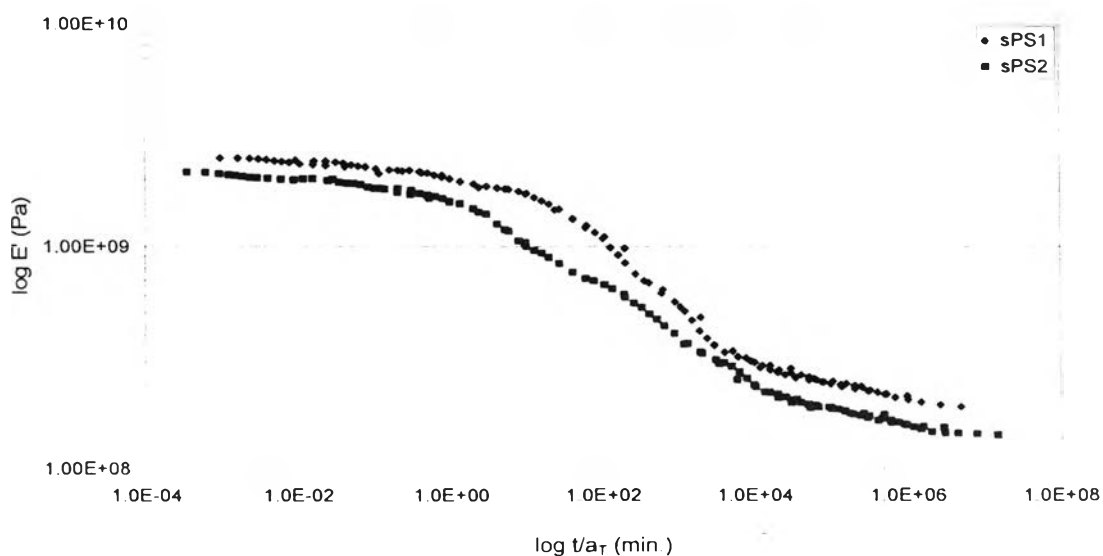
Figure 5.2.50 Master curve for sPS1 and sPS2 blended with PIP
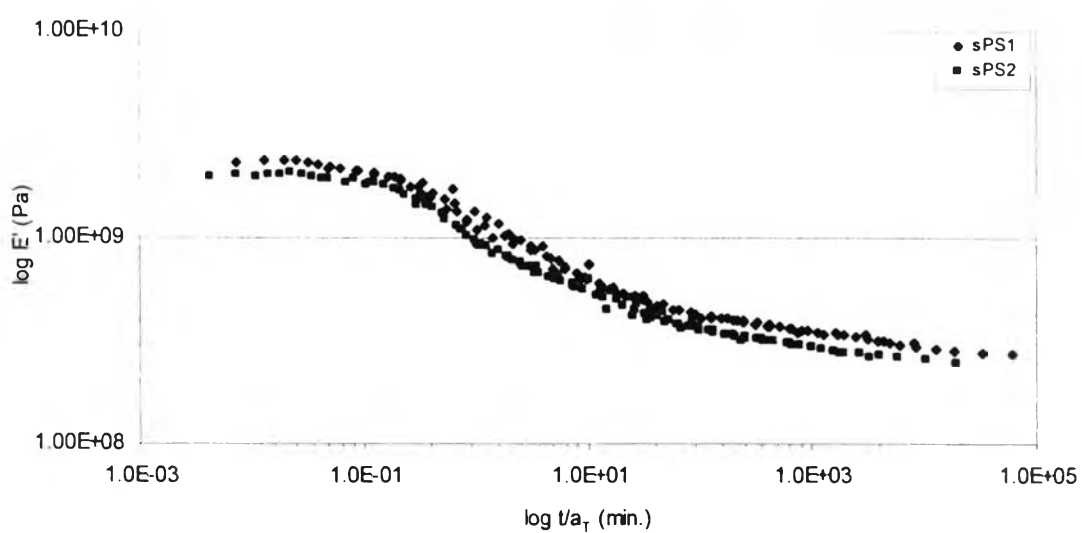
Figure 5.2.51 Master curve for sPS1 and sPS2 blended with PBMA

