

## Chapter 7

### Conclusions and Recommendations for future work

#### 7.1 Conclusions

Powdered natural rubber was successfully prepared by co-precipitation technique, using starch xanthate, SX, as the encapsulating agent. Natural rubber latex was co-precipitated with SX that were prepared by this method, to give powdered products. The properties of powdered rubber samples were examined and found to be satisfactory.

The conclusions drawn from the present work are summarized below.

The results showed that the DS and the loading of SX are the two critical factors in preparing powdered natural rubber. Out of the DS values used, DS of 0.07 was not suitable as it produced fine wet powders that were difficult to be filtered. Cost analysis showed that the DS of 0.35 was not economical since the increment of cost with the DS and loading of SX was high and was not proportional to that of yield. Hence the usage of SX with intermediate DS (i.e. 0.07 to 0.35) is more suitable in preparing powdered natural rubber and in the present work DS of 0.28 gave better results.

The results of the experiments on drying techniques suggested that

- Water washing of wet curds of natural rubber is essential in order to remove oxidizing agents and specially to remove non-rubber substances containing in the field latex.
- Anti-cake agents are needed to produce powders without agglomeration during drying. Irrespective of the type of an anti-cake agent, slow speed for a longer time has to be used during mixing with wet rubber curds. Some of the anti-cake agents like whiting gave unsatisfactory results but zinc stearate is more promising as an anti-cake agent as well as a facilitator for sulphur vulcanizing process.
- Two drying conditions were examined in the present work and found that the oven-drying was more suitable although sun-drying was cheaper, as oven-drying produced highly friable crumbs that could be ground to give fine powders.

Natural rubber powders with different particle sizes could be produced using co-precipitation method by changing the DS and loading of SX. The ease of grinding and the particle size distribution were improved with the increase of SX loading and also with DS values due to the decrease in rubber to starch weight ratio. When the starch amount in the mixture increases, it behaves as a partitioning agent and facilitates grinding.

Powdered natural rubber could be formulated by short period milling, avoiding high-shear mastication procedures that are required for bale rubbers. A progressive difficulty in milling was observed with the increase in SX loading due to high stiffness caused by the presence of starch, which acts as a filler.

Optimum cure time was reduced with low SX loading due to the accelerator activity of xanthates. However, further increase in SX loading increased optimum cure time, thus ruling out the possibility of accelerating cure by extra xanthates, providing an optimum level of SX for this phenomenon. The least optimum cure time was achieved with sample D35/20, out of the eight powdered rubber samples (having SX loading of a range 20-100 phr with two DS values - 0.28 and 0.35) used in the present work. Cure rate index, which is directly proportional to the rate of cure, was reduced with the increase of SX loading. This result confirmed the observations obtained on optimum cure time. However, scorch time was independent on effect of change of either DS or loading of SX.

The physical properties of powdered natural rubber gum vulcanizates were in the useful range in which the properties of most of the domestic and technical rubber goods lie. The results showed that the tensile strength was decreased with the increase of both DS and loading of SX. Thus a natural rubber powder with low SX loading is more suitable in producing high strength articles as it has an extra advantage of giving more freedom to add other conventional fillers and reinforcing agents. Modulus and hardness were increased and elongation at break, rebound resilience and abrasion resistance were decreased with the increase of both DS and loading of SX due to the loss of inherent rubbery properties of natural rubber by incorporation of SX. Compression set was increased with the increase of SX loading but was independent on DS of SX. Dynamic fatigue was very fast with high SX loading whereas samples with low SX loading (below 30 phr) resulted some resistance to fatigue. These observations suggest that the required properties could be achieved by varying the combinations of DS and loading of SX.

## 7.2 Recommendations for future work

Low DS and loading of SX showed better elastic recovery and some reinforcement, although there was a difficulty in preparing powders in mass-scale. The possibility of achieving better reinforcement with a little amount (less than 20 phr) of SX having high DS values can be examined in future.

Talc powder of 4 phr, too, behaved as an anti-cake agent to a certain extent. Since zinc stearate is expensive and hazardous, talc powder, which is a cheaper substitute, could be used with the intention of reducing the cost of production. However, in this case, loading above 4 phr has to be used. Studies can be carried out on the other possible types of anti-cake agents as well as on the effect of the amount and the method of addition of anti-cake agents.

