Rubber Technology

Dr. Pairote Jittham

National Metal and Materials Technology Center (MTEC), Thailand

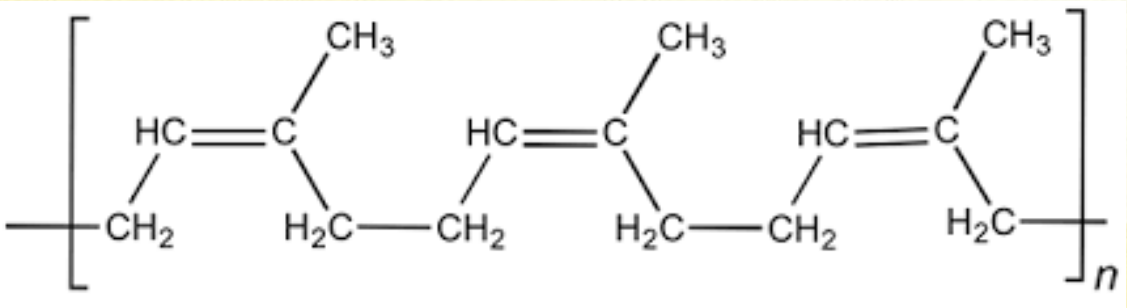
pairotej@mtec.or.th

Rubber Technology

- Rubber Types
- Rubber Ingredients
- Rubber Mixing and Testing

Part 1: Rubbers

1. Natural Rubber (NR)



cis-1,4-polyisoprene

Fresh latex

Concentrated latex

Dry rubber

Rubber sheet

Rubber bale

General properties of NR

- ✓ High elasticity
- ✓ High tack
- ✓ Non-polar rubber leading to poor oil resistance
- ✓ High double content leading to poor heat, oxygen and ozone resistances
- ✓ Crystallizable on stretching leading to excellent tear and tensile strengths

Tack = ability to stick to itself and to other materials

Products from NR

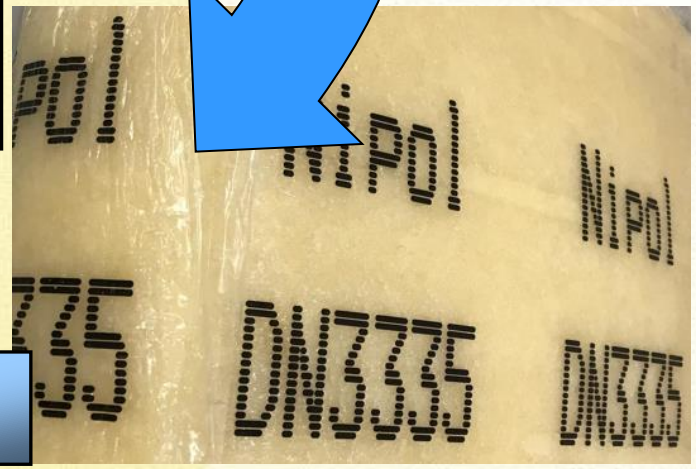
Latex : Condom, glove, balloon, thread

Dry rubber : Car tire, truck tire, airplane tire, conveyor belt, rubber band, engine mount, dock fender, pond or reservoir liner, automotive parts, etc.

2. Synthetic Rubbers

Monomers

Polymerization



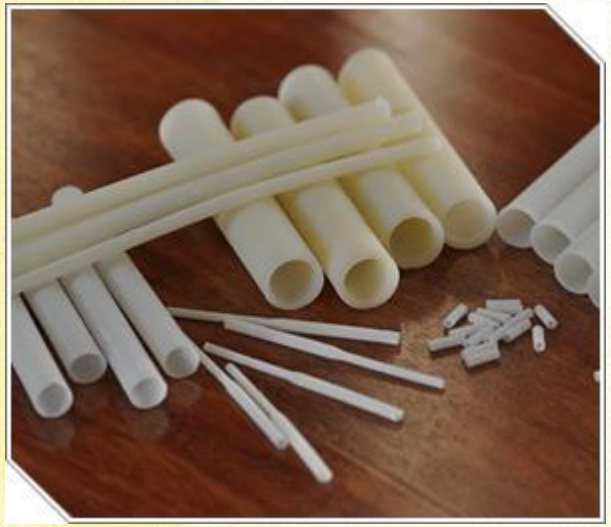
Synthetic rubbers

2.1 Polyisoprene (IR)

- Similar chemical structure and properties to NR
- Greater property consistency and higher purity