Figure 5.2.52 Master curve for sPS1 and sPS2 blended with PEMA

Figure 5.2.53 Master curve for sPS1 and sPS2 blended with PHMA

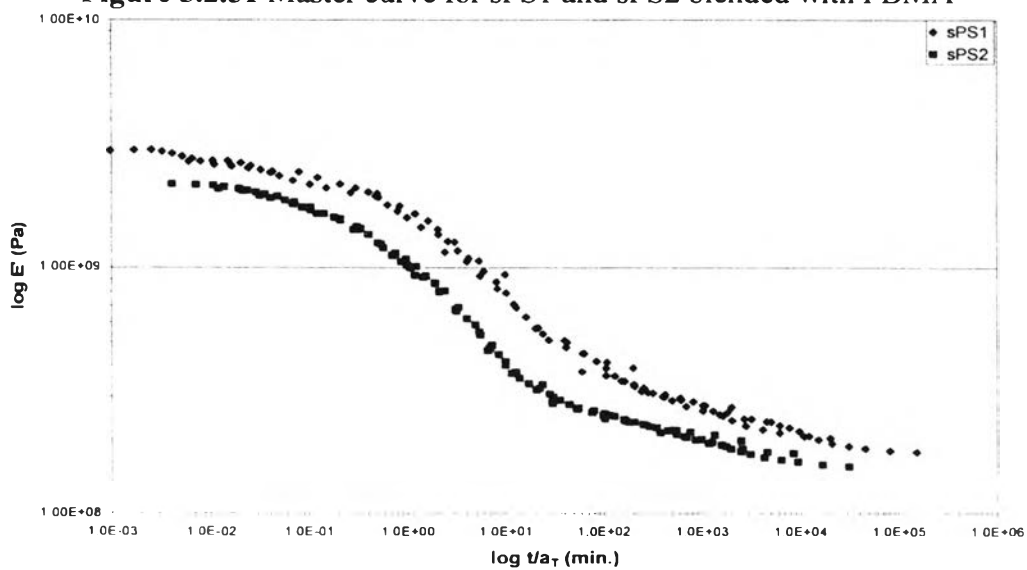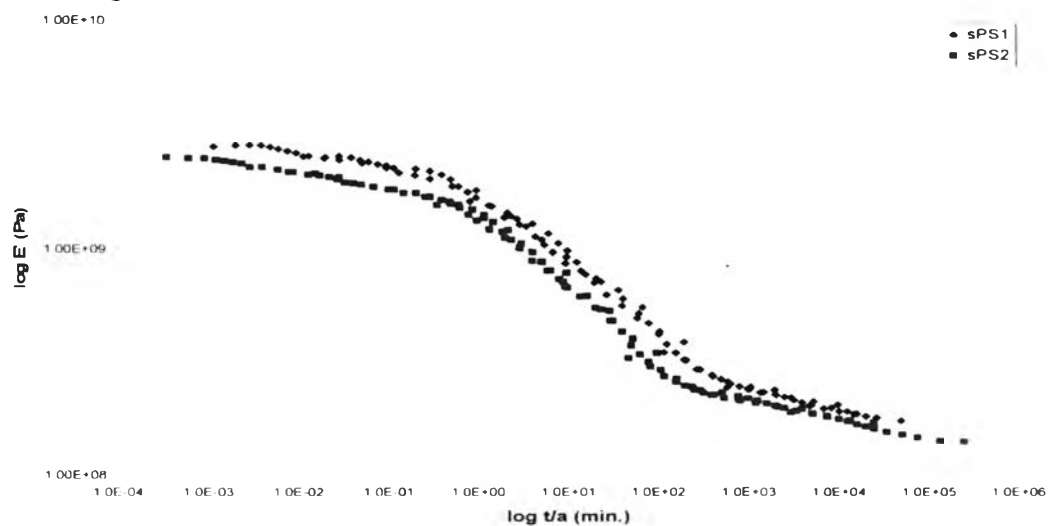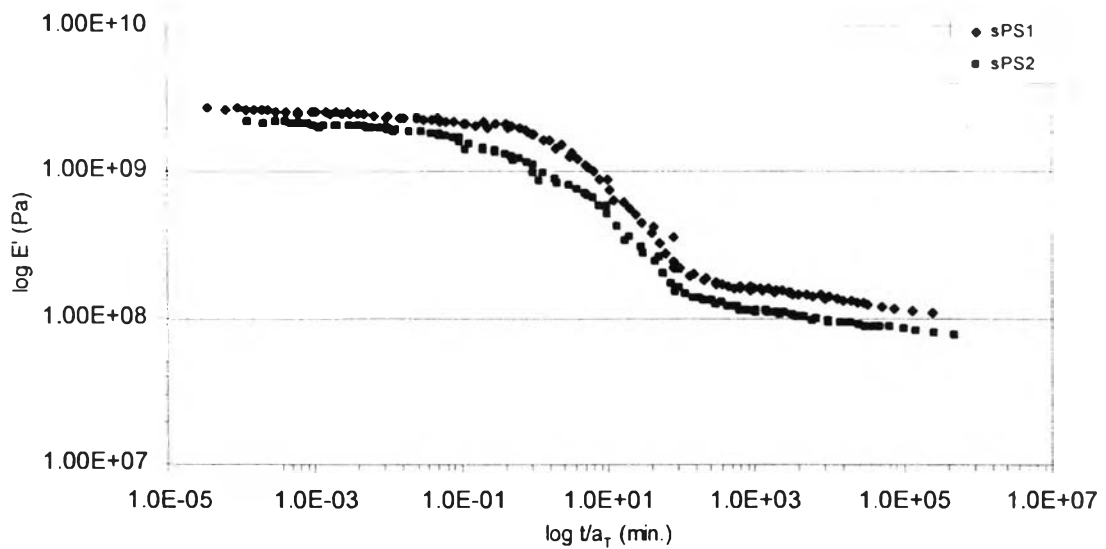**Figure 5.2.54** Master curve for sPS1 and sPS2 blended with PaMS

5.2.5 Williams Landel and Ferry (WLF) constants

The master curves can be obtained for all blend systems by using WLF equation, given by

$$\log a_T = \frac{C_1(T - T_g)}{C_2 + T - T_g}$$ 5.2.1

where a_T is the shift factor which the value was take to multiply for overlapping curve, T_g is the glass transition temperature and C_1, C_2 is WLF constants [26]. Then C_1 and C_2 can be obtained by fitting eq. 5.2.1 to linear equation [27].

$$\frac{-1}{\log a_T} = \frac{C_2}{C_1} \frac{1}{(T - T_g)} + \frac{1}{C_1}$$ 5.2.2

Then C_1 and C_2 were determined from slope and y-axis intercept of $-1/\log a_T$ versus $1/(T-T_g)$. Figure 5.2.55- 5.2.66 shown linear relationship of pure sPS and all blend systems in both time and frequency domain and Table 5.2.1 shown C_1 and C_2 for pure sPS and all the blend systems from the linear relationship explained above.

