

CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

2.1.1 Polymers

Two poly (methylmetacrylate) (PMMA's) of different molecular weights and a poly (styrene-acrylonitrile) (SAN), laboratory grade, were purchased from Polysciences Inc. U.S.A. The manufacturer's literature claims the molecular weights of 350000 and 75000 gram per mole for PMMA's where the content of styrene: acrylonitrile is 75:25 for SAN.

2.2.2 Solvent

Methyl Ethyl Ketone ($\text{CH}_2(\text{CH}_3)_2\text{CO}$), analytical grade, was purchased from Aldrich Chemical Company Inc. and used as solvent for preparing PMMA and SAN solutions.

2.2 Instruments

2.2.1 Rheometer

The rheometer (Rheometric Scientific Inc., model RES), parallel plate fixture, was used to measure viscoelastic moduli as functions of frequency, and the stress relaxation moduli as functions of time, at temperatures above and below the glass transition temperature, T_g .

2.2.2 Dynamic Scanning Calorimetry (DSC)

The dynamic scanning calorimetry, DSC, instrument (Netzsch instrument, model DSC 200) was used to determine the glass transition temperature, T_g , of the samples.

2.3 Methodology

2.3.1 Sample Preparations

2.3.1.1 *PMMA with 75000 grams per mole molecular weight.*

PMMA of molecular weight 75000 gmol^{-1} 10 grams was dissolved in ethyl methyl ketone, MEK, of 90 grams to obtain a solution of 10% w/w concentration. Then 80 ml of the solution were poured into a 10 cm diameter petridish and the solvent was evaporated slowly at 50°C for two days. To get rid of the trace amount of the solvent, the film was evaporated again in vacuum oven at 70°C for five days. Finally, a sheet of 0.86 mm thickness was cut into 25 mm diameter disk.

2.3.1.2 *PMMA with 350000 grams per mole molecular weight.*

PMMA of M_w 350000 gmol^{-1} 7.5 grams was dissolved in ethyl methyl ketone, MEK, of 92.5 grams to obtain the solution of 7.5 % w/w concentration. Then 120 ml of the solution were poured into a 10 cm diameter petridish and the solvent was evaporated slowly at 50°C for two days. To get rid of the trace amount of the solvent, the film was evaporated again in vacuum oven at 70°C for five days. Finally, a sheet of 1.07 mm thickness was cut into 25 mm diameter disk.

2.3.1.3 *SAN with styrene: acrylonitrile content 75:25.*

SAN with 75:25 styrene: acrylonitrile content 10 grams were dissolved in ethyl methyl ketone, MEK, of 90 grams to obtain the solution of 10 % w/w concentration. Then 90 ml of the solution were poured into a 10 cm diameter petridish and the

solvent was evaporated slowly at 50°C for two days. To get rid of the trace amount of the solvent, the film was evaporated again in vacuum oven at 70°C for five days. Finally, a sheet of 1.28 mm thickness was cut into 25 mm diameter disk.

2.3.1.4 PMMA/SAN blends. Binary blends containing SAN copolymer and PMMA were prepared. PMMA of M_w 75000 gmol^{-1} 10 grams was dissolved in ethyl methyl ketone, MEK, of 90 grams to obtain the solution of 10% w/w concentration. SAN with 75:25 styrene: acrylonitrile content of 10 grams were dissolved in ethyl methyl ketone, MEK, of 90 grams to obtain the solution of 10 % w/w concentration. Then the PMMA and SAN solutions were mixed together, and stirred slowly at room temperature for 24 hours. The mixture was poured into a 10 cm diameter petridish and the solvent was evaporated slowly at 50°C for two days. To get rid of the trace amount of the solvent, it was evaporated again in vacuum oven at 70°C for five days. Finally, a sheet of 1.14 mm thickness was cut into 25 mm diameter disk.

2.3.2 Rheological Measurements

Rheology is the science of deformation and flow of matter. It concerns with the response of materials to a mechanical force. That response may be irreversible flow, reversible elastic deformation, or a combination of both. The mechanical properties of an elastic solid may be studied by applying a stress and measuring the deformation of strain. By subjecting a polymer specimen to an oscillatory stress and determining the response, both elastic and viscous or damping characteristics can be obtained.

