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The RMWA Journal

GUJARAT'S FIRST RUBBER MAGAZINE

PROGRESS THROUGH RUBBER

In this edition

- ❑ Compounding Materials
- ❑ Injection Molding Machines
- ❑ Heat Resistance of Rubber
- ❑ Dynamic Properties of Polymer Materials and their Measurements.

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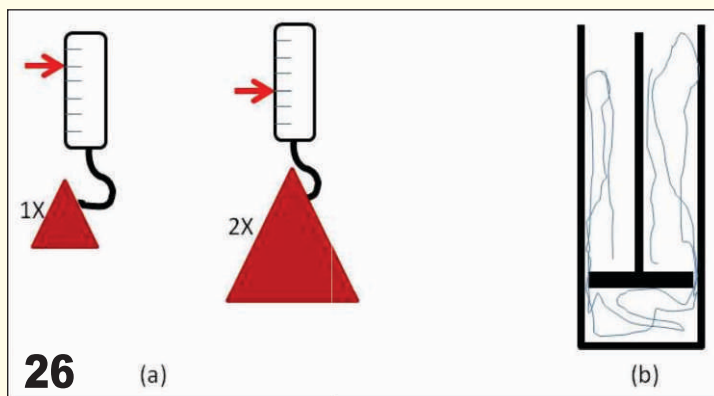
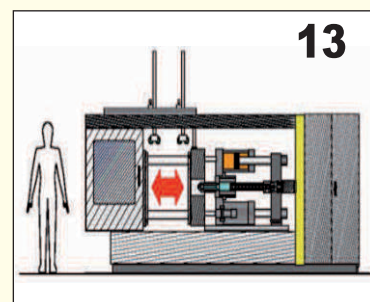
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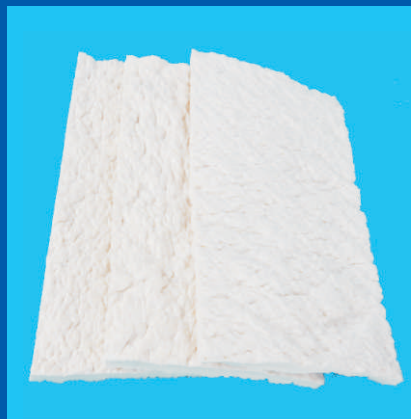
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From the Joint Secretary Desk

Snehal Shah
Jt. Secy, RMWA

Snehal Shah



“Help to Kerala”

Dear Members ,,,,

I feel honoured to address esteemed members of RMWA in the 5th edition of “The RMWA journal”.

We all are aware that in the beginning in July 2018, floods severely affected the south Indian state of **Kerala**, due to unusually high rainfall during the monsoon season. It was the worst **flooding in Kerala** in nearly a century. Kerala floods have not only taken several lives but it also has affected the rubber plantation industry. The floods in Kerala have caused extensive damage to rubber and other plantation crops in the state. Kerala produces around 85 per cent of rubber in the country which was destroyed due to floods in the state. Natural rubber is the heart of the rubber industry. It is our duty to come forward and help them to recover from this natural calamity. RMWA has sent out emails requesting members to donate to the CM relief fund in large numbers and show our solidarity with the rubber farmers. I hope our members will take up this cause sincerely.

Meanwhile, we are proud to announce that our membership number has reached 371 now with 38 members added this year. We are the biggest state association in rubber industry in India. RMWA has taken special initiatives to promote rubber product manufacturers by giving them incentives to participate in our 'India Rubber Expos'. 'The RMWA Journal' was started to provide techno-commercial information to members.

On 3rd August an AGM for 2017-18 had been called and new Trustees have been appointed for the years of 2018-19 and 2019-20. New committee for RMWA for the year 2018-19 has been formed in the trustee meeting on 31/08/1018, which will continue to work towards the benefit of the members of RMWA. I wish them all the best in their endeavours.

Here's wishing that this edition of The RMWA Journal will also be as useful to you as the previous ones.

