CHAPTER 2

EXPERIMENTAL TECHNIQUES
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The materials used and the experimental procedures adopted in the present investigations are given in this chapter.

MATERIALS

Poly(vinyl chloride)

The poly(vinyl chloride) (PVC) used in the study was suspension polymer with a K value of 65 as powder. The resin was obtained from National Organic Chemicals Ltd., Bombay.

Butadiene-acrylonitrile rubber

Butadiene-acrylonitrile (nitrile) rubber (NBR) used in the study had an acrylonitrile content of 33% and a Mooney viscosity of 40.9 (ML(1+4) at 100°C). The rubber was obtained from Synthetics and Chemicals Ltd., Bareilly.

Chloroprene rubber

Poly(chloroprene) (neoprene) rubbers (CR) used in the study were the following general purpose grades:

1. GN type, Mooney viscosity, ML(1+4) at 100°C, 46
2. W type, Mooney viscosity, ML(1+4) at 100°C, 47
3. W type, Mooney viscosity, ML(1+4) at 100°C, 42.
All the three grades were obtained from Du Pont, USA.

Natural rubber

The natural rubber (NR) used was crumb rubber, ISNR-5 obtained from the Rubber Research Institute of India, Kottayam. The Mooney viscosity of the rubber was 85.3 (ML(1+4) at 100°C).

Styrene-butadiene rubber

Styrene-butadiene rubber (SBR) was obtained from Synthetics & Chemicals Ltd., Bareilly. The rubber had a styrene content of 23.5% and a Mooney viscosity of 49.2 (ML(1+4) at 100°C).

Polybutadiene rubber

Polybutadiene rubber (BR) was obtained from Indian Petrochemicals Corporation Ltd., Baroda. The rubber was 97% 1,4 (cis) and had a Mooney viscosity of 48.0 (ML(1+4) at 100°C).

Polysulphide rubber

Polysulphide rubber used in the study was FA type with a Mooney viscosity of 82.0 (ML(1+4) at 100°C). It was supplied by M/s.J.B.Polymers, Bombay.

Magnesium oxide

Magnesium oxide used in the study was commercial grade calcined light magnesia with a specific gravity of 3.6.
Zinc oxide

Zinc oxide used in the study was commercial grade white seal with a specific gravity of 5.5.

Stearic acid

Stearic acid used in the study was commercial grade with a specific gravity of 0.92.

Tribasic lead sulphate

Tribasic lead sulphate \( (3\text{PbO}.\text{PbSO}_4.\text{H}_2\text{O}) \) (TBLS) used was commercial grade with a specific gravity of 7.0.

Dibasic lead stearate

Dibasic lead stearate \( (2\text{PbO}.\text{Pb(C}_1\text{H}_3\text{5COO})_2) \) (DBLS) used was commercial grade with a specific gravity of 1.9.

Red lead

Red lead \( (\text{Pb}_3\text{O}_4) \) used was commercial grade supplied by M/s. Glaxo India.

Dioctyl phthalate

Dioctyl phthalate (DOP) used was commercial grade with a specific gravity of 0.986 and viscosity 60 cps.

Epoxidized soyabean oil

Epoxidized soyabean oil used was commercial grade with a specific gravity of 0.993 and viscosity 400 cps.
Calcium stearate

Calcium stearate used was commercial grade.

Lauric acid

Lauric acid used was commercial grade.

Titanium dioxide

Titanium dioxide used was commercial grade.

Sulphur

Sulphur used in the study was commercial grade which conformed to the specifications given in I.S. 8851 (1978).

MBTS

MBTS (benzothiazyl disulphide) used was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

TMTD

TMTD (tetramethyl thiuram disulphide) used was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

CBS

CBS (N-cyclohexyl-2-benzothiazyl sulphenamide) was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.
DPG

DPG (diphenyl guanidine) was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

NA-22

NA-22 (ethylene thiourea) was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

PBN

PBN (phenyl-\(\text{p}\)-naphthylamine) was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

Carbon black

Carbon black used in the study was semi-reinforcing furnace black (N741) supplied by Phillips Carbon Blacks Ltd., Durgapur.