The shear stress modulus can be represented by a complex dynamic modulus G^* , which is the ratio of the complex stress and complex strain :

$$G^* = \sigma^*/\gamma^*. \quad (2.1)$$

The dynamic modulus can be resolved into two components :

$$G^* = G' + iG'', \quad (2.2)$$

where $|G^*| = \sqrt{(G')^2 + (G'')^2}$,

and $G' = G^* \cos \delta$,

$G'' = G^* \sin \delta$.

The ratio of G'' and G' give another measure of damping called the dissipation factor or loss tangent :

$$\tan \delta = G''/G' \quad (2.3)$$

2.3.2.1 Shear modulus In the rheological measurements a fixed strain was used at a given temperature, to ensure that measurements were taken well within the linear viscoelastic range of the materials investigated. To determine linear viscoelastic range of the materials, $G'(\gamma)$ and $G''(\gamma)$ were measured as functions of percent strain (γ) at a fixed temperature. Plots of $G'(\gamma)$ against (γ) and of $G''(\gamma)$ against (γ) show constant curves for an interval of γ . This range of γ implies the linear viscoelastic range of materials at that temperature. In order to choose an optimum strain, the highest strain amplitude which is somewhere within linear viscoelastic regime of glassy polymer (at the lowest measurement temperature) was chosen. The chosen strain amplitude is also in the linear viscoelastic regime of the rubbery polymer (at high temperature), and was used in the rheological measurement at all temperatures.

A model RES rheometer with 25 mm parallel plate fixtures was used to measure the isothermal dynamic storage and loss moduli data, $G'(\omega)$ and $G''(\omega)$, as functions of angular frequency (ω). The experimental frequency was varied from 0.01 - 100 rad/s, for each temperature. The range of temperature was from 60 to 190 °C. The strain values used were in the linear viscoelastic regime.

2.3.2.2 *Time-temperature superposition* Before constructing a master curve, the shift factors were determined empirically by a procedure as follows. First, a reference temperature T_0 somewhere within the range of the experiments was chosen (in our experiment, 190 °C). Then plots of $G' b_T$ ($b_T = T_0/T$) against $\log \omega$ and of $\tan \delta$ against $\log \omega$ at various temperatures were prepared. The horizontal distance between each pair of adjacent curve was measured and recorded as $\Delta \log a_T$. Where the values of $\Delta \log a_T$ from G' and $\tan \delta$ were the same within the reasonable error, the average was taken. The selected values of $\Delta \log a_T$ were then added progressively from T_0 to obtain $\log a_T$ at each temperature as shown in Table 2.1. Finally, plots of $G' b_T$ against $\log \omega a_T$ and of $\tan \delta$ against $\log \omega a_T$ at various temperatures were prepared and yield the G' and the $\tan \delta$ master curves respectively.

Table 2.1 Determination of a_T values for PMMA $M_w = 350000 \text{ gmol}^{-1}$

T(°C)	$b_T = T_0/T$	$\Delta \log a_T$		average $\Delta \log a_T$	$\log a_T$
		from G'	from tan δ		
190	1	0	0	0	0
180	1.0221	1.55	1.55	1.55	1.55
170	1.0451	0.70	0.56	0.63	2.18
160	1.0693	0.55	0.79	0.67	2.75
150	1.0946	0.41	0.3	0.35	3.10
140	1.1211	0.12	0.10	0.10	3.20
130	1.1489	0.11	0.33	0.21	3.41
120	1.1781	0.62	0.57	0.59	4.00
110	1.2089	0.48	0.24	0.30	4.30
100	1.2413	0.69	0.70	0.70	5.00
90	1.2755	0.59	0.40	0.50	5.50
80	1.3116	0.76	1.25	0.95	6.45

2.3.2.3 *Stress relaxation modulus* Before doing stress relaxation measurements, the linear viscoelastic range of materials was determined. The stress relaxation modulus, $G_R(t)$ was measured at many values of percent strain (γ) at a fixed temperature. The plots of $G_R(t)$'s against t showed nearly identical values for all times for a range of γ within the linear viscoelastic regime. A fixed γ in this range was chosen and used in the stress relaxation measurements.