Happy Reading

Editor's Note

Manoj Shah
Editor, RMWA

Manoj Shah



“Technical on Fluoro Polymer”

Dear Readers,,,,

Consumption of Fluoropolymer is increasing. Growth of automotive industries is mainly giving push to consumption of fluoropolymers. The characteristics such as good mechanical strength , high heat & chemical resistance are driving their upward consumption. Increasing demand is also observed in electronic & medical device. Fuel hose , gaskets and transmission system are the area where such polymers are largely used. In other application like cook-wear & semi-conductor cable, demand is likely to go up in coming years.

There are also certain restrain too. Fluoropolymers are not environment friendly. Natural degradation is not possible with these polymers. They may break down in chemicals which are toxic and can cause cancer.

Fluoropolymer market can be asserted either by product type or by application type. There are fluoro product like [1] polyvinyl diene fluoride [2] polytetrafluoroethylene [3] fluorinated ethylene propylene and [4] fluoro elastomers.

By application all above fluoropolymers have market share in automotive industries, industrial equipment, electrical & electronics industries and chemical processing industries.

Nowadays use of such polymers also started in industries like healthcare, aerospace & construction.

Happy Reading



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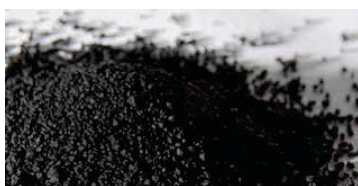
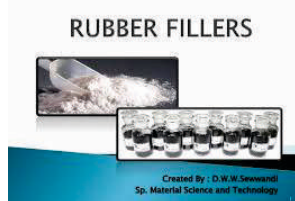
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Rubber Technology

Education

Compounding Material

Manoj Shah
Nitro Polymers



Chemistry of rubber compounding is a calculative art. The knowledge is essentially required on following points to design a rubber compound for rubber product. [1] Service condition [2] Properties of elastomer [3] Vulcanising system [4] Life of the product [5] Processing equipment and [6] Testing of compound & product.

There is a very long list of compounding material. Broadly they are classified as under. Elastomers or blend of elastomers

- ☐ Peptisers
- ☐ Vulcanising agents
- ☐ Accelerators
- ☐ Activators
- ☐ Antidegradents
- ☐ Softeners / Plasticizer
- ☐ Fillers
- ☐ Carbon blacks
- ☐ Special additives

A practical compound [recipe] is generally written on parts by weight. [P.B.W.] considering elastomer or blend of elastomer as 100 parts.

WE ARE OMITTING DETAILS ON ELASTOMERS AS THEY WERE DESCRIBED IN DETAILS IN PREVIOUS ARTICLE.

☐ PEPTISERS

These are chemical plasticizers. In general 2.0 pbw controls amount & speed of mastication.

Improve mixing and provides low power consumption.

When required viscosity is achieved, action of peptisers can be terminated by sulphur, accelerators & carbon black. They are useful in high viscosity rubber e.g. natural rubber.

Typical peptisers are MBTS, oil soluble sulphonic acid & pentachlorothiophenol.

All such chemicals consist of active -SH group [mercaptan].

☐ VULCANISING AGENT

- 1 These are cross linkers for rubber chain into 3D network.
- 2 Sulphur & sulphur bearing material and peroxides are well-known vulcanising agent.
- 3 Sulphur is widely used. 0-3 pbw for soft rubber product. 25-35 pbw for hard ebonite.
- 4 Rhombic sulphur S₈ is widely used. Amorphous sulphur is meta-stable due to high polymeric structure. It is insoluble in most solvent, known as insoluble sulphur. It prevents blooming of uncured stock & maintains building tack.
- 5 TMTD [3.5 %] when used, the product is heat resistant. Scorch safety is compromised & blooming is evident.
- 6 Peroxides are cross linking agent. E.g. benzoyl peroxide & di-cumyl peroxide.
- 7 They should be nontoxic.
- 8 Peroxide cured products are bloom free, heat



