

CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

2.1.1 Polymers

The following polymers were used as homopolymers in this investigation: polyisoprene (PI), polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Poly(styrene-*b*-isoprene-*b*-styrene) triblock copolymer (SIS) was used as a compatibilizer in this work. All the polymers were used as supplied without any further purification. This study can be divided into two parts; in each part we examined ternary blends. The ternary blend systems are PS/P(S-*b*-I-*b*-S)/PI system and a PPO/P(S-*b*-I-*b*-S)/PI system.

The laboratory grade polystyrene (PS) was purchased from Polyscience, Inc. The molecular weight of PS was given from the supplier as 50,000.

Two polyisoprenes (PI) were used in this work. For convenience, these polymer are designated as PI-100 and PI-4 to indicate the molecular weight of their polymers. The polyisoprene (PI-100) was a commercial product of the Japan Synthetic Rubber Co., Ltd. The viscosity average molecular weight, $M_v = 9.23 \times 10^5$, was obtained from viscometric measurements. The synthetic, *cis* polyisoprene (PI-4) was purchased from Aldrich Chemical Company, Inc. The molecular weight characterization by GPC was given from the supplier as 40,000.

The laboratory grade poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was purchased from Polysciene, Inc. having a quoted molecular weight of 50,000.

The poly(styrene-*b*-isoprene-*b*-styrene) triblock copolymer used is a commercial product of the Shell Chemical Company. This material, Kraton D 1125P, had a styrene content of 30 % by weight. The molecular weight characterization by GPC was 74,700.

2.1.2 Solvents

The analytical grade toluene, used as the solvent for polystyrene/polyisoprene solutions was purchased from J.T. Baker.

The analytical grade chloroform, used as the solvent for poly(2,6-dimethyl-1,4-phenylene oxide)/polyisoprene solutions was purchased from Ajex Chemical.

2.2 **Instrumentation**

2.2.1 Rheometer

The rheometer, Rheometric Scientific Inc., (model RES), with the parallel plates fixture, was used to measure the alpha transition temperature (T_{α}), the relaxation spectrum ($H(\lambda)$), the shear modulus (G), the shear yield stress (τ_y) and the shear yield strain (γ_y) of our samples.

2.2.2 Scanning Electron Microscope (SEM)

Blends were imaged with scanning electron microscope (SEM), JEOL 5200 2AE(MP52001), with a magnification range of 35-200,000 times, to identify the fracture surface morphology of our samples.

2.2.3 Transmission Electron Microscope (TEM)

The morphology of the blends was measured using a transmission electron microscope (TEM), JEOL model JEM-200CX, with a magnification range of 100-330,000 times.

2.3 Methodology

2.3.1 Sample Preparations

2.3.1.1 *Preparation of PS/PI-100/SIS (40/60/x)^a blends system.*

Binary blends containing PS and PI homopolymers were prepared. PS with M_w 50000 g mol⁻¹ of 2 grams and PI-100 with M_v 1.0×10⁶ of 3 grams were dissolved in toluene, a non-selective solvent for polystyrene and polyisoprene (Winey et al.,1991) of 95 grams to obtain the solution of 5% w/w concentration. Ternary blends containing PS, PI homopolymers and SIS triblock copolymer were prepared. In the case of the samples PS/PI-100/SIS (35/55/10), PS, PI and SIS of weights 1.75, 2.75 and 0.50 grams respectively were dissolved in toluene of 95 grams to obtain the solution of 5%w/w concentration. For convenience, these polymer blends are designated further by PS/PI-100/SIS (40/60/10) to indicate the % w/w of the SIS triblock copolymer when the ratio of PS/PI-100 was fixed at 40/60.

Then the polymers solution were stirred mechanically for homogeneity at room temperature for two days. The polymer blend solution of 160 ml was poured onto an aluminium foil placed on a petridish whose diameter was 10 cm.

^a x is referred to % w/w of SIS triblock copolymer.

The solution was evaporated slowly at room temperature for a period of 10-12 days. Due to the glassy nature of the polystyrene, a small amount of solvent remained in the films; therefore, the films were placed in a vacuum oven at 70°C for at least 3 days to remove this solvent. Solvent removal was completely accomplished since the glass transition temperature of the pure polymers prepared this way was nearly the same as those of the virgin materials.

After the solvent was removed from the casted films, the polymer films were allowed to relax at the room temperature over a period of two days to remove any residual stress. Then the polymer films were carefully removed from the aluminium foil. Finally, films of 0.7-1.0 mm. thickness were cut into 25 mm diameter disks.

2.3.1.2 Preparation of PPO/PI-100/SIS (40/60/x)^a blends system. Binary blends containing PPO and PI homopolymers were prepared. PPO of M_w 50000 g mol⁻¹ of 1.2 grams and PI-100 of M_v 1.0×10⁶ of 1.8 grams were dissolved in chloroform at 50°C (Hashimoto et al., 1991) of 97 grams to obtain the solution of 3 % w/w concentration. Ternary blends containing PS, PI homopolymers and SIS triblock copolymer were prepared. In the case of the samples PPO/PI-100/SIS (35/55/10), PPO, PI and SIS of weights 1.05, 1.65 and 0.30 grams respectively were dissolved in chloroform of 97 grams to obtain the solution of 3%w/w concentration. For convenience, these polymer blends are designated further by PPO/PI-100/SIS (40/60/10) to indicate the %w/w of the SIS triblock copolymer when the ratio of PPO/PI was fixed at 40/60.