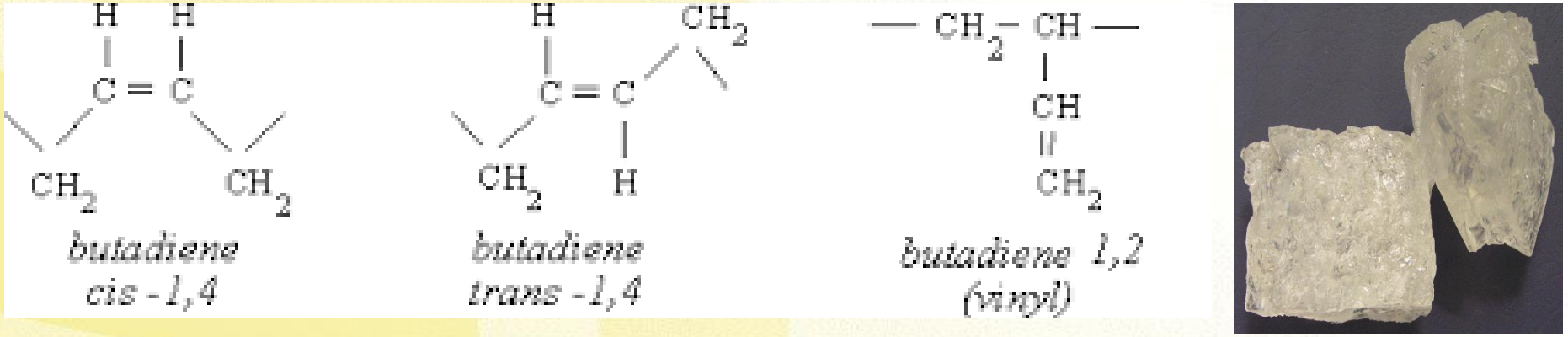
Products from IR

Teat and medical appliances



2.2 Butadiene rubber (BR)

- Structure : cis-1,4 or trans-1,4 or vinyl-1,2



- Poor tensile and tear strengths

General properties of BR

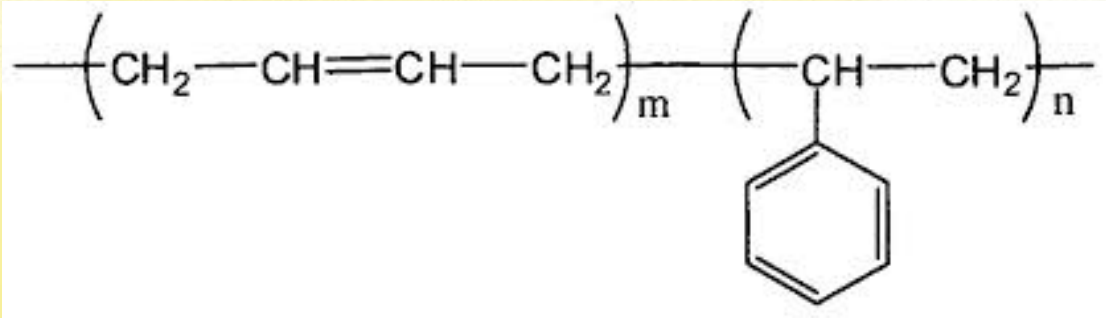
- Highest Elasticity
- Highest abrasion resistance
- Non-polar rubber leading to poor oil resistance/ high insulation
- High d/b content leading to poor aging resistance

Products from BR

Tire tread, shoe sole, conveyor belt, transmission belt, golf-ball core

2.3 Styrene butadiene rubber (SBR)

- Structure : random copolymer



- Styrene ~23% and butadiene ~77%
- General purpose rubber (the most widely used)

General properties of SBR

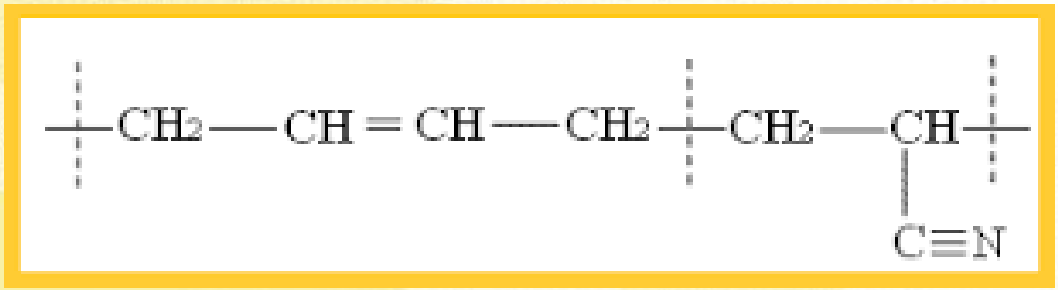
- High property consistency
- Non-polar rubber leading to poor oil resistance/ high insulation
- Lower elasticity and strength than NR
- High d/b content leading to poor aging resistance

Products from SBR

Tire, conveyor belt, hose, cable jacket

2.4 Acrylonitrile butadiene rubber or nitrile rubber (NBR)

- Structure : copolymer of butadiene and acrylonitrile



- Acrylonitrile ~ 18 – 51% by weight
- No strain-induced crystallization leading to poor strength

General properties of NBR

- High abrasion resistance (better than NR and SBR)
- High polarity (depending on ACN content)

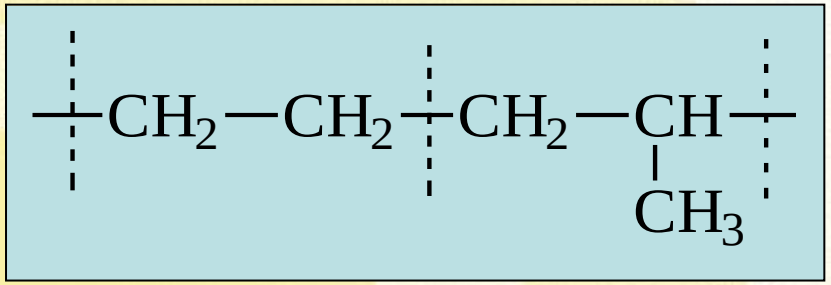
  leading to good oil resistance but poor insulation
- High double bond content leading to poor aging resistance

Products from NBR

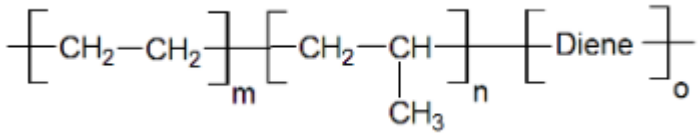
Good oil resistance products such as gasket, o-ring, conveyor belt, oil hose, shoe sole, etc.

2.5 Ethylene propylene diene monomer (EPDM)

- Structure : random copolymer of ethylene, propylene and diene



- Initially, only ethylene and propylene were linked together to form “EPM”.



- To allow sulfur vulcanization, diene is later added into EPM and the rubber is called EPDM.

General properties of EPDM

- No strain-induced crystallization leading to poor mechanical properties
- Non-polar rubber and, thus poor oil resistance/high insulation
- No double bond in the main chain leading to excellent aging and chemical resistances

Products from EPDM

Automotive parts (such as window gasket, steam hose, etc.),
conveyer belt, hose for washing machine, pond liner, cable jacket