Figure 5.2.55 Relationship between -1/ log a_T versus $1/(T\text{-}T_g)$ for sPS1

Figure 5.2.56 Relationship between -1/ log a_T versus $1/(T\text{-}T_g)$ for sPS2

Figure 5.2.57 Relationship between $-1/\log a_T$ versus $1/(T\text{-}T_g)$ for sPS1/PIP

Figure 5.2.58 Relationship between $-1/\log a_T$ versus $1/(T\text{-}T_g)$ for sPS2/PIP

Figure 5.2.59 Relationship between -1/ log a_T versus $1/(T\text{-}T_g)$ for sPS1/PBMA

Figure 5.2.60 Relationship between -1/ log a_T versus $1/(T\text{-}T_g)$ for sPS2/PBMA

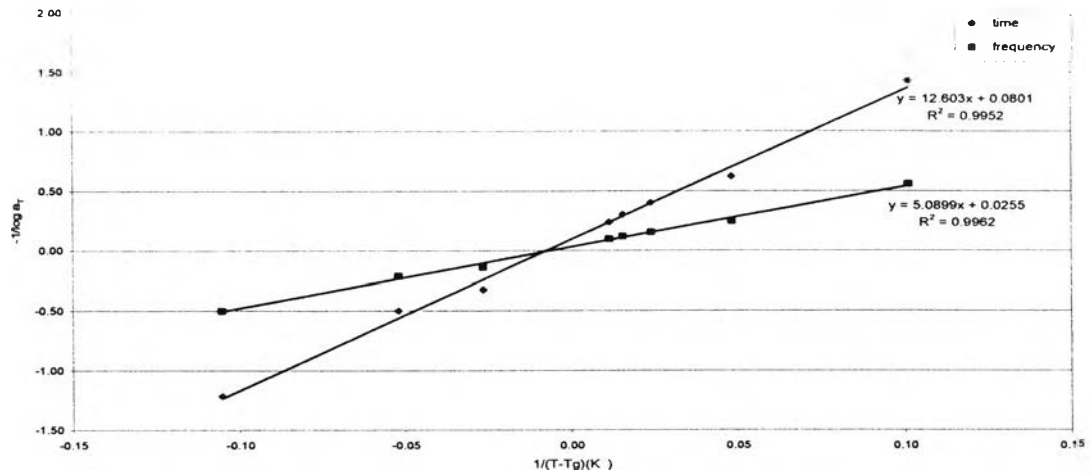**Figure 5.2.61** Relationship between -1/ log a_T versus $1/(T-T_g)$ for sPS1/PEMA

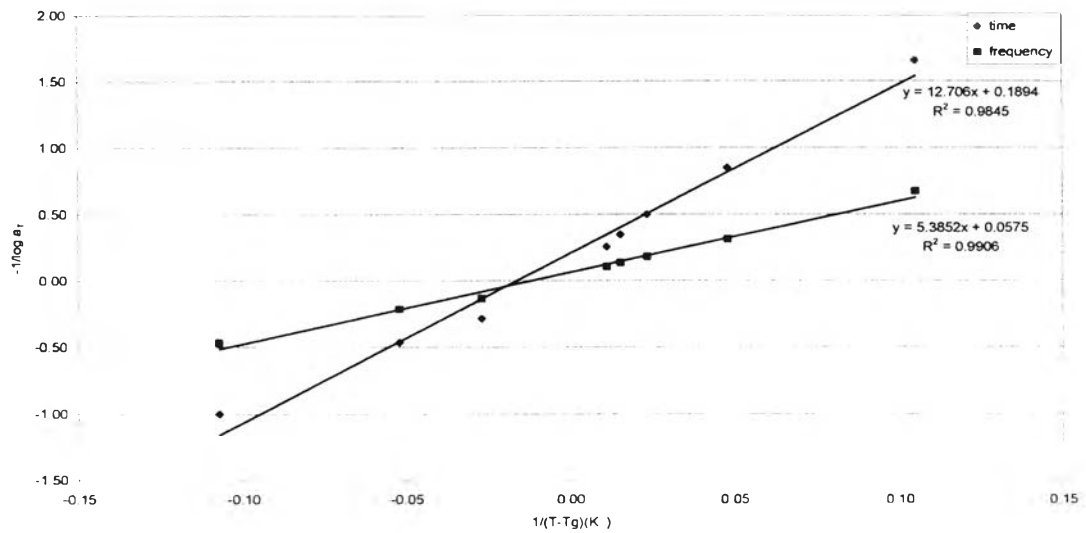**Figure 5.2.62** Relationship between -1/ log a_T versus $1/(T-T_g)$ for sPS2/PEMA

