

CHAPTER II EXPERIMENTAL

2.1 Materials

2.1.1 Polymers

The following polymers were used as homopolymer in this investigation: polypropylene (PP) and two high-density polyethylenes (HDPE) of different molecular weights ($M_w = 119,000, 122,000, \text{ and } 58,000$ gram per mole) were supplied by TPE. Polystyrene (PS) was another blending component supplied by TPI, with molecular weight of 109,000 gram per mole. These polymers are of commercial grade and were used without any purification. A laboratory grade polymer with a narrow weight average molecular weight, poly(methylmetacrylate) (PMMA) purchased from Polyscience Inc., was also used as a minor component in a blend, with molecular weight of 25,000 gram per mole. The polymer properties used in this study are summarized and shown in Table 2.1.

Table 2.1 The material properties of the five polymers.

Polymers	Grade	Source	M_w^a (g/mole)	T_m^b (°C)	T_d^b (°C)	MFI ^a (g/10 min)
PP	P640J	TPE	1.19×10^5	~165	407	10
HDPE(1)	H5840B	TPE	1.22×10^5	~134	380	0.4
HDPE(2)	H5418J	TPE	5.80×10^4	~134	380	5
PS	Singlite	TPI	1.02×10^5	($T_g=100$)	400	8.9
PMMA	Cat#04554	Polyscience	2.50×10^4	($T_g=105$)	320	-

^a quoted from company

^b reference (Shenoy, 1996)

2.1.2 Paraffin

Paraffin wax was used in preparing samples for optical microscope technique. Its melting point is about 50-54 °C.

2.2 Instruments

2.2.1 Brabender Mixer

The brabender mixer (Brabender Plasti-corder, model PL 2000), with a cam type mixer-measuring head consisting of figure-eight-shaped chamber in which two removable roller blades, was used to mix two polymer melts. It is the standard mixer for testing a large range of material (ASTM D2538). The volume of the mixer bowl is approximately 55 cm³. The maximum torque is 100 Nm, and the rotor speed range is 1 to 120 rpm. The temperature of chamber was controlled by oil bath enclosing the chamber. This oil heated measuring mixer can maintain its temperature up to 300 °C, and the melt temperature was measured by means of a thermocouple. The mixing parameters were temperature, mixing time, and rotor speed.

2.2.2 Rheometer

The rheometer (Rheometric Scientific Inc., model ARES) was used with a cone and plate fixture, with plate diameters of 8- or 25-mm and the cone angle of 0.1. A transducer was attached to the cone. This transducer was used to measure the resultant torque exertion by the sample in response to deformation. The torque range of transducer no.1 is 0.20-200 gm.cm, and 200-2000 gm.cm of transducer no.2. The temperature was controlled by oven (air chiller or LN₂) with the temperature range between 600 °C to -150 °C and a temperature resolution of 1 °C. This rheometer can apply the strain from 0.005% to 500% within a frequency range of 100-0.001 rad/s in the dynamic testing mode. For the steady state mode, it can apply shear rate up to 1000 s⁻¹.

2.2.3 Microtome Sector

The microtome sector (Rotary Microtome, MT 970) with a tungsten knife was used to cut the sample sheared by cone and plate rheometer. The sample can be cut in thickness ranges between 0.5 to 60 micrometers. Another microtome sector, supported by Botany Department, Chulalongkorn University, with stainless knife was also used to cut the sample. Its ability of cutting is 5 to 25 micrometers of thickness.

2.2.4 Optical Microscope (OM)

The optical microscope (Leoca, model DMRXE), connecting with 12V 100W transmitted light lamp, was used to image the morphology of polymer blends. It consists of 5 objective lens (10 times, 20 times, 40 times, 50 times, and 100 times). Both lens of 50 times and 100 times are oil objective lens. It has two moveable eye lenses (10 times and 16 times). The minor phase particle size was measured by image analysis software supplying with the microscope. The magnification range of microscope is from 100 times to 1600 times. The sample thickness was thinner than 20 micrometers that the light can pass through it.

2.3 Methodology

2.3.1 Sample Preparations

2.3.1.1 *Blending*

Each polymer blend was prepared by mixing two polymers in the brabender mixer. The volume of polymers in chamber was fixed at 44 cm³ at the mixing temperature of 200 °C. Since the melt density of each component was known, the polymer volume at various compositions could be calculated. The weight of sample was calculated as follow:

$$W(g) = \frac{V(cm^3) \times 100\%}{\left\{ \frac{X\%}{\rho_1} + \frac{(100-X)\%}{\rho_2} \right\}} \quad (2.1)$$

where W is total batch weight (g), V is volume of polymer melt in the chamber, 44 cm^3 , $X\%$ is %weight of i-component, and ρ_i is melt density of i-component. The weight of each component was calculated by multiplying the W by $X\%$ or $(100-X)\%$ respectively. The following table shows the calculated weights for polymer blends mixed by the brabender mixer.