Part 2: Compounding ingredients

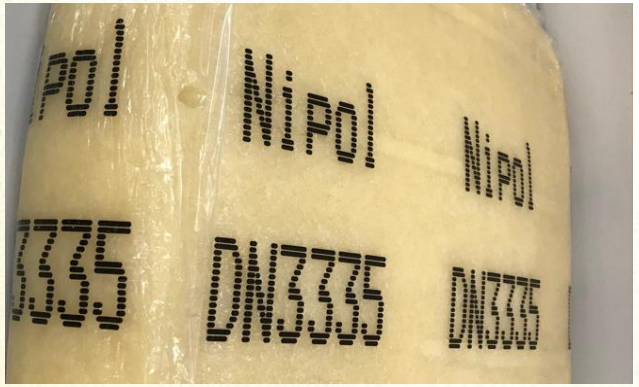
Compounding ingredients

1. Rubber
2. Vulcanizing agent
3. Accelerator
4. Activator
5. Anti-degradant
6. Filler
7. Plasticizer and processing aid

1. Rubber

Rubber type

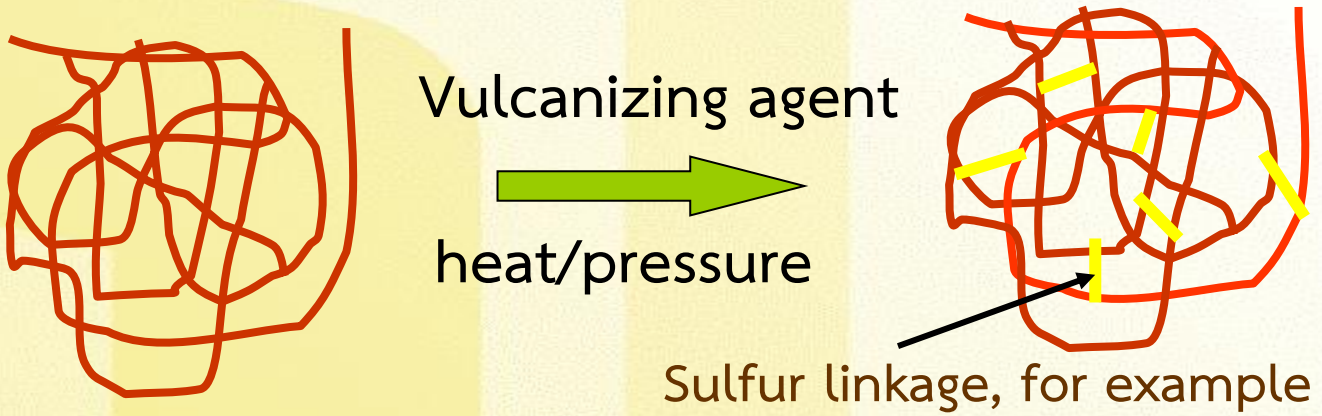
- Natural rubber (NR)
- Synthetic rubber (SR)



2. Vulcanizing or Curing Agent

- An ingredient necessary for vulcanization or curing process

- Added into the formulation to form crosslinks between individual rubber chains (form 3-dimensional network)



Before vulcanization
(Raw Rubber : Thermoplastic)

After vulcanization
(vulcanizate : Thermoset)

