

CHAPTER III

EXPERIMENTAL WORK

3.1 Materials

3.1.1 Polyamide 6

Injection grade polyamide 6, with a commercial name of nylon 6 was selected. It was manufactured by UBE Industries, Co., Ltd. Polyamide 6 is generally synthesized by ring-opening polymerization of caprolactam. Polyamide 6 resins is opaque, white in its colour. The density is 1.14 g/cc. Its molecular structure is shown in Figure 3.1.

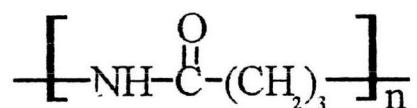


Figure 3.1: The chemical structure of polyamide 6.

3.1.2 High Impact Polystyrene

The high impact polystyrene or HiPS (Styron 470) for injection and extrusion applications was provided by Dow Chemical Company. It is used to blend with PA6. In general, HiPS is produced by the polymerization of a solution of polybutadiene and styrene. HiPS resin

is white in colour. It has a density of 1.05 g/cc. The morphology of HiPS is shown in Figure 3.2.

HiPS is a two-phase material. This was varified by a dynamic mechanical test. It is also supported by a microscopic evidence from TEM images which were obtained by preparing the specimen using a microtome to cut a thin film and then stain it with osmium tetroxide (OsO_4)

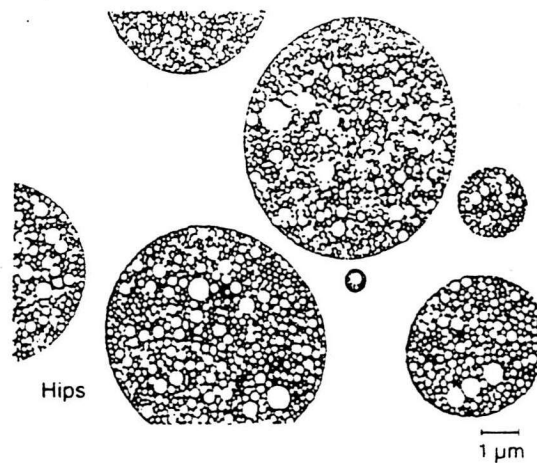


Figure 3.2: Morphology of the conventional HiPS.

The domain of HiPS contain relatively large inclusions of matrix material. Because of their appearance in the images, this type of domain is call “cell particles”. The inclusions enlarge the rubbery phase volume far beyond the existing rubber content.

3.1.3 Maleated Styrene-Ethylene/Butylene-Styrene Block Copolymer

The compatibilizer selected is Maleated styrene-ethylene/butylene-styrene thermoplastic block copolymer (SEBS-g-MA). Maleated styrenic block copolymer is appropriate for compatibilizing polyamide 6 and HiPS. The styrene end blocks of the maleated styrene block copolymers provide excellent compatibility with the high-impact polystyrene (HiPS) whereas the maleic anhydride on the ethylene/butylene middle block of this copolymer can react with the amine group of the polyamide 6. The chemical structure of SEBS-g-MA is shown in Figure 3.3.

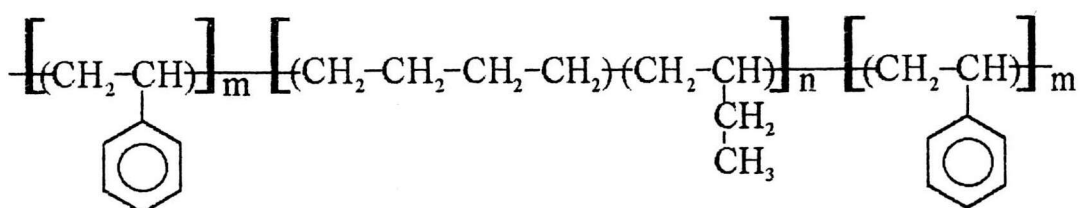


Figure 3.3: The chemical structure of SEBS block copolymers.

Maleated styrene-ethylene/butylene-styrene thermoplastic block copolymer (SEBS-g-MA) is modified from styrene-butadiene-styrene block copolymer (SBS), which is synthesized via homogeneous anionic polymerization in hydrocarbon solvents with hydrogenation reaction to the SEBS block copolymer. SEBS block copolymers can react with maleic anhydride in solution at 81°C with benzoyl peroxide as an initiator, or it can react in an extruder at about 260 °C with 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane as an initiator. The maleic anhydride adduct is illustrated in Figure 3.4.

