

## CHAPTER III

### EXPERIMENTAL WORK

#### 3.1 Materials

All of the materials used in the present study were commercial grade chemicals. A suspension polymerized PVC homopolymer (s-PVC) having a K-value of 71 was used. The plasticizers used were di-isononyl phthalate (DINP) and epoxidized soya been oil (EPO). A barium/cadmium/zinc Ba/Cd/Zn complex stabilizer was also applied. Ground calcium carbonate filler having top cut at 100% maximum of 32.0  $\mu\text{m}$  was added. Acrylonitrile butadiene (NBR) which contains 34% acrylonitrile was used. The specific gravity of NBR in the present study is 0.98. Details of the formulation dosage level are listed in Table 3.1.

**Table 3.1 The formulation of plasticized PVC prepared in the present study.**

Unit : phr

Material	NBR0	NBR20	NBR30	NBR40	NBR50
s-PVC	100	100	100	100	100
NBR	-	20	30	40	50
DINP	100	100	100	100	100
CaCO <sub>3</sub>	10	10	10	10	10
Ba/Cd/Zn	1	1	1	1	1
EPO	3	3	3	3	3

### 3.2. Mixing

The 10 L Papenmeier Laboratory mixer was used for mixing all of the material for PVC dryblend.

The mixer was initially preheated at 60°C. The PVC resin and all solid additives with the exception of NBR are fed into the mixing chamber. For pre-mixing, the mixer speed was set at 1,000 rpm for 2 minutes. Then, the mixing speed was increased to 2,000 rpm while the temperature was raised to 80°C. After that, the speed of mixing was lowered to 1,000 rpm. All liquid additives were put into the mixing chamber and the speed of mixing was raised to 2,000 rpm again while the temperature was elevated to 110°C. After lowering the mixing speed, the mixing chamber was cooled by cooling water. After cooling, NBR was fed into the mixing chamber. Mixing then was conducted at 1,000 rpm until the temperature

was decreased to 50°C. The dryblend was then discharged from the mixing chamber. Any residue dryblend which was stuck to the inner surface of the mixing chamber was scraped off.

### 3.3 Extrusion and Pelletization

The dryblended plasticized PVC with and without NBR were extruded and pelletized by a 30 mm single-screw extruder at the screw speed of 40 rpm. The single screw extruder has three heating zones and a die zone and they were set according to the conditions shown in Table 3.2.

**Table 3.2: Extrusion temperature profiles.**

Screw and Die	ZONE 1	ZONE 2	ZONE 3	ZONE 4 (Die)
Temperature(°C)	100	105	110	115

### 3.4. Sample Preparation

#### 3.4.1 Milled-Sheets

A two-roll mill was used. It consists of two parallel rollers rotating in opposite directions. There is a small gap or 'nip' between the rolls. The nip is adjustable. For mixing the plasticized PVC and plasticized PVC with NBR, the two-roll mill is set at a temperature around 140-170°C. The mixing takes place at the rolling bank which is created by the speed

difference between the two rolls. Diffusion of materials at the nip of the rolls occurs at a slow rate because of the closed-flow streamlines. To break up the streamlines after the material forms a blend against one roll, intermixing must be promoted by a technique call 'quartering', or 'cross cutting'. This is done by the mill operator, who will cut strips frequently, pull them away from the roll, and fold them to pass through the nip of the rolls. Sufficient shear stress must be applied to break up agglomerates and achieve sufficient dispersion. The fusion of PVC occurs from conductive and frictional heating. The sheet compound from the two-roll mill still requires subsequent fabricating and cutting process for further tests in the present study.

