CHAPTER IV

EXPERIMENTS

4.1 Materials

4.1.1 Styrene-Acrylonitrile Copolymer (SAN)

Commercial grade styrene-acrylonitrile copolymer (SAN) from Mitsubishi Corporation, Japan, under the trade name of "SANREX" was used in this study. It is a copolymer of styrene and acrylonitrile. It appears in blue transparent pellet. The repeating units of styrene and acrylonitrile are shown in Figure 4.1. Its viscosity-average molecular weight (M_v) determined in tetrahydrofuran (THF) at 25 °C is 165,200. The glass transition temperature (T_g) detected by differential scanning calorimeter (DSC) with 10 °C/min heating rate is about 105 °C and the acrylonitrile content examined by elemental analysis is 25.74 % by weight. The softening point temperature is about 200 °C.

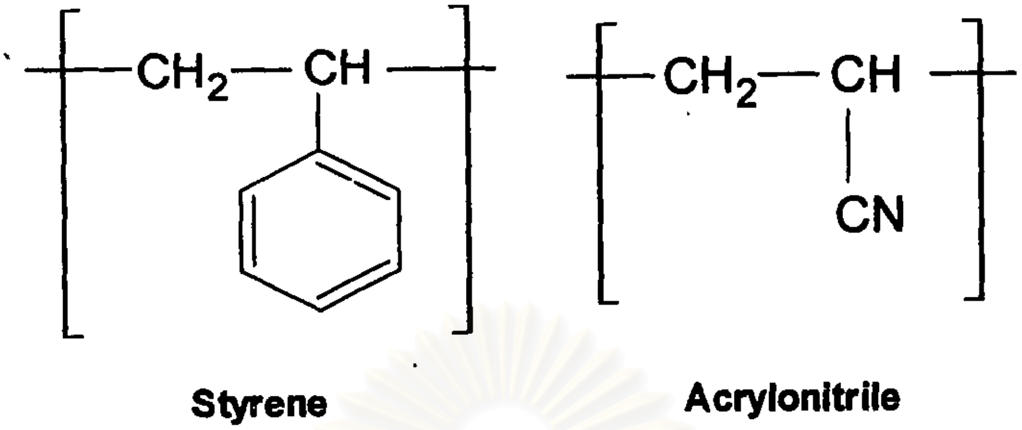
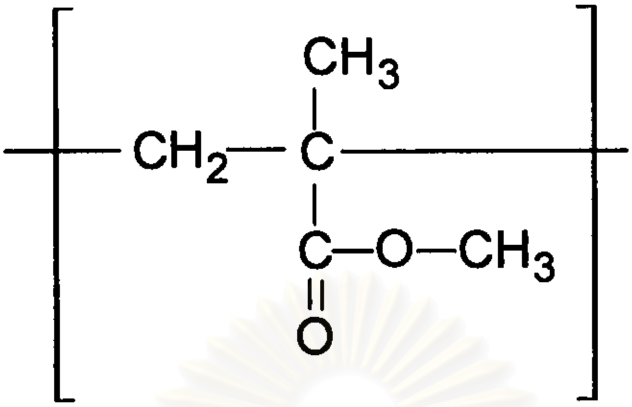


Figure 4.1 The repeating units of styrene and acrylonitrile.

4.1.2 Poly(methyl methacrylate) (PMMA)

Commercial grade poly (methyl methacrylate) (PMMA) under the trade name of "Acrylic Resins" manufactured by Thai Petrochemical Industry, Co. Ltd., was used to blend with styrene-acrylonitrile copolymer (SAN). It is in a transparent pellet form. The repeating unit of poly(methyl methacrylate) is shown in Figure 4.2. The viscosity-average molecular weight (M_v) of poly(methyl methacrylate) determined in 1THF at 25 °C is 108,600. The glass transition temperature (T_g) determined with 10 °C/min heating rate by DSC is 115 °C. The softening point temperature is about 200 °C.



Methyl Methacrylate

Figure 4.2 The repeating unit of poly(methyl methacrylate).

