

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Polyamide12 (Nylon12)

Polyamide12 (Nylon12) is a commercial grade polyamide (Grilamid® L25 natural 6112), which was supplied by EMS-Chemie (Asia and America). The polymer is in a pellet-bead form. The melting point is 178 °C. The polymer properties are reported in Table 3.1.

Table 3.1 Polymer properties of polyamide12 (Nylon12)

Properties	Grilamid®L25	ASTM
Melt Flow Rate, (275 °C, 5 kg), g/10 min	20	D1238
Density, g/cm ³	1.09	ISO 1183
Tensile Strength at Yield, MPa	45	D638
Elongation at Yield, %	11	D638
Flexural Modulus, MPa	1660	D790
Notched Izod Impact Energy, J/m	144	D256
Deflection Temperature 0.46 MPa (66 psi)	146	D648

3.1.2 Natural Rubber (NR)

Natural rubber (NR) grade Standard Thai Rubber (STR) 5L was purchased from Banpan Research Laboratory (Thailand) in yellow solid bulk form. The specification of STR-5L is presented in Table 3.2.

Table 3.2 Specification of STR-5L

Properties	STR-5L
Density (g/cm ³)	0.93
Glass Transition Temperature (°C)	-70.0
Dirt Content (max, wt%)	0.04
Ash Content (max, wt%)	0.40
Nitrogen (max, wt%)	0.60
Volatile Matter (max, wt%)	0.80
Initial Plasticity (Po) (min)	35.00
Plasticity Retention Index (PRI) (min)	60.00
Color Lovibond Scale (individual value, max)	6.00
Color Coding Marker	Light green

3.1.3 Polystyrene (PS)

Polystyrene (PS) is a commercial grade polystyrene (STYRON™ 666D), which was supplied by Americas Styrenics. The polymer properties are reported in Table 3.3.

Table 3.3 Polymer properties of polystyrene (PS)

Properties	STYRON™ 666D	ASTM
Melt Flow Rate, g/10 min	8	D1238
Density, g/cm ³	1.04	D792
Tensile Strength at Yield, MPa	44.8	D638
Elongation at Break, %	1.6	D638
Flexural Modulus, MPa	3150.9	D790
Notched Izod Impact Strength, J/m	16	D256
Deflection Temperature 0.46 MPa (66 psi)	85.6	D648

3.1.4 Maleic Anhydride (MA)

Maleic anhydride (MA) with purity of 99.0 % was purchased from Acros Organics to use as a reactive functional group. This material was used in form of white opaque pellets with melting point of 52.8 °C and density of 1.48 g/cm³.

3.1.5 Dicumyl Peroxide (DCP)

Dicumyl peroxide (Luperox[®] DCP) with purity of 99.0 % and active oxygen content of 5.92 % was purchased from Sigma-Aldrich to use as an initiator. This material was used in form of white opaque flakes with melting point of 39 °C and density of 1.56 g/cm³ at 25 °C.

3.2 **Blend Preparation**

3.2.1 Mastication of NR

The solid block natural rubber was masticated on a two-roll mill (Lab Tech, LMR 110) as shown in Figure 3.1 for 10 min at room temperature, and then cut into small pieces.



Figure 3.1 Two-roll mill.

3.2.2 Non-Reactive Compatibilization

3.2.2.1 *Polystyrene/Natural Rubber [60/40 wt%] Blend*

Polystyrene/Natural rubber (PS/NR) blend used as a non-reactive compatibilizer in Nylon12/NR blend was prepared in a twin-screw extruder (Labtech) with a screw diameter of 20 mm and a length/diameter ratio of 44 (Figure 3.2). Prior to blending, PS was dried in a vacuum oven at 60 °C for 12 hours in order to remove the absorbed water. Then PS (60 wt%), DCP (0.5 wt%) and NR (40 wt%) were fed into the extruder and mixed at different screw speeds (30-45 rpm). The operating temperatures of the extruder were maintained at 100, 120, 135, 150, 160, 165, 165, 165, and 165 °C that order from hopper to die. The extrudate was cooled in a water bath before being cut with a granulator into pellet form.