Figure 5.2.63 Relationship between -1/ log a_T versus $1/(T-T_g)$ for sPS1/PHMA

Figure 5.2.64 Relationship between -1/ log a_T versus $1/(T-T_g)$ for sPS2/PHMA
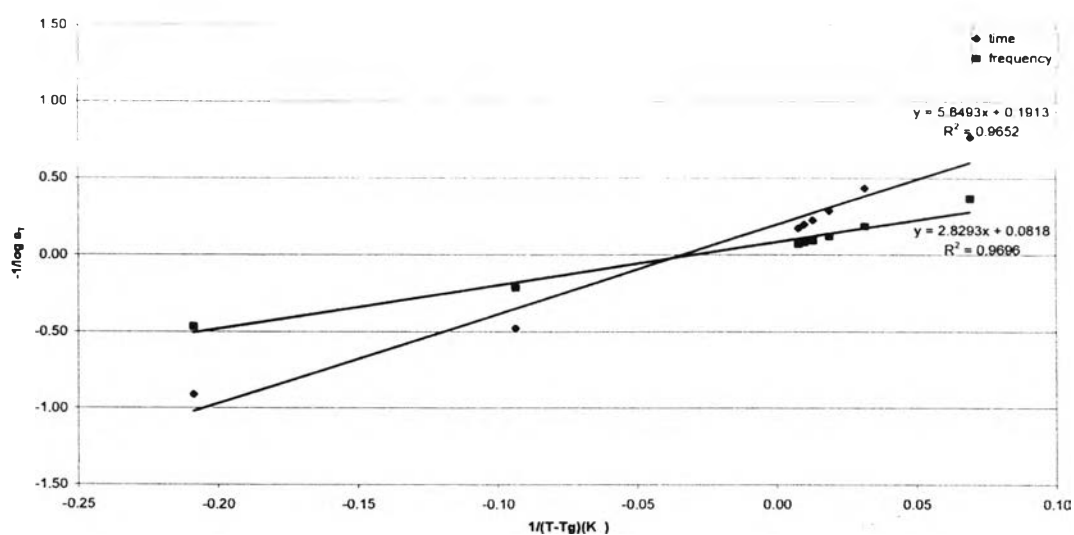