CHAPTER II

EXPERIMENTAL DETAILS

2.1 Materials

The polymers used in this work were polystyrene [PS] and poly(2,6-dimethyl-1,4-phenylene oxide) [PPO]. The commercial grade polystyrene used in this work, trade-name "SINGLITE", was purchased from the Thai Petrochemical Industry Co., Ltd. [TPI]. The molecular weight of PS, measured by using GPC technique, was found to be $M_w = 102,393$. The other polymer, PPO, was purchased from the Polysciences, Inc. The weight average molecular weight (M_w) and the number average molecular weight (M_n) of PPO, as given by the supplier, were 50,000 and 20,000, respectively.

The analytical grade toluene was used as the solvent of both polymers, PS and PPO. It was purchased from the Farmitalia Carlo Erba Company, Inc.

2.2 Sample Preparation

For measuring mechanical properties, physical aging, the blends of PS and PPO were used in the form of film. Both polymers, PS and PPO, were first dissolved in toluene as a stock solution with the concentration of 15 % weight/volume. The stock solution was warmed first to get a homogeneous solution before being diluted to become the 5 % solution used for preparing solutions of the blends.

The compositions of the blends were given on a volume fraction of PS and PPO solutions. Consequently, compositions were varied from 0 to 100 percent, by volume, for PPO and from 100 to 0 percent, by volume, for PS.

The blend solutions were slowly stirred and heated at 50 °C for 2 hours to get miscible blends in all proportions. The mixed solution was then poured onto a smooth surface glass plate.

To obtain homogeneous single-phase films, the glass plates contained solution were heated up to 65-70 °C until we obtained the dry films. These dried films were further treated by vacuum drying at 60 °C for 2 days for getting rid of the solvent which remained in the films after evaporation.

2.3   Experimental Techniques

T_g values were determined as a function of composition by differential scanning calorimetry (DSC) using the Du Pont Instruments, Thermal Analysis 2000.

The mechanical properties, creep, were measured by dynamic mechanical analysis (DMA) using the Perkin-Elmer DMA-7e.

Principle of DMA-7e

DMA technique is used to measure the change in mechanical behavior of a sample while it is subjected to a change in temperature, time, frequency, stress or a combination of these parameters. The schematic representation of DMA-7e themal analysis system is shown in fig. 2a.

DMA is widely used to study the properties of polymers and other materials under various experimental conditions in the temperature range from -200 to approximately 850 °C.
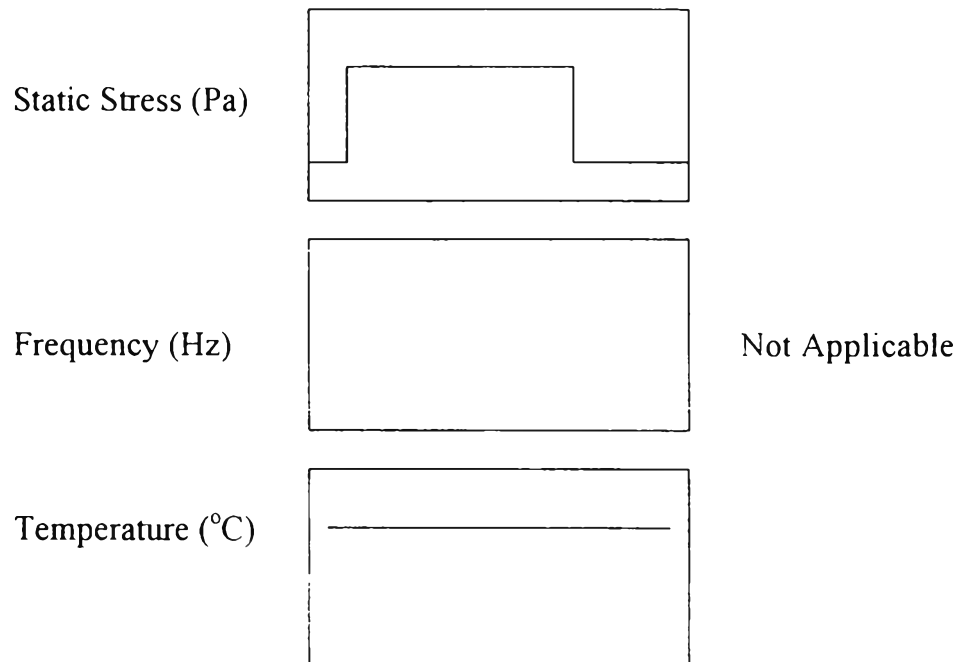

Static Stress (Pa)	
Frequency (Hz)	Not Applicable
Temperature (°C)	

Figure 2a   System creep-recovery mode.

In our experiment, the creep-recovery mode was operated for measuring creep. The film extension probe or holder was used as the measuring system.
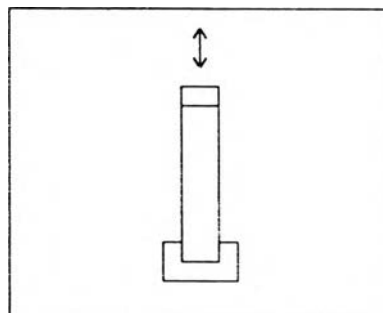

Figure 2b   Film extension.

Creep-Recovery of a Polymer

Creep is time-dependent strain observed when a viscoelastic material is subjected to a constant load and at a particular temperature. Recovery is the relaxation of strain observed when the load is completely or partially removed.