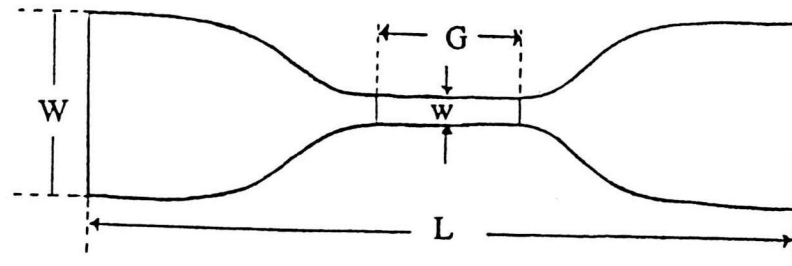
### **3.4.2 Pressed Sheets**

The samples from section 3.4.1 was pressed in a hot press under a pressure of 160 kg/cm<sup>2</sup> for 5 min. The temperature of the hot press was set at 150°C. All samples were pressed to the required thickness specified in each subsequent test.

### **3.4.3. Specimens for Tensile Test**

For tensile test, dumbbell-shaped specimen was cut from the pressed sheet so that the length of the specimen was parallel with the milled direction. The dimensions of the test specimen are shown in Fig 3.1.





where  $W$  = overall width = 25 mm

$w$  = width of narrow section = 5 mm

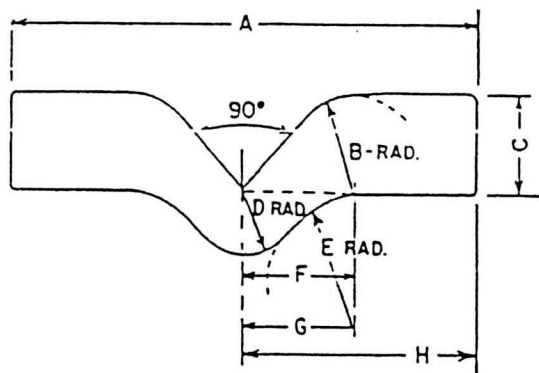
$L$  = overall length = 100 mm

$G$  = gauge length = 25 mm

**Fig 3.1: Specimen for tensile test.**

#### **3.4.4. Specimens for Tear Strength Test**

Specimens for tear strength test were stamped out of the pressed sheets with a steel die. The dimensions of the die are shown in Fig 3.2. The cutting edge of the die was kept sharp and free of all nicks to avoid leaving ragged edge on the specimen. The apex of the 90 deg angle die was sharpened to provide a sharp corner. Specimens were considered acceptable when the cut edges are perpendicular to the other surfaces of the specimen and have minimum concavity.



DIE C

Dimension	Millimetres		Inches	
	Value	Tolerance	Value	Tolerance
A	102	±0.50	4.0	±0.02
B	19	±0.05	0.75	±0.002
C	19	±0.05	0.75	±0.002
D	12.7	±0.05	0.5	±0.002
E	25	±0.05	1.0	±0.002
F	27	±0.05	1.061	±0.002
G	28	±0.05	1.118	±0.002
H	51	±0.25	2.0	±0.01

**Fig 3.2: Die dimensions for tear strength specimen (Die C).**

### 3.4.5 Specimens for Compression Set

A circular die was used to prepare standard test specimens for compression set. The die has an inside diameter of  $13.00 \pm 0.2$  mm ( $0.51 \pm 0.01$ in). The thickness of the pressed sheet is  $6.0 \pm 0.2$  mm ( $0.24 \pm 0.01$ in).

### 3.4.6 Specimens for Hardness Measurement

Specimens can be of any shape as long as the thickness is not less than 6 mm. The surface of the specimens for hardness measurement should always be flat and smooth.

### **3.4.7 Specimens for Abrasion Resistance Test**

Like hardness test specimens, the samples for abrasion resistance test should be flat and smooth. Pressed sheet of 6 mm in thickness was punched to make cylindrical specimens of 16 mm in diameter.