4.1.3 Solvents

Solvents used in this study were methylene chloride (MC), acetone (AC), tetrahydrofuran (THF), methyl ethyl ketone (MEK) and 1,2-dichloroethane (DC). All are reagent grade solvents. The properties of the solvents are summarized in Table 4.1.

Table 4.1 The properties of solvents [Brandup and Immergut, 1989].

Solvent	Boiling Point (°C)	Solubility Parameter $(\delta, MPa)^{1/2}$	Hydrogen Bonding Interaction
Methylene chloride	39.50	19.8	Weak
Acetone	56.24	20.3	Moderate
Tetrahydrofuran	64-65	18.6	Moderate
Methyl ethyl ketone	79.60	19.0	Moderate
1,2-Dichloroethane	83.50	20.1	Weak

4.2 Equipment

4.2.1 Digital Hot Plate Stirrer

The Cole-Parmer hot plate/stirrer 04644 series model no. 731-2C-P which is a programmable, digital laboratory hot plate with stirrer was used for preparing the solvent casting samples and studying the phase diagram of the blends. The desired plate temperature, stirrer speed and the heating rate are settable from a digital front panel keyboard and display. For studying the phase diagrams of the blends, the controllable heating rate at 5 °C/min was used.

4.2.2 Vacuum Oven & Pump

The HotPack vacuum oven model no. 207380, which has the temperature range from 40 °C to 280 °C with 1.5 cubic feet chamber, was used for preparing the solvent casting samples. It can be vacuummed down to -30 inch Hg.

The vacuum oven is equipped with Edwards two stage rotary vacuum pump model no. 1102180403.

4.2.3 Twin Screw Kneader

The Kurimoto twin screw kneader model S-1 was used to prepare the melt mixing samples. It is a co-rotating type and can be operated at a maximum capacity of 2 kg/hr. The dimension of the twin screw kneader is 540 mm wide, 1000 mm long and 1260 mm high. The mixing temperature and screw speed are settable from the front panel of the equipment.

4.2.4 Press Roller & Barrel Temperature Controller

The Kurimoto press roller was used to calender the molten blend from the twin screw kneader. The size of the press roller is 600 mm in width, 920 mm in length and 894 mm in height. It has a maximum capacity of 2 kg/hr. The surface of the press roller can be heated to prevent sticking of the sample during calendering. Clean water is used as a heating medium. The temperature of the heating medium is controlled by the Kurimoto barrel temperature controller model MC3-15H. The barrel temperature controller dimensions are 233 mm wide, 506 mm long and 538 mm high. It has a temperature range from 60 to 120 °C. It requires the supply voltage of 220 volt, 3ϕ AC at 50 Hz.

4.2.5 Hydraulic Hot Press

The local made hydraulic hot press was used for preparing the flat melt mixing samples. It can be compressed up to 350 kg/cm^2 and heated up to 600 °C.

4.2.6 Surface Temperature Probe & Digital Thermometer

The Cole-Parmer surface temperature probe model E-08516-60 with 0.5 inch tip diameter, which has a temperature range from -250 to 649 °C, was used to measure the temperature at which the first indication of cloudiness developed on heating in both solvent casting and melt mixing samples. It was connected to the Fluke digital thermometer model 52, which can display the temperature up to 1370 °C with a reading resolution of 0.1 °C and has a reading time of 1 sec/reading.

4.2.7 Differential Scanning Calorimeter (DSC)

The glass transition temperature (T_g) of samples was determined by using a differential scanning calorimeter (DSC).

DSC is a thermal analysis technique that measures heat flow into or out of a sample and a reference as a function of time or temperature. A Dupont DSC model 2910 was used in this work. About 10 mg of the sample was placed in open aluminum pan and the heating rate was set at 10 °C/min. The temperature reading was calibrated with indium (m.p. 156.3 °C) and the obtained data were collected by computer connected to the DSC.