The model RES rheometer with 25 mm diameter parallel plate fixtures was used to measure the isothermal stress relaxation moduli data $G_R(t)$ as functions of time, t . The experimental time ranged from 0 to 35 seconds for

each temperature. The range of temperature was 60 to 190 °C. The fixed strain values used were in linear viscoelastic regime.

The stress relaxation as functions of time (t) can be written by Kohlrausch equation [Palade et al. 1996] as :

$$G_R(t) = G_R(0)\exp[-(t/\tau^*)^\beta] \quad (2.1)$$

where $G_R(0)$ is the plateau modulus, τ^* is the effective relaxation time, and β is the coupling parameter or the bandwidth of the distribution spectrum of relaxation time, t .

β and τ^* at a fixed temperature were defined from a fit of the fractional exponential of Kohlrausch (equation 2.1) to the stress relaxation measurements. Ngai and Plazek (1986) stated that most of the terminal relaxation in entangled linear monodisperse polymer melt could all be fitted by equation 2.1 with β_η in the narrow range of 0.55-0.6. In the α relaxation region, the values of β_α are different depending on sample preparing conditions and different measurement techniques.

The plots of $\ln G_R(t)$ against t^β at trial β 's from the range given by Ngai and Plazek (1986) at each temperature yielded straight lines. β was chosen from a straight line with the best fitting coefficient. The slope of the straight lines give us $-(1/\tau^*)^\beta$. And τ^* was obtained from this slope. An example β and τ^* for PMMA $M_w = 75000 \text{ gmol}^{-1}$ at 130 °C is shown in Figures 2.1- 2.2. The result was $\beta_\eta = 0.39$ and $\tau^* = 1.0162 \text{ s}$.

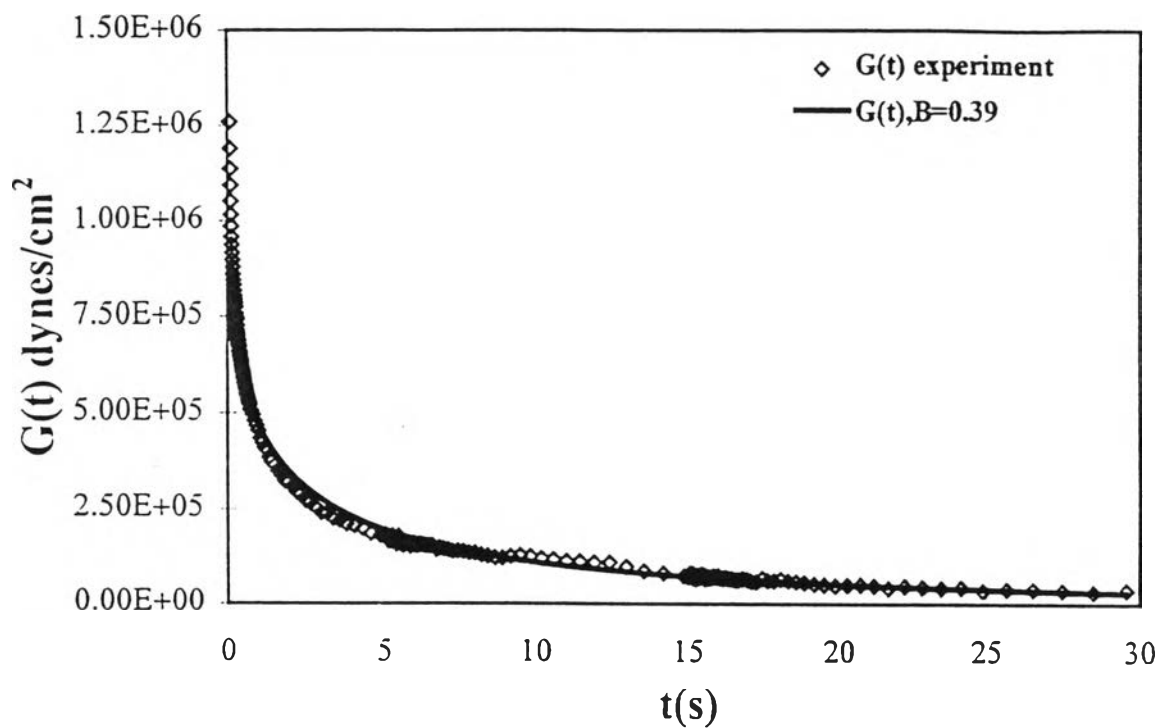


Figure 2.1 A fit of theoretical stress relaxation moduli, $G_R(t)$, for $\beta = 0.39$ to experimental data of PMMA $M_w = 75000 \text{ g mol}^{-1}$ at temperature $130 \text{ }^\circ\text{C}$.