Table 2.2 The weight of polymer for mixing in the brabender mixer.

Polymer blends (minor/major)	%weight		Melt density ^c at 200 °C (g/cm ³)		Total batch weight (g)	Weight of homopolymer (g)	
	minor	major	minor	major		minor	major
PS/PP	10	90	0.957	0.754	33.89	3.39	30.50
PS/HDPE(2)	10	90	0.957	0.753	33.85	3.38	30.47
PMMA/HDPE(1)	10	90	1.106	0.753	34.22	3.42	30.80

^c reference (James, 1996)

The conditions of mixing for all blends were controlled and shown in Table 2.3. After mixing, the polymer blend was removed from the brabender and allowed to cool down slowly to room temperature. Finally, a bulk of polymer blend was cut into small size by shredder consisting of 4-mm diameter of screen.

Table 2.3 The conditions of mixing for blend systems.

Temperature (°C)	Rotor speed (rpm)	Mixing time (min)	Loading time (sec)
200	10	17	~30
200	50	12	~30

2.3.1.2 Shearing by the Cone and Plate Rheometer

The polymer blend was sheared by the cone and plate rheometer using steady state shearing mode with gap of 0.050 mm. The conditions of shearing such as temperature, shear strain rate and shearing time, were controlled. Then the sample was taken off in the rod shape of 2-mm diameter. The following table shows the conditions of shearing.

Table 2.4 The conditions of shearing for equilibrium morphology.

Shear rate (1/s)	Temperature (°C)	Shearing time (s)
1	200	1800
10	200	300
100	200	60
200	200	45
400	200	30
800	200	20

2.3.1.3 Sectioning by Microtome Sector

The sample in rod-shape was embedded in paraffin wax at ~50 °C contained in a foil mold. As soon as the paraffin was hard enough to keep the pieces of sample from moving, the mold was floated in a pan of cold

water. When the paraffin was thoroughly cooled, the sample was peeled off and the foil mold was discarded. The paraffin around the piece of sample was trimmed into rectangular shape, with the sample approximately centered in the paraffin. The sample was also vertically centered in the paraffin. The sample embedded in paraffin was then put on a stub, which was the mounting block, to hold the sample during sectioning. The sample was cut into pieces with of a thickness of 14 μm by microtome sector. Finally, the thin sample was heated to 55-60 $^{\circ}\text{C}$ on a hot plate to remove any residual paraffin covering the sample surface. After that the thin sample was put on and covered by a glass slide.

2.3.2 Rheological Measurements

2.3.2.1 *Shear Viscosity (η)*

Shear viscosity of homopolymers was carried out by the rheometer ARES using 25-mm cone and plate fixture. The measurement was performed on the steady rate sweep default testing mode. Using continuous rotation, the strain provided a constant shear strain rate. During deformation, shear strain rate was applied. the shear stress (τ) was measured as a function of the shear strain rate ($\dot{\gamma}$). The stress-to-shear strain rate ratio yields the shear viscosity (η).

Procedures: Before the measurement was taken, the rheometer was heated to 200 $^{\circ}\text{C}$, and the gap was calibrated. Then the polymer was loaded. As polymer melted, the gap was set at 0.050 mm. The measurement conditions were shown in Table 2.5. During measurement, torque was checked to make sure that the responded torque was within a transducer range.

2.3.2.2 *The First Normal Stress Difference (N_1)*

The first normal stress difference was carried out by the rheometer ARES using 25-mm cone and plate fixture. When elastic material is strained, a stress will develops in a direction parallel to the shear strain force, and another will develops in a direction perpendicular to the shear strain

direction. This measurement was performed simultaneously with the viscosity testing on steady rate sweep default testing mode which the shear strain rate range was between 0.1 to 1000 s⁻¹ at 200 °C. At very high shear strain rates, 500-1000 s⁻¹, the edge fracture instabilities usually occur. So the normal stress difference measurement at these shear strain rate was done quickly before fracturing started.

Table 2.5 The conditions of shear viscosity and the first normal stress difference measurement.

Shear strain rate sweep (1/s)		Temperature (°C)	Soak time (s)	Measurement (point per decade)
Initial	Final			
0.1	100	200	3	5
100	500	200	3	5
500	1000	200	3	5

2.3.2.3 Dynamic Modulus (G' , G'' , and G^*)

The dynamic mechanical testing was used to obtain storage modulus G' , loss modulus G'' , complex modulus G^* of materials. The measurement was performed on the ARES rheometer using 25-mm cone and plate fixture in a frequency sweep default testing mode.

Procedure: Before the measurement was taken, the rheometer was heated to 200 °C, and the gap was calibrated. The polymer was then loaded. As polymer melted, the gap was set at 0.050 mm. At the first step, the polymer was tested in strain sweep default testing mode to find the % strain where G^* was independent of % strain, or in the linear viscoelastic regime. The following table shows the conditions of the strain sweep test.