Drying techniques are important on the physical characteristics of dried crumbs. Oven drying showed better performance compared to sun drying. However improving of drying in the oven can be further examined by adding a fan or a fluidized bed to the system.

Particle size of the rubber powders is important in preparing adhesives. Finer particles could be achieved with high SX loading. Screening the powder from the first grinding pass and recycling the coarse fraction can further reduce the particle sizes. However, high SX loading give rise to change the physical properties significantly and hence further work can be aimed at producing finer particles with low SX loading.


Powdered natural rubbers are suitable for wide spectrum of end uses. Low SX encased powdered rubbers can be used in general purpose applications using conventional rubber equipment with short milling periods. Finer natural rubber powders are beneficial in adhesive and paste applications, whereas coarser/intermediate size natural rubber are suited for different applications such as blending with thermoplastics, use as an additive for cement and bitumen in order to improve water proofing and elasticity respectively. Further research works can be aimed to improve these areas of application, as they are useful in developing respective industries in Sri Lanka.

Feasibility of using SX encased powdered natural rubber as a substitute to bale rubber in certain areas can be studied by monitoring the following effects.

- I. Effect of adding some fillers like hard clay, hydrated silica and HAF black on properties of vulcanizates of SX encased natural rubber powders.
- II. Effect on accelerator activity of SX in cure characteristics and hence change the conventional formulations.
- III. Compound formulation by powder mixing procedures and fabrication into finished articles by powder processing techniques common in the plastic industry.



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## Appendix 1

### Natural and synthetic rubbers

Natural rubber, NR, is produced in Sri Lanka, using natural rubber field latex, in the form of sheets and block. The rubber particles in field latex is in the form of spherical particles, each protected by a layer of phospholipid and protein, which prevent coagulation. The chemical structure of NR is formed with stereo-chemical *cis*-1,4 polyisoprene repeating units. Hence, NR is one of the few stress-crystallizing elastomers. Its ensuring high strength, without reinforcement by particulate fillers, leads to many product applications.

Synthetic rubbers can be either of homopolymers, copolymers or terpolymers that are produced by polymerization of monomer/s. Monomers are obtained as chemical modifications of by-products from crude oil distillation. Characteristic properties of synthetic rubbers can be varied, unlike NR, by changing the methods and further the conditions of polymerization. 98% *cis* 1,4 polyisoprene, IR, which is very similar to NR, can be produced by stereo-specific polymerization.

Mastication of NR reduces its molecular weight and narrows distribution as a result of breakdown of the very high molecular weight fraction, providing low-molecular-weight internal plasticization. The presence of non-rubber ingredients in the NR seems to help this process. IR behaves like masticated NR for processing.

World rubber usage of around 15 million metric tons is split between natural rubber, which constitutes about 35% of global consumption, and synthetic rubber, of which styrene-butadiene rubber (SBR) accounts for about 18%. The balance of synthetic rubbers (47%) consists of polybutadiene and a range of speciality polymers such as urethanes, halogenated polymers, silicones and acrylates. Traditionally, the growth of synthetic and natural rubber consumption is virtually in line. Global natural rubber consumption is split among tyres (75%), automotive mechanical products (5%), non-automotive mechanical products (10%) and miscellaneous applications such as medical and health-related products (10%).



## Appendix 2

### Specifications of field latex

*Total Solids Content (TSC)*: is the solids (all rubber and non-rubber substances) fraction of the latex, which is relatively non-volatile at temperatures in the region of 100°C. In practice, about 10 g of latex is taken into a flat dish and an even film is formed. Then the film is dried at 100°C.

$$\text{TSC, percentage of mass} = (m_1/m_0) * 100$$

Where,  $m_0$  = mass, in grams, of the test portion

$m_1$  = mass, in grams, of the dried sheet

*Dry Rubber Content (DRC)*: is the solid fraction of the latex which, is coagulated under carefully controlled conditions. Usually, DRC is considered as the quantity of rubber hydrocarbon content. In practice, rubber particles are separated from the serum by coagulating with acetic acid. Then the coagulum is pressed to a sheet form and it is dried at 70°C.



$$\text{DRC, percentage of mass} = (m_1/m_0) * 100$$

Where,  $m_0$  = mass, in grams, of the test portion

$m_1$  = mass, in grams, of the dried sheet

*Alkalinity*: is the content of ammonia, grams per 100 grams of latex, if latex is preserved with ammonia. In practice, latex is titrated (with standard sulfuric acid) to pH 6.0 in the presence of a stabilizer and its alkalinity is calculated from the quantity of acid, which is required.