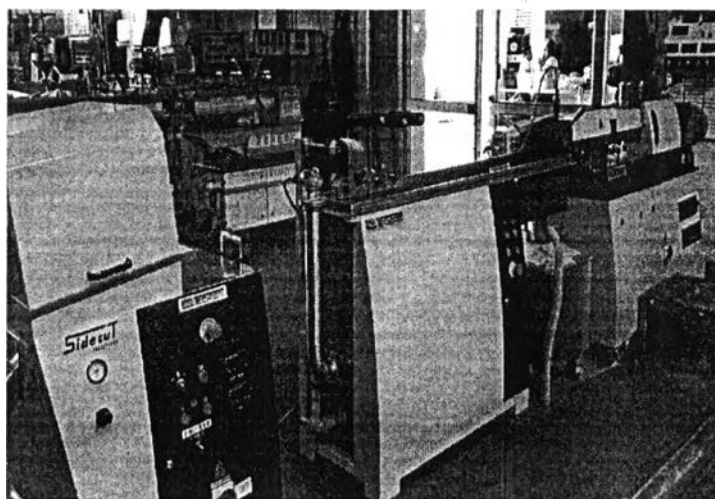


Figure 3.2 Co-rotating twin-screw extruder (Labtech).

3.2.2.2 *Determination of Grafting Ratio*

In PS/NR melt blending process using DCP as an initiator, many kinds of end products were produced in free radical reaction system, e.g., crosslinked NR, unreacted PS (PS short chain), a graft copolymer of PS and NR. To purify the blend, the crosslinked NR (gel) was extracted by using toluene for 24 h at 120 °C while the PS short chain (unreacted PS) was extracted by methyl ethyl ketone

for 24 h at 90 °C. The contents of gel and unreacted PS including graft ratio (GR) were calculated by using Equations (3.1-3.3).

$$\text{Gel (wt\%)} = \left[\frac{\text{weight of gel}}{\text{weight of crude blend}} \right] \times 100 \quad (3.1)$$

$$\text{Unreacted PS (wt\%)} = \left[\frac{\text{weight of unreacted PS}}{\text{weight of crude blend}} \right] \times 100 \quad (3.2)$$

$$\text{Graft ratio (GR)} = \frac{\text{weight of purified blend (PS - g - NR)}}{\text{weight of crude blend}} \quad (3.3)$$

3.2.2.3 Nylon12/NR [80/20 wt%]/[PS/NR] Compatibilizer Blends

Prior to blending, the crude blend of PS/NR and Nylon12 were dried in the vacuum oven at 60 °C for 12 h in order to remove the absorbed water. Then Nylon12, NR and PS/NR blend with various contents (5-25 phr) were fed into the twin-screw extruder and mixed at screw speed of 40 rpm. The operating temperatures of the extruder were maintained at 170, 175, 180, 185, 190, 200, 200, 205, 210, and 210 °C that order from hopper to die. The extrudate was cooled in a water bath before being cut with the granulator into pellet form, and then dried in the vacuum oven at 60 °C before further use. The blend compositions are shown in Table 3.4.

Table 3.4 Blend compositions of [Nylon12/NR]/[PS/NR] blends for Chapter IV

Materials	Nylon12 (wt%)	NR (wt%)	PS/NR (phr)
Neat PA12	100	-	-
NR	-	100	-
Nylon12/NR	80	20	-
[Nylon12/NR]/[PS/NR]			
5	80	20	5
10	80	20	10
15	80	20	15
20	80	20	20
25	80	20	25

3.2.3 Reactive Compatibilization

3.2.3.1 *Polystyrene/Natural Rubber [60/40 wt%]/Maleic Anhydride Blend*

Prior to mixing, PS was dried in a vacuum oven at 60 °C for 12 hours in order to remove the absorbed water. Then PS-NR-MA blend was prepared via reactive blending in a Brabender mixer (Figure 3.3) by using two different mixing procedures as shown in Figure 3.4. The blend compositions are shown in Table 3.5.

