

CHAPTER III

EXPERIMENTAL PART

3.1 Materials

3.1.1 Polymers

In this study, three main types of polymers were used as homopolymer matrices: polystyrene (Dow Chemical, PS680A), high density poly(ethylene) (BPE, HDPE5200B) and poly(vinyl acetate) (Aldrich, PVAc500). Poly(isoprene) (Japan Synthetic Rubber, PI), with the quoted molecular weight of 10^6 gram per mole, was used as a minor component. All of these polymers were laboratory grade. Poly(styrene-b-isoprene-b-styrene) triblock copolymer (Shell Chemical Company, Kraton D1125P), with the quoted molecular weight of 74,700 gram per mole (30%PI), was used as a compatibilizer.

Polymers were chosen on the basis of the interfacial tension between the major and the minor component, the interfacial tension between PS segment of block copolymer and the major components and the viscosity ratio (η_r). Interfacial tensions of all polymer pairs were chosen to differ for studying the effect of interfacial tension on the morphology whereas the viscosity ratio of each polymer pairs was fixed in the range of 0.1-4 (Ica and Tadmor, 1994). All polymer properties were shown in table 3.1.

Table 3.1 Properties of homopolymers using in this work

Polymer	Source	M_w # (g/mole)	M_w + (g/mole)	M_v ++	M_n + (g/mole)	M_w/M_n
PS680A	Dow Chemical	-	$1.87 \cdot 10^5$	$1.99 \cdot 10^5$	$5.72 \cdot 10^4$	3.27
PI	Japan Synthetic Rubber	$1.00 \cdot 10^6$	$1.03 \cdot 10^6$	$1.05 \cdot 10^6$	$6.47 \cdot 10^4$	15.92
HDPE5200B	BPE	-	$7.60 \cdot 10^3$	-	$5.02 \cdot 10^4$	15.14
SIS bcp	Shell Chemical Company	-	$7.47 \cdot 10^4$	-	-	
PVAc500	Aldrich	$5.00 \cdot 10^3$	$5.79 \cdot 10^3$	$5.40 \cdot 10^3$	$7.91 \cdot 10^4$	6.32

quoted from company

+ from GPC

++ from Ubbelohde viscometer

Moreover, the value of surface tension, interfacial tension and viscosity ratios of each polymer pairs are also shown in Table 3.2.

Table 3.2 Surface tension, interfacial tension, and viscosity ratio of each polymer

Polymers (X)	Surface tension * (dyn/cm) (at 220°C)	Interfacial tension + (dyn/cm) at 220°C (X-PS segment)	Viscosity ratio # (η_r) (X-PI)
PS	26.380	0.000	0.519
PE	25.455	4.688	0.506
PVAc	23.280	1.930	0.365

* reference (Polymer handbook , 1989)

+ from calculation (Appendix C)

from experiments

3.1.2 Solvent

Toluene and chloroform were used as solvents for casting film. Chloroform was purchased from Labscan Asia Co.,Ltd. whereas toluene was purchased from J.R.Baker. The solvent properties are shown in Table 3.3.

Table 3.3 Properties of the solvents (Brandrup and Immergut, 1989)

Solvent	Source	T _m * (°C)	T _b * (°C)	density * (g/ml)	viscosity * (centipoise)
toluene	J.R.Baker	-95	110.6	0.86	0.526-0.590
chloroform	Labscan Asia Co.,Ltd.	-63.5	61.7	1.48	0.514-0.568

* reference

3.1.3 Commercial Paraffin Wax

A paraffin wax was used to prepare thin samples for studying the morphology with an optical microscope. Its melting point is about 40°C without decomposition (Mark *et al.*, 1987).