The solution was then stirred at room temperature for two days. The polymer blend solution of 160 ml was poured onto an aluminium foil placed on a petridish whose diameter was 10 cm. The solvent was slowly

evaporated over a period of 5-6 days at room temperature. The cast films was further dried in a vacuum oven for at least 1 week at 70°C. Testing for solvent removal was done in the same manner described above. After the solvent was removed from the cast films, the polymer films were allowed to relax at the room temperature over a period of two days to remove any residual stress. Then the polymer films were carefully removed from the aluminium foil. Finally, films of 0.6-0.9 mm. thickness were cut into 25 mm diameter disks.

2.3.2 Sample Characterization

Molecular weight can be simply determined by viscometric measurements. Molecular weights of samples used in this study were summarized in **Table 2.1**. Both K_m and a are specific values depending on range of molecular weight and type of polymers (Brandrugs et al., 1975).

Table 2.1 The average molecular weight (M_v) of the four polymers

Polymers	M_w^a	M_v^b	$K_m \times 10^3$ (ml/g)	a	$[\eta]$ (ml/g)
PS	50,000	49,920	9.2	0.720	22.21
PPO	50,000	50,808	48.3	0.640	49.63
PI-100	-	9.23×10^5	20.0	0.728	44.08
PI-4	40,000	35,466	8.51	0.770	27.12

^a quoted from the company.

^b Viscometric measurement.

For polymer solutions, the ratio η_{sp}/C exhibits a concentration dependence:

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{sp}/C) \quad (2.1)$$

where

- $[\eta]$ = intrinsic viscosity
- η_{sp} = specific viscosity
- C = concentration of polymer solution, mg/l.

The intrinsic viscosity $[\eta]$ is related to the molecular weight by the Mark-Houwink relation:

$$[\eta] = K_m M_v^a \quad (2.2)$$

where

- K_m = a parameter determined by the combination of polymer and solvent at a given temperature
- M_v = the viscosity average molecular weight
- a = the given polymer-solvent combination at constant temperature remains constant over a wide range of molecular weights

2.3.2.1 *The molecular weight of polystyrene (PS).* The constant K_m and a can be obtained empirically for a given polymer, solvent and temperature. From Chinai et al. (1956), for PS in toluene at 30°C, the constants K_m and a are 9.2×10^{-3} (ml/g) and 0.72 respectively. So

$$[\eta] = 9.2 \times 10^{-3} \text{ (ml/g) } M_v^{0.72}. \quad (2.3)$$

Intrinsic viscosity, $[\eta]$ was obtained from an extrapolation of the specific viscosity η_{sp} , divided by the concentration C_p , to zero concentration as shown in **Figure 2.1**.

We obtained the intrinsic viscosity, $[\eta]$, of 22.20997 ml/g. Thus the viscosity average molecular weight of PS is 49,920.

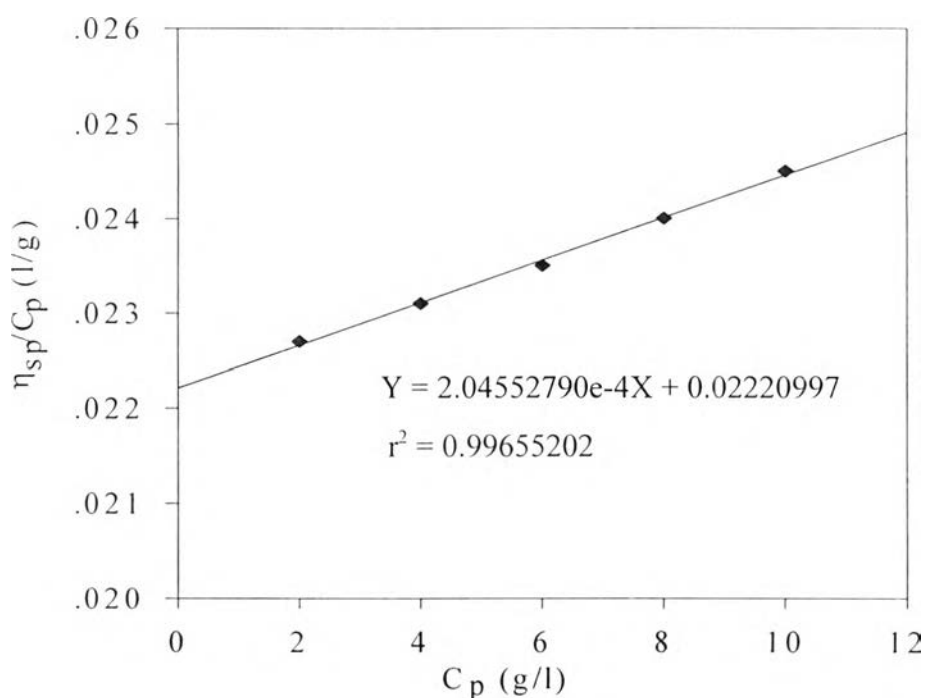


Figure 2.1 Schematic of a plot of η_{sp}/C_p and extrapolation to zero concentration to determine $[\eta]$. The polymer was PS.