$$\text{Alkalinity, percentage of NH}_3 = (1.7 * N * V) / m_0$$

Where,  $N$  = normality of sulphuric acid used

$V$  = volume, in ml, sulphuric acid used

$m_0$  = mass, in grams, of the test portion



*Volatile Fatty Acid Number (VFA)*: is the number of grams of potassium hydroxide equivalent to the volatile fatty acids in latex containing 100g of total solids content. In practice, 50 ml of 30 wt% ammonium sulphate solution is added to 50 g of latex while stirring. Then the mixture is heated in a 70°C water bath until it coagulates. The serum is filtered and is acidified with 5 ml of 50 wt% sulphuric acid. 10 ml of acidified serum is steam distilled and the condensate is titrated with barium hydroxide.

$$\text{VFA} = (67.32 * N * V / m_0 * \text{TSC}) * \{50 + m_0 * (100 - \text{DRC} / 1000\rho)\}$$

Where, N = normality of the barium hydroxide solution  
V = volume, in mm<sup>3</sup>, of barium hydroxide solution required to neutralize the distillate  
DRC = dry rubber content  
m<sub>0</sub> = mass, in grams, of test portion  
ρ = specific gravity of the serum, 1.02  
TSC = total solids content



## Appendix 3

### Testing equipment for measuring properties of powdered natural rubber

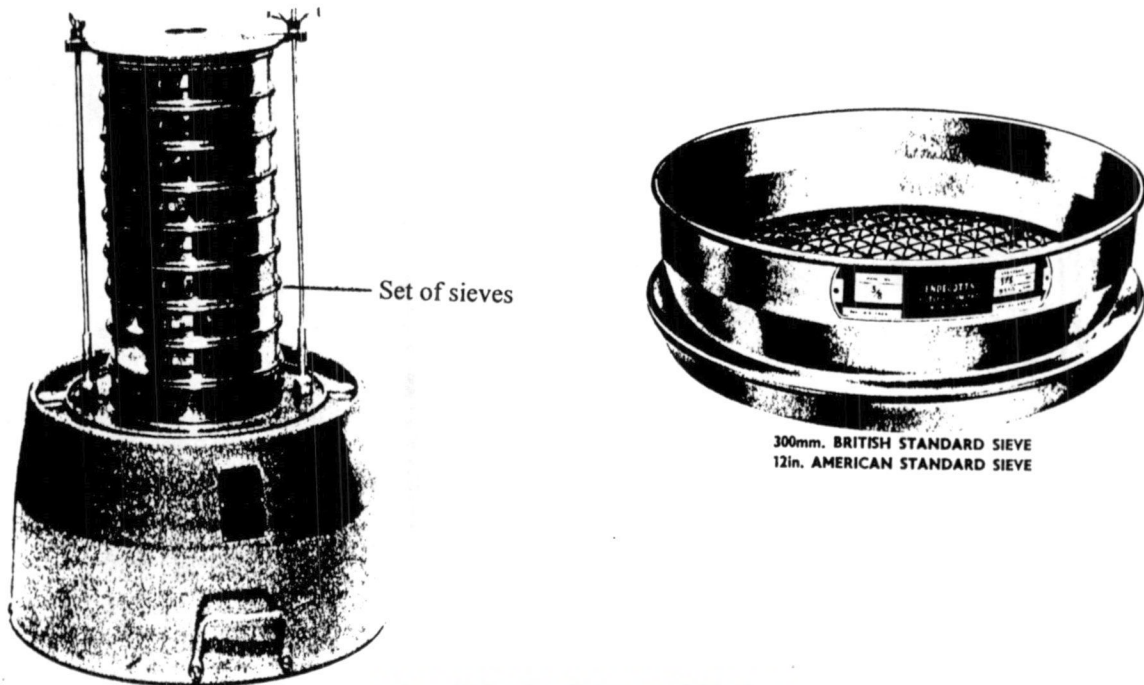


Figure A.3.1 A sieve and an Endecott testing sieve shaker for the analyze of particle size distribution of any powder/granular material