4.2.8 Tensile Testing Machine

The Lloyd 2000R instrument which can be operated in both tension and compression mode was used to perform tensile testing of the melt mixing samples with and without solvent. The main frame dimension of the instrument is 1550 mm in height, 500 mm in depth and 600 mm in width. It has an overall force range from 0.25 N to 10 kN by using interchangeable load cells. The crosshead speed is settable in the range of 0.1 to 500 mm/min with the accuracy of ± 0.5 % of the set speed.

4.3 Phase Diagram Studies

4.3.1 Sample Preparation

Two methods, solvent casting and melt mixing, were used to prepare samples for the studies of the phase diagrams of SAN/PMMA blends.

4.3.1.1 Solvent Casting

Styrene-acrylonitrile copolymer (SAN) and poly(methyl methacrylate) (PMMA) were weighed to prepare SAN/PMMA blends at desired compositions at following weight ratio: 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10. Seventeen ml of solvent was added to 0.85 g of the total solid weight of the polymers to form 5% (w/v) solution. The mixture was stirred at 400 rpm by digital hotplate/stirrer at room temperature until all polymers were dissolved and continuously stirred overnight to ensure complete miscibility. Methylene chloride, acetone, tetrahydrofuran, methyl ethyl ketone and 1,2-dichloroethane were used as common solvents.

The solution was cast onto 22x22 mm coverslips placed in petri dishes by variable volume pipette. Each coverslip contained about 0.15 ml of solution. The petri dishes were covered and the solvent was allowed to slowly evaporate at room temperature in a fume cupboard for 24 hr. The resulting clear films with 0.05 mm thickness were further dried under reduced pressure of -30 inch Hg in a vacuum oven at 75 °C for 1 to 7 days.

4.3.1.2 Melt Mixing

The desired weight ratio (10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10) of styrene-acrylonitrile copolymer (SAN) and poly(methyl methacrylate) (PMMA) was weighed to 1 kg. Pellets of the weighed composition were dry-blended in a v-shaped mixer at 32 rpm for 10 min before continuously melt mixing in a twin screw kneader. Melt mixing was performed at 200 °C, 100 rpm screw speed and the feed rate was kept constant at 0.36 kg/hr. The blends came out from the kneader in molten and unshaped form, so the scissors were used to take samples every 30 seconds and then the cut samples were calendered by a press roller to make small pieces of samples with smooth surfaces. Each piece of sample was about 3 to 4 g.

Pieces of blends were compressed at 200 °C under a pressure of 300 kg/cm^2 into thin sheets by a hot press. The resulting sheets were approximately 0.3 mm in thickness but the edge of each sheet was thinner and the thickness was only 0.1 mm. The 0.1 mm thick parts were cut to study the phase diagram, whereas the rests with 0.3 mm thickness were used in tensile testing.

4.3.2 Determination of Phase Diagrams

In this study the phase diagrams of polymer blends both cast from various solvents and melt mixing were constructed by plotting the cloud point temperature against the blend compositions. The cloud point temperatures at which phase separation occurred on heating for each blend formulation were determined as follows.

For the solvent casting blends, two pieces of films with 0.05 mm thickness were attached together to form the 0.1 mm thick film sandwiched between two coverslips. The film should be thicker than 0.08 mm to diminish the influence of the film thickness on the observed cloud point temperature [Guo and Higgins, 1990]. The 0.1 mm thick film was then placed on a covered hot plate. Prior to the observation, the surface of the hot plate was covered by a blackened aluminum foil to make the cloud point more easily judged by eyes. The film was heated from 200 °C at a heating rate of 5 °C/min until the first cloudiness was occurred. The cloud point temperature was taken as the temperature where the blend started to turn from clear to cloudy.

For the melt mixing blends, the 0.1 mm thick film was cut to a size of 10 mm x 10 mm and was sandwiched between two coverslips. It was then placed on the covered hot plate. The cloud point temperature was observed in the similar way as mentioned in the solvent casting blends.

4.4 Tensile Test

4.4.1 Tensile Specimen Preparation

The melt mixing sheets with 0.3 mm thickness as prepared in section 4.3.1.2 were cut to rectangular pieces of 10 mm x 90 mm with a scalpel. Each specimen was visually checked to be free of flaws or imperfections along the cutting edges.