2.3.2.2 *The molecular weight of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO).* The constant K_M and a can be obtained empirically for a given polymer, solvent and temperature. From Barrales-Rienda and Pepper (1966), for PPO in chloroform at 25 °C, the constants K_M and a are 48.3×10^{-3} (ml/g) and 0.64 respectively. So

$$[\eta] = 48.3 \times 10^{-3} (\text{ml/g}) M_v^{0.64}. \quad (2.4)$$

Intrinsic viscosity, $[\eta]$ was obtained from an extrapolation of the specific viscosity η_{sp} , divided by the concentration C_p , to zero concentration as shown in **Figure 2.2**.

We obtained the intrinsic viscosity, $[\eta]$, of 49.6300171 ml/g. Thus the viscosity average molecular weight of PPO is 50,808.

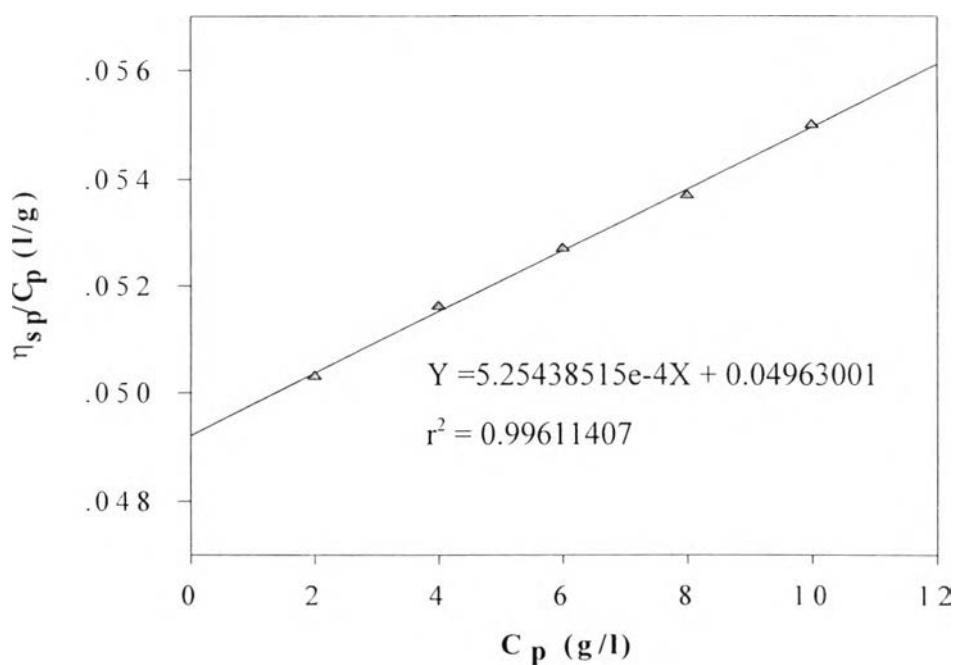


Figure 2.2 Schematic of a plot of η_{sp}/C_p and extrapolation to zero concentration to determine $[\eta]$. The polymer was PPO.

2.3.2.3 *The molecular weight of polyisoprene (PI-100).* The constant K_{η} and a can be obtained empirically for a given polymer, solvent and temperature. From Beattie and Booth (1963), for PI in toluene at 30°C, the constants K_{η} and a are 20.0×10^{-3} (ml/g) and 0.728 respectively. So

$$[\eta] = 20.0 \times 10^{-3} \text{ (ml/g)} M_v^{0.728}. \quad (2.5)$$

The intrinsic viscosity was 44.081 ml/g. Thus the viscosity average molecular weight of PI-100 was 9.25×10^5 (Pokaew et al., 1997).

2.3.2.4 *The molecular weight of polyisoprene (PI-4).* The constant K_{η} and a can be obtained empirically for a given polymer, solvent and temperature. From Abe et al. (1969), for PI in toluene at 30°C, the constants K_{η} and a are 8.51×10^{-3} (ml/g) and 0.77 respectively, So

$$[\eta] = 8.51 \times 10^{-3} \text{ (ml/g)} M_v^{0.77}. \quad (2.6)$$

Intrinsic viscosity, $[\eta]$ was obtained from an extrapolation of the specific viscosity η_{sp} , divided by the concentration C_p , to zero concentration as shown in **Figure 2.3**.

We obtained intrinsic viscosity, $[\eta]$, of 27.12 ml/g. Thus the viscosity average molecular weight of PI-4 is 35,466.