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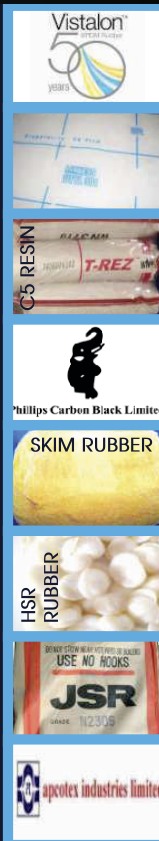


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□ ACTIVATORS

- 1 Activator activates accelerator & increase cure rate. They are alkaline e.g DEA & TEA
- 2 Inorganic activators are ZnO, MgO, & PbO.
- 3 Organic activators are stearic acid, high molecular weight fatty acids e.g Lauric and Oleic acid.
4. Generally used around 0-5 phw but it depends on curing system.

□ ACCELERATORS

- 1 Broadly classified into 5 types. They accelerate the crosslinking reaction.
- 2 DITHIOCARBAMATE type are ultra fast accelerator for unsaturated rubber however they are used as primary accelerator for saturated rubber like butyl & EPDM. They are non-discolouring in light coloured compound. Examples are ZDC, ZDBDC etc. They are used in latex compound.
- 3 THIURAM type are fast accelerator. Normally not used as primary accelerator with unsaturated rubber. However they are used as booster to primary accelerator. They are non-discolouring in light coloured compound. Well-known examples are TMTD & TMTM. Zinc oxide & stearic acid are necessary for sulphur & non-sulphur curing.
- 4 SULPHENAMIDE type accelerator are widely used. They are reaction product of MBT with alkaline substances. They provide long flow period yet cures rapidly. Mainly used in heavy dynamic stresses. [tyres, mechanical goods & conveyor belts] Examples are CZ, DZ, MOZ etc.
- 5 THIOZOLE types are semi fast accelerators. Examples are MBT & MBTS. The former is faster in curing while the latter is safe processing. Mainly used in footwear & mechanical goods.
- 6 SPECIAL types are used for specific polymer or purpose. NA-22 for neoprene. PF resin & paraquinonediimine for butyl. HMDA [Diak] for viton. DPG / DOTG for abonites & high modulus product.

□ SOFTENERS & PLASTICIZERS

- 1 They improve mixing of carbon black & fillers. They produce low hardness compound.
- 2 They improve building tack & plasticity of compound. They reduce power consumption. Petroleum oils are widely used. They can be classified as aromatic, naphthenic & paraffinic. Aromatic oils are highly unsaturated, naphthenics are moderate & paraffinics are saturated.
- 3 Vulcanised vegetable oils are also used as softener. E.g. factices.

- 4 Esters of organic acids are used as plasticizer for nitrile rubber.

D.O.P., D.B.P. & C.I. resin are used widely in nitrile rubber.

- 5 Pine tar oil is good tackifier for natural & SBR rubber.

□ FILLERS

- 1 There are two types of filler [1] reinforcing [2] extenders
- 2 Precipitated Silica, Calcium silicate and Aluminium silicate are reinforcing filler.
- 3 Hard clay and calcium carbonate are semi reinforcing filler.
- 4 Ground whiting, barytes & talc are extenders.
- 5 Silica & clay are acidic, may retard cure.

□ CARBON BLACKS

- 1 There are mainly three types of carbon blacks namely furnace, thermal & channel.
- 2 Furnace blacks are reinforcing fillers. Particle size is main property to determine the reinforcement. Lower the particle size, higher is the reinforcement. Furnace blacks are largely used. There are different types of furnace blacks. Space does not permit to go in more details.
- 3 Thermal blacks are used in resilient rubber product at comparatively higher loading. They consist higher particle size.
- 4 Useful in 'V' belt due to low heat built up. Also used in inner lining compound & inner tubes. Use is restricted due to high cost.
- 5 Channel blacks are not used as they are acidic and retards cure. The very low yield 5% is other reason. They are easy processing with good reinforcement.
- 6 Acetylene black is basically thermal black. It is pure form of carbon. Mainly used to produce electrically conductive compound.
- 7 Previously blacks are classified by their manufacturing process and the property it imparts to rubber compound. A.S.T.M. classification is based on particle size.