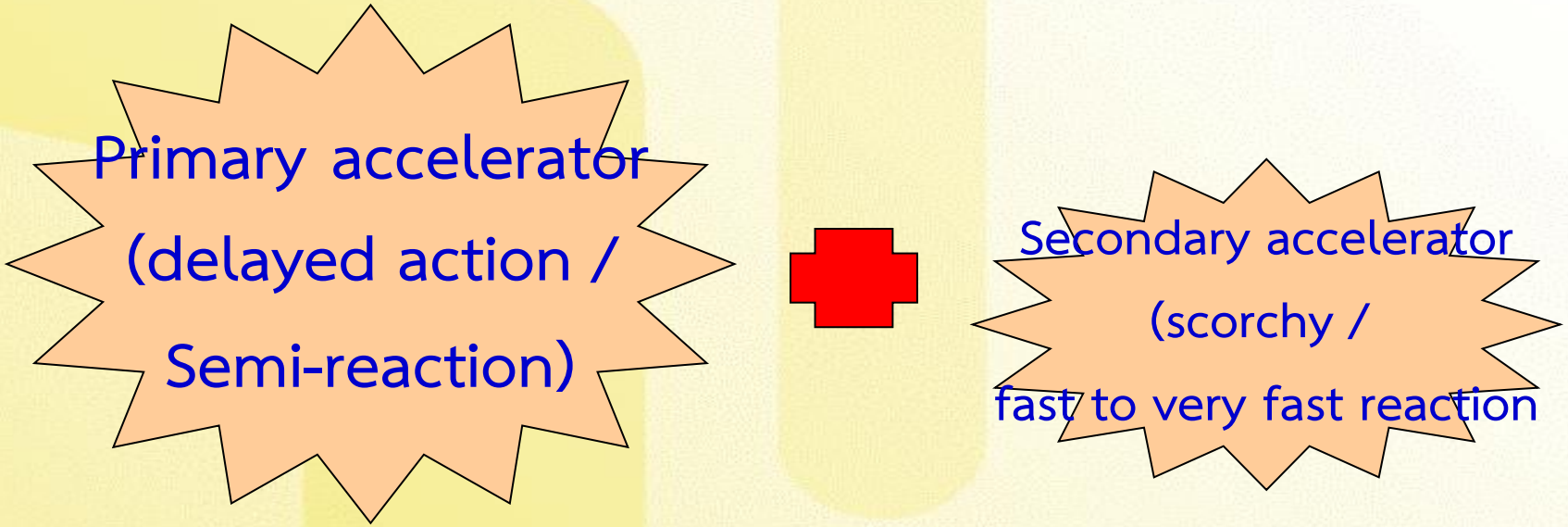
2.1 Sulfur

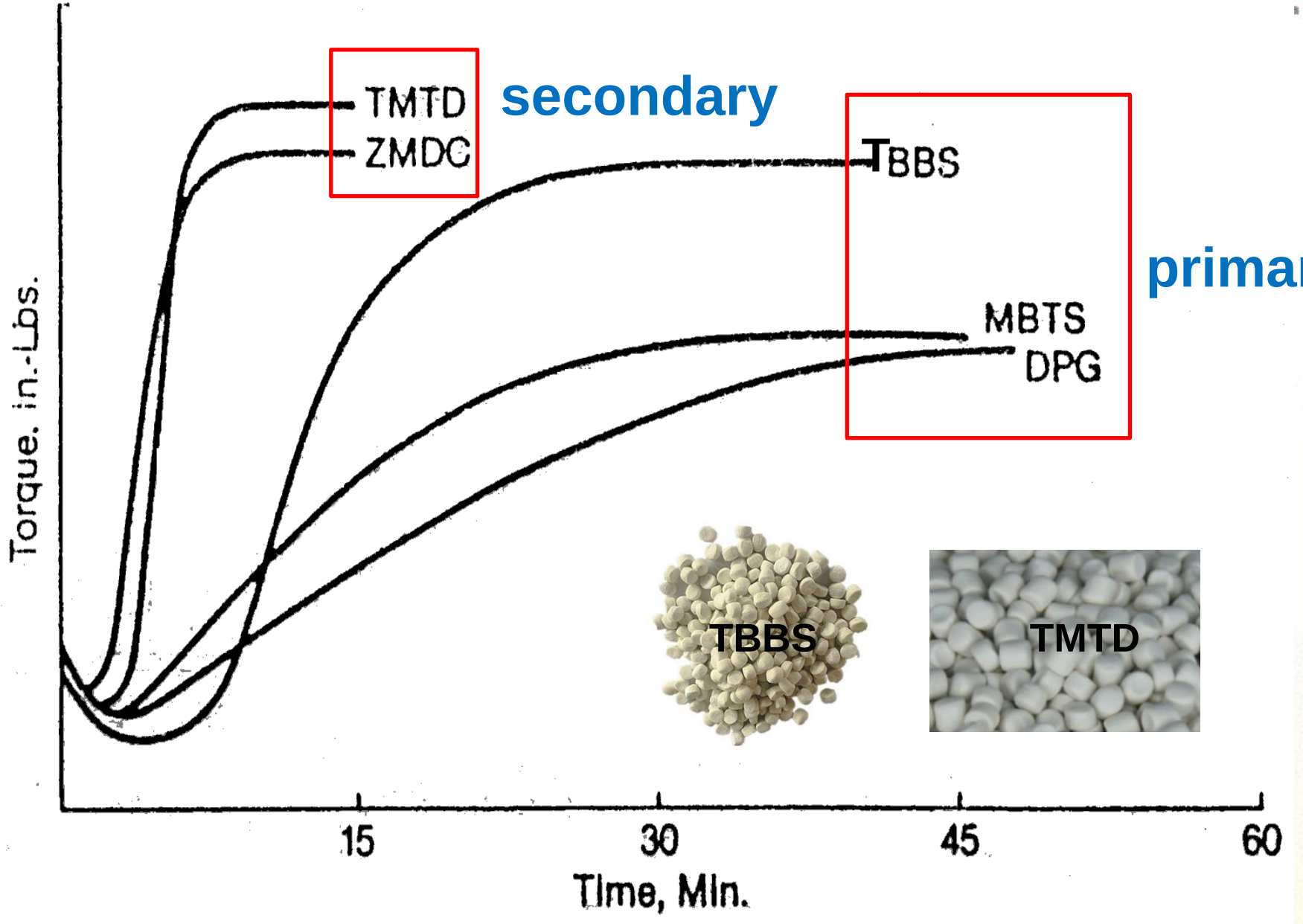
- Low cost (the most widely used in rubber industry)
- Common dosage : 0.5-3.0 phr
- Fast reaction when used with accelerator(s)
- Good mechanical properties

Note : can be used only with unsaturated rubbers

3. Accelerator

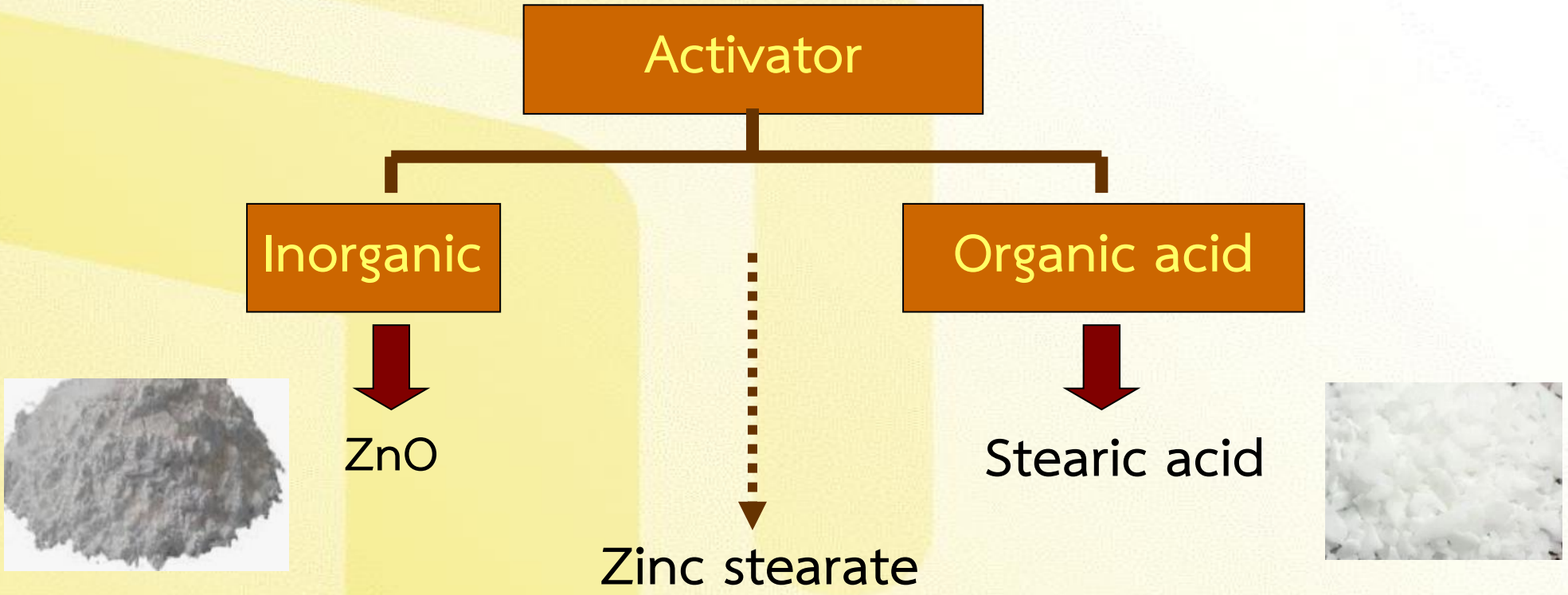
- Speed up sulfur vulcanization reaction
- Necessary for sulfur vulcanization
- Generally used more than 1 type to yield "synergistic effect"




TMTD
ZMDC
secondary
TBBS
primary
MBTS
DPG
Torque, in.-Lbs.
15
30
45
60
Time, Min.
TBBS
TMTD

4. Activator

- Activate sulfur vulcanization
- Make accelerator become more effective



5. Anti-degradant

An ingredient added to protect rubber from heat, oxygen and ozone

- Widely used in unsaturated rubbers
- Normal dosage : 1-3 phr

Anti-degradant

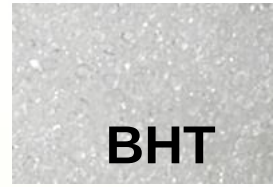
Discoloration

- Phenylene diamine derivatives, e.g.,
  - Isopropyl phenylene diamine (IPPD)*
  - Dimethyl butyl phenylene diamine (6PPD)*
- Dihydroquinoline derivatives, e.g.,
  - Trimethyl dihydroquinoline polymerized (TMQ)**