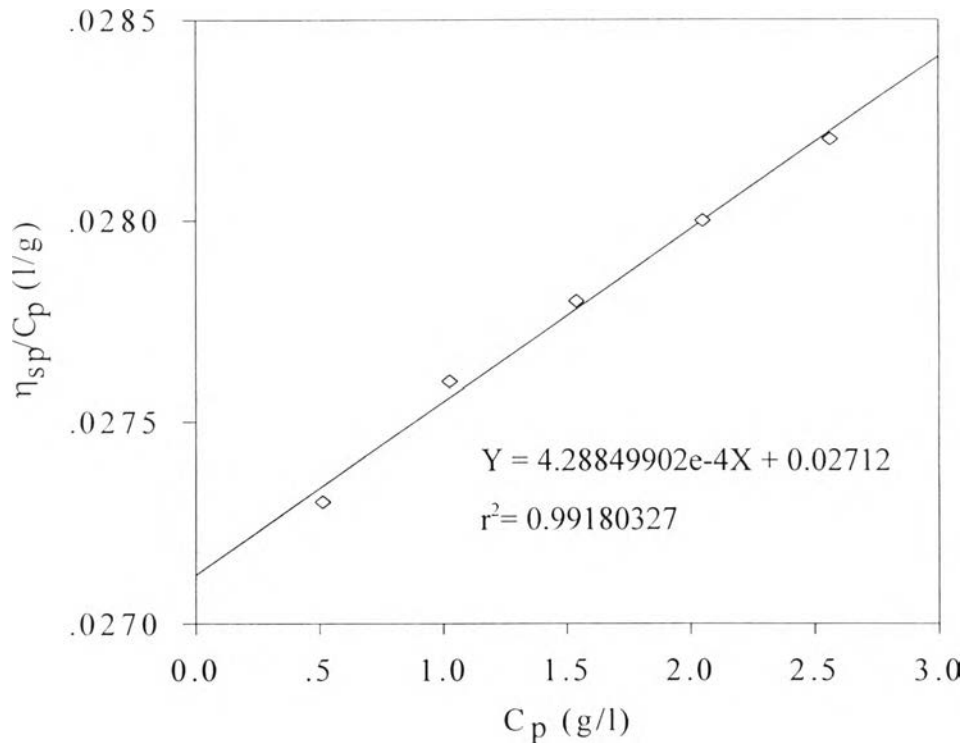


Figure 2.3 Schematic of a plot of η_{sp}/C_p and extrapolation to zero concentration to determine $[\eta]$. The polymer was PI-4.

2.3.3 Rheological Measurements

Principle

This instrument is a mechanical spectrometer that is capable of subjecting a sample to either a dynamic (sinusoidal) or steady (linear) shear strain (deformation), then measuring the resultant torque expended by the sample in response to the shear strain. Shear strain is applied by the motor, torque is measured by the transducer.

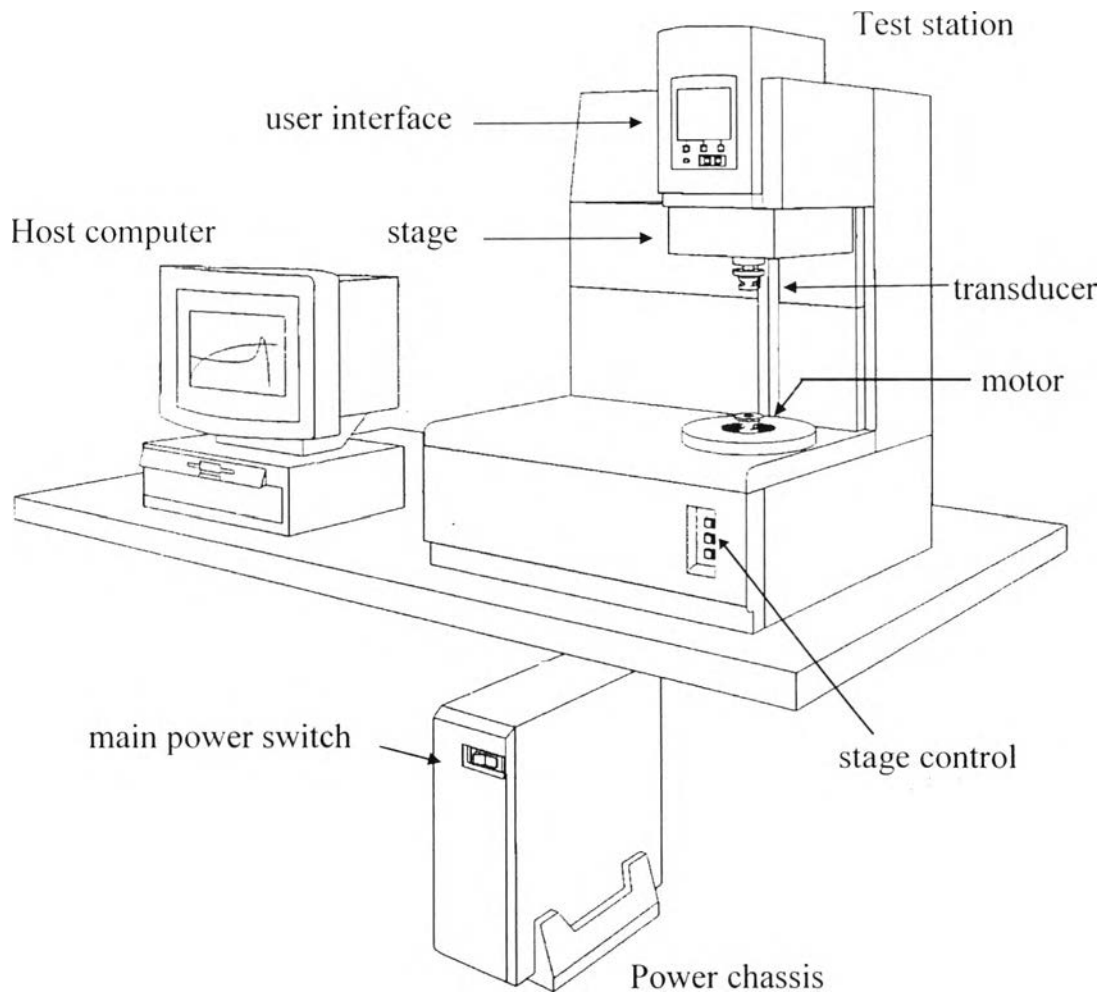


Figure 2.4 Instrument components.

Rheology is the science that studies the deformation and flow of materials. It concerns with the response of materials to a mechanical force, in term of the material's elasticity and viscosity. Elasticity is the ability of a material to store deformation energy. Viscosity is a measure of a material's resistance to flow and reflects the rate of dissipation of deformational energy through flow.