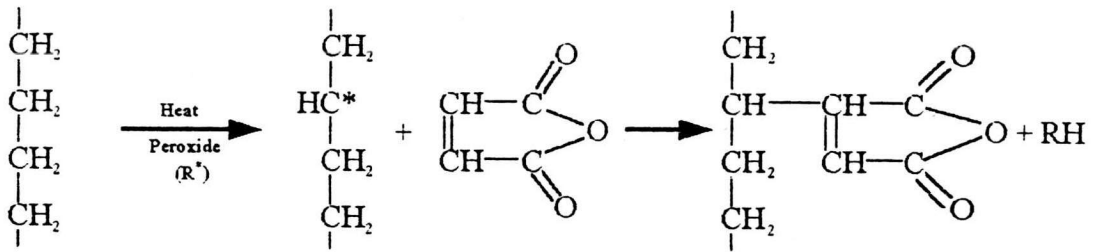


Figure. 3.4: Maleic anhydride reaction with saturated hydrocarbon elastomers.

3.2 Mixing and sample preparation

3.2.1 Mixing

A dry blend of Polyamide 6 and HiPS was performed according to the formulation shown in Table 3.1. The blend was then melted and mixed in an internal mixer until the blend was homogenized.

Table 3.1: Formulations of the PA6/HiPS blends.

Weight fraction of polyamide 6 (X_1)	Weight of polyamide 6 (g)	Weight of HiPS (g)
0.0	0.00	42.00
0.2	8.53	34.14
0.4	17.35	26.02
0.6	26.45	17.64
0.8	35.86	8.97
1.0	45.60	0.00

The temperature of the mixer was set between 215 and 255 °C. The rotor speed was kept constant at 50 rpm. Mixing time is for a period of 5 or 10 min. The formulations were designed such that the volume of the material in each mix was 40 cc.

3.2.2 Mechanical blending

PA 6 was dried in a vacuum oven at 80 °C for 8 hr. The purpose of the drying was to remove any absorbed moisture before the process of blending. Each formulation was dry blended then mixed in the melt state in a counter rotating twin screw extruder at a screw speed of 50 rpm. The temperature of the barrel and the die was adjusted to 235 °C. The dry blended materials were fed by a screw feeder at a rate of about 20 g/min. A couple of strands were extruded, quenched in a water bath and pelletized. Table 3.1 shows all the formulations of PA6/HiPS blends with and without the SEBS-g-MA compatibilizer.

Table 3.2: Formulations of PA6/HiPS blends using a twin screw extruder.

Sample	Quantity by weight of (g)		
	Polyamide 6	HiPS	SEBS-g-MA
No compatibilizer			
HiPS	0	100	0
20%Polyamide 6	20	80	0
40%Polyamide 6	40	60	0
60%Polyamide 6	60	40	0
80%Polyamide 6	80	20	0
Polyamide 6	100	0	0
Compatibilizer 2.5 phr			
HiPS	0	100	2.5
20%Polyamide 6	20	80	2.5
40%Polyamide 6	40	60	2.5
60%Polyamide 6	60	40	2.5
80%Polyamide 6	80	20	2.5
Polyamide 6	100	0	2.5
Compatibilizer 5.0 phr			
HiPS	0	100	5.0
20%Polyamide 6	20	80	5.0
40%Polyamide 6	40	60	5.0
60%Polyamide 6	60	40	5.0
80%Polyamide 6	80	20	5.0
Polyamide 6	100	0	5.0
Compatibilizer 7.5 phr			
HiPS	0	100	7.5
20%Polyamide 6	20	80	7.5
40%Polyamide 6	40	60	7.5
60%Polyamide 6	60	40	7.5
80%Polyamide 6	80	20	7.5
Polyamide 6	100	0	7.5
Compatibilizer 10 phr			
HiPS	0	100	10
20%Polyamide 6	20	80	10
60%Polyamide 6	40	60	10
80%Polyamide 6	60	40	10
Polyamide 6	80	20	10
	100	0	10