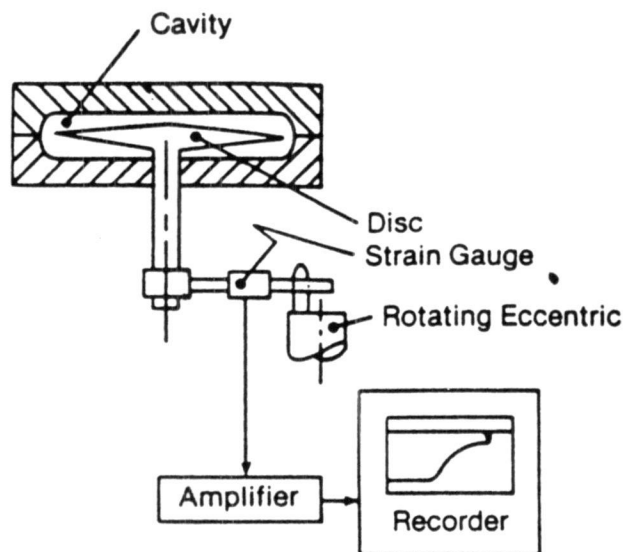


Figure A.3.2 Sketch of an Oscillating disc rheometer, which is used to monitor the cure characteristics.

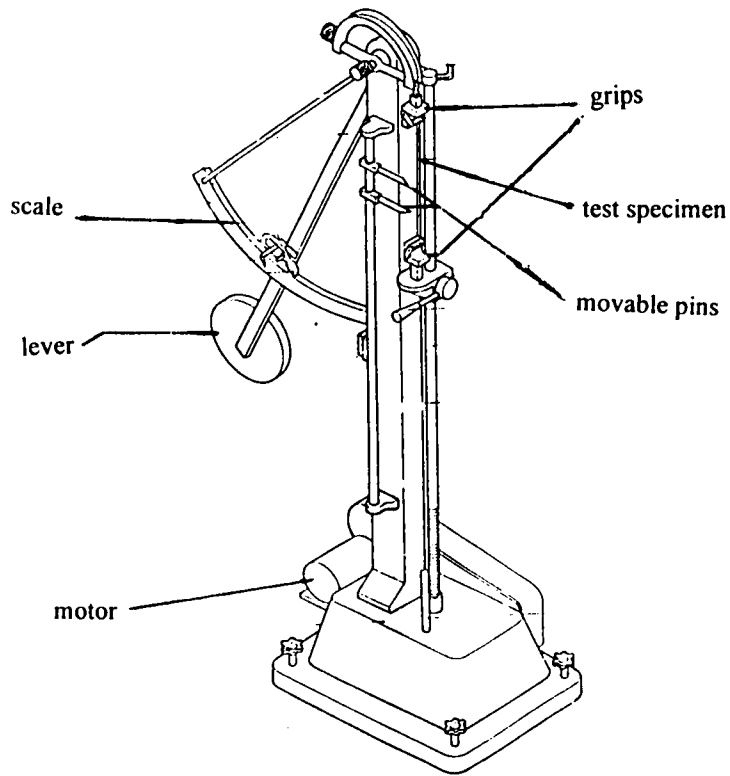


Figure A.3.3 A pendulum/general type tensile strength tester, which measures force and elongation at specified time or at break

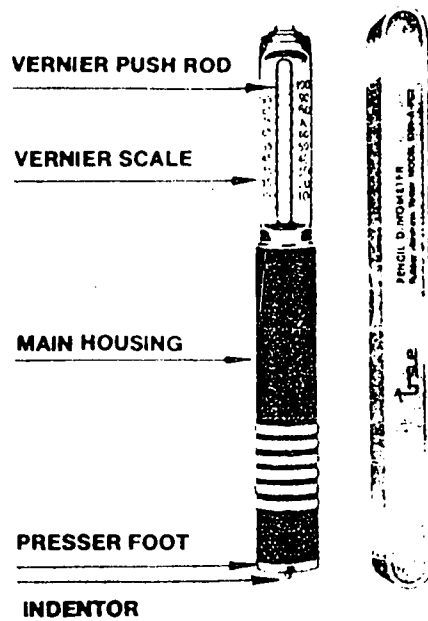
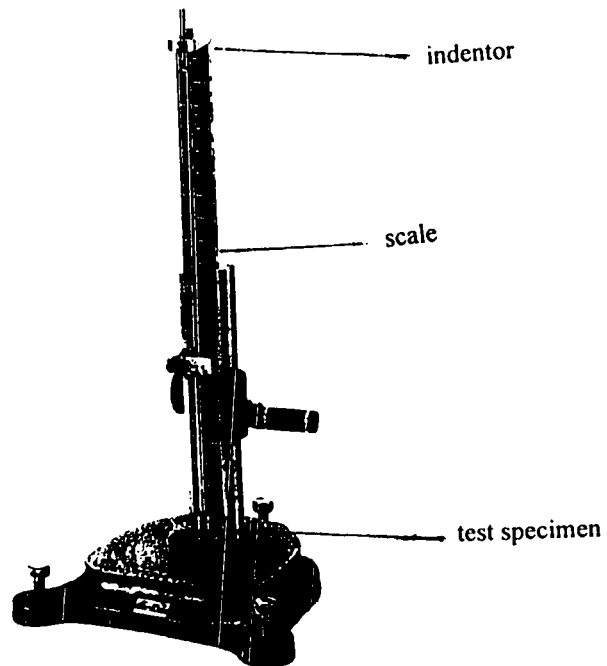