2.3.3.1 *Alpha transition temperature (T_α)*. Dynamic mechanical testing was used to obtain T_α of our samples. This testing measures the response of a material to a sinusoidal or other periodic stress. Since the stress and strain are generally not in phase, two quantities can be determined : a modulus and a phase angle or a damping term.

Dynamic mechanical results are generally given in terms of complex moduli. The complex moduli are defined by

$$G^* = G' + iG'' \quad (2.7)$$

where G^* is called the complex shear modulus, G' is called the storage modulus, G'' , the loss modulus and i is the imaginary unit ($i = \sqrt{-1}$).

The ratio of the loss modulus to the storage modulus is the tangent of the phase angle shift δ between the stress and the strain. Thus

$$G'' / G' = \tan \delta \quad (2.8)$$

This measures the damping ability of the material. $\tan \delta$, a damping term, is a measure of the ratio of energy dissipated as heat to the maximum energy stored in the materials during one cycle of oscillation.

The dynamic mechanical behavior of an ideal polymer is illustrated in **Figure 2.5**.

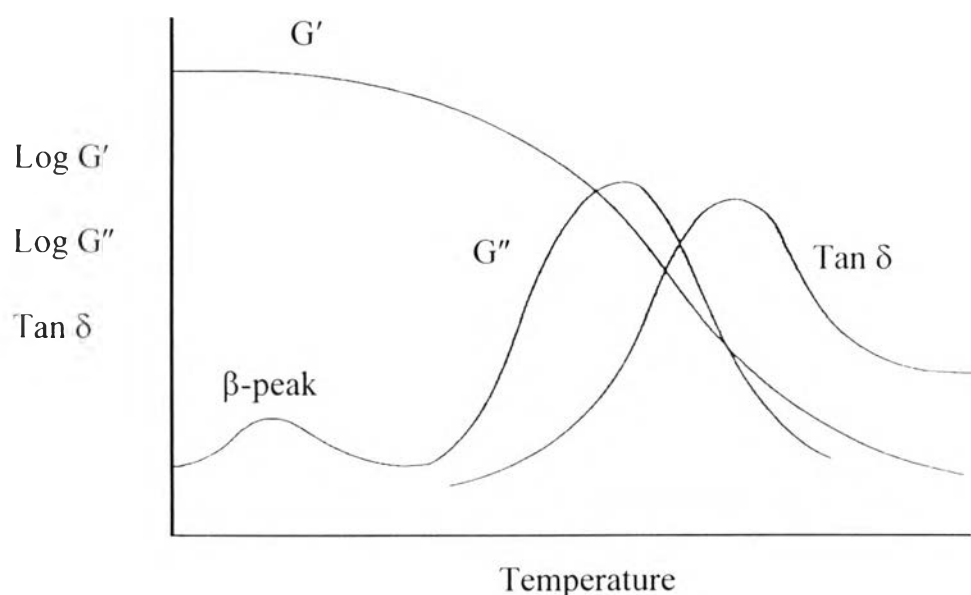


Figure 2.5 The dynamic mechanical behavior of an ideal polymer.

The maxima in G'' and $\tan \delta$ are sometimes used as the definition of T_{α} . For the α -transition, the portion of the molecule excited comprises from 10 to 50 atoms or more (Brandruys and Immergut, 1975). The width of the transition and shifts in the peak temperatures of G'' or $\tan \delta$ are sensitive guides to the exact state of the material, molecular mixing in blends and so on (Sperling, 1993).

Procedures

The measurements were performed on a rheometer, Rheometric Scientific model RES using 25-mm.diameter parallel plate test fixtures in the temperature step mode at a constant frequency of $1 \text{ rad}\cdot\text{s}^{-1}$ and soak time of 3 min before each measurement. The sample film was cut into a dish shape of 25 mm in diameter and 0.6-1.0 mm in depth. Strain sweep experiment was performed at constant frequency (ω) and temperature to ensure linear viscoelasticity behavior in which G' and G'' are independent of strain. From

this experiment at constant ω (1 Hz) and T (30°C), a small strain values in the linear viscoelastic range (0.1-5.0%) was chosen.

In the temperature step mode, G'' was measured as a function of temperature at a heating rate of 2-3°C/min. The range of temperature was from -80°C to 150°C for PS/PI/SIS blends and -80°C to 250°C for PPO/PI/SIS blends. This temperature range is well above the glass transition temperatures reported earlier for these materials¹. Low temperature (-80 to 25°C) was attained by cooling with liquid nitrogen. High temperature (25 to 250°C) was attained by a controlled air heater.

2.3.3.2 Stress relaxation ($G(t)$) and Relaxation spectrum ($H(\tau)$).

Principle

Stress relaxation is the most fundamental transient experiment used for characterizing the viscoelastic properties of such materials. A stress relaxation test consists of suddenly applying a strain to the sample, and following the stress as a function of time as the strain is held constant. When the Maxwell element, as illustrated in **Figure 2.6**, is strained instantaneously, only the spring can respond initially to a stress of $G\gamma_0$, where γ_0 is the constant applied strain and G is the elastic modulus.

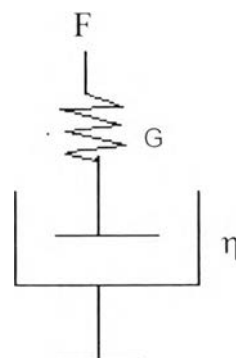


Figure 2.6 Maxwell model.