- One-step Mixing

PS (60 wt%) was fed into the chamber of the Brabender mixer to melt at a processing temperature of 170 °C and a rotor speed of 60 rpm for 3 min. Next, DCP (0.5 wt%) was added and mixed for 3 min. Finally, MA (3 and 5 wt%) and masticated NR (40 wt%) were fed into the chamber and mixed further for another 4 min. The blends were called PS/NR/MA.

- Two-step Mixing

At the first step, masticated NR was induced in the Brabender mixer for 3 min at the processing temperature of 135 °C and the rotor speed of 60 rpm. MA was then incorporated, mixing it at the same temperature and rotor speed for 5 min. Finally, the NR functionalized with MA, so called “maleated natural rubber (MNR)”, was removed from the chamber.

At the second step, PS was added and melted for 3 min at the processing of temperature of 170 °C and the rotor speed of 60 rpm. Next, DCP was added and mixed for 3 min. Finally, MNR was added to the molten PS and mixed for 4 min. The blends were called PS/MNR.

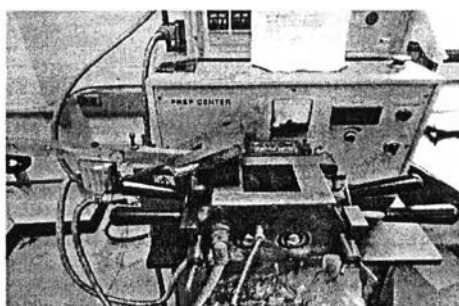


Figure 3.3 Brabender mixer (Prep Center) with roller blades.

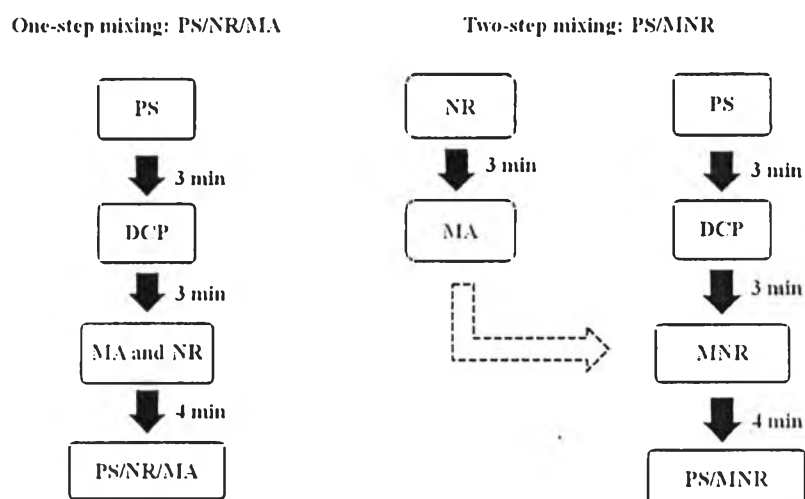


Figure 3.4 Two different mixing procedures for preparation of PS/NR/MA (one-step mixing) and PS/MNR (two-step mixing).

Table 3.5 Blend compositions of PS-NR-MA blends for Chapter V

Materials	PS (wt%)	NR (wt%)	DCP (wt%)	MA (wt%)	No. Step of Mixing
PS	100	-	-	-	1
PS/NR	60	40	0.5	-	1
PS/NR/MA-3	60	40	0.5	3	1
PS/NR/MA-5	60	40	0.5	5	1
PS/MNR-3	60	40	0.5	3	2
PS/MNR-5	60	40	0.5	5	2