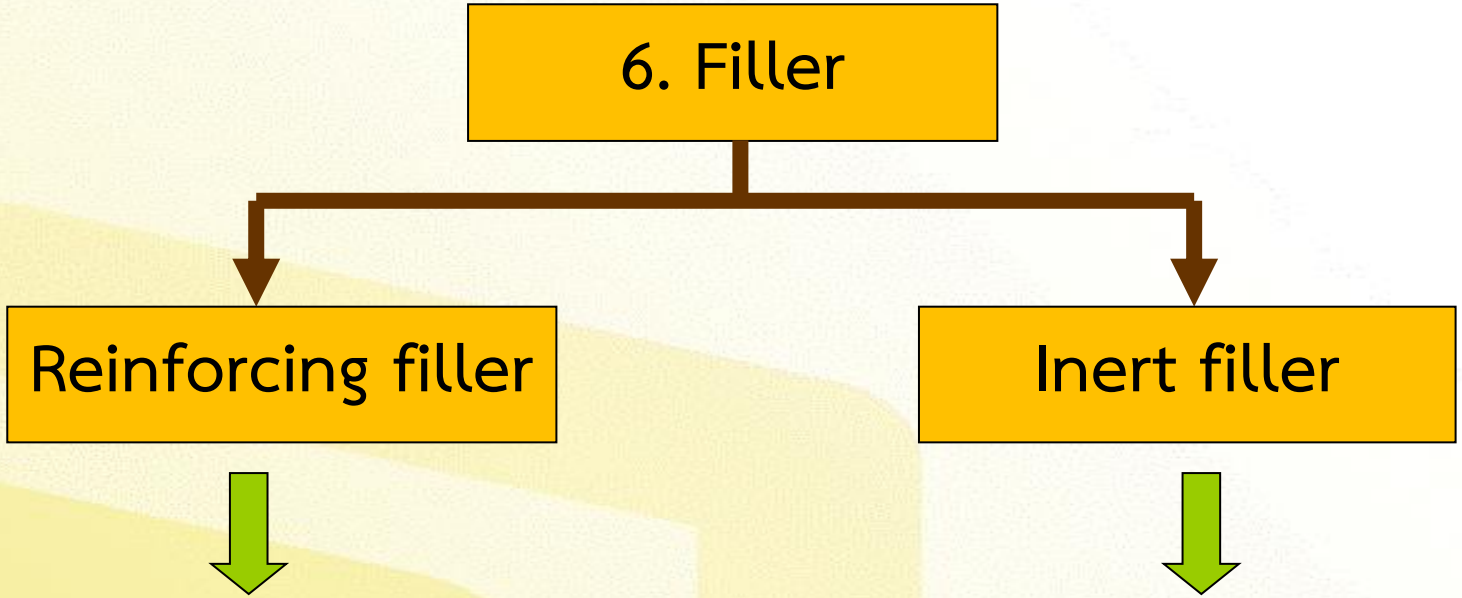
* Protection from oxygen and ozone

Non-discoloration

- Phenol derivatives, e.g.,
  - Dibutyl-p-cresol (BHT)**
  - Methylene methyl butyl phenol (BPH)**
  - Styrenated phenol (SPH)*



** Protection from oxygen only


6. Filler
Reinforcing filler
Inert filler
• carbon black
• silica
• clay
• talcum
• $CaCO_3$

6.1 Carbon black (CB)

- The most widely used reinforcing filler
- Good interaction with rubber

6.2 Silica

- Silica used in rubber compounding is precipitated silica.
- It is an amorphous form of silica or silicon dioxide (SiO_2)
- It is widely used to reinforce light colored products
- It has relatively high polarity (lower interaction with rubbers compared to CB)

6.3 Clay

- Aluminium silicate : $Al_2O_3.2SiO_2.2H_2O$
- Very low cost (most widely used for cost reduction)
- Low to medium reinforcing filler

6.4 Calcium carbonate ($CaCO_3$)

- Non-reinforcing to low reinforcing fillers
- Basic in nature leading to faster vulcanization reaction

6.5 Talcum

- Silicate of Magnesium
- Non-reinforcement filler
- Help to reduce gas permeability of rubber

7. Plasticizer or Processing Aid

- Improve processability
- Improve filler distribution

	NR	SBR	BR	NBR	CR	CSM	EPDM	IIR
Paraffinic	+	+	+	-	-	-	+	+
Naphthenic	+	+	+	0	0	0	+	0
Aromatic	+	+	+	+	+	+	0	-

Note: + compatible - incompatible 0 compatible under conditions

General rubber formulation

Ingredient	Content (phr)
Rubber	100
Activator	1-5
Anti-degradant	1-3
Reinforcing filler	0-60
Inert filler	0-120
Plasticizer or processing aid	0-20
Accelerator	0.5-2
Curing agent	0.5-3.5
Other ingredients (pigment, etc.)	As appropriate