3.2.3 Molding and specimens preparation

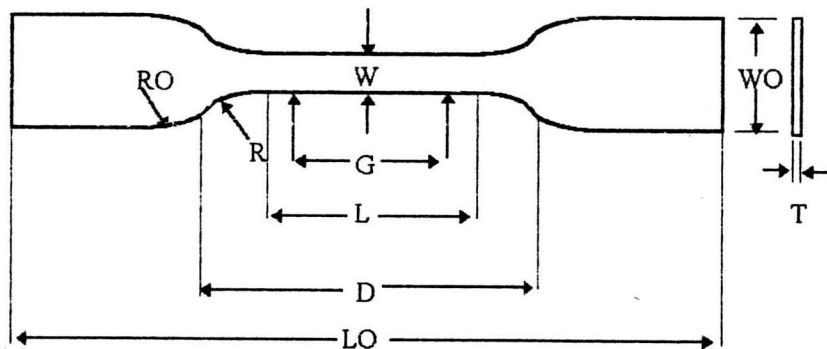
The PA6/HiPS blend pellets of each formulation were dried and compression molded into 150 mm square plate with 2 mm and 3 mm in thickness. The molding was done at 265 °C under a pressure of $4.9 \times 10^6 \text{ N/m}^2$ (or 50 kg/cm²). Then the hot molded plate was quenched to 160 °C and subsequently cooled to 55 °C at a cooling rate of 15 °C/min under a pressure of $4.8 \times 10^5 \text{ N/m}^2$ (or 70 psi). The specimens which contained air bubbles were discarded.

Specimens for standard tensile test were prepared by using a Laser cutting equipment with a computer controller. Specimens for heat-distortion temperature (HDT) test were cut by hand by using a cutting saw to the size and shape slightly larger than the specified size. Then they were ground and polished by using a grinder and polisher to the correct standard size. The Izod impact and the dynamic mechanical thermal analysis (DMTA) specimens were prepared by using a diamond saw. After machining, each test specimen was stored in an auto-dehumidified desiccator for at least 7 days to remove any adsorbed moisture and to prevent water sorption.

3.3 Mechanical Test

3.3.1 Tension test

A tensile test was conducted to obtain the stress-strain behaviour by stretching each PA6/HiPS blend at a constant rate. The force required for stretching was measured. Tensile testing was performed on the LLOYD 2000R in accordance with the condition and procedure set in the ASTM D638. Dumbell specimens of Type IV were used in this test. Figure 3.5 shows the dimensions of the dumbell specimen of Type IV.



SPECIMEN DIMENSIONS OF TENSILE TEST

DIMENSION (SEE DRAWING)	ASTM standard D638 TYPE IV, in.(mm)
W - Width of narrow section	0.25(6)
L - Length of narrow section	1.30(33)
WO - Width over-all, min	0.75(19)
LO - Length over-all, min	4.5(115)
G - Gage length	1.00(25)
D - Distance between grips	2.5(64)
R - Radius of fillet	0.56(14)
RO - Outer radius	1.00(25)

Figure 3.5: The dimensions of the dumbell specimens of type IV.

The crosshead speed was kept constant at 5 mm/min. Each blend formulation was tested under tension for at least five times. Only the average values were reported.