## **3.5. Testing**

### **3.5.1. Mechanical Tests**

#### **3.5.1.1 Tensile Tests (ASTM D412)**

Tensile elongation and tensile modulus measurements are the most important indications of strength in a material. They are the most widely specified properties of plastic materials. Tensile test, in a broad sense, is a measurement of the ability of a material to withstand forces that tend to pull it apart and to determine to what extent the material stretches before breaking. Tensile modulus is an indication of the relative stiffness of a material, it can be determined from a stress-strain diagram. Different types of plastic materials are often compared on the basis of tensile strength, elongation and tensile modulus data. Many plastics are very sensitive to the rate of straining and environmental conditions. Therefore, the data obtained by this method cannot be considered valid for applications involving load-time scales or environments widely different from this method. The tensile property data are more useful in preferential selection of a limited use in actual design of the product. This is because the test

does not take into account the time-dependent behaviour of plastic materials.

In this experiment, the prepared specimen is clamped between two jaws of the test apparatus. One jaw is stationary and the other moves at a constant rate. In this study, the crosshead speed was set constant at 200 mm/min and load cell used has a maximum capacity of 5 kN. All specimens were tested at standard testing condition of  $23 \pm 2^\circ\text{C}$  and  $50 \pm 10\%$  relative humidity.

### 3.5.1.2 Compressive Properties (ASTM D395)

Compression set tests were conducted to measure the ability of the rubber compounds to retain elastic properties after prolonged action of compressive stress. The actual stressing service may involve the maintenance of a definite deflection, the constant application of a known load, or the rapidly repeated deformation and recovery resulting from intermittent compressive forces. The compression set under constant deflection (ASTM D395 method B) was used for the present study. The specimen was tested under  $70^\circ\text{C}$  for 22 hours.

Calculation of the compression set can be expressed as a percentage of the original deflection as follows:-

$$C = [(t_0 - t_i)/(t_0 - t_s)] \times 100 \quad [3.1]$$

where  $C$  = compression set expressed as percentage of original deflection  
 $t_0$  = original thickness of specimen  
 $t_i$  = final thickness of specimen  
 $t_s$  = thickness of the spacer bar used

### 3.5.2 Physical Tests

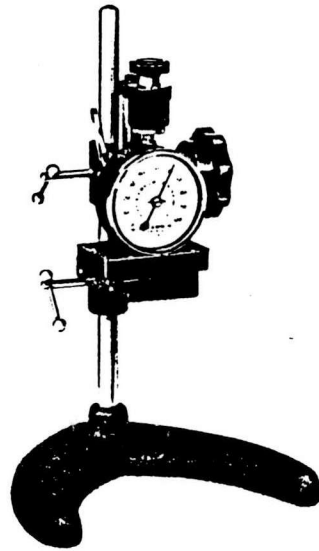
#### 3.5.2.1 Hardness (ASTM D2240)

Hardness is defined as the resistance of a material to deformation, particularly permanent deformation, indentation or scratching. Hardness is purely a relative term and should not be confused with wear and abrasion resistance of plastic material. Many tests have been devised to measure hardness. Only one type of the hardness test is not adequate to cover the entire range of hardness properties encountered.

Two of the most commonly used hardness tests for plastics are the 'Rockwell hardness test' and 'Durometer hardness test'. Rockwell hardness is used for relatively hard plastics such as acetal, nylons, acrylics. For softer materials such as flexible PVC, thermoplastic rubbers and polyethylene, durometer hardness is often used.

The durometer hardness test is mostly used for measuring the relative hardness of soft polymeric materials. The test method is based on the penetration of a specified indenting forced into the material under the specified conditions.

Two types of durometers are most commonly used, type A and type D. The basic differences between the two types are the shape and the dimension of the indenture. The hardness numbers derived from either scale are just numbers without any units. Type A durometer is used with relatively soft material while type D durometer is used with slightly harder material. A commercially available durometer measuring instrument is shown in Fig 3.3 [85].



**Fig 3.3: Durometer hardness tester.**

### **3.5.2.2 Specific Gravity (ASTM D792)**

Specific gravity is defined as the ratio of the weight of a given volume of a material to that equal volume of water at a state temperature. The temperature selected for determining the specific gravity of a plastic part is 23°C.