3.2 Instruments

3.2.1 Rheometer

A strain-controlled rheometer (Rheometric Scientific Inc., model ARES) was used with 8 mm and 25 mm cone and plate fixtures. The cone angle was 0.1 radian. A transducer was attached to the cone to measure the resultant torque exerted by samples in response to deformation. A transducer no.1 was used for torque between 0.2 to 200 gm.cm whereas transducer no.2 was used for torque between 200 to 2000 gm.cm. The temperature was controlled by an oven between -150 to 600°C. The rheometer can be used into 3 modes: steady state mode, dynamic mode and transient mode. The strain can be varied from 0.005% to 500% within a frequency range of 0.001-

100 rad/s for the dynamic testing mode whereas it can apply shear rate from 0.01 to 1000 s⁻¹ in steady state mode.

3.2.2 Microtome Sector

A microtome sector (Rotary Microtome, MT 970) was used to cut the sample with thickness varied between 0.5 to 60 micrometers after mixing by the cone and plate rheometer. The knife was made from tungsten.

3.2.3 Optical Microscope (OM)

An optical microscope (Leica, model DMRXE), connecting with 12V 100W transmitted light lamp, was used to examine the phase morphology of polymer blends before and after the shear flow experiments. There are 2 movable eye lens: 10 and 16 magnifications. It consists of 5 objective lens (10, 20, 40, 50 and 100 magnifications) in which the lens of 50 and 100 magnifications are oil objective lens. So the magnification of this microscope can vary from 100 to 1,600 times. A suitable thickness of sample should be between 10 to 20 μm (shown in Appendix D1.3) so that the light can pass through it, the drops do not overlap with each other and that the drop size seen is the actual size, not its smaller cross section. The minor phase's particle size was measured by image analysis software supplying with the microscope.

3.2.4 Compression Molding

A compression molding (Wabash, model V50H-18-CX) was used to prepare samples by a melt mixing process. It consists of 2 heated plates: the upper plate is stationary whereas the lower plate is movable. The temperature of both plates was controlled by using air and water system. The pressure required to press the samples were between 0 to 15 tons.

3.3 Methodology

There were two processes, the solvent casting process and the melt mixing process, that were used in this work to study the effect of block copolymer on blend morphology. The sample preparation and procedure of these two processes are different as described below:

3.3.1 Solvent Casting Process

PS/PI blend was chosen to study the effect of block copolymer on blend morphology.

3.3.1.1. Sample Preparation

PS/PI blend was dissolved in toluene to prepare the solution in the concentration of 5 g/100ml at room temperature. The composition ratio between major and minor components was fixed at 0.9:0.1 and the amount of SIS triblock copolymer was varied between 0 to 20% in the blend system without changing the composition ratio. The weights of each polymer in blending are listed in Table 3.4.

Table 3.4 Weight of each homopolymer and block copolymer for blending in the composition ratio 0.9:0.1

% SIS block copolymer	weight of minor phase (PI) (grams)	weight of major phase (grams)	weight of SIS block copolymer (grams)
0	0.500	4.500	0.000
2	0.490	4.410	0.100
5	0.475	4.275	0.250
10	0.450	4.050	0.500
15	0.425	3.825	0.750
20	0.400	3.600	1.000

The samples in the solvent casting process were produced from two methods:

a. Casting film on glass slide method.

PS/PI blend with block copolymer was dissolved in toluene and stirred at room temperature for 3 days. After that, the solution was poured onto a glass slide. The solvent was evaporated slowly at room temperature for 2 days and dried under a vacuum oven at 70°C for 1 days to remove the solvent. Then 5 to 30 microns of film were obtained.

b. Forming the thick samples and sectioned with microtome method.

PS/PI blend with triblock copolymer was mixed in its suitable solvent and stirred at room temperature for 3 days. After dissolution, the solution was poured onto an aluminium foil sheet placed on a beaker of the size 10 cc. The solvent was evaporated slowly at room temperature for 2 weeks and dried in a vacuum oven at 70°C for 2 days to remove the solvent. Then it was allowed to relax at room temperature for 2 days. The sample thickness typically about 0.5 cm was formed.

The thick sample was cut to be a rod shape and embedded in a piece of paraffin wax at about 50°C in the foil mold as soon as the melted-paraffin was hard enough to prevent the sample from moving. This mold was soaked in cold water to cool down the temperature of paraffin and the sample was peeled off and the foil mold was discarded. Then the sample was embedded in paraffin on a base to support the sample during section. The sample was cut to make a thin film having a thickness between 10-20 microns. Finally, the paraffin covering the thin sample was removed out and this sample was placed on a glass slide.

