CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Polymers

The homopolymers chosen for polymer blends were polypropylene (PP) and polystyrene (PS) with different melt flow indexes and molecular weights. Polypropylenes with melt flow indices 11, 4, 3, and 2.5 were kindly supplied by HMC Polymer Company Limited. Polystyrenes, as supplied by Dow Chemical, were of two commercial grades (685D26W and 656D26W), and as supplied by Aldrich Company, was of laboratory grade (MFI 14). The commercial grade polypropylenes and polystyrenes were used without any purification.

Table 3.1 The polymer properties of polypropylene and polystyrene.

Polymers	Grade	Source	MFI* (g/10 min)	M_w* (g/mole)*	M_n * (g/mole)	PDI (M_w/M_n)
PP(1)	6631	HMC Polymer	2.5	8.53×10^6	4.40×10^5	19.39
PP(2)	pd382	HMC Polymer	3	7.35×10^6	3.60×10^5	20.39
PP(3)	6531	HMC Polymer	4	6.78×10^6	5.43×10^5	12.49
PP(4)	pd943	HMC Polymer	11	5.10×10^6	3.31×10^5	15.39
PS(1)	685D26W	Dow Chemical	-	-	-	-
PS(2)	656D26W	Dow Chemical	-	-	-	-
PS(3)	Cat# 43,011-0	Aldrich	14	-	-	-

* quoted from company

3.2 Equipments

3.2.1 Compression Moulding Machine

A compression moulder (Wabash, Model V50H-18-CX) was used to compress in order to obtain polymer blend samples in a disk form. The compression moulding machine is consisted of 2 plates, an upper and a lower. The upper plate is stationary while the lower platen is movable to compress the sample. The temperature was controlled by heater. The load can be applied in the range of 0 to 50 tons

3.2.2 Rheometer

A strain-controlled rheometer (Rheometric Scientific Inc., model ARES) equipped with a cone and plate geometry having a diameter of 25 mm and the cone angle of 0.1 radian was used for rheological measurements. The advantage of this geometry is that the shear strain rate applied is the same everywhere in the liquid. Two transducers attached to the cone were used to measure the torque exerted by the sample deformation. The torque range of transducer no.1 is from 0.2 to 200 gm.cm and of transducer no.2 is from 200 gm.cm to 2000 gm.cm The temperature was controlled by an oven (air chiller or LN_2), ranging from -150 ± 0.01 to 600 ± 0.01 °C. The measurement can be carried out in 3 modes, steady state mode, dynamic mode, and transient mode. Shear strain rate can be varied from 0.001 to 1000 s^{-1} and strain from 0.005% to 500% within the frequency range of 0.001-100 radian/s.

3.2.3 Microtome Sector

A microtome sector (Rotary Microtome, model MT 970) with a tungsten knife was used for cutting specimen as sheared by cone and plate rheometer. The sample thickness that this sector can cut the specimen is from 0.5 to 60 micrometers.

3.2.4 Optical Microscope (OM)

An optical Microscope (Leica, model DMRXE), connecting with a 12V 100W transmitted light lamp, was used to image morphology of polymer blends. The microscope composes of five objective lens (10 times, 20 times, 40 times, 50 times, and 100 times) and two eye lens (10 times and 16 times). Both lens of 50 times and 100 times are oil objective lens. An Image Analysis Software supplied with microscope was used for determining the minor phase droplet size and statistics.

3.3 Methodology

3.3.1 Pre-Processing Rheological Characterization

3.3.1.1 Dynamic Modulus (G', G", and G)*

The linear viscoelastic behavior of polymeric material is investigated from the response to a small-amplitude oscillatory shear in terms of the storage modulus G', the loss modulus G", and the complex modulus G*. The three oscillatory shear modulus measurements were performed on the strained-control rheometer ARES using a 8-mm cone and plate geometry. Before measurement, the rheometer was heated to a particular temperature, and the gap was calibrated by means of auto-zero gap. Then polymer sample in disk form was loaded. As polymer melted, the gap was set at 0.051 mm and the excess polymer was striped out from the edge of cone and plate. The measurement was performed on the dynamic testing mode with strain sweep test for 0.1-500% strain at the frequency of 1 rad/s to determine a linear viscoelastic regime such that G^* was independent on

%strain. Then the frequency sweep test was carried out to characterize molecular weight with the frequency of 0.1-100 rad/s at a particular % strain from the previous test.