Specific gravity values represent the main advantage of plastic over the other materials, namely, light weight. All plastics are sold today on a cost per weight basis, not on a cost per unit volume basis. Such a practice increases the significance of the specific gravity considerably in both purchasing and production control. Two basic methods have been developed to determine the specific gravity of plastics, depending upon the form of the plastic material. Method A is used for specimens in various forms such as sheets, rods, tubes, or molded articles. Method B is suitable for pellets, flakes, or powder.

Method A was selected for this study. The test specimen of any convenient size and shape was weighed in air. Then, the specimen was suspended from a fine wire attached to the balance and immersed completely in distilled water. The weight of a specimen in water was determined. The specific gravity of the specimen was calculated as follows:

$$\text{Specific gravity} = \frac{a}{[(a+w)-b]} \quad [3.2]$$

where  $a$  = weight of specimen in air

$b$  = weight of specimen and wire in water;

$w$  = weight of totally immersed sinker and partially immersed wire.

### **3.5.2.3 Color**

The CIE lab testing was used for measuring the color of plasticized PVC with and without NBR in terms of a Yellow Index (YI) based upon the yellowness of samples.

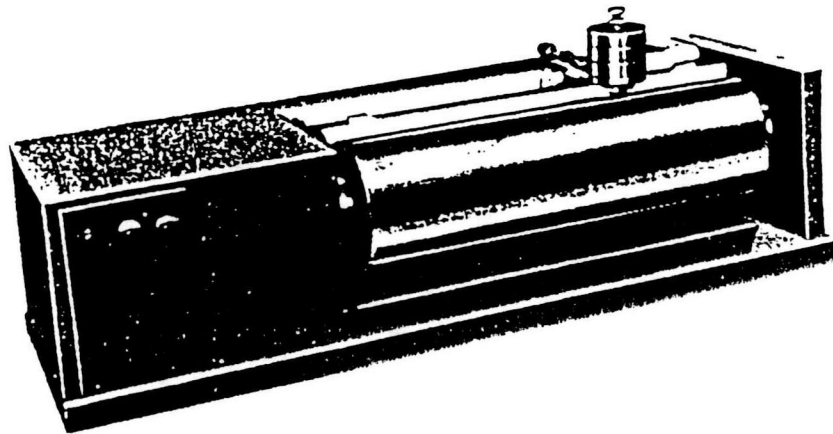
### **3.5.2.4 Abrasion Resistance Tests (JIS K 6369)**

Abrasion resistance of polymeric materials is a complex subject. Many theories have been developed to support the claim that abrasion is closely related to frictional force, load, and true area of contact. An increase in any one of the three generally results in greater wear or abrasion. The hardness of the polymeric materials has a significant effect on abrasion characteristics. For example, a harder material with considerable asperities on the surface will undoubtedly cut through the surface of a softer materials to an appreciable depth, creating grooves and scratches. The theory is further complicated by the fact that the abrasion process also creates oxidation on the surface from the build up of localized high temperature. The resistance to abrasion is also affected by other factors, such as the properties of polymeric material, resiliency and the type and amount of additives.

All the above-mentioned factors make abrasion a difficult mechanical property to define as well as to measure adequately. Resistance to abrasion is defined as the ability of a material to withstand mechanical action that tends progressively to remove material from the surface. In the present study, the abrasion resistance is a measure of the volume of



material loss when pressed against abrasive paper on a revolving drum by using the abrasion tester as shown in Fig 3.4.



**Fig 3.4 : Abrasion tester.**

### **3.5.3 Thermal Tests**

#### **3.5.3.1 Differential Scanning Calorimeter (DSC)**

Whenever a material undergoes a physical transformation or a chemical reaction, heat is either absorbed (endo thermic reaction) or released (exothermic reaction). Many such transformations or reactions are initiated by the temperature of the material.

For this study, a differential scanning calorimeter (DSC) was applied to determine the glass transition temperature ( $T_g$ ) of the test samples. Perkin Elmer DSC7 was used. The DSC is designed to determine the

enthalpies by measuring directly the amount of heat supplied to the sample or reference to compensate for these heat of reactions. The temperature of the sample and that of the reference is programmed to rise or cool at a control rate, or to hold isothermally.

