

## **CHAPTER III**

### **EXPERIMENTAL**

#### **3.1 Chemicals**

1. Prevulcanized natural rubber latex : Revertex(Thailand) Ltd.
2. Methyl methacrylate monomer : Siam Chemical Industry Co., Ltd.
3. Sodium hydroxide, AR grade : Merck
4. Divinyl benzene : Merck
5. Oleic acid : Fluka
6. Ammonia solution : Fluka
7. Aluminum oxide, for chromatography: Fluka
8. Irganox 1076 : Ciba-Guigy Ltd.
9. Polypropylene (2500 TC) : Thai Petrochemical Industry (Public),Ltd.
10. EPDM (JSR EP35) : Japan Synthetic Rubber Co., Ltd.
11. Polyolefin (Engage 8100) : PI industry Co., Ltd.

#### **3.2 Glasswares**

1. 4-Necked round bottom reactor, 500 cm<sup>3</sup> capacity
2. Condenser
3. Nitrogen gas tubing
4. Other general laboratory glassware



### 3.3 Equipments

1. Transmission Electron Microscopy : JSM 200CX, STREC CU
2. Scanning Electron Microscopy : JSM 35CF, STREC CU
3. Two roll mill : Lab Tech Engineering, CU
4. Crushing machine : Lab Tech Engineering, CU
5. Compression molding machine : Lab Tech Engineering, CU
6. Durometer hardness : Zwich, RRIT
7. Universal testing machine : Instron Corporation SerielX, RRIT
8. Flexural strength testing : Instron Corporation Model 4302, MTEC
9. Impact testing machine : Impact Radmana ITR2000, MTEC
10. Differential Scanning Calorimeter : Perkin Elmer DSC7, STREC CU
11. Thermogravimetric Analyzer : Perkin Elmer TGA7, STREC CU

### 3.4 Experimental Procedure

#### 3.4.1 Purification of Monomer

Methyl methacrylate monomer (MMA) was washed with 10 wt% aqueous sodium hydroxide solution followed by deionized water until neutral, and then dried using anhydrous sodium sulfate, and pass through an activate aluminum oxide column to remove the residual inhibitor. The purified MMA was stored in the refrigerator.