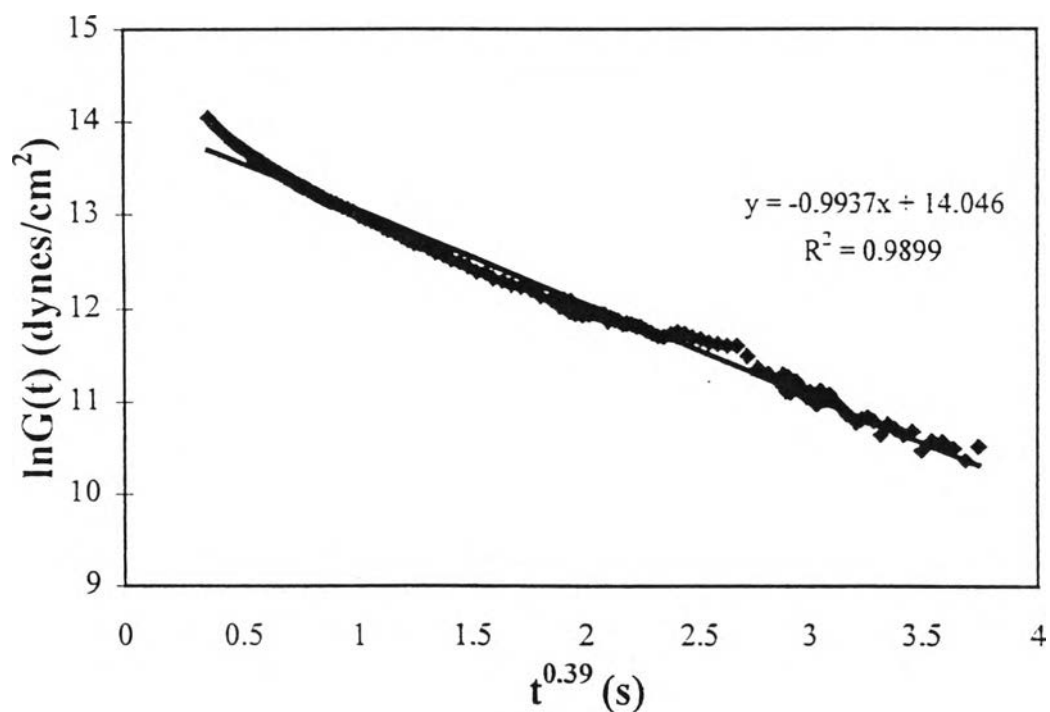


Figure 2.2 The plot of $\ln G_R(t)$ vs t^β of the data corresponding with figure 2.1.

2.3.3 Differential Scanning Calorimetry (DSC) Measurements

The glass transition temperatures, T_g 's (onset), of PMMA $M_w = 75000 \text{ gmol}^{-1}$, PMMA $M_w = 350000 \text{ gmol}^{-1}$, SAN with 75: 25 styrene: acrylonitrile content, and PMMA/SAN 30/70 blends were determined by differential scanning calorimetry, DSC. All the samples were annealed above T_g before each measurement. All DSC runs were made under a nitrogen atmosphere with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$.

The T_g 's (onset) of all the samples are shown in Table 2.2. The T_g 's of all the samples are measuring 85 to $100 \text{ }^\circ\text{C}$.

Table 2.2. The glass transition temperature (onset) of all the samples as determined by DSC

SAMPLES	T_g ($^\circ\text{C}$)
PMMA $M_w = 350000 \text{ gmol}^{-1}$	91.6
PMMA $M_w = 75000 \text{ gmol}^{-1}$	99.1
SAN 75: 25	88.0
PMMA/SAN 30/70 Blend	86.4