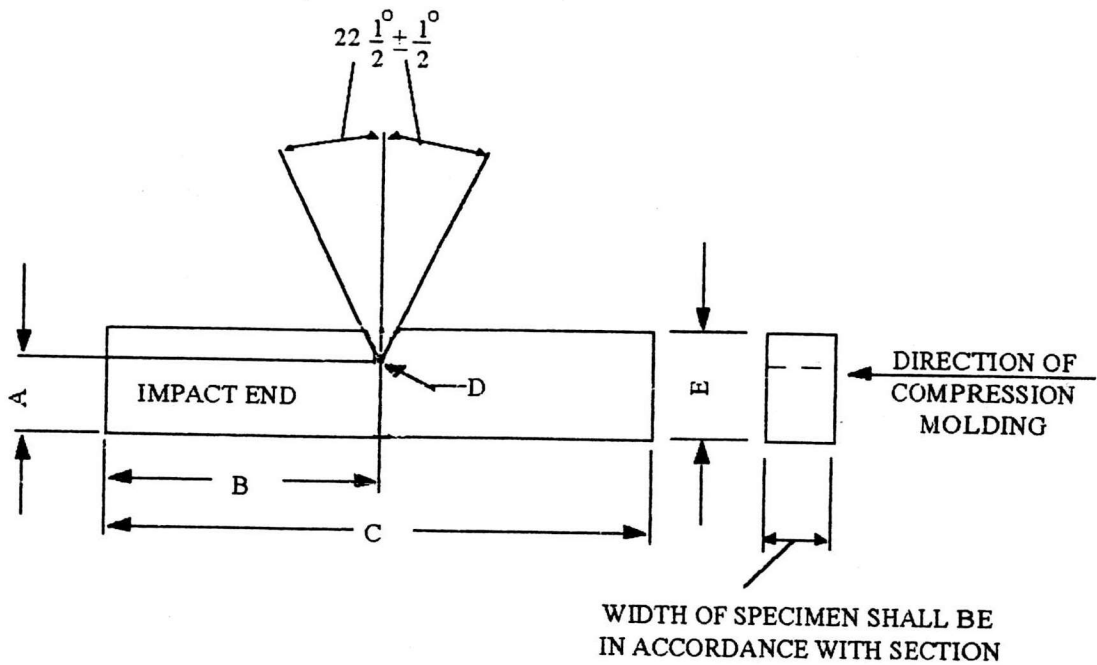
3.3.2 Impact test

Toughness is a concept most people can appreciate. Equally broadly accepted term is the work done in breaking a specimen. In practice, there is a great interest mainly in the toughness under conditions of rapid deformation. In other words, the concept of impact resistance or impact strength is widely appreciated.

Standard impact tests for plastics can be divided into two groups of test namely (i) pendulum impact tests e.g. Izod test, Charpy test, tensile impact test and (ii) the falling weight test.

3.3.2.1 Izod impact test

The Izod impact test is a cantilever beam type of pendulum impact test. It was conducted based upon the ASTM D256 method A. Dimensions of the Izod test specimen are illustrated in Figure 3.6. A notch of 3-mm wide is introduced in each specimen by using the notch cutting apparatus. The Izod impact test was performed on the Izod Tester. Each blend formulation was tested for five times and only averaged values were reported.



	mm	in.
A	10.16 \pm 0.05	0.400 \pm 0.002
B	32.00 max 31.50 min	1.260 max 1.240 min
C	63.50 max 60.30 min	2.500 max 2.375 min
D	0.25R \pm 0.05	0.010R \pm 0.002
E	12.70 \pm 0.15	0.500 \pm 0.006

Figure 3.6: The dimensions of the Izod impact test specimens.

3.3.2.2 Falling weight test

In falling weight test, energy is provided by a mass, usually a sphere or a hemispherical indenter, falling vertically onto the test specimen. The falling weight test was conducted according to the procedure set in the ASTM D3029. A compressed specimen of 150 mm square plate with 2 mm in thickness was used. The test was performed on the Energy Absorption tester. It was conducted at room temperature.

Five specimens were tested for each blend formulation. Only averaged values were reported.

3.3.3 Heat-distortion temperature (HDT)

The HDT was determined by using the procedure set in the ASTM D648. A rectangular bar of specimen of 13 x 127 mm with 3 mm in thickness was tested for the temperature at which it would deflect by 0.25 mm. The condition of loading is that the specimen was under a standard flexural load of 1,820 kPa (264 psi) \pm 2 1/2%. The load was placed at the specimen center. Figure 3.7 illustrates the apparatus for the deflection temperature test. The test was performed on the Advanced HDT/VICAT system Advanced Auto Softening point system.