3.3.1.2 Shear Viscosity (η)

When shear strain rate was applied, the shear stress was measured as a function of the shear strain rate. The stress-to-strain rate ratio yields the shear viscosity. Shear viscosity measurement was carried out by the strained-control rheometer ARES using the 25- and 8-mm cone and plate fixtures. Before each measurement, the rheometer was heated to 220 ^{o}C, and the gap was calibrated by means of the auto-zero gap. Then polymer sample in disk form was loaded. As polymer melted, the gap was set at 0.051 mm. and the excess polymer was striped out from the edge of cone and plate. The measurement was performed on the steady state mode with the strain sweep test for 0.1 – 1 s^{-1} and the transient mode with step rate test for the shear strain rate higher than 1 s^{-1} to avoid or minimize the edge fracture instabilities. During each measurement, the torque measured was checked to confirm that it was in the transducer range.

3.3.1.3 The First Normal Stress Difference (N_1)

When elastic material is strained by a given shear stress, stresses are generated normal to the shearing direction. The difference between the stress in parallel direction and perpendicular direction to the shear strain force yields the first normal stress difference, which is a positive function of the shear strain rate. The first normal stress difference test was performed at the same time as the viscosity measurement using the steady state mode and the transient mode.

3.3.2 Post-Processing Rheological Characterization

After long time shearing in cone and plate rheometer, all of homopolymers were characterized for their rheological properties again.

3.3.2.1 Shear Viscosity (η)

Before each measurement, the rheometer with 25-mm cone and plate fixture was heated to 220 °C, and the gap was calibrated by means of the auto-zero gap. Then polymer sample in disk form was loaded. As polymer melted, the gap was set at 0.051 mm. and the excess polymer was striped out from the edge of cone and plate. The measurement was performed on the transient mode with the step rate test. After shearing, the processed samples were cooled and taken out from the 25-mm cone and plate fixture. The processed samples were characterized for their shear viscosities again using the 8-mm cone and plate fixture on the transient mode.

3.3.2.2 The First Normal Stress Difference (N_1)

The first normal stress difference test was performed at the same time as the viscosity measurement.

3.3.3 Sample Preparation

3.3.3.1 Blending

Each polymer blend having a 20 wt% of minor phase was roughly mixed and compressed into a 25-mm disk form with the thickness of 1 mm by the compression moulder at the temperature of 175 °C. The compression cycle was preheated for 5 min, compressed under a load of 10 tons for 3 min and cooled under compression by means of water and air until the temperature of 40 °C was reached.

3.3.3.2 Shearing by the Cone and Plate Rheometer

For a homogeneous blending, the blended samples were sheared at various shear rates on the rheometer with the 25-mm cone and plate geometry. The transient mode with step rate test was used and the strain unit required was around 5000 for a morphological equilibrium on the ensemble mean basis and was around 10000 for a morphological equilibrium on statistical basis. The shearing conditions are shown in Table 3.2. Then the sample was cooled and taken off from the cone and plate fixture.

Table 3.2 The conditions of shearing time required for the ensemble mean equilibrium and the statistical equilibrium of the blend system at 220 ^{0}C

Shearing rate (s^{-1})	Shearing time (s)	
	Ensemble mean equilibrium	Statistical equilibrium
10	500	1000
20	250	500
30	170	350
50	100	200
70	75	145
100	50	100
200	25	50

3.3.3.3 Sectioning by Microtome Sector

The sample was cut to rod-shape and embedded vertically into the center of melt paraffin wax covered by a cylindrical foil mold. When paraffin wax was thoroughly cooled by cold water, the foil was peeled off. Then the sample embedded in paraffin wax was put on a stub to stabilize the sample during section. The sample was cut by the microtome sector into pieces with the thickness of 16 μm. The suitable thickness for cutting was determined in a preliminary test by varying the thickness of sample. It was found that the drop could not be observed clearly when the sample thickness was less than 16 μm. In contrast, if the sample thickness were too high, the overlapping of drop would be observed. At last, the sample was stripped from the paraffin covering around the sample edge and then the sample was put on and covered by glass slide.

3.3.4 Morphology Investigation

The image of the specimen after cutting was taken by using the optical microscope with the magnification of 500 times. The dispersed phase size was observed and measured by the Image Analysis Software installed in the computer connecting to the microscope. The average, standard deviation and size distribution function of this droplet size diameter of dispersed phase were obtained from the drop ensemble containing at least 200 drops.