### 3.4.2 Preparation of IPNs NR/PMMA Composites

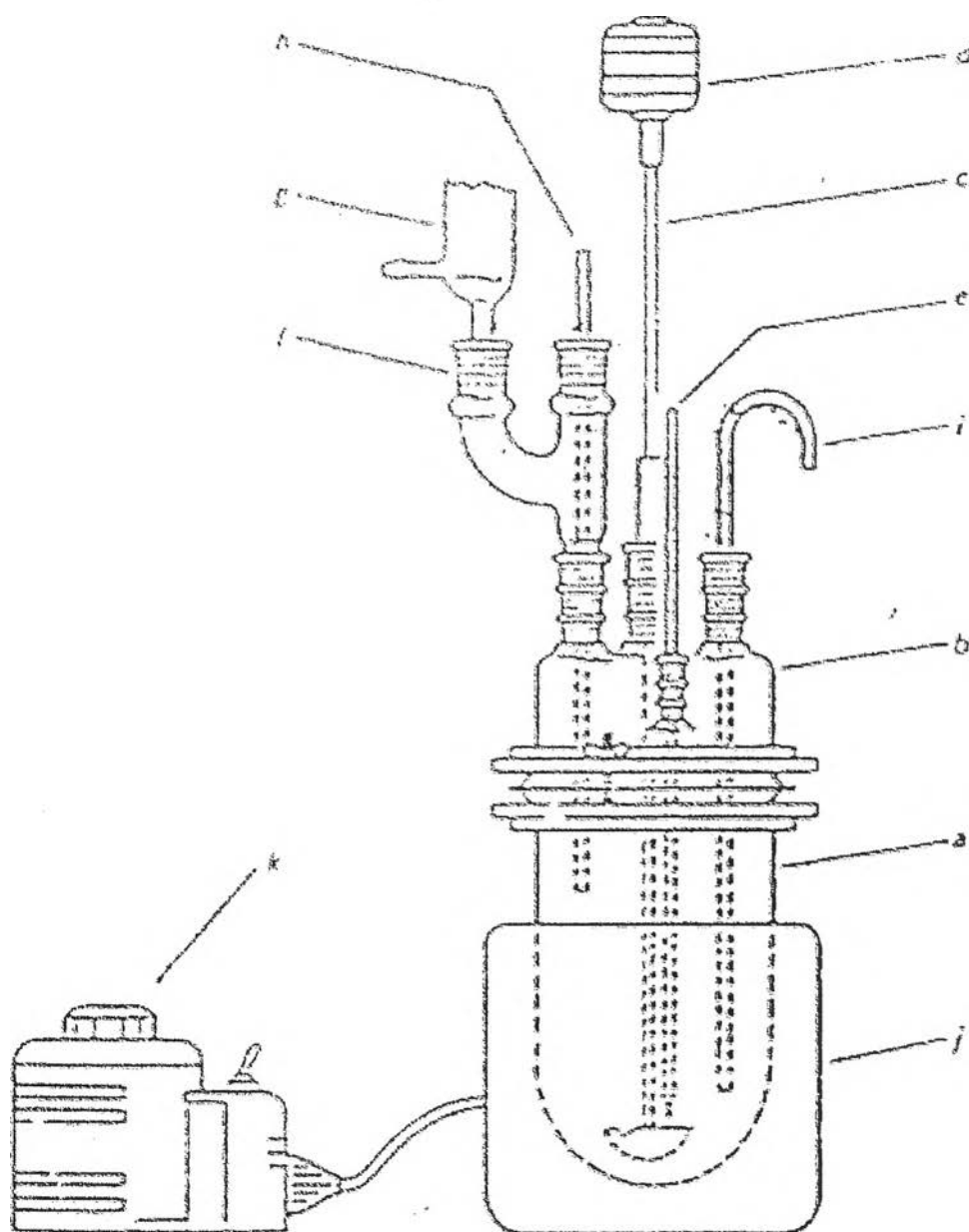
Interpenetrating polymer networks of natural rubber with polymethyl methacrylate were prepared from prevulcanized natural rubber latex by emulsion polymerization method. The equipment setup is shown in Figure 3.1

Prevulcanized natural rubber latex (50g, DRC 60%) was placed in a round bottom reactor along with 1000 cm<sup>3</sup>. Bubbling the nitrogen gas for approximately 30 minutes at room temperature deoxygenated the mixture. The MMA monomer (10, 20, 30, 40 phr) was then added continually while stirring for 15 minutes to allow the prevulcanized natural rubber latex particles to attain swelling. *Tert*-butyl hydroperoxide as an initiator (0.5-2.0 phr) was added at temperature between 50-80 °C. The reaction was then allowed to proceed for 2,6,8 hours under continuous stirring to complete the polymerization. The obtained IPNs latex of NR/PMMA was casted at room temperature on open trays. Once dry, the sheet was removed from the tray and transferred to the oven at 70 °C for approximately 24 hours to remove any traces of monomer that may be retained. The dried sheet was then leached with distilled water to remove any water-soluble impurities from rubber. Finally the sheet was then returned to the oven until it was thoroughly dried.

An appropriate condition for interpenetrating polymer networks with emulsion polymerization could be obtained by varying the initiator concentration, reaction temperature, monomer concentration and reaction time as shown in Table 3.1