For molecular weight characterization of homopolymers, the frequency sweep default testing was done after strain sweep testing. For Palierne's theory study part, the sample was pre-sheared in steady state mode before a frequency sweep default testing.

Table 2.6 The strain sweep testing conditions of homopolymers and polymer blends.

Frequency (rad/s)	% Strain sweep		Temperature (°C)	Soak time (s)	Measurement (point per decade)
	Initial	Final			
1	1	500	200	3	5
0.1	1	500	200	3	3

Pre-shearing: Both homopolymers and the blends were pre-sheared by the cone and plate rheometer at steady state shearing mode with gap of 0.050 mm, to get an equilibrium morphology. The following table showed the conditions of pre-shearing.

Table 2.7 The conditions of pre-shearing for dynamic modulus testing.

Shear rate (1/s)	Temperature (°C)	Shearing time (s)
1	200	1800
10	200	300
100	200	60

The conditions of frequency sweep testing are shown in Table 2.8. If the torque was below the range of that transducer, higher %strain was chosen to obtain a high enough value of torque.

Table 2.8 The frequency sweep testing conditions of homopolymers and polymer blends at 200 °C.

Samples	% strain	
	$\omega=100-0.1$ (rad/s)	$\omega=1.0-0.001$ (rad/s)
Homopolymer	20%	100%
Polymer blend	20%	100%

2.3.3 Morphology Investigation

The thin sample was imaged by an optical microscope with magnification of 400 times or 500 times. The dispersed phase was observed and the Image Analysis Software installed with the microscope allowed measurement of minor phase droplet size. About 200-300 drops were picked and measured to obtain the average size diameter.

2.4 Calculation of Interfacial Tension of Polymer Blends

The interfacial tension, Γ_{12} , between 2 homopolymers making a immiscible blend was calculated from the surface tension of each component, assuming that no chemical reaction took place. Both surface and interfacial tension decrease with increasing temperature. The values of surface tension for the homopolymers have been published (Brandrup, 1989). The surface tension of a polymer at any temperature can be calculated from the temperature coefficient of surface tension and surface tension at a reference temperature as

$$\gamma_T = \gamma_r - \frac{d\gamma}{dT}(T - 20) \quad (2.2)$$

where γ_T is surface tension at required temperature, γ_r is surface tension at reference temperature, $(d\gamma/dT)$ is temperature coefficient, and T is temperature

(°C). The surface tension consists of disperse-contribution and polar-contribution, $\gamma = \gamma^d + \gamma^p$. The polar-contribution of surface tension is equal to the surface tension at that temperature multiplied by polarity. The polarity of polymer does not depend on temperature; it only depends on chemical structure of polymer. Then the interfacial tension was calculated by using the Harmonic mean equation (Mark *et. al*, 1986):

$$\Gamma_{12} = \gamma_1 + \gamma_2 - 4 \left[\frac{\gamma_1^d \gamma_2^d}{(\gamma_1^d + \gamma_2^d)} + \frac{\gamma_1^p \gamma_2^p}{(\gamma_1^p + \gamma_2^p)} \right] \quad (2.3)$$

where Γ_{12} is an interfacial tension between polymer pair, γ_i is surface tension of polymer against polyethylene, reference material, superscript-d shows the dispersed contribution part, and superscript-p shows the polar contribution part. The summation of two-contribution part is the resultant surface tension.

The surface tension and interfacial tension at temperature 200 °C are shown in Table 2.9 and Table 2.10 respectively.

Table 2.9 Surface tension of homopolymers.

Polymers	γ at reference temperature (20 °C)	polarity	$-\frac{d\gamma}{dT}$ (dyn/cm-K)	Calculation for 200 °C		
				γ (dyn/cm)	γ^p (dyn/cm)	γ^d (dyn/cm)
PP	29.4	0	0.056	21.56	0	21.56
HDPE	36.8	0	0.056	28.96	0	28.96
PS	40.7	0.168	0.072	30.62	5.14	25.48
PMMA	41.1	0.281	0.076	30.46	8.89	21.90

Table 2.10 Interfacial tension of polymer blends.

Polymer blends (minor/major)	Γ_{12} at 200 °C from calculation (dyn/cm)	Γ_{12} at 200 °C from references (dyn/cm)
PS/PP	4.99	5.00 ^d , 5.00 ^e
PS/HDPE	4.93	4.92 ^f , 4.80 ^d
PMMA/HDPE	8.76	8.00 ^d , 10.0 ^d

^d Brandrup and Immergut, 1989

^e Sandararai and Macosko, 1995

^f Utracki and Sammut, 1991

The surface tension of polymer can also be calculated by thermodynamic interaction, chi-parameter (χ), but it can only apply to polymer fluids not polymer melts (Mark, Bikales, and Overberger, 1993).