4.4.2 Experimental Procedures

The tensile tests were performed according to ASTM D882 to measure tensile strength at break of melt mixing blend with and without solvent. The specimens without solvent were placed in the grips and the grips were tightened to minimize slipping of the specimen during test. The initial gauge length was fixed at 50 mm. The rate of grip separation or the crosshead speed was kept constant at 50 mm/min. The test condition was 23 ± 2 °C. Twenty specimens of each blend formulation were tested and the test results were recorded as load versus extension. An example of the test result diagram of SAN/PMMA blend is shown in Figure 4.3.

For the blends with solvent, the specimens were suspended in vapor of the solvent in a vacuummed dessicator for 20 min and then left to dry outside the dessicator at the test climate for 1 hr before performing the tensile test in the same manner as described above. The solvents used were methylene chloride, acetone, tetrahydrofuran, methyl ethyl ketone and 1,2-dichloroethane. A set of apparatus for preparing the blends with solvents is shown in Figure 4.4.

4.5 The Studies of Glass Transition Temperature

4.5.1 Sample Preparation

The specimens of SAN/PMMA blends at various compositions without solvent from section 4.4 and blends with different solvents from section 4.4 were cut into small pieces. An amount of 10 mg of blends at each composition with or without solvent was used to study the glass transition temperature (T_g) using DSC.

4.5.2 Experimental Procedures

The glass transition temperature (T_g) of blends without solvent and blends with solvents is determined by using a differential scanning calorimeter (DSC).

The piece of blend, which was cut and weighed as described in section 4.5.1 was placed in open aluminum pan. Heating process was performed from 30 °C to 200 °C and the heating rate was set at 10 °C/min.

The glass transition temperature of each sample was determined from the inflection point of the T_g curve as shown in line A of Figure 4.5.