3.2.3.2 Determination of Gel Content and MA Grafting Efficiency

After mixing, the gel (crosslinked NR) content was measured by using solvent extraction method. Gel was extracted by dissolving the crude blend of PS-NR-MA (2.0 g) in toluene (100 ml) for 24 h at 120 °C. After vacuum drying at 100 °C for 24 h, the gel (insoluble part) content was then calculated by using Equation (3.1). For purification, the soluble part (the blend without gel) was precipitated into 100 ml of acetone. The precipitate was then filtered and washed with acetone several times. At this step, the unreacted MA was also removed. After vacuum drying, the blend without gel was extracted by methyl ethyl ketone (good solvent for PS) for 24 h at 90 °C. The solution (unreacted PS) was then precipitated into 100 ml of ethanol, and its content was calculated by using Equation (3.2). The purified product was specified as the PS-g-MNR copolymer, and the graft ratio was calculated by using Equation (3.4).

$$\text{Graft ratio (GR)} = \frac{\text{weight of purified blend (PS - g - MNR)}}{\text{weight of crude blend}} \quad (3.4)$$

For MA grafting efficiency, the purified product (1.0 g) was dissolved in 100 ml of toluene with the addition of 0.2 ml of distilled water at refluxing temperature for 2 h. By this procedure, the water plays a role in hydrolyzing anhydride functions into carboxylic acid functions. The carboxylic acid concentration was determined by titration with 0.1 N ethanolic KOH, after adding five drops of 1 % phenolphthalein in ethanol as an indicator. The carboxylic acid concentration was converted to the MA content by using Equation (3.5), and the MA grafting efficiency was then calculated by using Equation (3.6).

$$\text{MA (wt\%)} = \left[\frac{98.06 \times N \times V}{2 \times W} \right] \times 100 \quad (3.5)$$

$$\text{MA grafting efficiency} = \left[\frac{\text{weight percentage of MA grafted}}{\text{weight percentage of MA added}} \right] \times 100 \quad (3.6)$$

where N = concentrations (mol/l) of KOH
 V = volume (l) of KOH
 W = weight (g) of purified product

3.2.3.3 Nylon12/NR [80/20 wt%]/Compatibilizer Blends

The blends of Nylon12/NR with PS/MNR-3 as a reactive compatibilizer at various contents (1, 3, 5, 7 and 10 phr) were prepared by melt-mixing process in the Brabender mixer. The condition was set at 210 °C for processing temperature and 70 rpm for rotor speed. First, Nylon12 was fed into the chamber and molten for 3 min. Then PS/MNR and masticated NR were added and mixed for another 4 min. Finally, the blends were taken out of the chamber, cooled down to room temperature, and ground into small pieces for further study of phase morphology, rheological, thermal, and mechanical properties.

Table 3.6 Blend compositions of [Nylon12/NR]/[PS/MNR-3] blends for Chapter VI-VII

Materials	Nylon12 (wt%)	NR (wt%)	PS/MNR-3 (phr)
Neat PA12	100	-	-
NR	-	100	-
Nylon12/NR	80	20	-
[Nylon12/NR]/[PS/MNR]			
1	80	20	1
3	80	20	3
5	80	20	5
7	80	20	7
10	80	20	10

3.2.3.4 Determination of Nylon12-g-MNR

To determine the content of Nylon12-g-MNR (succinimide linkage), the crude blends of [Nylon12/NR]/[PS/MNR] was dissolved in toluene at temperature of 120 °C for 3 days. At this step, unreacted NR was removed. After vacuum drying for 24 h at 100 °C, the blends were then dissolved in formic acid at 70 °C for 4 days to remove unreacted Nylon12. The purified products were specified as Nylon12-g-MNR, and their contents (graft ratio) were calculated by using Equation (3.7).

$$\text{Graft ratio} = \frac{\text{weight of purified blend (Nylon12 - g - MNR)}}{\text{weight of crude blend}} \quad (3.7)$$

3.3 Characterizations

3.3.1 Non-Reactive Compatibilization

3.3.1.1 *Fourier Transform Infrared Spectrometer (FTIR)*

Infrared spectra were recorded with a Fourier transform spectrometer (PerkinElmer 1760-X) in the range of 4000-400 cm^{-1} with a resolution of 16 cm^{-1} . The PS, NR and graft copolymer of PS and NR were dissolved in toluene and then analyzed as films.