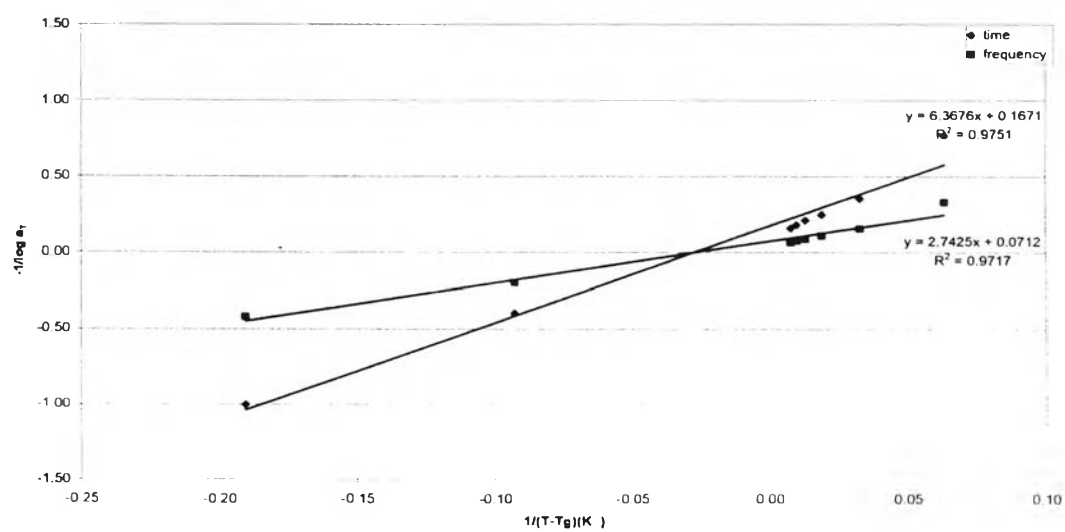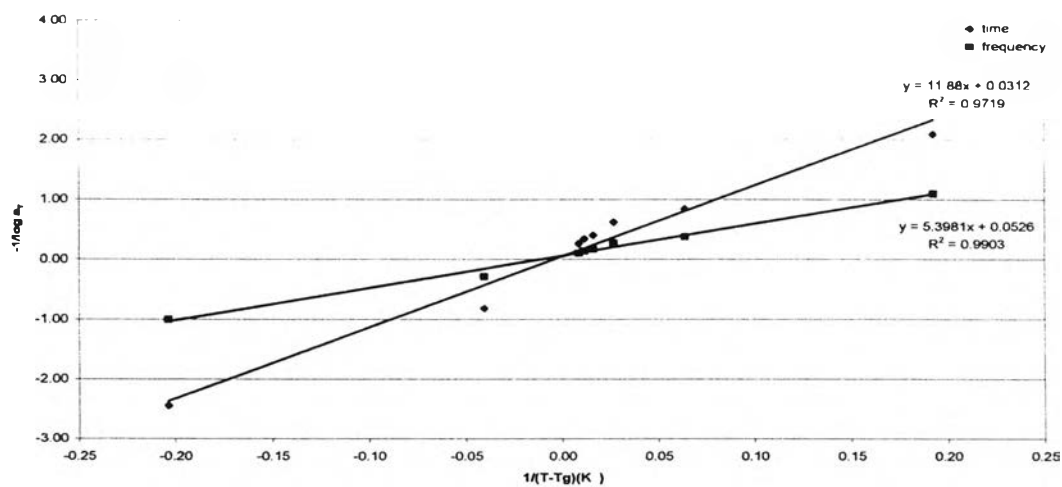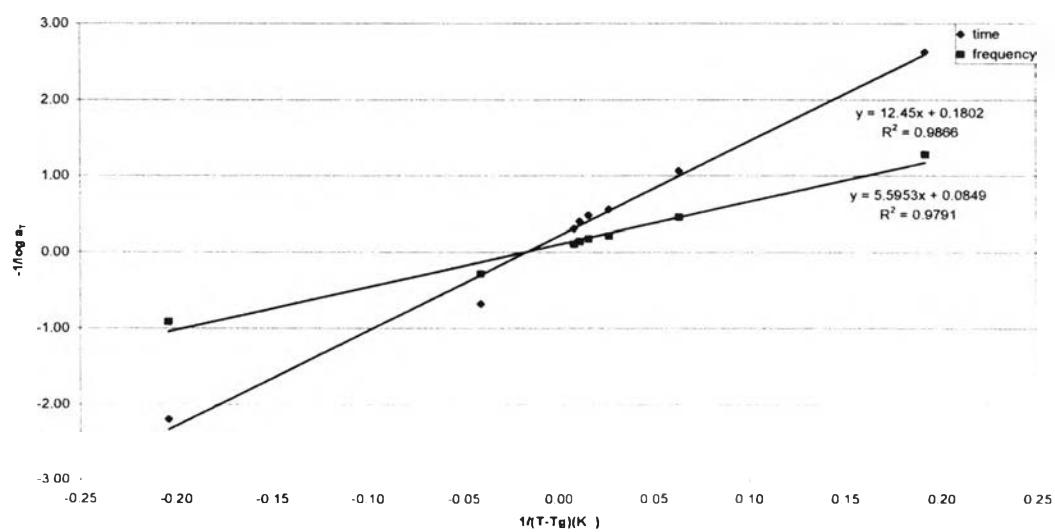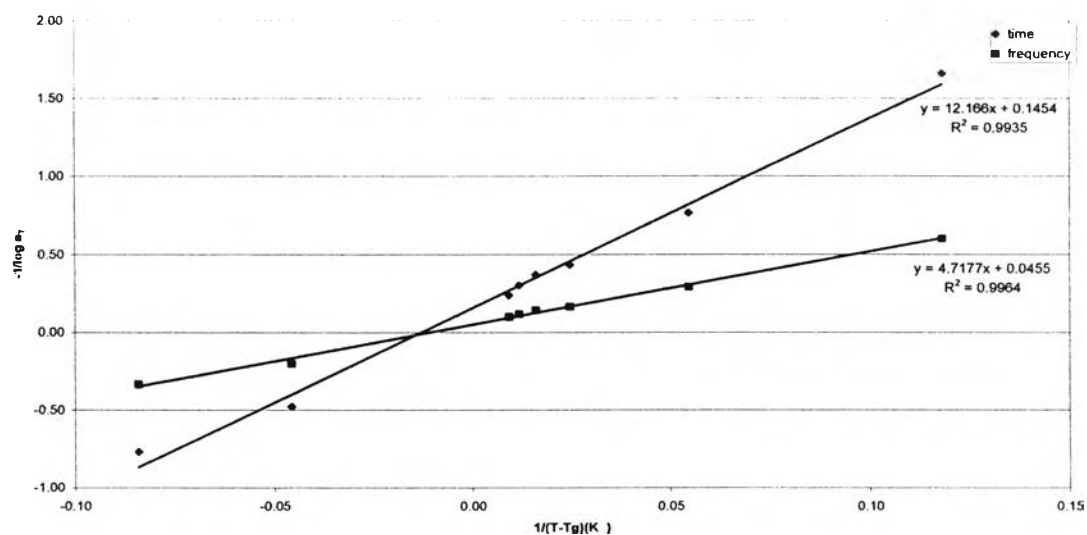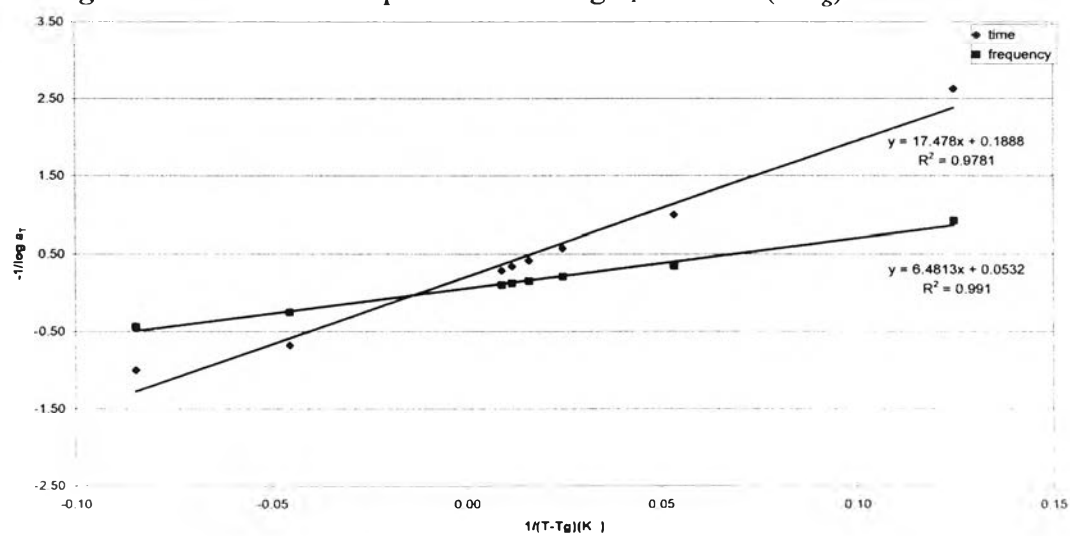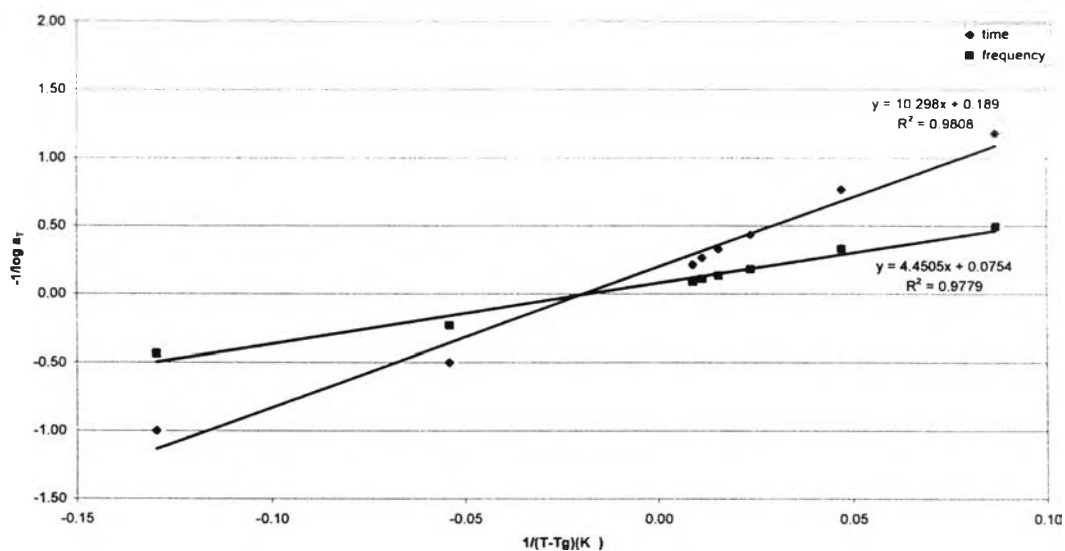