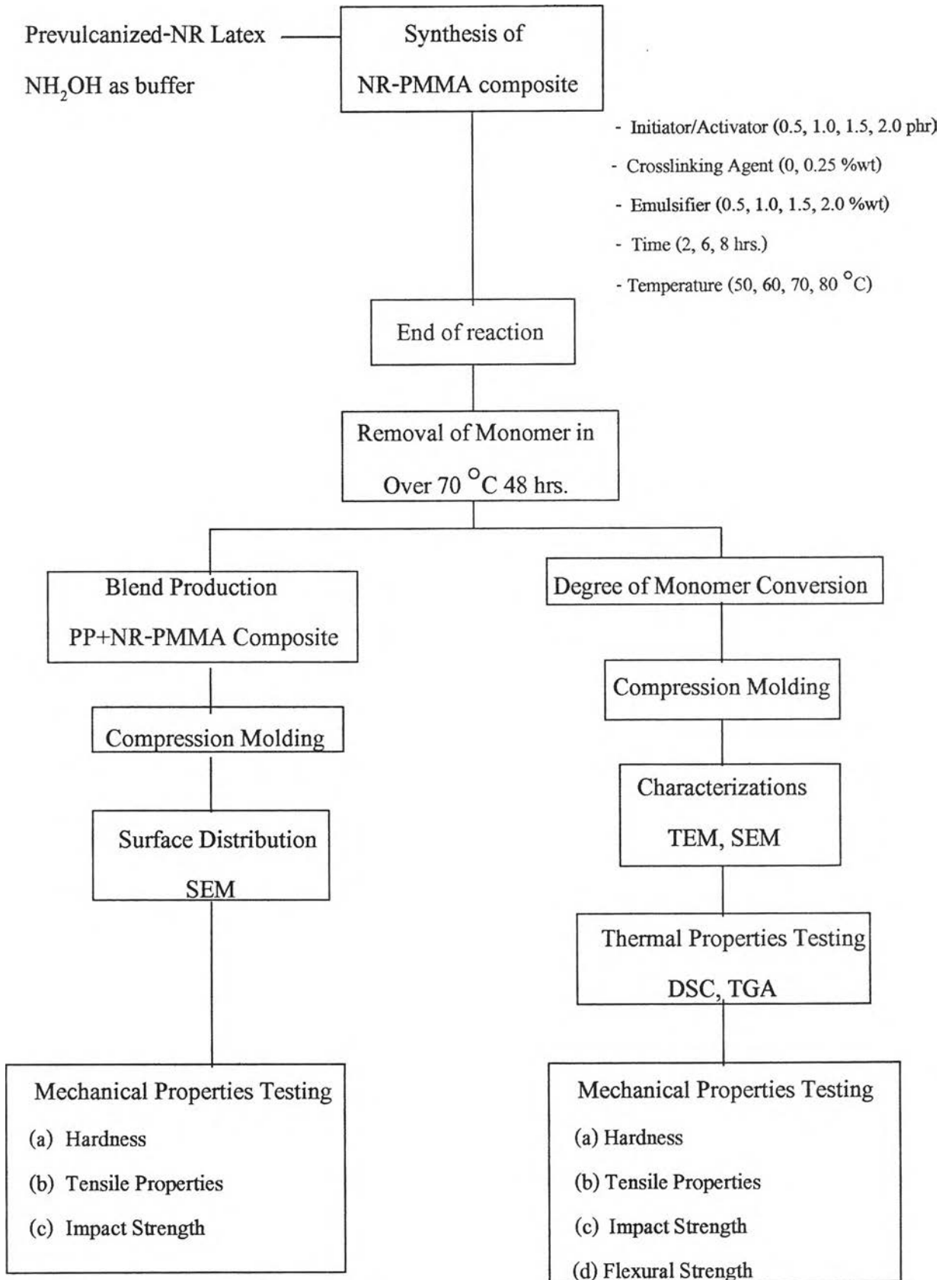
**Table 3.1** The recipes investigated in the polymerization process.

Ingradient	Quantity	Unit
Initiator/activator (1/1)	0.5, 1.0, 1.5, 2.0	phr
Crosslinking agent	0, 0.25	%wt of monomer
Emulsifier	0.5, 1.0, 1.5, 2.0	%wt of monomer
Reaction temperature	50, 60, 70, 80	°C
Reaction time	2, 6, 8	Hours
Ratio NR/PMMA	90/10, 80/20, 70/30, 60/40	-



**Figure 3.1** Apparatus for emulsion polymerization of NR/PMMA IPNs

- |                             |                          |
|-----------------------------|--------------------------|
| (a) Reaction kettle bottom  | (g) Condenser            |
| (b) Reaction kettle top     | (h) Nitrogen-inlet tube  |
| (c) Stainless steel stirrer | (i) Sampling tube        |
| (d) Air motor               | (j) Water bath           |
| (e) Thermometer             | (k) Variable transformer |
| (f) Adapter                 |                          |