The extended spring then begins to contract, but the contraction is resisted by the dashpot. The more the spring retracts, the smaller is its restoring force, and the rate of retraction drops correspondingly. Solution of the differential equation with $\dot{\gamma} = 0$ and the initial condition $\tau = G\gamma_0$ at $t = 0$ shows that the stress undergoes a first order exponential decay:

$$\tau(t) = G\gamma_0 e^{-t/\lambda} \quad (2.9)$$

where γ_0 is the constant, initial applied strain, G the elastic modulus, τ the stress and λ the relaxation time. In terms of a *relaxation modulus*, $G_r(t) \equiv \tau(t)/\gamma_0$, So

$$G_r(t) \equiv \tau(t)/\gamma_0 = G e^{-t/\lambda} \quad (2.10)$$

Again, the relaxation modulus $G_r(t)$ is a more general means of representing stress relaxation response because it is independent of the applied strain for linear materials (Rosen, 1993).

In most cases, the stress relaxation behavior of polymers cannot be described by the Maxwell model. The flow process normally extends over a much wider time interval than predicted by Eq. (2.11). Thus, for polymers a single relaxation time is not sufficient in describing the relaxation behavior. By coupling a number of Maxwell models in parallel the time region of flow can be broadened. The corresponding stress time relation of this generalized model is given as

$$G_r(t) = G_\alpha \gamma_0 + \gamma_0 \sum_{i=1}^n G_i e^{-t/\lambda_i} \dots\dots\dots(2.11)$$

Here G_i is the modulus of the i :th Maxwell model and λ_i the corresponding relaxation time. The term $G_\alpha \gamma_0$ denotes the stress level approached after very long times.

A more practical description of the relaxation process is achieved by introducing a continuous distribution of relaxation times. Equation (2.13) then takes in the following form

$$G_r(t) = G_\alpha \gamma_0 + \gamma_0 \int_{-\infty}^{\infty} H_d(\lambda) e^{-t/\lambda} d \ln \lambda \quad (2.12)$$

where $H_d(\lambda) = \lambda G(\lambda)$ is the distribution of relaxation times λ (the relaxation spectrum) (Brostow and Corneliusen, 1989).

Procedures

Relaxation spectrum ($H(\tau)$) measurements were carried out in a rheometer, model RES with 25 mm diameter parallel plate test fixtures in stress relaxation mode. The sample film was cut into a dish shape of 25 mm in diameter. Before doing stress relaxation measurements, the linear viscoelastic range of materials was determined by using strain sweep mode at constant ω ($\omega=1 \text{ Hz}$) and T ($T=50^\circ\text{C}$). The stress relaxation modulus, $G(t)$ was measured at many values of percent strain (γ) at a fixed temperature ($T=50^\circ\text{C}$). The plots of $G(t)$'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 ($\gamma=0.4\%$) and used in the stress relaxation measurements. The experimental time ranged from 0 to 1000 seconds.

2.3.3.3 Stress-Strain Tests.

Principle

In stress strain tests, the buildup of force (or stress) is measured as the specimen is being deformed at a constant rate. Occasionally, stress-strain tests are modified to measure the deformation of a specimen as the force is applied at a constant rate. Also, since a polymer's properties are time dependent, the shape of the observed curve will depend on the strain rate and temperature.

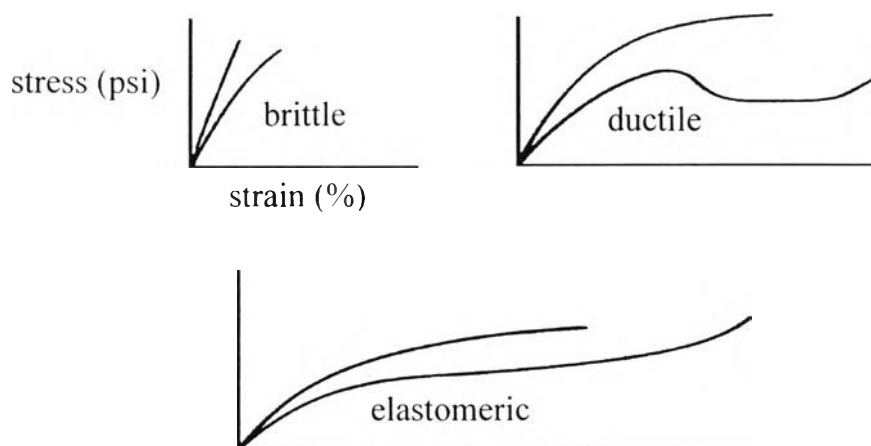


Figure 2.7 Variation in stress-strain behavior of polymers as measured at a constant rate of strain.

The relationship between stress and strain can be given by an equation (2.13).

$$F/A = \sigma = E\varepsilon \quad (2.13)$$

where F is the force, A is the cross-sectional area, σ is the stress (force divided by area), ε is the strain, and E is the proportionality factor which is called the

modulus, sometimes referred to as *Young's modulus* for the tensile stress case. The modulus is the slope of the stress strain curve. If the modulus is large (corresponding to a steep angle of the curve), the material resists deformation strongly. Such materials are said to be *stiff*.

In a shear test, the equation describing the stress strain curve are of the same form with tensile but difference in symbols. The stress-strain equation is given in Equation (4.12) as follows:

$$\tau = G\gamma \quad (2.14)$$

where τ is the shear stress, G is the shear modulus, γ is the shear strain.