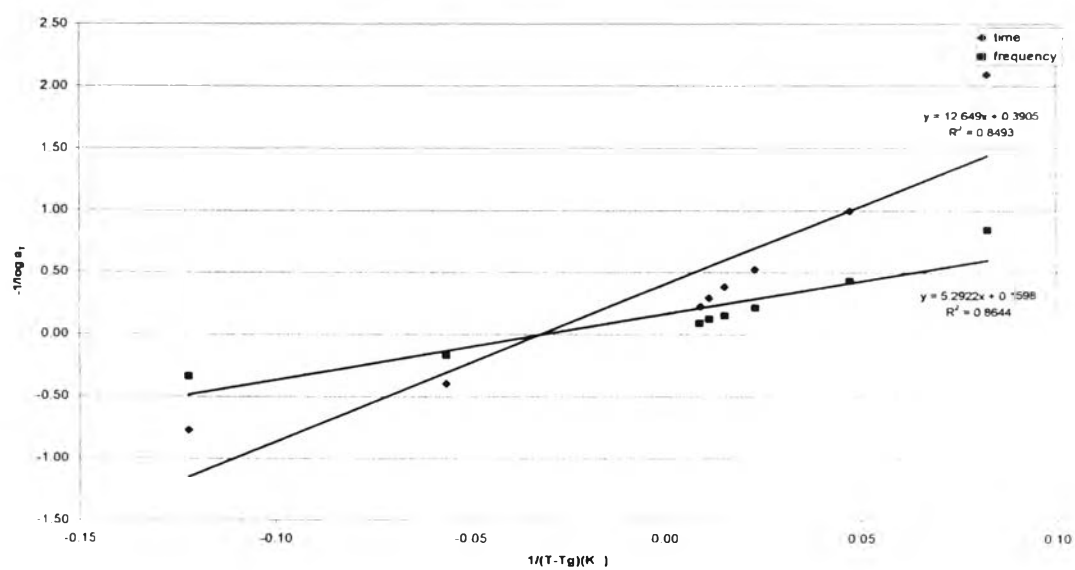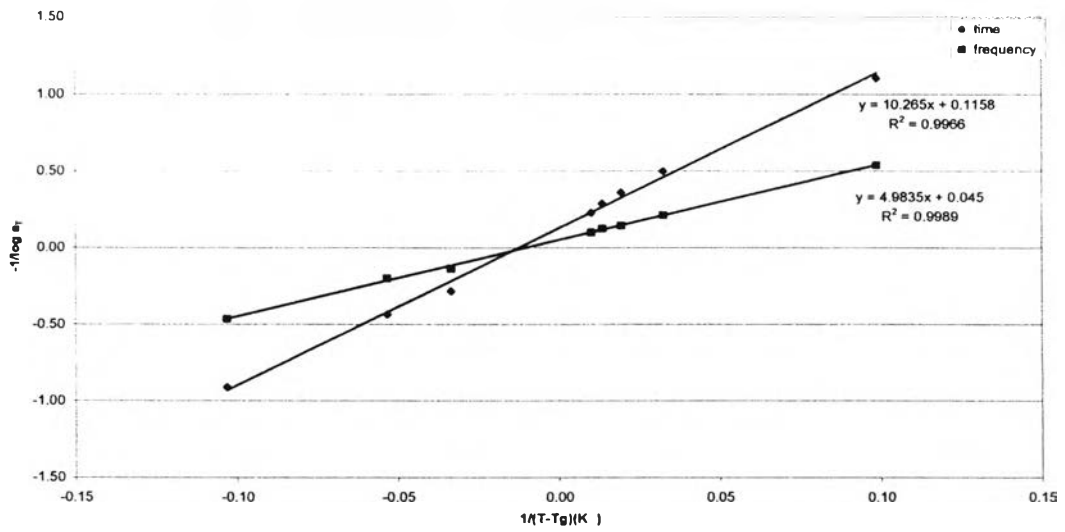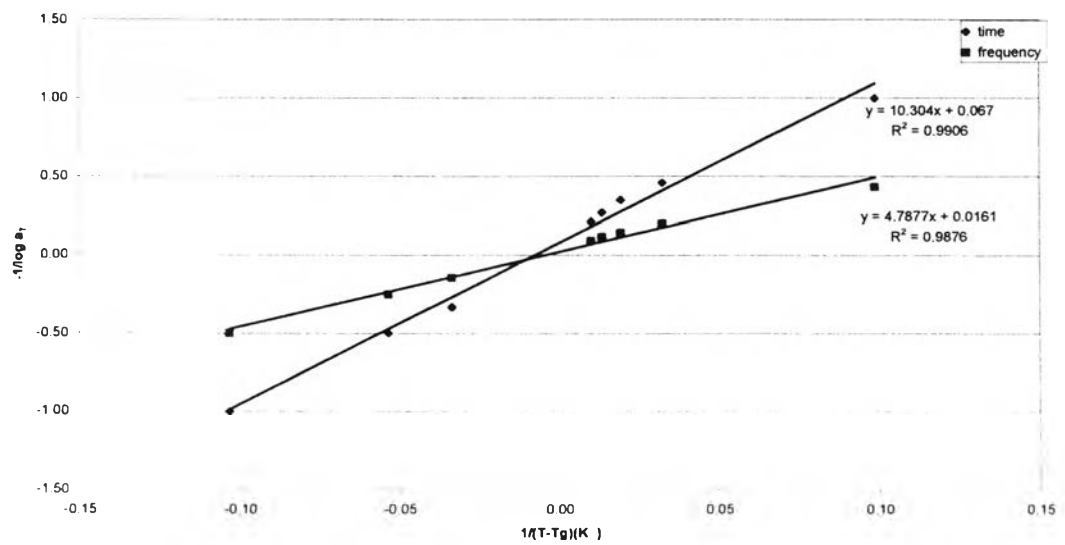
Figure 5.2.65 Relationship between -1/ log a_T versus $1/(T\text{-}T_g)$ for sPS1/PaMS