**Figure 3.2** Experimental scheme of NR/PMMA composite

### **3.5 Characterization**

#### **3.5.1 Determination of the morphology of NR/PMMA composite**

##### **Transmission Electron Microscopy (TEM)**

Transmission electron microscopy was used in order to observe ultramicrotome sections of NR/PMMA composite, which were prepared in the following way. First, a smooth surface of the NR/PMMA composite was dipped in osmium tetroxide solution for 48 hrs in order to stain the NR phase. The staining not only enhanced the contrast for the microscopic viewing of the blends but also hardened the rubber phase. In this way, ultramicrotome sections could be prepared without altering the particle morphology of the no longer soft natural rubber particles.

##### **Scanning Electron Microscopy (SEM)**

Scanning electron microscope was used for the examination of NR/PMMA composite, which were prepared by coating the gold vapor deposition before viewing.

#### **3.5.2 Determination of Thermal Properties of the Composite Product**

##### **Differential Scanning Calorimetry (DSC)**

A 10-20 mg sample of a dried sample was placed into an aluminum pan and measured between 50 and 180 °C in a Perkin Elmer DSC7 thermal analyzer. The heating and cooling rate was 10 °C/min. DSC measures enthalpy and determines the temperature and enthalpy of the changes in the material's physical state, such as  $T_g$  and  $T_m$ .

## **Thermogravimetric Analyzer (TGA)**

Thermogravimetric analyzing system was used to follow the weight loss of 10-mg sample between 50 and 800<sup>o</sup> C while the system was purged with air. The heating rate was 20<sup>o</sup>C/min. TGA measures changes in mass and helps determine the thermal stability and the decomposition curves.

### **3.6 Mechanical Testing**

The ASTM and ISO test methods were used for investigating the mechanical properties of composite products as follows:

#### **-Hardness**

(ASTM D2240 Standard test method for rubber property-Durometer Hardness)

The assignment of the specimen for hardness testing was at least 6 mm in thickness. The surface of the specimen was flat and covered a sufficient area to permit the presser foot to contact the specimen. For materials having hardness values above 50 type D Durometer, the thickness of the specimen was at least 3 mm and measurements should not be made closer than 6 mm to any edge.

According to the thickness assignment, the test specimens in this experiment were composed of plied pieces to obtain the necessary thickness. The type D Durometer was used in this experiment. The conditions in testing are shown as follows:

Temperature	:	25 <sup>o</sup> C
Relative humidity	:	50%
Number of pieces plied	:	2 pieces



For all of the property measurement, at least five samples were tested to obtain a reliable average and standard deviation.

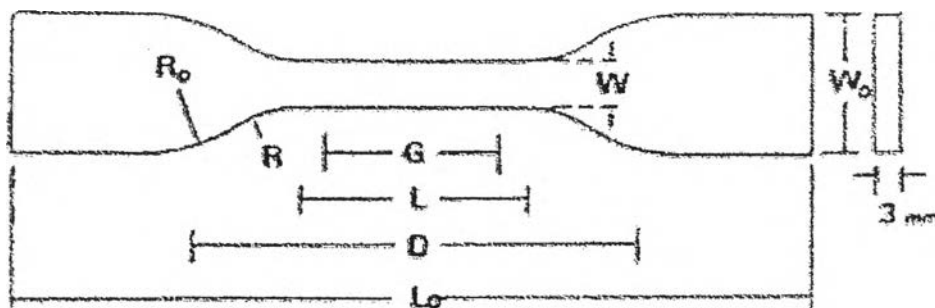
### -Tensile properties

(ASTM D638: Standard test method for tensile properties)

The tensile properties were measured according to ASTM D638 using Universal Testing Machine Model LR 30K. The dumbbell specimen of type IV was used. Figures 3.3 and 3.4 indicated the dimensions of dumbbell specimen of type IV and schematic of tensile test set-up.