In the absence of physical or chemical transformations as a base line, endothermic reaction will cause the plot to deviate in the positive direction while the exothermic reaction will cause the plot to deviate in the negative direction in the Y-scale. The X-scale depicts the temperature of the sample when analyzing in the dynamic scanning mode

The glass transition temperature is the temperature at which the polymer transforms from a glassy state to a rubbery state. It is frequently referred by its abbreviated symbol,  $T_g$ . Below  $T_g$ , the molecules are "frozen" and rigid but above  $T_g$  they become "flexible". This transformation is accompanied by drastic change in the physical properties of material. At  $T_g$ , the polymers undergo enthalpies of relaxation which appear as a positive deviation from the DSC baseline resulting from the increase in specific heat above  $T_g$ . The glass transition usually takes place within a range of temperature.  $T_g$  is often defined as a mid point of the step change in energy. The step change in energy is sample size dependent, larger sample size will result in a more distinct and higher step change in energy. The onset of the step change in energy is sometimes quoted as a glass transition temperature.

In this experiment, the Perkin Elmer DSC7 was used for the study of compatibility of NBR and PVC in their various composition of blends by

observing the  $T_g$  as the mid point in the step change of test samples. The temperature was scanned from  $-100^{\circ}\text{C}$  to  $100^{\circ}\text{C}$  at a constant heating rate of  $10^{\circ}\text{C}/\text{min}$ .

### 3.5.3.2 Thermal Gravimetric Analyzer (TGA)

One of the methods to measure the quality of a mixture of different materials involves weighing the samples while heating it and then measuring how much the weight changes. Since different chemicals boil off at different temperatures, one can measure the amount of each in the original mixture. This technique is known as thermal gravimetric analysis (TGA). A typical apparatus consists of an analytical balance supporting a platinum crucible for the specimen. The crucible is situated in an electric furnace.

In the present study, the Perkin Elmer TGA7 was used for the analysis of the content of the NBR in plasticized PVC with and without NBR. Each specimen was scanned from the temperature of  $50^{\circ}\text{C}$  to  $900^{\circ}\text{C}$  at a constant heating rate of  $20^{\circ}\text{C}/\text{min}$  in the atmosphere of nitrogen.

### **3.5.4 Analytical Test**

#### **3.5.4.1 Fourier Transform Infrared Spectroscopy (FTIR)**

FTIR was used as a tool to study the characteristics of the material in plasticized PVC with and without NBR. The characteristic peak of NBR was easy to observe by the CN absorption peak of the acrylonitrile in NBR which shows up at the wave number of  $2,238\text{ cm}^{-1}$ .

### **3.5.5 Environmental Test**

#### **3.5.5.1 Oil Resistance Test**

Since monomeric plasticizers are easily extracted from plasticized PVC compounds when they are in contact with aggressive materials such as solvent, unleaded gasoline and motor oil, it seems desirable to detect some changes in properties in the environments of these chemicals.

This experiment was carried out to determine any physical and mechanical changes after an immersion of plasticized PVC with and without NBR in three petrol reagents, motor oil, unleaded gasoline and hexane. To test for the resistance in motor oil, the dumbbell specimens were immersed in the motor oil at  $80^{\circ}\text{C}$  for 48 hours. For the resistance in hexane and unleaded gasoline, the dumbbell specimens were immersed in each of the liquid at  $30^{\circ}\text{C}$  for 48 hours.

### 3.5.6 Fractography

Scanning electron microscope (SEM) was used to study the characteristics of fracture surface of the plasticized PVC with and without NBR prepared in the present study. The SEM used in the present investigation was the JEOL JSM5410 scanning electron microscope. The observation was made on surfaces fractured at low temperature close to that of liquid nitrogen. The surfaces were sputtered with gold. The thickness of the gold coat is around 300 Å. The fracture morphology was observed at the accelerating voltage of 10, 20 and 25 kV.