Part 3: Rubber Mixing and Testing

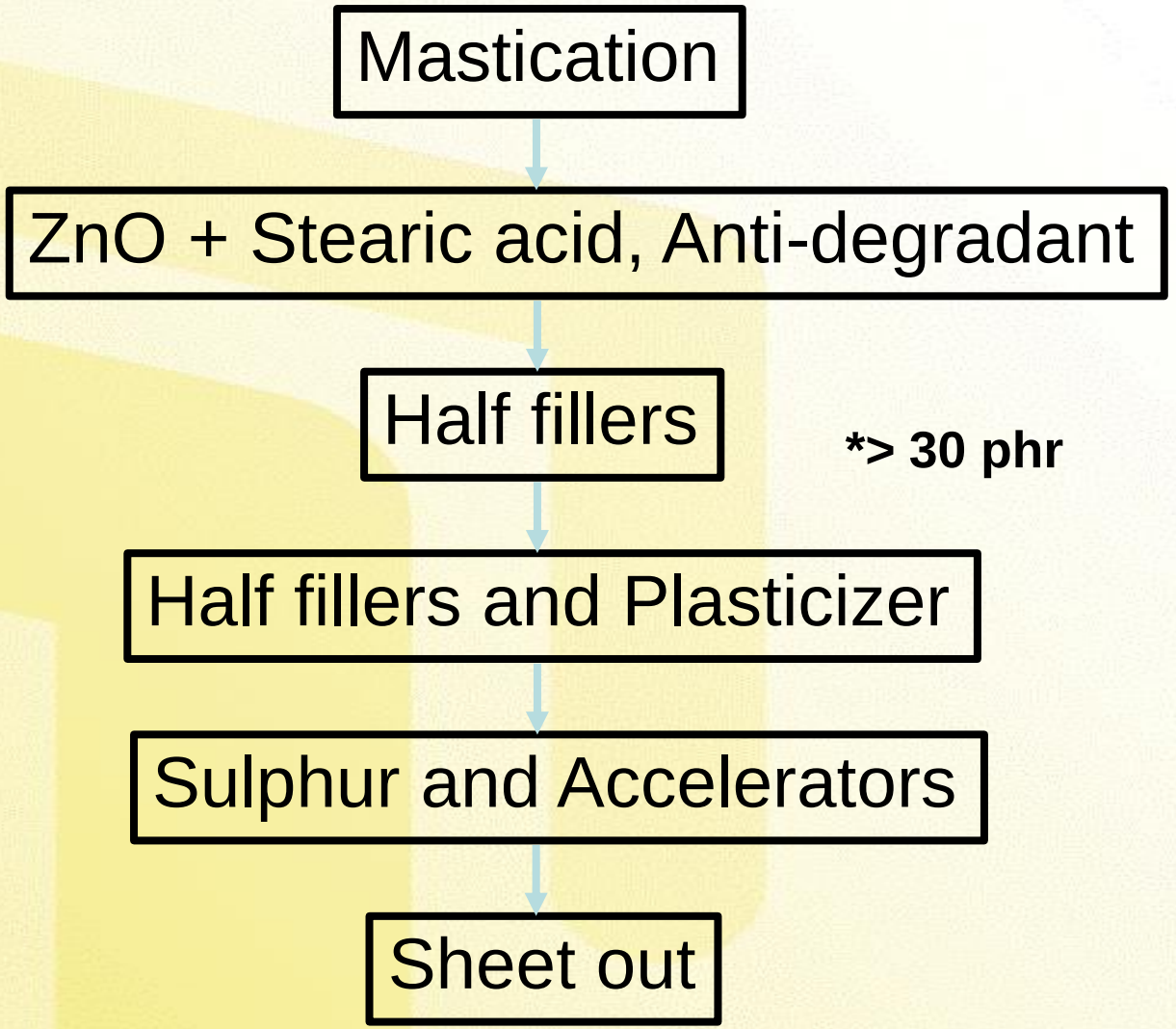
1. Rubber mixer

After having rubber formulars. Rubber ingredients need to be mixed together using rubber mixers. The rubber ingredients after mixing called “rubber compound”

Two roll-mill

Internal mixer

2. Rubber mixing step



3. Rubber compound properties

After mixing, normally, 3 properties of rubber compounds are measured.

- Density
- Mooney viscosity
- Cure characteristics

3.1 Density

Densiometer

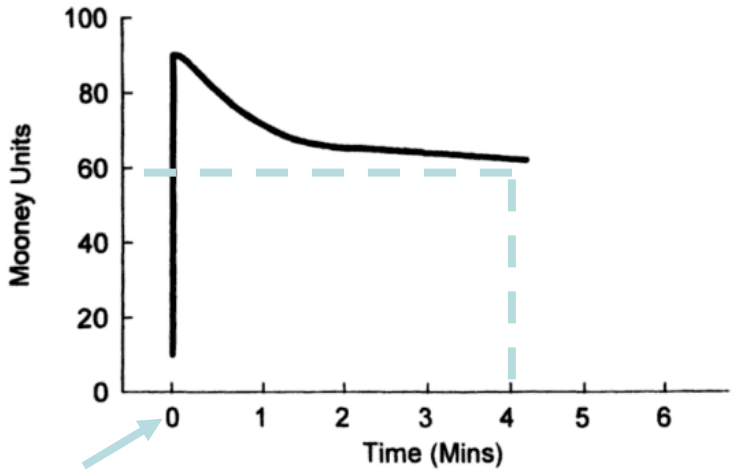
- ASTM D297

$$\text{Density at 25C (mg/m3)} = \frac{(0.9971 \times A)}{A-(B-C)}$$

A = mass of rubber specimen in air
B = mass of rubber specimen and supporting wire in water
C = mass of supporting wire in air

3.2 Mooney Viscosity

- ASTM D1646
- Heat the rotor up to the desired temperature (100C for NR)
- Make a sheet of rubber compound and weight it around 23±3 g
- Cut it into round shape, ϕ 47 mm (2 pcs)
- Put the round shape samples on the top and bottom of the rotor
- After 1 min., start rotor with speed 2±0.02 rpm, measure Mooney viscosity after the rotor rotation for 4 min.
- Generally, use large rotor (ϕ 36.10±0.03 mm)
- For high viscosity rubber compound, use small rotor (ϕ 30.48±0.03 mm)
- Mooney viscosity unit is MU