Figure A.3.4 Basic parts of a pencil durometer that is used to measure the hardness of rubbers



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Figure A.3.5 A Rebound resilience tester for finding resilience property/elasticity of rubber and other polymers

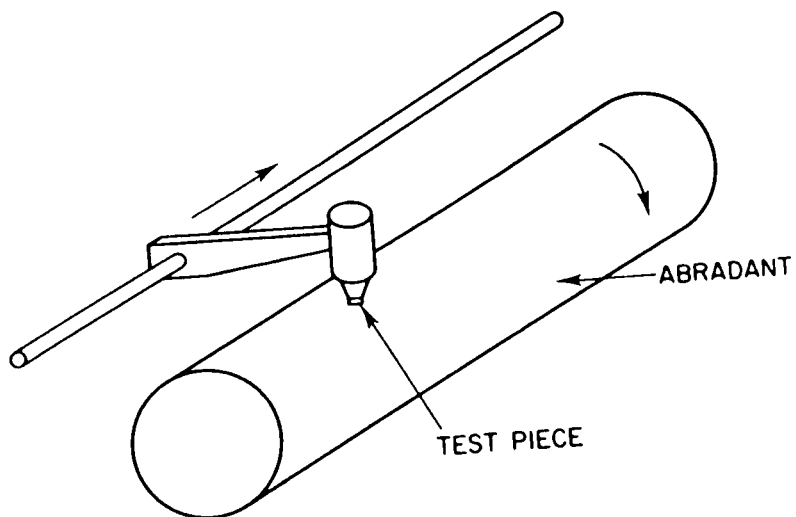
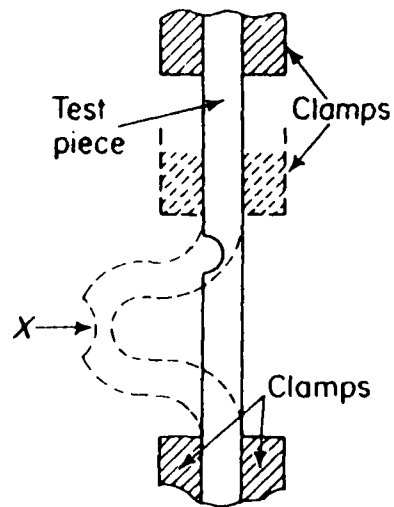


Figure A.3.6 Sketch of a Din abrader that is used to measure abrasion resistance



*Figure A.3.7* The mechanism of the De-Mattia flexing machine that is used to find the crack initiation and the rate of growth of cracks



## Appendix 4

### Data related in testing of properties of powdered natural rubber

1. *Table A.4.1* Particle size distribution

Sample No.	D07/80	D07/100	D28/60	D28/80	D28/100	D35/30	D35/40	D35/60
Sieve aperture								
5000 microns	-	-	10.95	-	-	34.38	-	-
4000	-	-	11.63	1.1	-	19.43	7.75	-
3350	-	-	11.82	6.90	-	12.42	15.19	-
2800	28.44	23.83	13.64	22.93	0.25	6.72	34.39	1.31
2000	16.37	23.23	20.23	19.20	0.48	12.27	39.26	7.98
1400	20.7	17.70	15.23	20.85	4.96	8.28	2.3	19.40
1000	13.57	10.88	7.93	17.30	17.19	3.86	1.27	24.00
500	15.42	16.7	6.97	9.66	49.54	2.60	0.11	37.5
pan	6.13	8.29	1.60	2.15	27.63	0.40	0.00	10.62