Naphthenic oil

Naphthenic oil used in the study was commercial grade procured from M/s. Hindustan Petroleum Corporation.

Aromatic oil

Aromatic oil used in the study was commercial grade procured from M/s. Hindustan Petroleum Corporation.
ASTM reference oil

ASTM reference oil used in the study was ASTM reference oil 3 which conformed to the specifications given in ASTM D471 (1983).

Solvents

Solvents used in the study (chloroform, toluene, acetone, carbon tetrachloride, methanol, acetic acid and methyl ethyl ketone) were of analytical grade.

EXPERIMENTAL PROCEDURES

Preparation of PVC compounds

The dry blending technique was employed for the preparation of PVC compounds. PVC resin and the stabilizers were subjected to vigorous stirring. When the temperature rose to about 70°C - 80°C, plasticizer was added which got absorbed into the polymer particles to give dry, free flowing powders.

Studies on a Brabender Plasticorder

Brabender Plasticorder (Torque rheometer) manufactured by M/s. Brabender OHG Duisburg, West Germany has been widely used for measuring processability of polymers,
rheological properties of polymer melts, for blending of polymers, modelling processes such as extrusion etc.\textsuperscript{1-6}. A plasticorder model PL3S was used in this study.

The Brabender torque rheometer is essentially a device for measuring in metergrams the torque generated due to the resistance of a material to mastication or flow under pre-selected conditions of shear and temperature. The heart of the torque rheometer is a jacketed mixing chamber whose volume is approximately 40 cc for the model specified. Mixing or shearing of the material in the mixing chamber is done by two horizontal rotors with nogs or protrusions. The resistance which is put up by the test material against the rotating rotors in the mixing chamber is made visible with the help of a dynamometer balance. The dynamometer is attached to a precise mechanical measuring system which indicates and records the torque. By means of a lever and weight system different measuring ranges could be adjusted. For the present model the minimum span is 0-1000 metergrams, the intermediate span 0-2500 metergrams and the maximum span 0-5000 metergrams. A D.C. thyristor controlled drive is used for speed control of the rotors (range 0 to 150 rpm). The temperature of the mixing chamber is controlled by circulating hot oil. The temperature could be set at any value up to 300\textdegree C. Stock temperature thermocouple coupled with a temperature recorder is
used for temperature measurement. Different types of rotors could be employed depending upon the nature of the polymers. The rotors can be easily mounted and dismounted due to the simple fastening and coupling system. Once test conditions have been decided (rotor type, rpm and temperature), and set, sufficient time should be given for the temperature to attain the set value and to become steady. Then the materials could be charged into the mixing chamber to obtain a torque-time curve or a plastogram. A typical torque-time curve for a PVC compound is shown in Fig.2.1 (for formulation A, table 3.6). The following observations could be made from the torque-time curve.

A - begin of the curve
This is the point at which the material is heated.

B - maximum torque
This is the point at which maximum torque is attained due to the melting of PVC phase.

C - torque stabilizes at a value
This is the point at which torque stabilizes to a constant value, when the fusion and homogenization is complete. The torque shown is a measure of the melt viscosity at the corresponding stock temperature.

D - degradation break
This is the point at which crosslinking of the molecules due to accelerated molecular degradation starts.
Fig. 2.1 A typical Brabender torque-time curve for a PVC compound
E - maximum crosslinking

This is the point at which the degree of crosslinking reaches maximum. Thereafter the material crumbles down to powder and the torque drops to zero.