Yield stress, σ_y is the 0.2% offset yield stress that was obtained from the initial slope of the stress-strain curve with a line parallel to this which is offset by 0.2% from the origin. **Figure 2.8** shows the definition and determination of the yield stress and the yield strain.

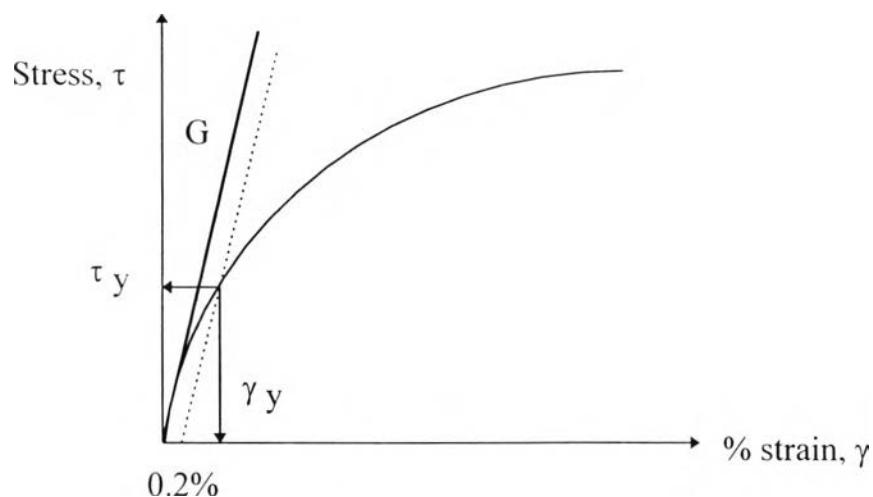


Figure 2.8 0.2% offset yield stress and yield strain on the stress-strain curve.

Procedures

A model RES rheometer with 25 mm parallel plate test fixtures was used to measure the stress-strain tests in the step rate test mode. The sample was cut into a dish shape of 25 mm in diameter. The experimental temperature was 25 °C. The experimental shear rate was 0.05 s⁻¹ for PS/PI blends. The experimental shear rate was 1.0 s⁻¹ for PPO/PI blends. Both shear rate are in linear viscoelastic behavior. The range of time was from 0-10 seconds for each measurements.

2.3.4 Morphology Measurements

2.3.4.1 *Scanning Electron Microscope (SEM).*

Principle

The principle of scanning electron microscope is illustrated in **Figure 2.9**. A finely focused electron probe scans the specimen surface and the secondary and backscattered electrons, etc., are emitted from the specimen surface. These signals are then detected and fed to a detector. This detector is composed of secondary electron correction electrode (collector), scintillator and photomultiplier tube (PMT). The signal intensities of secondary electron and backscattered electron are converted to intensity of light by scintillator, and then converted into electrical signals and amplified with PMT. Finally, a specimen image is displayed on the cathode ray tube (CRT) screen and photographs the image was photographed with a camera.