#### 2. Cure characteristics

*Rheograph* - rheometer chart or cure curve gives a clear picture of the overall kinetics of cross-links formation and even cross-link disappearance for a given rubber mix. Figure A.4.1 illustrates the regions of delay, curing and over cure. Delay region is the safe region to permit mixing, shaping and flowing in the mould before vulcanization. Cross-link formation takes place during the curing region and hence the torque value increases. The disappearance of cross-links and hence the degradation of the rubber takes place in the over cure region. According to the reactivity of the vulcanizing system, the curve can be of normal increase (due to formation of some cross-links), a plateau or a reversion.



*Cure characteristics* - are the time elapsed before cross-linking starts, the rate of cross-link formation once it starts, and the extent of cross-linking at the end of the process.

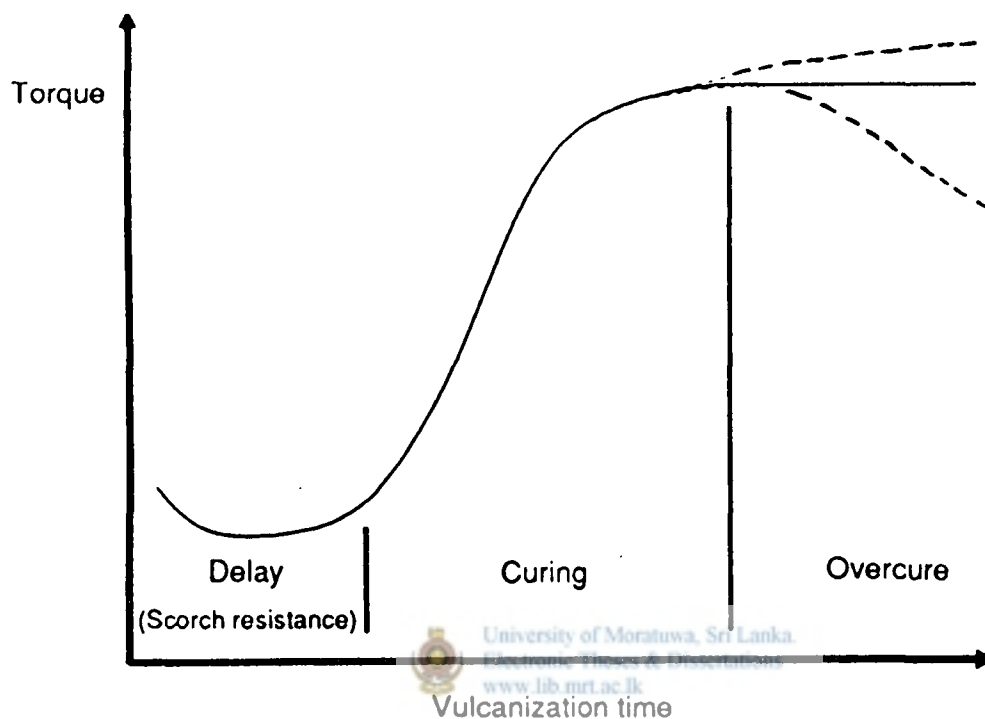


Figure A.4.1 Rheometer cure curve

3. Table A.4.2 Observations on Tensile test

Experiment No.	1	2	3	4	5	6	7	8	9
t, mm	1.47	1.60	1.58	1.57	1.98	1.75	1.74	1.72	1.62
A, mm <sup>2</sup>	4.41	4.80	4.74	4.71	5.94	5.25	5.22	5.16	4.86
f, N @ 300%E	3.9	-	-	-	-	26.5	37.0	-	-
f, N @ 100%E	-	14.7	24.5	27.0	-	-	-	24.5	29.4
f, N @ break	127.5	28.7	36.8	36.0	49.1	112.6	81.4	34.3	35.3