Figure 5.2.66 Relationship between -1/ log a_T versus $1/(T\text{-}T_g)$ for sPS2/PaMS

Table 5.2.1 C_1 and C_2 for pure sPS and all blend systems

System	Time dependence		Frequency dependence	
	C_1	C_2	C_1	C_2
sPS1	12.48	157.34	39.22	199.60
sPS1/PIP	5.23	30.58	12.22	34.59
sPS1/PBMA	32.05	380.77	19.01	102.63
sPS1/PEMA	6.88	83.67	21.98	103.69
sPS1/PHMA	5.29	54.49	13.26	59.03
sPS1/PaMS	8.64	88.64	22.22	110.74
sPS2	5.28	67.09	10.39	93.66
sPS2/PIP	5.98	38.11	14.04	36.16
sPS2/PBMA	5.55	69.09	11.78	65.90
sPS2/PEMA	5.30	92.57	18.80	121.83
sPS2/PHMA	2.56	32.39	6.26	33.12
sPS2/PaMS	14.93	153.79	62.11	297.37

5.2.6 Effect of blended polymer type

There are 5 systems for syndiotactic polystyrene of each molecular weight blend such as sPS/PIP, sPS/PBMA, sPS/PEMA, sPS/PHMA and sPS/PaMS blend systems. All blend systems were evaluated for the strength of sPS. It was the main purpose to developing sPS blend that stiffness and brittleness are lower than the pure sPS. Figure 5.2.67 and 5.2.68 show storage modulus (E') master curve as a frequency dependence for all the blend systems which have blended with the same molecular weight of sPS. Reference temperature for all blend sysytems were 100.25 °C.
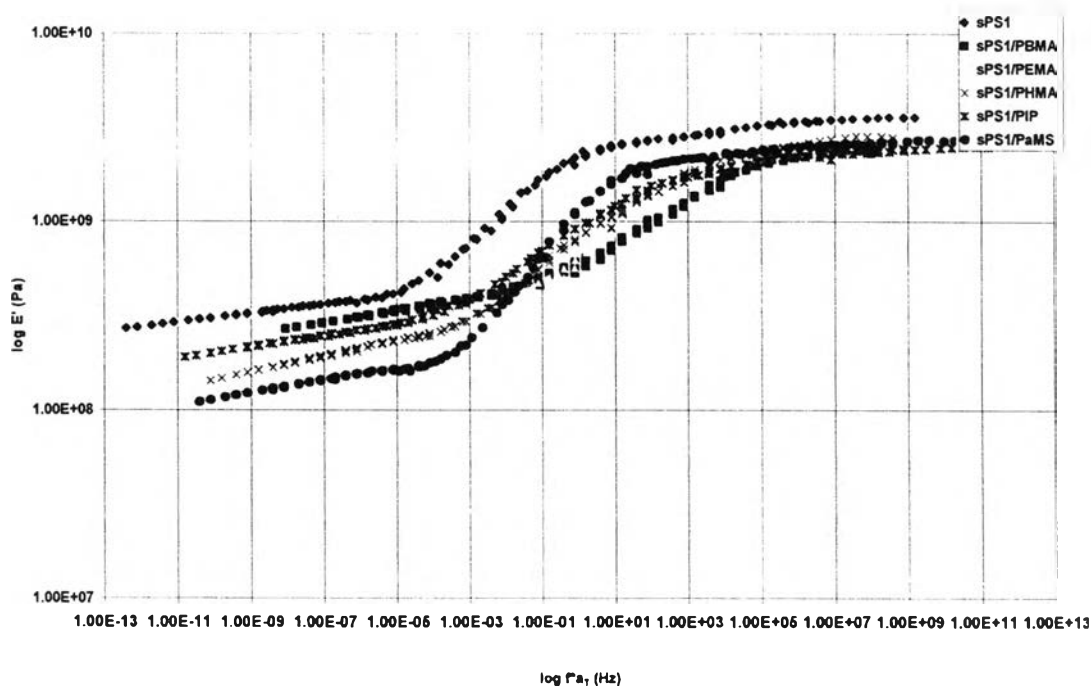
Figure 5.2.67 E' master curve for all sPS1 blend systems
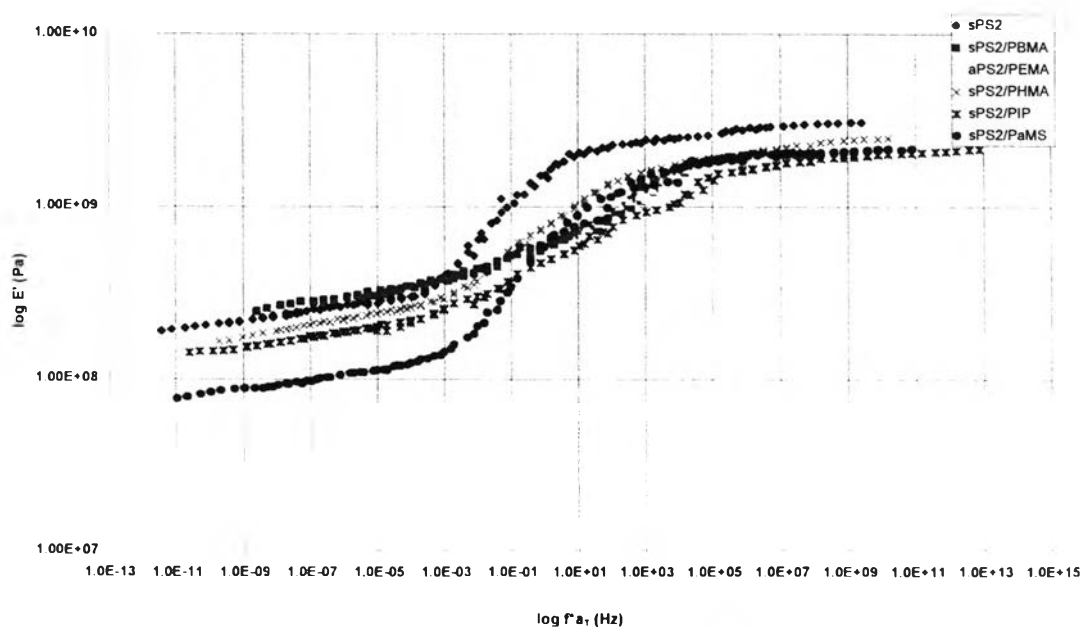