3.3.2 Melt Mixing Process

3.3.2.1. Sample Preparation

Polyisoprene minor phase and SIS block copolymer were dissolved in chloroform. The weight ratios between PI and SIS are shown in table 3.4. This homogeneous solution was evaporated at room temperature and followed by drying in a vacuum oven for 1 day at 70°C to form film. This film was then dry-mixed with the major phase and molded by a compression-molded machine at 170°C for 4 minutes to form 25-mm diameter of disks. Finally, air and water system were used to cool down the samples. The weight of each sample's disk was typically between 0.76-0.80 grams.

a. Mixing Sample's Disk by Cone and Plate Rheometer

The disks of the polymer blends from compression molding were melt-mixed with the 25 mm of cone and plate rheometer at 220°C. Steady state shearing mode was used with a gap of 0.05 mm. All conditions of mixing such as temperature, shear rate were controlled to find the mixing time which gave the equilibrium morphology of blending.

Table 3.5 Mixing time for equilibrium morphology at 220°C of each polymer pairs

Mixing shear rate (s ⁻¹)	PS/PI system		PE5200B/PI system		PVAc/PI system	
	temperature (°C)	mixing time (s)	temperature (°C)	mixing time (s)	temperature (°C)	mixing time (s)
10	220	600	220	600	220	600
100	220	-	220	60	220	-

b. Shearing by the Cone and Plate Rheometer

The polymer blend after mixing was sheared by the 25 mm of cone and plate rheometer using steady state shearing mode with gap of 0.05 mm and shear rate was varied from 10 to 200 s⁻¹ to study the effect of block

copolymer as a function of shear rate. The conditions of shearing such as temperature, strain unit, were controlled. So the equilibrium strain units were illustrated in Table 3.6.

Table 3.6 The conditions of shearing for PE/PI, PS/PI and PVAc/PI blends

Shear rate (s ⁻¹)	Shearing time (seconds) at 220°C		
	PE/PI blend	PS/PI blend	PVAc/PI blend
10	600	600	600
20	300	300	300
30	200	200	200
50	120	120	120
100	60	60	60
200	30	30	30
Strain unit (γ *time)	6.00*10 ³	6.00*10 ³	6.00*10 ³

c. Sectioning by Microtome Sector

The blends was formed to be a rod shape after melt mixing and sectioned by the microtome to obtain a thin film and the droplet size and the droplet size distribution were measured by the optical microscope. The procedure was the same as in section 3.3.1.1b

3.4 Rheological Characterization

3.4.1 Shear viscosity (η)

Rheometer ARES with the 25-mm cone and plate fixture was used to measure shear viscosity of each homopolymer. This measurement was performed on the steady state sweep default-testing mode for the shear rates of 0.1 to 10 s⁻¹ whereas the transient mode was used for the higher shear rate.

As shear rate ($\dot{\gamma}$) was applied, the shear stress (τ) was measured as a function of shear rate. The ratio of shear stress to shear rate represented the apparent shear viscosity. Before measurement, the fixture was heated up to 220°C and then gap calibration was carried out. After that, the sample disk was loaded and the gap was adjusted to 0.050 or 0.051 mm as the polymer was melted. The excess polymer melt was then removed out in the next step. During measurement, the torque was always checked to confirm that the responded torque was in the transducer ranges.

3.4.2 The First Normal Stress Difference (N_1)

Rheometer ARES with 25-mm cone and plate fixture was used to measure N_1 of each homopolymers. In general, N_1 is a positive function of the shear rate and it may also have a power-law behavior over a range of shear rate. (Barnes, Hutton and Walters, 1991). The same procedure was carried out as in the shear viscosity measurement.

3.5 Morphology Investigation

The droplet size and droplet size distributions were measured by the optical microscope with the magnification of 500 times: objective len is x50 whereas the eye len is x10. At least 150 drops were measured to obtain the average size diameter.