The distance between A and D in minutes is a measure of the heat stability of the material under investigation. The stability time of the present compound is about 37 minutes. A long stability time indicates processing safety. When the material is used in processing operations such as extrusion, the complete processing time should be well below the stability time of the material. The Brabender torque rheometer could also be used for a variety of other applications such as measuring processability, rheological behaviour of polymers, blending of two polymers etc. In processes such as blending, the operation should be completed in the stable period of the polymers in order to prevent any degradations in the matrix. In the present work the Brabender plasticorder was used for the assessment of heat stability of PVC compounds, blending of PVC with other polymers, for examining the compatibility of PVC with other polymers etc. The details of the procedure adopted are given in the relevant chapters.

Heat stability testing

Heat stability tests on PVC compositions and products are important in the practical contexts of processing and
service. Evaluation of the suitability and effectiveness of stabilizers, and stabilizer/plasticizer/lubricant systems in protecting PVC against degradation both under processing conditions and in use, is one of their main applications.

Determination of stability time on a Brabender plasticorder, or in other processing equipments like internal mixer, extruder or two roll mill, is specified as a dynamic test method since the stability of the material is determined in actual processing conditions. In equipments like the mill where a torque-time curve cannot be obtained, stability is assessed by periodically checking other effects used as the degradation index (commonly colour development in the material). By their nature, dynamic tests are primarily relevant to the effects of processing on PVC compositions. Indeed, the test equipment, temperature and running conditions are often chosen with a view to relating the test results to a particular process.

In static tests, the test treatment essentially consists in heating specimens of PVC material at the test temperature. The specimens are often pieces of sheet of standard size, but they may also be standard weights of powder or pellets of PVC polymer or composition.

1. Oven stability test

The oven stability test was the static test on stability conducted in this study. In this test, the heating
equipment was an air-circulation oven, the specimens being placed inside the oven. The oven was set to a temperature suitable for the particular composition and stability was determined in terms of heating time to reach a certain level of the degradation index used in the test: this may be the first appearance, or attainment of a certain degree of discoloration in the composition. The results of static tests are more relevant to the effects of heat in service than in processing of PVC materials. However, because the test procedures are simpler than those of dynamic tests, oven stability test is sometimes used to obtain indications of likely stability in processing with suitable correlations. An oven used for static heating test must be reliable with good control and even distribution of temperature. ASTM D2115 (1974) gives a useful summary of requirements in this regard.

A sequence of colour change is established by preparing a series of strips of PVC sheet degraded to the colours listed below:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<tbody>
<tr>
<td>0</td>
<td>clear</td>
</tr>
<tr>
<td>1</td>
<td>barely detectable change</td>
</tr>
<tr>
<td>2</td>
<td>very slight change</td>
</tr>
<tr>
<td>3</td>
<td>slight yellow tinge</td>
</tr>
<tr>
<td>4</td>
<td>pale yellow</td>
</tr>
<tr>
<td>5</td>
<td>yellow</td>
</tr>
</tbody>
</table>
6 faint tinge of red
7 pale red
8 red
9 deep red
10 very deep red/black.

2. **Congo red test**

Another test on heat stability conducted in this study was the Congo red test. The principle of this method is the detection or determination of HCl evolved by PVC material on heating. Enough sample of the compound was taken in a test tube to fill the test tube to a depth of 50 mm. Congo red paper strip (30 mm x 10 mm) was centrally mounted on the test tube above the specimen. Then the test tube was placed in an oil bath kept at 180°C. Time in minutes for red colour to change to transient violet or permanent blue was recorded. Mean values of times obtained in duplicate determinations for each specimen was recorded as the stability time. The details of the method are given in DIN 53381.

**Mixing and homogenization on the mixing mill**

Mixing and homogenization of polymers and compounding ingredients were also done on a laboratory size two roll mixing mill (15 cm x 33 cm) at a friction ratio of 1:1.
The polymers were blended initially and temperature of the rolls was maintained at 40°C-50°C during this time. Proper blending of the polymers was ensured by careful control of temperature, nip gap, time of mastication and by uniform cutting operation. The compounding ingredients were then added as per ASTM D3184 (1980) and 3182 (1982) in the following order: activators, fillers, accelerators and curing agent(s). Before the addition of accelerators and sulphur, the batch was thoroughly cooled.