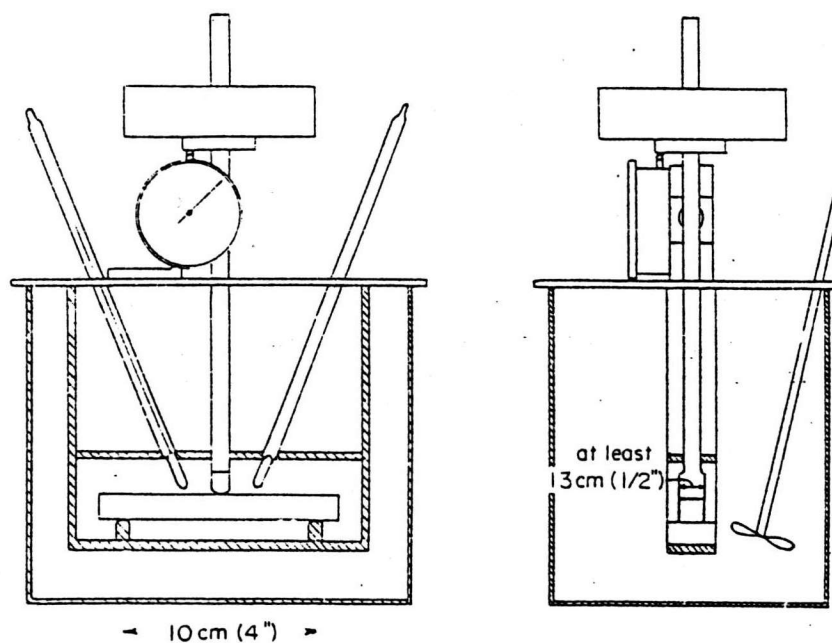


Figure 3.7: Apparatus for the heat deflection temperature test.

3.4 Characterization

3.4.1 Density

A density gradient column was prepared from a mixture of carbon tetrachloride and toluene. The mixture covered the density range from 0.87 to 1.59 g/cm³. Each part of the mixture in the column was separately mixed and then it was poured gently to the column. The pouring started with the high density composition (i.e. pure carbon tetrachloride) which stayed at the bottom of the column to the low density composition (i.e. pure toluene) which stayed at the top of the column. The whole mixture in the column was allowed to stand for 24 hr to ensure its equilibrium state. Then, the height of the liquid and the density column was calibrated by dropping drops of known density solution e.g. zinc chloride solution. The density of zinc chloride solution was previously measured separately by using a pycnometer.

3.4.2 Dynamic mechanical test

The dynamic mechanical analysis is a method to measure the viscoelastic properties as a function of temperature and time (or frequency). In dynamic mechanical test, a stress is measured as a function of strain that is of some periodic function of time; usually it is a sine wave. The stress will also be a sine wave. The phase angle between the stress wave and the strain wave is called δ .

The phase angle (δ) is a measure of the viscous response of the material to the dynamic strain. In the case of an ideal elastic solid, it follows from Hook's law that the stress is always in phase with the strain, i.e. $\delta = 0$. In contrast, the stress of an ideal viscous fluid is always 90° out of phase with the strain, i.e. $\delta = \pi/2$. At temperature below T_g , polymeric materials behave more as Hookean solids at small deformations, but at higher temperatures their behaviour is distinctly viscoelastic. Over the test temperature range of -150 to 185°C , δ will have a temperature-dependence value between 0° (totally elastic) and 90° (totally viscous). For polymeric materials, the maxima in $\tan \delta$ occurs at T_g .

$\tan \delta$ and storage modulus E' were measured using a dynamic mechanical thermal analyzer (DMTA). It consists of a combined head oven, an analyzer (Mark III) and a temperature programmer (CPC 706). The test was conducted in a single cantilever mode at a frequency of 1 Hz; the strain amplitude is $32\ \mu\text{m}$. A bar of specimen of $10 \times 25\ \text{mm}$ with 2 mm in thickness was tested. In the first series of the test, the blends were cooled to -100°C by using liquid nitrogen. Then the temperature was increased to 150°C at a ramp rate of $5^\circ\text{C}/\text{min}$. In the second series of the test, the blends were cooled to -150°C by using liquid nitrogen. Then the temperature was increased to 185°C at a ramp rate of $3^\circ\text{C}/\text{min}$.

3.4.3 Differential Scanning Calorimeter (DSC)

The heat of fusion for the blends and corresponding melting points for each blend formulation were measured by using a differential scanning calorimeter. DSC samples were taken from compression plates. Each sample was weighed to 10 ± 0.5 mg in weight. Then it was placed in an open aluminium pan. The heating or scan rate used was 5 °C/min. Specimens were heated from 35 °C to 285 °C.

3.4.4 Fractography

Plates of each blend formulation was machined to small rectangular bars. Each bar was then immersed in liquid nitrogen for about fifteen minutes until all the bubbles deminished. Then, cleavage was induced by cracking the immersed specimens to pieces. The cracked surfaces were coated with gold/palladium by sputtering at a plasma discharge current of 10 mA and a plate time of 4 min. The fracture surfaces were examined microscopically using the JEOL JSM-5400 scanning electron microscope.