□ SPECIAL ADDITIVES

- 1 Deodorants are used in erasers. Blowing agents are used to produce sponge rubber Products. Abrasives are used to produce buffing wheel. Benzoic acid is good retarder. Inorganic & organic compounds are used in coloured rubber products. Boric acid is flame retardant.

This article shows brief details about compounding material. Each category of compounding material requires one special article. Time & space does not permit to include full details.

Injection Moulding Machines

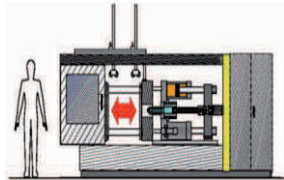
- Desma

DESIGNS

Horizontal machines

- well suited for small articles without inserts
- can easily be automated
- □ gravity supports article demoulding

The mould is almost always injected centrally through the fixed mounting platen (Z)

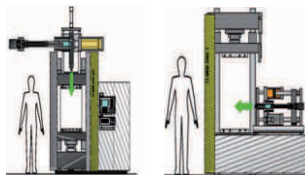


Vertical machines

- Are preferably used for:
- articles with inserts
- production with cyclic intervention by operator

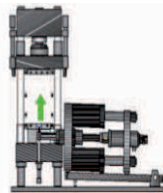
Injection centrally from top (ZO)

- little space required
- most frequent vertical design



Split line injection (T)

- recommended for a very large injection volume
- very flexible, since a diverting block also permits ZO and ZU moulds to be used

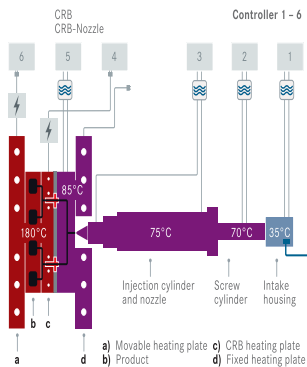


Injection centrally from below (ZU)

- advantageous for liquid silicone (LSR) processing



Vertical machine D 968.400 ZO BENCHMARK S3
and horizontal machine D 969.300 Z SEALMASTER S3



5.1 TEMPERATURE CONTROL

Cavity-forming mould components are usually heated with **electric heating elements**. Larger systems sometimes use hot steam.

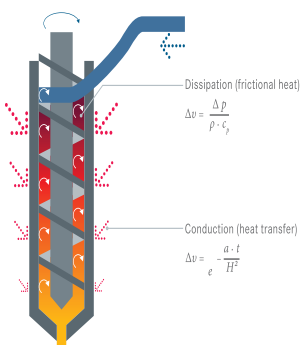
The temperature of areas in which the elastomer must remain liquid during production (injection unit and CRB), in contrast, is **temperature-controlled with liquid**. This means that a water- or oil-based medium is first adjusted in a heating or cooling device (temperature-control unit) to the required temperature. Next, the medium flows through the component that is to be temperature-controlled. The temperature of the medium is thus transferred to the component. This permits a very uniform temperature distribution. Furthermore, it permits the components to be cooled down very rapidly at the end of production (crash cooling). This prevents the compound from scorching.

Heating the compound in the screw cylinder improves its flowability (plasticizing). The screw permanently mixes the compound. This ensures gentle heating and a homogenous compound temperature (without temperature peaks).