The tensile testing conditions were as follows:

Temperature	23°C
Relative humidity	54%
Speed of testing	50.00 mm/min
Gauge length	25.00 mm/min



**Figure 3.3** Dimension of tensile test specimen (TypeIV)

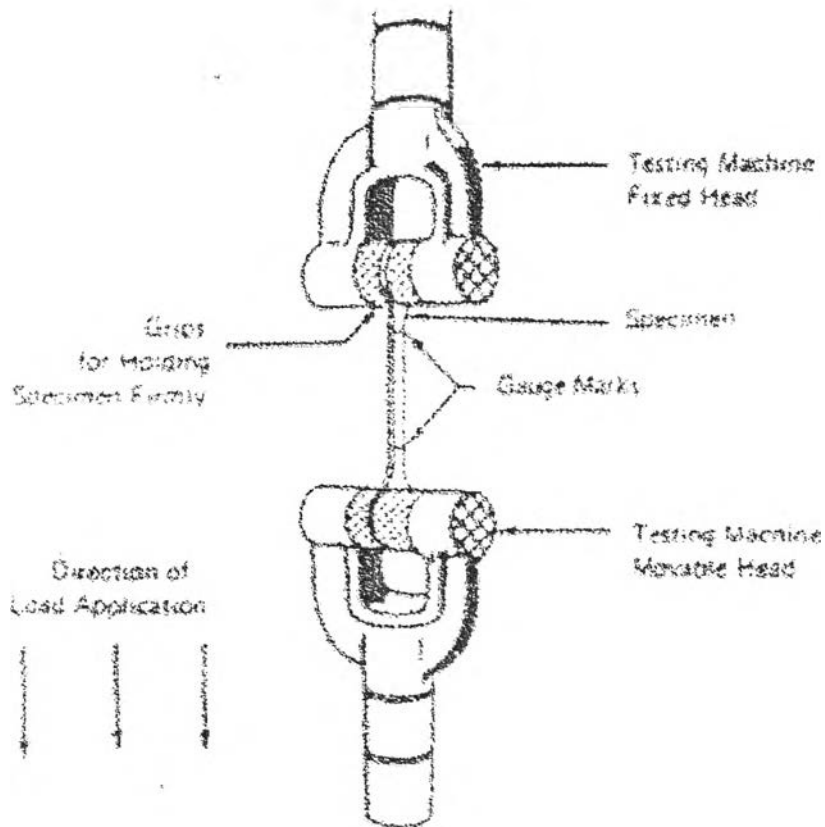


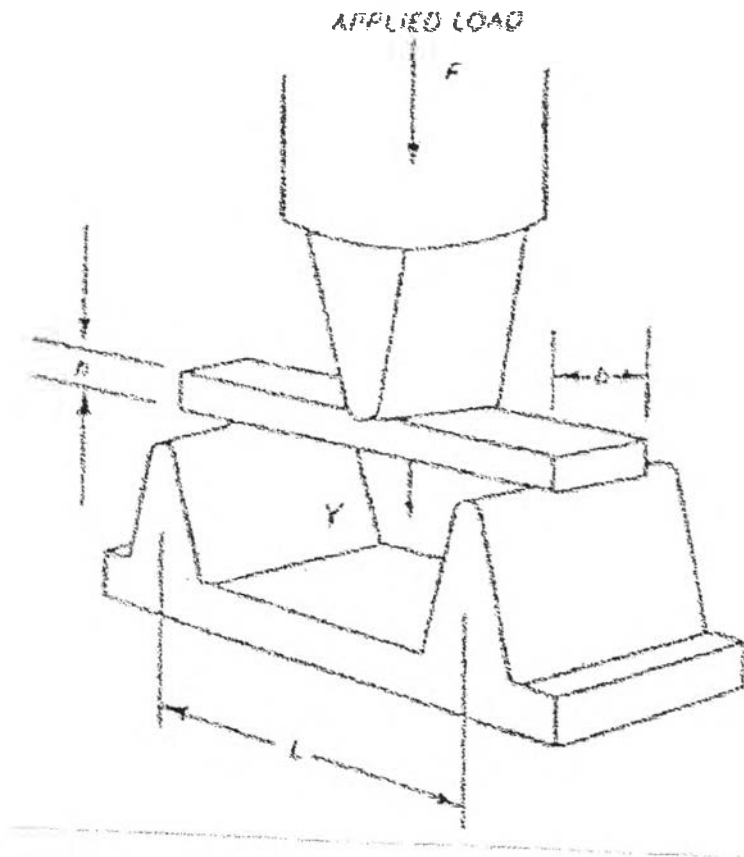
Figure 3.4 Schematic of tensile test set-up