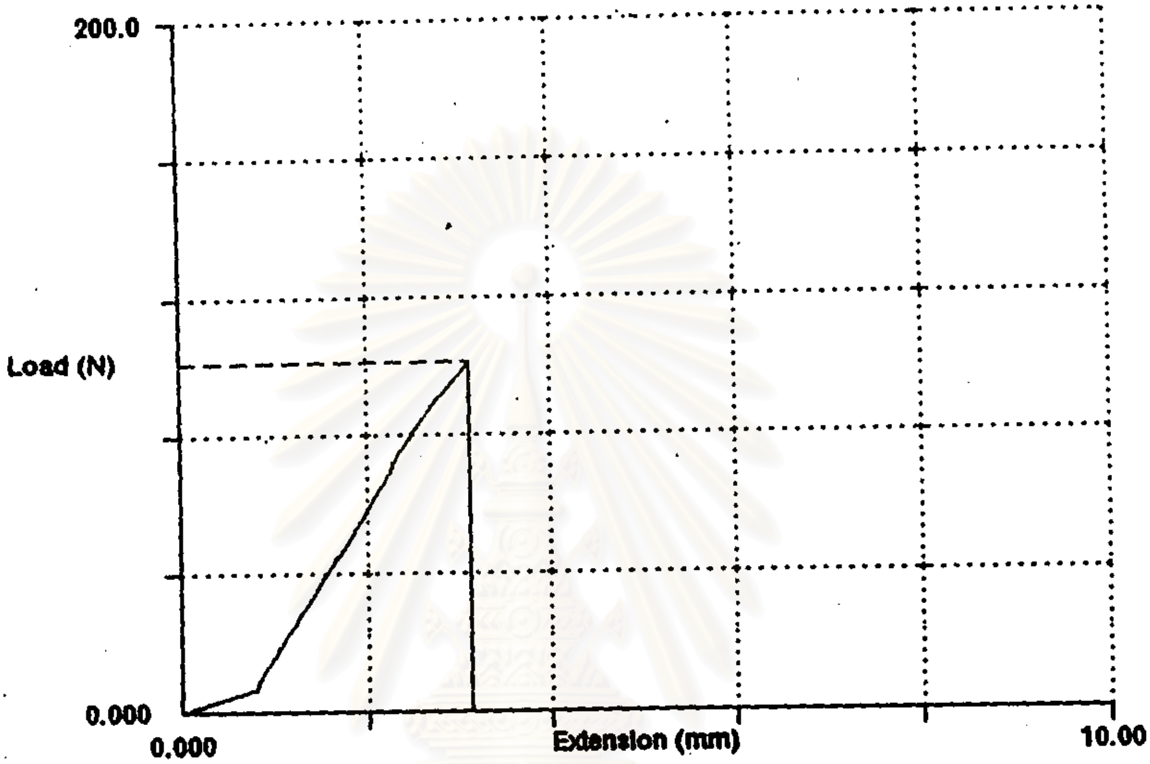


Figure 4.3 An example of the tensile result of SAN/PMMA blend.

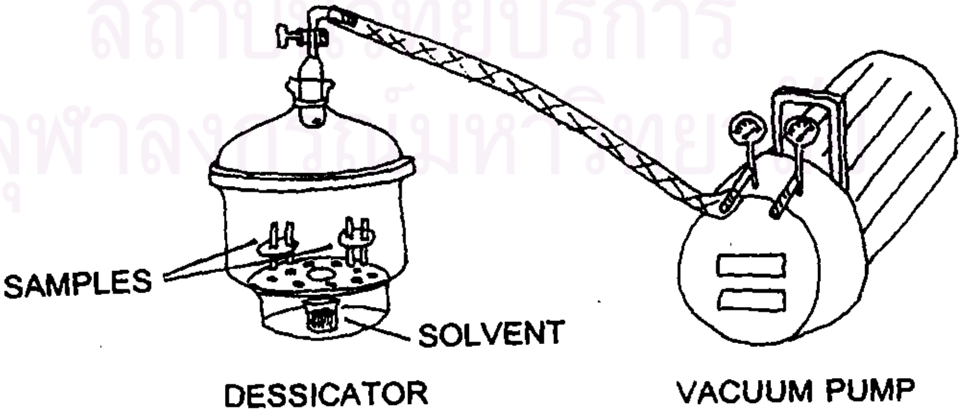


Figure 4.4 A set of apparatus for preparing the blends with solvents.

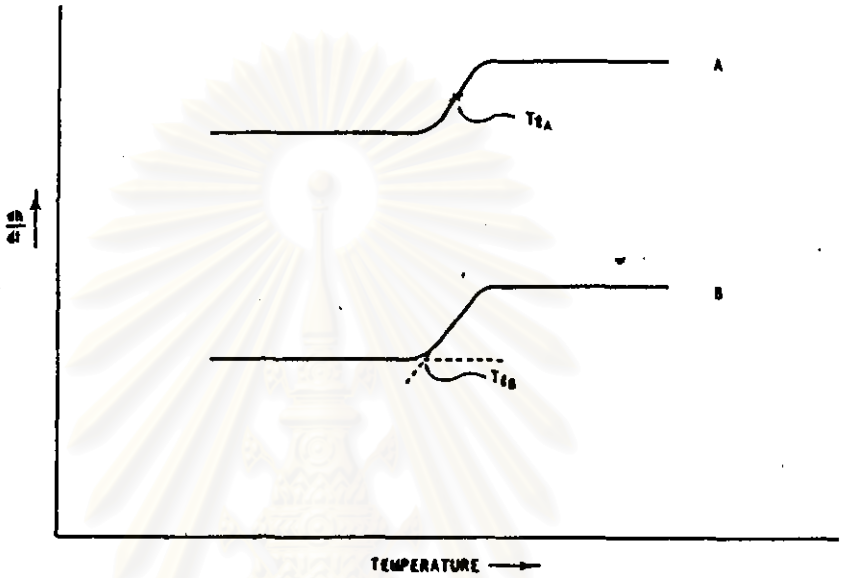


Figure 4.5 Two manners in which the glass transition temperature has been defined. A) the glass transition temperature is taken to be the inflection point of the curve (T_{gA}); B) T_g is chosen to be the extrapolated onset temperature (T_{gB}) [Fava, 1980].