The compound is preheated / plasticized by:

- Friction in the compound (dissipation), resulting from the different flow rates of the mass layers
- Heat transfer (conduction) from the temperature-controlled steel to the compound

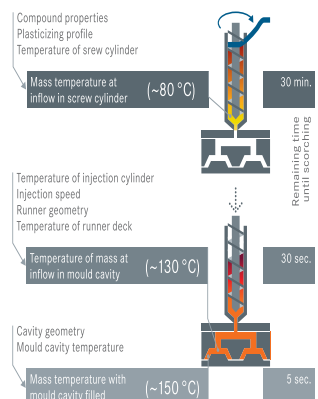
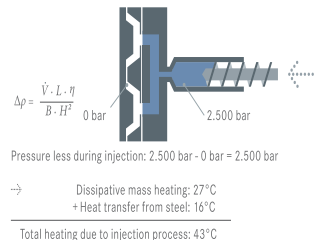
The resulting compound temperature must be kept at a constant value until the injection phase begins. This means that the temperature in the peripheral zones (contact zones to the steel surface) should neither rise nor drop. The temperature of the injection cylinder is therefore adjusted to the compound temperature in this area.



The movement of the injection piston (or the screw) during the injection process increases the mass pressure in the injection cylinder until the compound flows briskly into the mould cavities. The necessary pressure chiefly depends on the viscosity of the compound, and on the geometry of the injection channels. Currently, the maximum possible specific injection pressure (compound pressure in the injection cylinder) of injection moulding machines is approximately 3,500 bars.

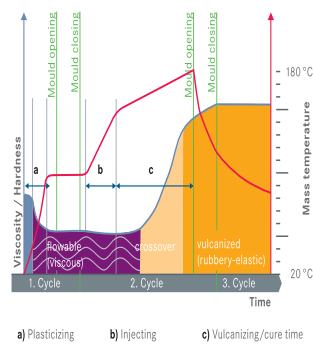
On its way through the hot mould channels, the mass also absorbs conductive heat. The exact amount chiefly depends on the surface temperature and the contact time (flow rate and length).

The sum of dissipative and conductive heat produces a major temperature rise during the injection process. There are two reasons why this is welcome: It reduces the necessary cure time, and it reduces the difference between mass temperature and mould temperature.



Ideally, the compound filling temperature and the steel mould surface temperature are exactly the same. In this case, the inner cavity pressure even of thick-walled articles remains almost constant during the entire cure time, and a very uniform cross-linking degree can be obtained.

In practice, however, this is (still) difficult or impossible. In particular with thick-walled articles, the difference between filling temperature and mould temperature leads to continuously rising pressure in the mould cavity (thermal expansion). Problems like flash, backrinding, or poorly shaped injection points are frequently the results. Furthermore, the compound is significantly stronger vulcanized on the article surface than it is inside the article.

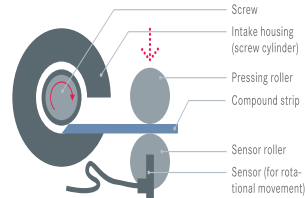


5.2 INJECTION UNIT

Tasks:

- Taking in the compound
- Monitoring the intake
- Dosing the exact compound quantities
- Preheating the compound gently and homogeneously (plasticizing)
- Keeping the compound temperature at a constant level until it is injected
- Ensuring an exact injection velocity profile
- Ensuring an exact injection volume
- Ensuring an exact dwell profile
- Best flushing effect possible (little)

STRIP INTAKE WITH MONITORING



5.2.2 GENERAL DESIGNS

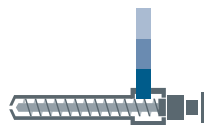
FIFO (First In, First Out)

Once design corresponds to the FIFO principle: The compound that is taken in first, is injected first. This is significant because the latent period (time remaining to the start of vulcanization) elapses relatively quickly as soon as the temperature is increased. The heat load of the compound that flows first into the injection cylinder is always highest. This component is exposed to an increased temperature during the entire plasticizing time. The compound last taken in, in contrast, is still

very fresh. This different heat load can now be compensated for when the part of the component that sits longest in the injection cylinder is injected right at the beginning of the injection phase. The FIFO principle also improves the flushing effect. The risk of contamination with old rubber (prevulcanized particles in the injection compound) is reduced since there are less or no „blind spots“ where material can deposit.