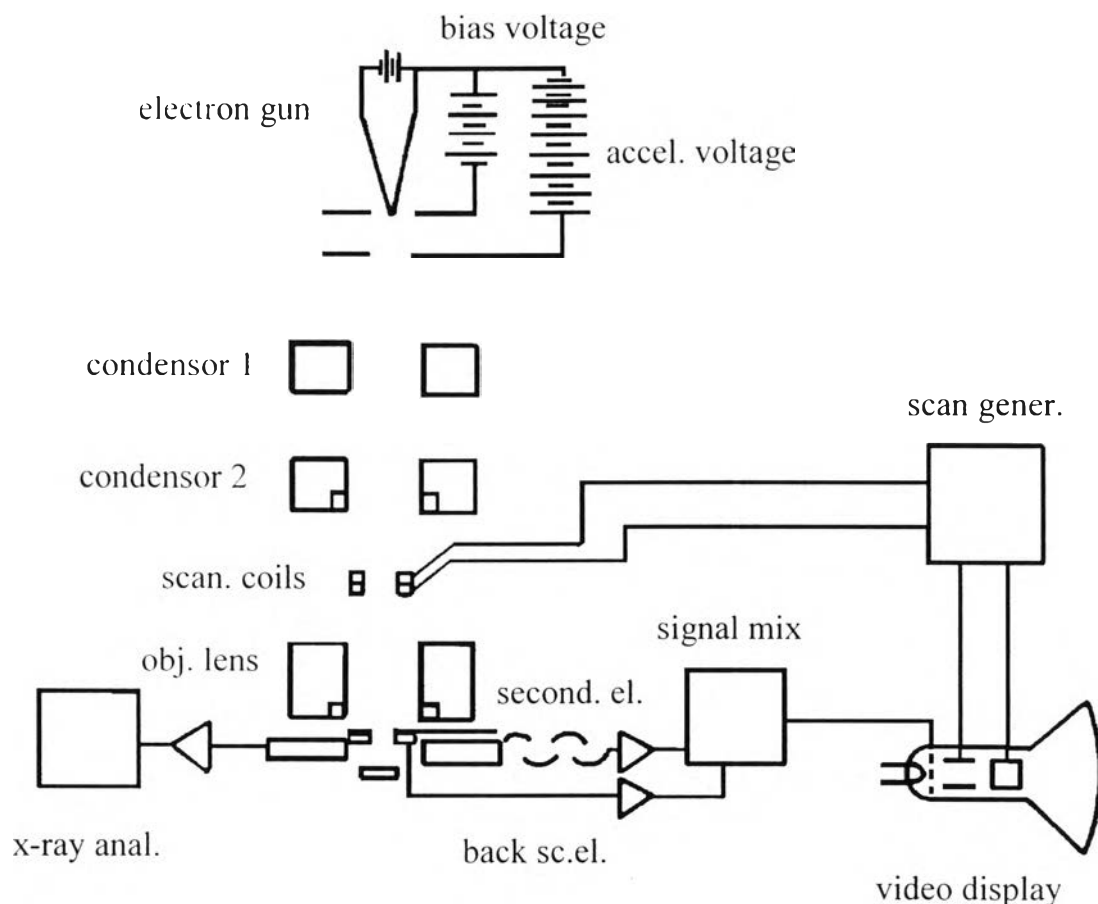


Figure 2.9 Schematic diagram of a scanning electron microscope (SEM).

Procedures

The sample films to be examined, chosen carefully from an ensemble of many samples, were then fractured by manual methods, after immersion in liquid nitrogen. The fractured specimen was placed on double sided sticky tape on a specimen stub, then coated with gold for 4 min. to obtain a thickness of approximately 300 \AA . Coated sample morphology was observed in a cross sectional view perpendicular to the fracture surface, using an accelerating voltage of 10-15 kV and 200-1500 times magnification. The digitized pictures from the specimen at various magnifications were taken with

the SemAfore program. Then the saved digitized pictures were printed out directly from the computer.

2.3.4.2 *Transmission Electron Microscope (TEM).*

Principle

The principle of transmission electron microscope is illustrated in **Figure 2.10**. A narrow electron beam scans the specimen surface are provided by the electron gun. The current density of the electron beam can be controlled by the gun bias, condenser lens aperture and defocus of the condenser lense. The specimen stage is placed in the center of the objective lens which is used for focusing. The magnification is obtained by two projective lenses. The intermediate lens also provides some magnification but is mainly used to change the focusing point from the specimen (image) to the back focal plane of the objective lens (diffraction). The objective lens aperture is used to cut off the scattered or diffracted beams and thus enhancing area. The image is viewed on a fluorescent screen which converts electron energy to visible light. The photographic camera is placed under the fluorescent screen and is basically a storage and a transport mechanism for the photographic plates.

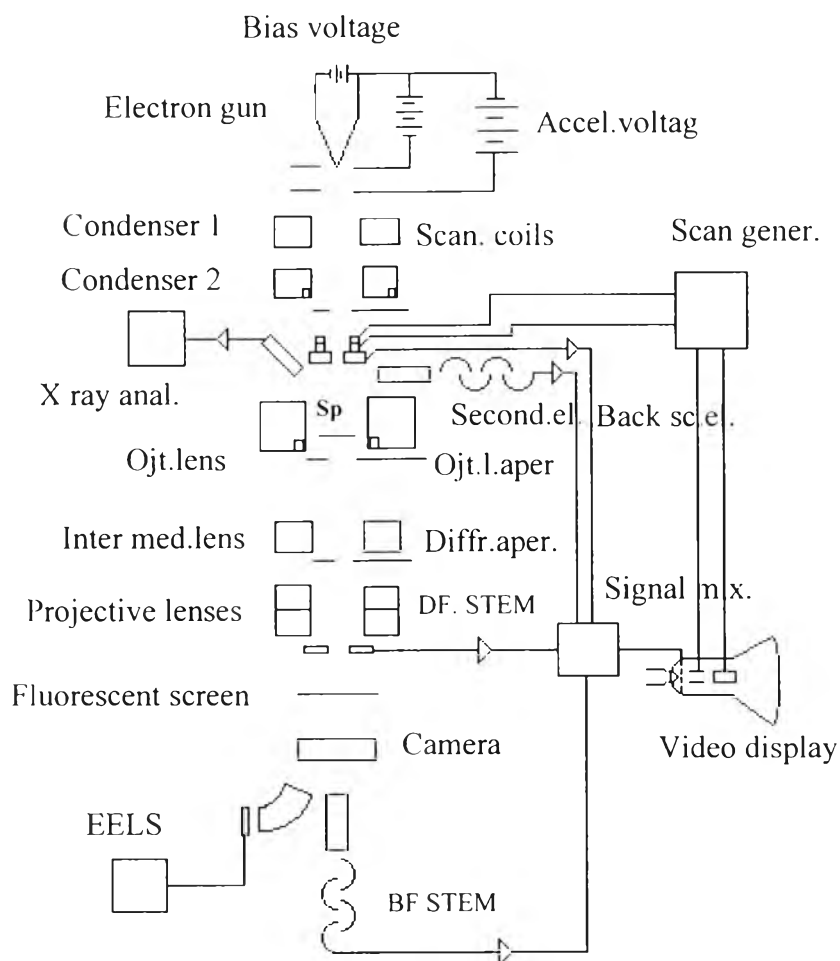


Figure 2.10 Schematic diagram of a transmission electron microscope (TEM).

Procedures

The sample films were cut with a cryomicrotome from bulk samples to obtain ultrathin sections (≈ 70 nm). Cryomicrotomy was conducted at -100°C using a glass or a diamond knife, then stained in the vapor of a 3% aqueous osmium tetroxide solution (OsO_4), this treatment selectively stains the polyisoprene microphase.