### -Flexural properties

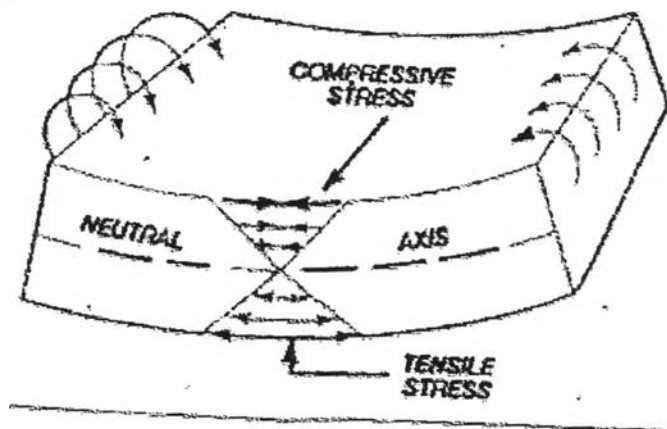
(ASTM D790M: Standard test method for flexural properties)

Flexural properties were measured using a Universal Testing Machine Model LR 30K. Specimen having 10 mm in width and 4 mm in depth and 80 mm in length was used for testing flexural strength and flexural modulus of the sample. Figures 3.5 and 3.6 illustrated the schematic of flexural test set-up and schematic of stress in flexed sample.

For a 3-point bending of flexural testing, the length of the support span depends upon the thickness. In this case, 64-mm span length was used in order to have support span to thickness ratio 16:1. A test specimen was loaded at a 10.05-mm diameter of crosshead loading nose by using the rate of crosshead motion at 1.7 mm/min.



**Figure 3.5** Schematic of flexural test set-up



**Figure 3.6** Schematic of stress in flexed sample

## -Impact resistance

(ASTM D256: Standard test method for impact resistance)

Impact strength was measured according to ASTM D256 on a Universal Impact Tester. The test specimen dimension for Izod type test and schematic of Izod test are shown in Figures 3.7 and 3.8

The machine parameters and testing conditions of the impact test were listed below:

Temperature	23°C
Relative humidity	54%
Pendulum capacity	5.5 J

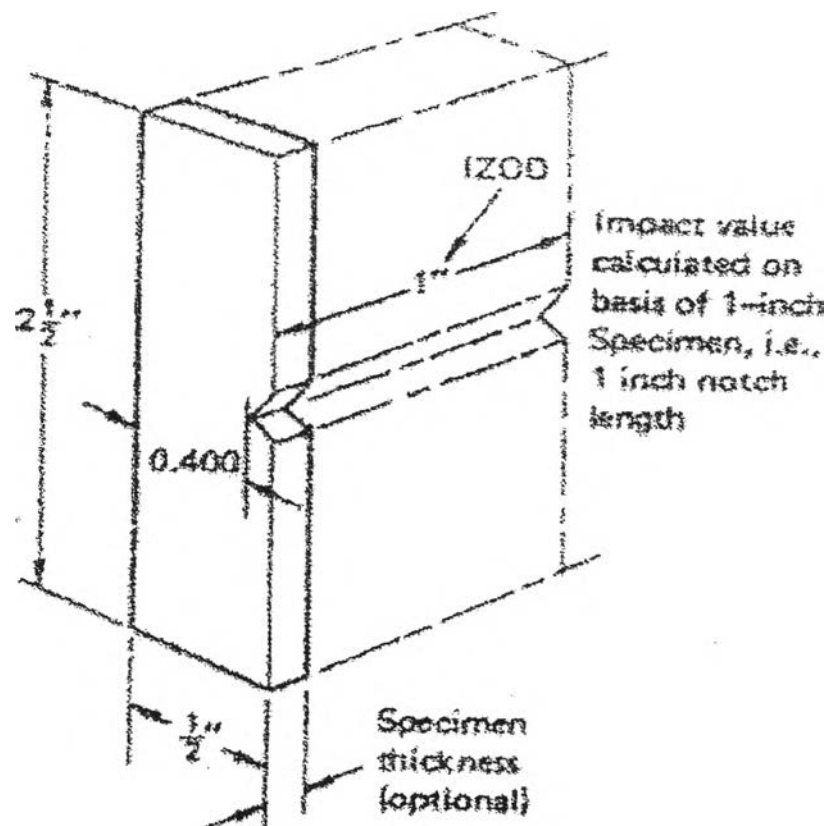


Figure 3.7 Dimensions of Izod type test specimen

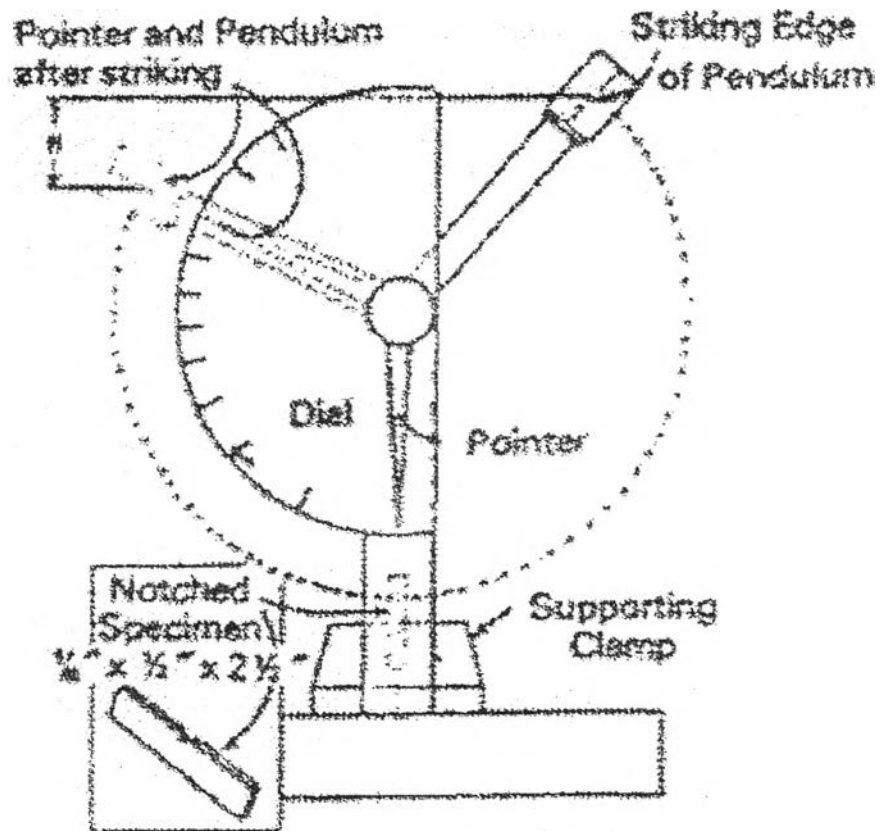


Figure 3.8 Schematic of Izod test

### 3.7 NR-PMMA product and PP blends

The isotactic polypropylene (100 phr) and 5 to 20 phr NR/PMMA composite were prepared by blending all of the components on a two-roll mill at 165°C for 5 min. The PP was first preheating for 2 minutes and followed by the composite product, and antioxidant, respectively. Furthermore, EPDM and Engage 8100 were used to replace the composite product in order to compare the mechanical properties. A batch was mixed for at least 10 minutes after blending. Distance between the rolls (the roll nip) was adjusted to facilitate mixing.

The thin sheet from the two-roll mill was grinded by crushing machine. The sheet was then pressed by compression molding at 200°C, and 1,000 psi for 5 min; the sheet thickness was 3 mm. The sheet was cut into the standard specimens according to the ASTM and ISO method.