2.4 T_g Characterization

T_g values were determined on approximately 8 mg. samples hermetically sealed in aluminum pans, with the heating rate of 10 °C/min. The T_g values obtained from DSC are shown below :

Table 2.1 T_g values as a function of compositions.

Composition, % PPO	T_g, °C
0	72
10	77
30	92
50	100
70	110
90	137
100	194

As mentioned above that PS used in this word was of the commercial grade. A possible effect which cause the lower T_g of PS than the nominal value of 100°C is the unknown additives. It can be surmised that T_g of blends, made with this PS, were veered from the nominal values. For the pure PPO, of a high purity, T_g is close to the quoted value.
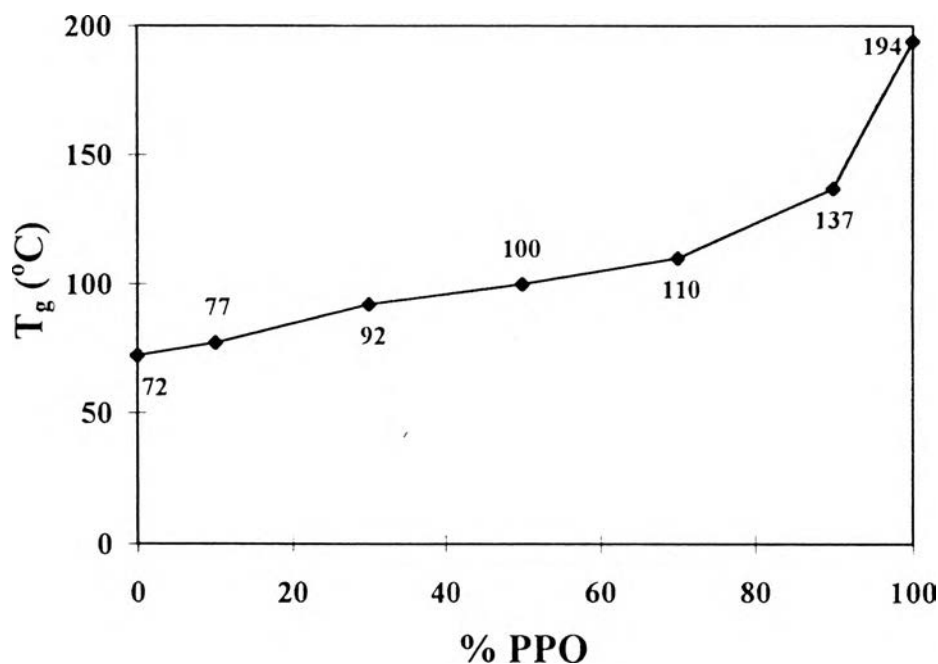
Figure 2c T_g values as a function of compositions.

2.5   Creep Measurements

To be sure that experiments were carried out in the linear viscoelastic region, the force scanning for each sample composition was carried out. The force rate was 500 mN/min and the force was applied from 0 to 200 mN.

The elongation of the sample was found to be proportional to the applied force in the force range of 90-200 mN. This indicates that the experiments could be carried out with the applied force within the range of 90-200 mN.

Experiments were performed with DMA. The sample films were used in rectangular shape with the width about 2.2 mm and 12.5 mm < length < 13 mm. The two ends of sample were tightly held by the film extension probe and stored in a furnace for temperature controlling.

The sample was annealed at temperature above T_g, $T_g + 10\ ^\circ C$, with the rate of 20 $^\circ C$/min to erase all thermal history and left at that temperature for 4 minutes. Then, the sample was quenched to the measuring temperature (T_a), $T_a = T_g - 12^\circ C$, and kept at that temperature for the isothermal creep measurement.

After keeping for a certain time (the aging time), the force (180 or 200 mN) was suddenly applied to the sample. And the strain was measured. The initial strain, $\varepsilon(0)$, was found by dividing the applied stress by the slope obtained from the force scanning, stress-strain curve.

By heating samples above T_g, as pointed out above, all previous thermal history is erased. In this way, several tests can be done with one sample, and the possible difficulty of differences in properties between different samples has been circumvented. The duration of creep experiments was limited to 10 % of the aging time [S. Vleeshouwers, A.M. Jamieson, and R. Simha; 1989].

It is very time consuming to have to heat and store the sample for every test. Struik [1978] suggests a more convenient procedure: once the sample is quenched, it is subjected to a series of creep experiments. The experiment with the shortest aging time is carried out first, and subsequent experiments are performed after increasing the aging time.

We examine the applicability of equation: $\varepsilon(t) = \varepsilon(0)\ \exp\ [(t/t_0)^\beta]$. To determine β, all curves were fitted to the above equation individually. For each curve individually, the parameter β and $\varepsilon(0)$ were calculated. The values for β for all curves were compared, and an average value was used for further fitting. With this average value for β, all data were again fitted to the above

equation, obtaining for every curve values for t_0 and $\varepsilon(0)$. All curves were superimposed, and then the generated master curve was compared with the above equation. Our results were found to produce more or less equivalent master curves [S. Vleeshouwers, A.M. Jamieson, and R. Simha; 1989].

Aging shift factors could be obtained. We used the t_0 values for creep curves of different t_a generated by fits to the master curve and computed the shift factor, a, as

$$a = t_0 (t_a) / t_0 (t_{a,ref}). \qquad (2.1)$$