After completion of mixing, the stock was sheeted out and passed six times end wise through a tight nip and finally sheeted out at a nip gap of 3 mm. Mixing time and temperature were controlled during the studies.

**Determination of cure characteristics**

1. **Using Monsanto Rheometer**

   The cure characteristics of the compounds were determined mostly on a Monsanto Rheometer model R 100 at 150°C. In this test, the polymer specimen is contained in a cylindrical cavity 50 mm x 10 mm and has embedded in it a biconical rotor of diameter 37 mm which is oscillated sinusoidally through a small arc amplitude. The cavity and specimen are maintained at a temperature of ±0.50°C and the force required to oscillate
the disc is measured. The following data could be taken from the torque-time curve (ASTM D1646 (1981)):

(i) Minimum torque - This is the torque attained by the mix after homogenizing at the test temperature before the onset of curve.

(ii) Maximum torque - This is the torque recorded after the curing of the mix is completed.

(iii) Optimum cure - This is the time taken for attaining 90% of the maximum torque.

(iv) Scorch time - This is the time taken for 2 units rise above the minimum torque.

If the mix exhibits a reverting cure behaviour, the torque decreases after reaching the maximum value.

2. **Using Göttfert Elastograph**

   This is a rotorless curemeter and the torque-time curve is generated by the oscillation of the lower half of cavity in which polymer mix is charged. An Elastograph model 67.85 was used in this study. This is a microprocessor controlled curemeter and hence has the capacity of generating
so many other data such as the cure-rate curve. However, the torque-time curve of the Elastograph is similar to that of the Rheometer and all the relevant data could be taken accordingly.

**Mooney viscosity measurement**

The Mooney viscosities of the raw rubbers were measured on the Mooney viscometer which is designed for measuring the shearing viscosity of rubber and rubber like materials by a disk rotating in a shallow cylindrical cavity set at 100°C and filled with the rubber under test. In running a viscosity test, the sample was allowed to warm up for one minute after the platens were closed. The motor was then started. Reading taken after 4 minutes was reported as the Mooney viscosity of the rubber (ML(1+4) at 100°C) (ASTM D1646 (1981)).

**Moulding of test sheets**

The test sheets for determining the physical properties were prepared in standard moulds by compression moulding on a single daylight electrically heated press having 30 cm x 30 cm platens at a pressure of 45 kg/cm² on the mould. In the case of rubber(s) and blends in which rubbers constituted the major fraction, the compounds were vulcanized upto their respective optimum cure times at 150°C. Mouldings were cooled quickly in water at the end of the
curing cycle and stored in a cold and dark place for 24 hours and were used for subsequent physical tests. For samples having thickness more than 6 mm (compression set) additional times based on the sample thickness were used to obtain satisfactory mouldings. In the cases of mixes showing a thermoplastic nature, the mouldings were prepared in specially designed moulds which could be immediately cooled after curing with the samples still kept inside under compression. The same technique was used for compression moulding of thermoplastics. However, in the case of thermoplastics moulding temperatures and times were determined by trial and error methods (ASTM D3182 (1982)).

Physical test methods

1. Tensile strength, elongation at break and modulus

In the present work these tests were carried out according to ASTM D412 (1980) using dumb-bell specimens on a Zwick Universal Testing Machine model 1445. All the above tests were carried out at 25±2°C. Samples were punched from compression moulded sheets parallel to the grain direction using a dumb-bell die (C-type). The thickness of the narrow portion was measured by bench thickness gauge. The sample was held tight by the two grips, the upper grip of which was fixed. The rate of separation of the power actuated lower
grip was 500 mm/minute. Tensile strength, elongation at break and modulus (stress at a given elongation) were printed out after each testing.

2. **Hardness**

Shore-A type Durometer was employed to find out the hardness of the moulded samples. The instrument uses a calibrated spring to provide the indenting force. Readings were taken after 15 seconds of the indentation after firm contact had been established with the specimens. The method employed was ASTM D2240 (1981).