Figure 5.2.68 E' master curve for all sPS2 blend systems

From both Figures above, the storage modulus of pure sPSs were higher than all the blends systems for both sPS systems. All the partially miscible polymer blended with sPS can modify the mechanical property of sPS by reduction of stiffness. In each graph, the properties of the blend as a function of $\log f^*a_T$ can be

roughly divided into three sections of frequencies that are in range over 1×10^5, range between 1×10^{-3}-1×10^5 and range under 1×10^{-3} Hz. All the curves can be divided by same limits to grouping the similar behavior.

For sPS1 blend system, storage modulus of all blend systems was near or similar in the first range (high frequency range). At this range, the samples were applied by force with short time duration or high frequency; the situations can be compared with receiving the impact strength i.e. the samples are strike at short time by force. Second range, all the blend systems were changing by decreasing of storage modulus according with the decreasing in frequency. These decreasing changes will depend on the glass transition temperature and the steepness of the curves. Last range (low frequency range), storage modulus of four systems blends that are sPS1/PIP, sPS1/PBMA, sPS1/PEMA and sPS1/PHMA were similar in laying between pure sPS1 and sPS/PaMS. It can also be seen that these blended polymers show the first attributes of a rubbery plateau [28] for low frequency or long time.

For sPS2 blend system, all ranges have the same trend with sPS1 blend system but with the difference magnitudes. They showed the same behavior as the systems of sPS1 blend.

Moreover, then calculated average storage modulus difference ($\Delta E'_{avg}$) between that of pure sPS and that of blended polymer. Table 5.2.2 showed average storage modulus different of all blend systems for two sections.

$$\Delta E'_{avg} = E'_{sPS} - E'_{blended\ polymer} \qquad\qquad 5.2.3$$

Table 5.2.2 Average storage modulus difference of all blend systems for two sections

Range (Hz)	$\Delta E'_{avg}$ of sPS1 blend system				
	PIP	PBMA	PEMA	PHMA	PaMS
Over1×10^5	1.23E+09	1.18E+09	9.68E+08	7.88E+08	8.76E+08
Under1×10^{-3}	1.70E+08	1.35E+08	2.13E+08	2.36+08	2.92E+08

Table 5.2.2 *(Cont.)*

Range (Hz)	$\Delta E'_{avg}$ of sPS2 blend system (Pa)				
	PIP	PBMA	PEMA	PHMA	PaMS
Over 1×10^5	1.16E+09	8.81E+08	1.97E+09	7.59E+08	9.17E+08
Under 1×10^{-3}	8.51E+07	-2.74E+07	7.61E+07	6.89E+07	1.74E+08

Table 5.2.2 showed the $\Delta E'_{avg}$ of sPS1 and sPS2 blend systems for two ranges of frequencies. For sPS1 blend system, $\Delta E'_{avg}$ of sPS1/PIP and sPS1/PBMA blend systems were higher than the other blend systems at high frequency range (over 1×10^5 Hz) and the $\Delta E'_{avg}$ of sPS1/PaMS blend system was highest at low frequency range (under 1×10^{-3} Hz). The three systems mentions were less brittle than the other systems so the blends can improve mechanical property of sPS. For sPS2 blend system, $\Delta E'_{avg}$ of sPS2/PIP and sPs1/PEMA blend systems were higher than the other blend systems at high frequency range (over 1×10^5 Hz) and that of sPS1/PaMS blend system at low frequency range (under 1×10^{-3} Hz).