3.3.1.2 *Molding*

The blends were dried at 60 °C for 12 h before being injected. Then the blends were molded in an injection molding machine (Asia Plastic – 90 Injection molding) into tensile specimens (Type I; length of 165 mm, width of 10.0 mm, and thickness of 3.2 mm) and impact specimens (length of 63.5 mm, width of 12.7 mm, and thickness of 3.2 mm). The typical operating conditions used were a 250 °C nozzle temperature and a 90 °C mold temperature.

3.3.1.3 *Mechanical Testing*

Tensile properties of the blends were carried out by an Instron universal testing machine model 4206. All specimens were tested according to ASTM D638 at room temperature with the gauge length of 50 mm, the load cell of 100 kN and the crosshead speed of 50 mm/min.

Impact energy of the blends was studied by an Izod pendulum impact tester (Zwick model 5113). All specimens were V-notched on the center of one longitudinal side and tested with the pendulum 21.6 J according to ASTM D256 at room temperature.

3.3.1.4 *Blend Morphology*

A JEOL JSM 5800LV scanning electron microscope (SEM) with magnification 2,500 times was used at 15 kV to investigate the morphology of the cross-sectional surface after coating by gold, a conductive material. For the preparation of the cross-sectional surface, the samples were cryogenically broken after dipping in liquid nitrogen for 1 h and then the rubber phase was removed by etching with toluene for at least 3 days at 100 °C.

3.3.1.5 Rheological and Extrudate Swell Measurements

A CEAST Rheologic 5000 twin-bore capillary rheometer (see Figure 3.5) was used to investigate the melt rheology and the extrudate swell of Nylon12/NR]/[PS/NR] blends. The inner diameter and the length of the barrel used were 15 and 300 mm, respectively, while the length-to-inner diameter (L/D) was 0.5/1, 5/1 and 20/1 for the Bagley correction. All measurements were made at four test temperatures of 205, 210, 215 and 220 °C and the range of apparent shear rates varied from 100 to 4000 s⁻¹. The hold-on time and hold-on pressure for stages 1-3 were 200 s at 10, 20, and 30 Pa, respectively. For the apparent shear stress (τ_{app}), it is defined as shown in Equation (3.8).

$$\tau_{app} = \frac{R\Delta P}{2L} \quad (3.8)$$

where R is the radius of the die (mm), ΔP is the pressure drop across the die (Pa), and L is the length of the die (mm); and the apparent shear rate ($\dot{\gamma}_{app}$) is defined as shown in Equation (3.9).

$$\dot{\gamma}_{app} = \frac{4Q}{\pi R^3} \quad (3.9)$$

where Q is the volumetric flow rate. Then the procedures of Bagley (Brydson, 1970; Cogswell, 1996) and Rabinowitsch (Cogswell, 1996) will be used to correct the actual shear stress and the actual shear rate, respectively. According to these corrections, the actual shear stress is defined as shown in Equation (3.10).

$$\tau_{actual} = \frac{R\Delta P}{2(L + eR)} = \frac{\Delta P}{2\left(\frac{L}{R} + e\right)} \quad (3.10)$$

where e is a multiplication factor according to the Bagley correction; and the actual shear rate ($\dot{\gamma}_{actual}$) is defined as shown in Equation (3.11).

$$\dot{\gamma}_{\text{actual}} = \frac{3n'+1}{4n'} \dot{\gamma}_{\text{app}} \quad (3.11)$$

where n' is the slope from a plot (in a double logarithmic scale) between the apparent shear rate and the apparent shear stress that was fitted to the Rabinowitsch correction. According to these values, the actual shear viscosity (η_{actual}) can be calculated by using Equation (3.12).