4. Approximate relationships between Shore A, Shore D and IRHD scales

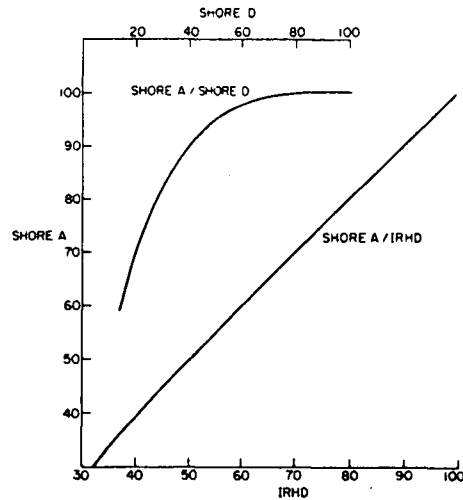


Figure A.4.2 Correlation curve [Refer - Brown (1979) p124]

5. Table A.4.3 Observations on Abrasion Resistance test

Experiment No.	1	2	3	4	5	6	7	8	9
Wt. of test piece, g	1.31	1.55	1.58	1.59	1.67	1.42	1.51	1.56	1.58
Density, g/cm <sup>3</sup>	0.945	1.17	1.129	1.136	1.193	1.14	1.79	1.114	1.129
Wt. Loss, g	0.16	0.142	0.97	0.142	0.114	0.80	0.69	0.12	0.114
Vol. loss, cm <sup>3</sup>	0.17	0.87	0.86	0.96	0.96	0.79	0.2	0.92	0.11
Abrasion resist., /cm <sup>3</sup>	58.44	11.90	11.64	10.46	10.46	12.66	12.12	10.9	9.9

6. Table A.4.4 Observations on compression set test

Experiment No.	1	2	3	4	5	6	7	8	9
t <sub>0</sub> , mm	12.56	13.4	13.9	12.95	13.2	13.11	13.1	13.2	13.0
t <sub>i</sub> , mm	11.45	10.9	10.17	10.22	10.9	10.95	10.41	10.31	10.49

## Glossary

*abrader*: abrasion testing machine

*antioxidant*: a compounding ingredient used to retard deterioration caused by oxygen

*ASTM*: the abbreviation for American Society for Testing and Materials

*blank*: piece of mix of suitable volume for the mould

*cpm*: cycles per minute

*calender*: machine with two or more rolls for converting rubber, or a combination of rubber and other materials, into a sheet of controlled thickness

*compound/ing*: intimate mixture/mixing of a polymer(s) with all the ingredients necessary for the finished article

*compression moulding*: moulding process in which the blank is placed directly in the mould cavity and compressed to a shape by closure of the mould

*doctor blade (spreading knife)*: blade used for spreading dough or latex smoothly and uniformly

*dough*: paste-like mass of smooth texture consisting of a mix and solvent for spreading

*durometer*: an instrument for measuring hardness

*equipment supplier*: develop a process and equipment concept together with the raw material supplier and rubber processor in view of quality and economics

*extruder*: machine for extrusion, generally with driven screw, for continuous forming of rubber or plastic through a die

*formulation (recipe)*: statement of all ingredients and their proportions to be contained in a mix

*IRHD*: International Rubber Hardness Degrees

*injection moulding*: moulding process in which mix is forced into a closed heated mould from a separate heating chamber

*master batch*: intermediate rubber compound that consists only of common ingredients needed for further processes

*mastication*: process of plasticising raw rubber irreversibly by the combined action of mechanical work and oxygen frequently at elevated temperature

*mill*: machine with two driven rolls forming a nip for masticating, plasticising, mixing and sheeting

*phr*: parts per hundred rubber (by weight)

*powder technology*: the technology used to mix powder materials of average particles less than 1 mm (mainly use in plastic industry)

*proofing*: process of coating a fabric with rubber to impede penetration by a fluid usually water; the rubber coating of such fabric

*RSS (ribbed smoke sheet) rubber*: a type of rubber available in the form of sheet that is dried with smoke

*raw rubber producers*: supply raw materials in powder or crumb form to meet the requirements of the equipment suppliers and rubber processor

*rheometer (Monsanto)*: one type of curemeter

*roll*: roller or hollow cylinder forming a major moving member of a rubber processing machine

*rubber processors*: cooperate in process development and compound reformulation to meet specific compound requirements

*SAF (superior abrasion furnace) black*: a type of carbon black, which is commonly used as a reinforcing filler for black rubber compounds

*scorch*: premature vulcanization of a rubber mix

*substrate*: a rigid indenter

*tensometer*: a tensile testing machine

*vulcanizate*: main product of vulcanization