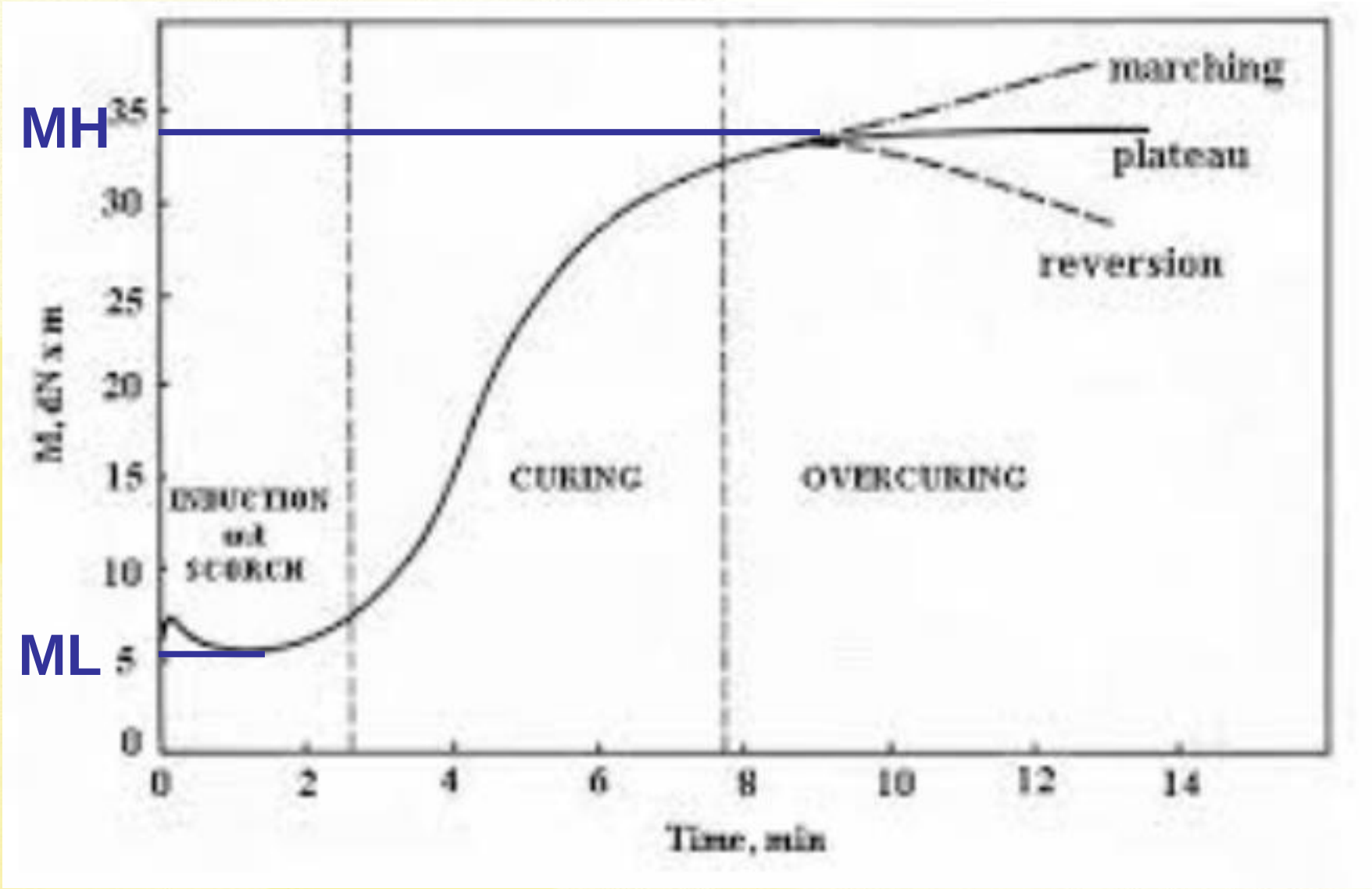
Mooney Viscometer

Roger Brown, Handbook of Polymer Testing: Physical Method, Rapra Technology Ltd, England, 1999

3.3 Cure Characteristics

- ASTM D2084
- Use rubber compound approx. 3-5 cm^3
- Put the sample between lower and upper dies and press the start button
- Lower die will oscillate at 0.5 or 1 degree, frequency is 1.67 Hz or 100 rpm

Moving Die Rheometer (MDR)


MH
ML
marching
plateau
reversion
INDUCTION
SCORCH
CURING
OVERCURING
M, dN x m
Time, min
0
5
10
15
20
25
30
35
0
2
4
6
8
10
12
14

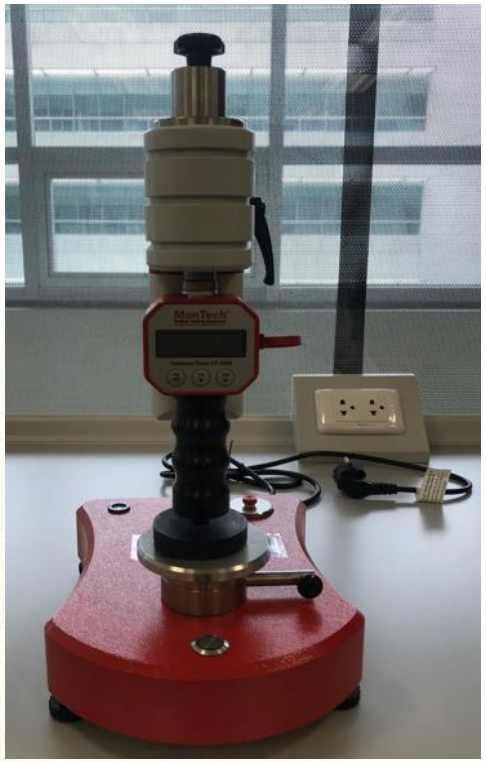
4. Rubber Vulcanizates Testing

There are many properties of vulcanized rubbers (rubber vulcanizates) to be measured, for example,:

- Hardness test
- Tensile properties test
- Heat resistance test

4.2 Hardness Measurement

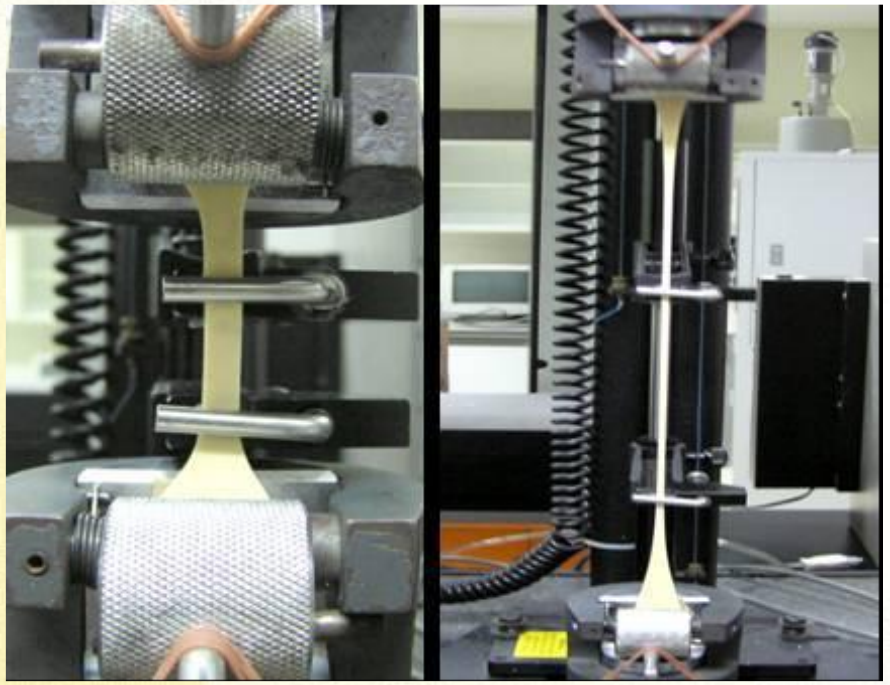
- ASTM D 2240
- Hardness is the resistance of rubber to indentation
- Hardness gauge has a needle on a spring protruding from one end
- Place the needle against the rubber
- Read the measurement gauge for rubber hardness
- Generally, Shore A Hardness is used for rubber
- Measure 5 points and use average value
- Sample 6 mm thick & 12 mm from edge