$$\eta_{\text{actual}} = \frac{\tau_{\text{actual}}}{\dot{\gamma}_{\text{actual}}} \quad (3.12)$$

For extrudate swell, it was measured by using an attached KEYENCE VG laser analytical device, which comprises a laser light source and a light sensor. The extrudate swell (B) is reported as the percentage of extrudate swell (%) seen Equation (3.13).

$$\%B = \frac{(D_e - D) \times 100}{D} \quad (3.13)$$

where D_e and D are the diameter of the extrudate and the die, respectively.

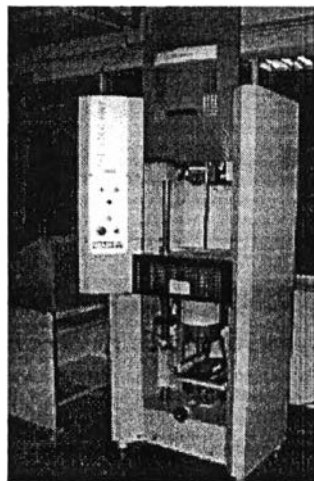


Figure 3.5 CEAST Rheologic 5000 twin-bore capillary rheometer.

3.3.1.6 Thermogravimetric Analysis

The thermogravimetric analysis (TGA) was performed with a thermal analyzer (Perkin-Elmer Pyris). The blends were analyzed at temperature of 30-600 °C with the heating rate of 10 °C/min under the nitrogen gas atmosphere.

3.3.2 Reactive Compatibilization

3.3.2.1 Solid-state NMR

The presence of MA in the formerly prepared MNR and PS/MNR blend was determined by solid-state ^{13}C NMR. The blends were packed into the ZrO_2 rotor (4 mm in diameter). The experiments were performed at 50 MHz at room temperature with an Inova-200 solids NMR spectrometer using a cross polarization (CP)/magic angle spinning (MAS) probe. For this present work, a rotor spinning frequency of 7 kHz was used.

3.3.2.2 Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR).

ATR-FTIR was used to study the chemical structure of [Nylon12/NR]/[PS/MNR] blends after purification. FTIR spectra of the materials were recorded using a Nicolet 6700 in the range of 4000-600 cm^{-1} with a resolution of 4 cm^{-1} .

3.3.2.3 Rheological Test

Rosand RH7 capillary rheometer (see Figure 3.6) was used to investigate the flow properties; shear viscosity, flow activation energy and extrudate swell of the [Nylon12/NR]/[PS/MNR] blends. A capillary die with the length-to-inner diameter (L/D) of 32/1 was used. All measurements were made at three test temperatures of 200, 210 and 220 °C and the range of apparent shear rates varied from 10 to 500 s^{-1} . The apparent values of shear stress, shear rate and shear viscosity were calculated using a derivative of the Poiseuille law for capillary flow (Cogswell, 1996). The apparent shear stress (τ_{app}) and the apparent shear rate ($\dot{\gamma}_{\text{app}}$) were calculated by using Equations (3.8) and (3.9).

According to these values, the apparent shear viscosity (η_{app}) is defined as the ratio of apparent shear stress to apparent shear rate as shown in Equation (3.14).

$$\eta_{app} = \frac{\tau_{app}}{\dot{\gamma}_{app}} \quad (3.14)$$

Then the percentage of extrudate swell or die swell (B) is reported by using Equation (3.13).



Figure 3.6 Rosand RH7 capillary rheometer.