3. **Compression set**

The samples (1.25 cm thick and 2.8 cm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hr in an air oven at 70°C. After the heating period, the samples were taken out, cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

\[
\text{Compression set (\%)} = \frac{t_o - t_1}{t_o - t_s} \times 100
\]

where \(t_o\) and \(t_1\) are the initial and final thickness of the specimen and \(t_s\) is the thickness of the spacer bar used. The method used was ASTM D395 (1982) method B.
4. Tear resistance

This test was carried out as per ASTM D624 (1981). Unnicked, 90° angle test pieces were used. The samples were cut from the compression moulded sheets parallel to the grain direction. The test was carried out on a Zwick Universal Testing Machine. The speed of extension was 500 mm/minute and the temperature 25±2°C.

Aging studies

Dumb-bell specimens for evaluation of physical properties were prepared and aged in an air oven at pre-determined temperatures for specified periods suitable for the test material. Physical properties like tensile strength, elongation at break, modulus etc. were measured before and after ageing and the percentage retention of these properties was evaluated for assessing the effect of ageing (ASTM D573).

Ozone resistance test

The ozone resistance of samples was assessed as per ASTM D1171 (1974) using a Mast ozone chamber. In this chamber, ozonised air is generated with the help of an ultraviolet lamp. Test pieces of triangular cross-section with specified dimensions were prepared and were then bent into a loop for keeping the samples under strain. After mounting, the samples
were allowed to condition for a specified period of time at room temperature in an ozone-free atmosphere. The samples were then introduced into the ozone chamber at an ozone concentration of 50 parts per hundred million (pphm). The temperature of the test was 40±1°C. The samples were exposed for 20 hours and visual assessment of crack intensity was made at 10 hours interval.

For estimating the ozone concentration a known volume of air is passed into a 4% solution of potassium iodide buffered to pH 7. The liberated iodine is titrated against 0.002 N sodium thiosulphate solution and ozone concentration calculated.

Swelling studies

Samples of approximately 1 cm diameter, 0.25 cm thickness and 0.30 gm weight, were punched out from the central portion of the compression moulded sheets, weighed and allowed to swell in excess of the respective solvents at laboratory temperature (30±2°C) for the specified period of time. Then the samples were taken out, quickly dried with a filter paper and weighed. The percentage increase in weight was calculated. The procedure given in ASTM 471 (1983) was followed.
Infrared spectroscopy

Infrared (IR) spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm\(^{-1}\) by organic molecules. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are indicative of the bond strengths and structural geometry in the molecule. Absorption at around 1700 cm\(^{-1}\) was made use of in this study because it is appropriate for carbonyl group determination\(^{8-11}\). The IR spectra given in this investigation were taken in KBr pellets using a Perkin Elmer model 983.

Scanning electron microscopy

Scanning electron microscope (SEM) was first introduced in 1965 and it has since become a very useful tool in polymer research for studying morphology\(^{12-14}\). In this technique an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors and magnified. An image of the investigated microscopic region of the specimen is thus photographed.

If the specimen under investigation is not a good conductor, it should be coated with a thin layer of conducting
material like gold or platinum. This is done by placing the specimen in a high vacuum evaporator and vaporizing the conducting material held in a tungsten basket (vacuum dispersion).

The SEM observations reported in the present investigation were made on the fracture surface of tensile test specimens using a Philips 500 model scanning electron microscope. The fracture surfaces of the samples were carefully cut out from the failed test pieces without disturbing the surface. These surfaces were then sputter coated with gold within 24 hours of testing. The SEM observations were made within one week after gold coating. The gold coated samples were kept in desiccators before the SEM observations were made. The shapes of the test specimens, direction of the applied force and portions from where the surfaces have been cut out for SEM observations are shown in Fig.2.2.
Fig. 2.2 SEM scan area of the tensile failure surface.
References