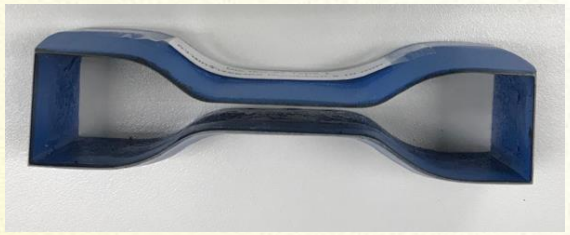


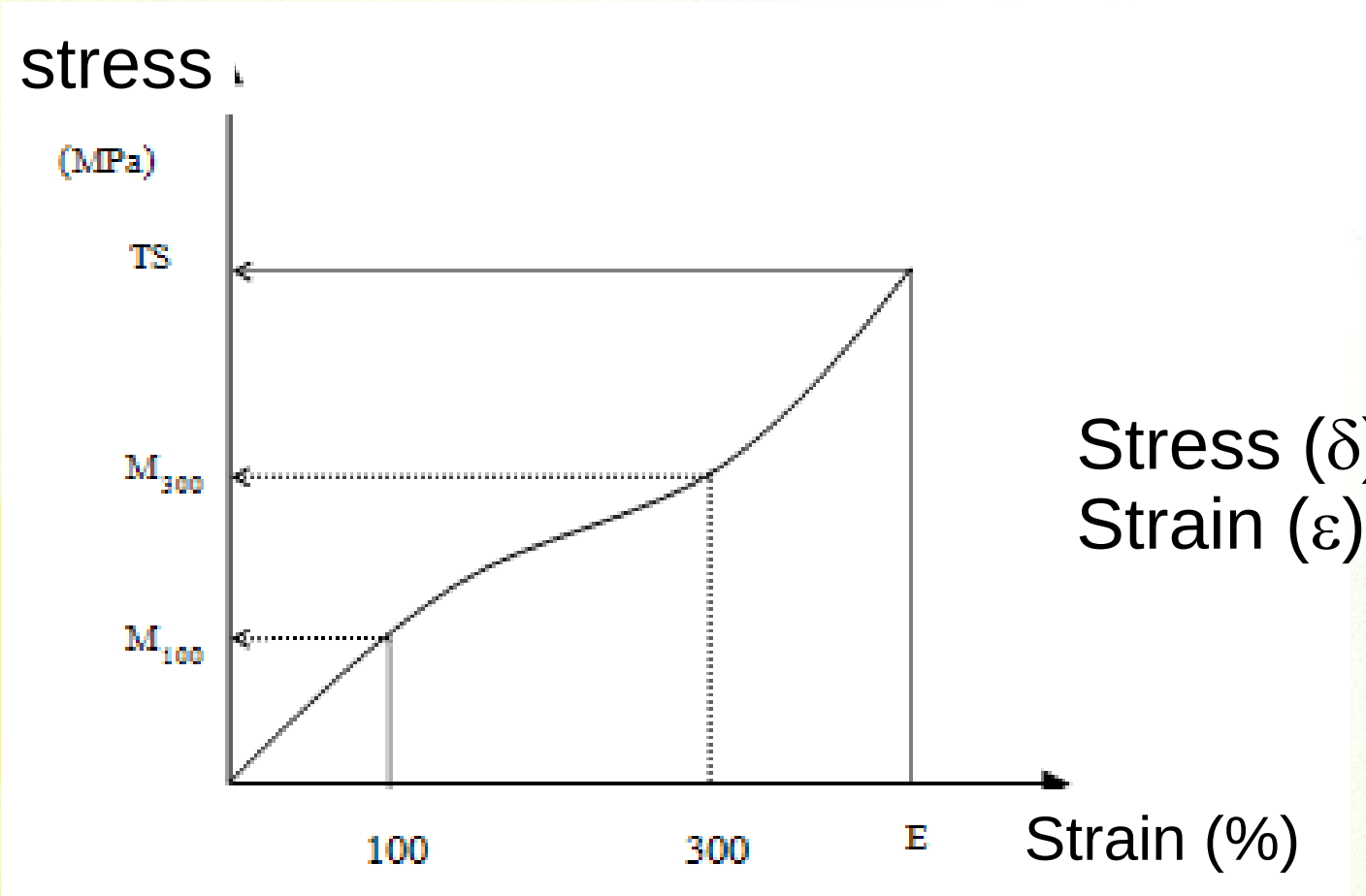
Durometer

4.3 Tensile Properties Test

- ASTM D412
- Use Universal Testing Machine (UTM)
- Tension speed 500±50 mm/min
- Gauge length = 25 mm
- Specimens = 3mm thick, 6mm wide Dumbbell shape type-C
- First, measure thickness of 3 points, use average value
- Then, measure tensile properties 3-5 times, use median value
- Results from tensile properties test are:
  - Tensile Strength (TS)
  - Elongation at Break (EB)
  - Modulus(M)







Stress (δ) = F/A

Strain (ε) = $(\Delta l/l_0)x100$

F = force

Δl = change of length

A = cross sectional area

L_0 = original length

4.5 Heat resistance test

- ASTM D573 (ISO 188)
- To determine the physical properties of vulcanized rubber under elevated temperature
- Dumbbell-shaped type-C is the most use (ASTM D412)
- Measure original properties of specimen, such as TS, EB and hardness
- Place the specimen in oven at specified temperature and time period (for example, 70C for 72hrs).
- Remove the specimen from the oven and allow to cool at room temperature for at least 16 hrs. (not more than 96 hrs.)
- Measure final properties of the specimen.
- Report a percent change of the TS, EB;
- Report hardness change in hardness points.

Hot air oven

Thank You for Your Attention.

Q&A