3.3.2.4 Thermal Property

Crystallization parameters were measured by using differential scanning calorimeter (DSC Q2000). The samples were heated from -20 to 210 °C at 10 °C/min in order to eliminate any thermal history of the material, and then, cooled from 210 to -20 °C at a rate of 5 °C/min. The samples were then heated from -20 to 210 °C at a rate of 10 °C/min. All these steps were carried out in a dry nitrogen atmosphere in order to avoid any possible thermal degradation. The peak temperatures of the corresponding exothermal and endothermal curves were taken as the crystallization temperature (T_c) and the melting temperature (T_m), respectively,

and normalized to the unit weight of the sample. The degree of crystallinity (X_c) can be calculated by using Equation (3.15).

$$X_c = \frac{\Delta H_b}{\Delta H_0} \times 100 \quad (3.15)$$

where ΔH_b was the enthalpy of fusion (area under the endotherm) of Nylon12 in the blends, and ΔH_0 was the enthalpy of fusion for a 100 % crystalline Nylon12 which was taken to be 245.69 J/g (Pyda, 2013).

3.3.2.5 Phase Morphology

A JEOL JSM 7401 Scanning Electron Microscope (SEM) with magnification 500 times for PS-NR-MA blend (Chapter V) and 5,000 and 10,000 times for [Nylon12/NR]/[PS/MNR] blends (Chapter VII) was used at 10 kV to investigate the phase morphology. For preparation of the cross-sectional surface, the impact bar specimen of each blend was cryogenically broken after dipping in liquid nitrogen for 5 min (PS-NR-MA blends). For [Nylon12/NR]/[PS/MNR] blends, all samples were cryogenically broken after dipping in liquid nitrogen for 15 min and then the rubber phase was removed by etching with mixed solvent of toluene (90 wt%) and isopropanol (10 wt%) for at least 3 days at 100 °C to get complete dissolution. Samples were then coated by silver to be a conductive material.

3.3.2.6 Impact Energy

Impact energy of all blends was studied by Izod pendulum impact tester (TMI No. 43-1). All specimens were obtained from mini-injection molding (see Figure 3.7) with a length of 60 mm, a thickness of 3 mm, and a width of 12 mm. The specimens were then V-notched on the center of one longitudinal side, providing a width of 10.2 mm under notch. The test was done according to ASTM D256 with the pendulum 13.6 J for PS-NR-MA blends (Chapter V) and 40.6 J for [Nylon12/NR]/[PS/MNR] blends (Chapter VII) at room temperature. For each blend, ten replications were tested.

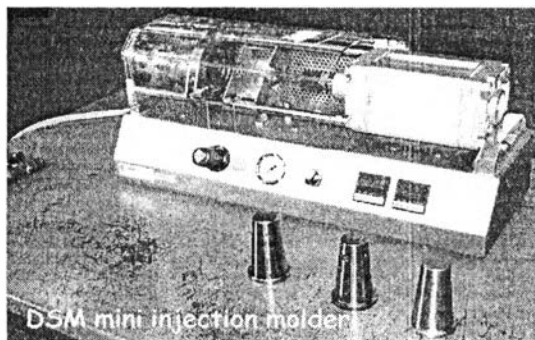


Figure 3.7 DSM mini injection molder.

3.3.2.7 *Tensile Properties*

An Instron universal testing machine (Model 5567) was used to measure the tensile properties; Young's modulus, tensile stress at yield, and elongation at break of [Nylon12/NR]/[PS/MNR] blends with a crosshead speed of 10 mm/min and 10 kN load cell. Tensile specimens (Type IV) were obtained from mini-injection molding with a specimen length of 60 mm, a gauge length of 32 mm, and a thickness of 3 mm. At least ten specimens were used for each blend to determine an average and standard deviation according to ASTM D638 at room temperature.

3.3.2.8 *Flexural Properties*

The flexural stress, the flexural modulus and the flexural strain of [Nylon12/NR]/[PS/MNR] blends were determined by using an universal testing machine (Model 4206). Samples were obtained from compression molding with a depth of 3 mm, a width of 25 mm, and a length of 80 mm. All specimens were then tested according to ASTM D790 (Three Point Bending) with a crosshead speed of 2 mm/min, a load cell of 5 kN, and a support span of 50 mm. Five specimens were used for each blend to determine an average and standard deviation.