FIRST IN, FIRST OUT

1. Start of plasticizing



2. End of plasticizing, start of injection phase



3. End of injection phase



5.2.1 MATERIAL FEEDING

Rubber compounds are usually processed in strip shapes. The screw can take in the compound strip directly. The intake speed can be monitored with a sensor. If the strip tears off, this is detected and screw rotation is stopped to prevent the material from overheating.

Silicone rubber is processed as:

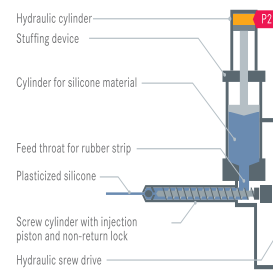
- Solid silicone or paste silicone (HTV)
- Liquid silicone (LSR)

In either case, strip intake is difficult / impossible due to the too soft and sticky consistency. Adequate auxiliary equipment is therefore used here. The material supply is usually monitored indirectly via the dosing time (and limit switch for material shortage).

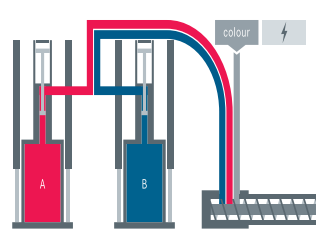


ActiveFeed - Actively driven feed roller

STUFFING DEVICE FOR PASTE SILICONE (HTV)



MIXING AND DOSING DEVICE FOR LIQUID SILICONE (LSR)



Currently, we know three different basic concepts of injection moulding machines for polymer materials:

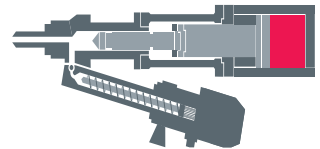
1) Screw piston (injection unit)

- corresponds to the FIFO principle
- Standard in thermoplastics injection moulding machines
- unsuitable for rubber processing, because effective screw length is not constant



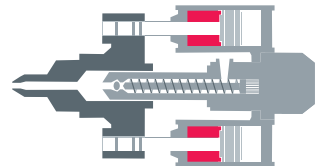
2) Injection unit with separate screw and injection cylinder

- does not correspond to the FIFO principle
- steady compound strip intake
- Standard injection unit for elastomers up to approximately 1990



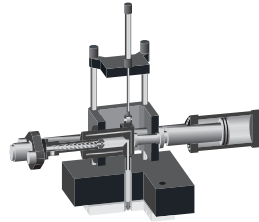
3) Injection unit with screw cylinder injection piston

- corresponds to the FIFO principle
- Combines the benefits of type 1 and type 2
- Permits shortest cycle times
- Since approximately 1995 common technique for elastomer injection moulding

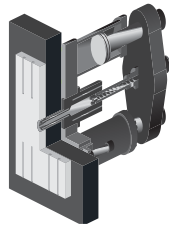


5.2.3 CURRENT DESMA DESIGNS

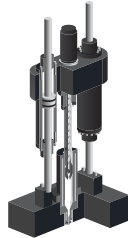
DESMA FIFO-A with retractable nozzle
For vertical machines (injection from top):



DESMA FIFO-B with retractable nozzle
For horizontal machines and for split line injection:



DESMA FIFO-C with fixed-lying nozzle
For C-frame machines and small shot volumes:

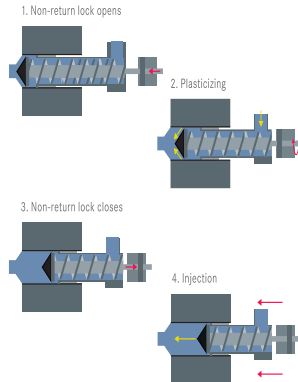


Current technique

In autumn 2010, DESMA first presented an injection unit with a patented active non-return lock (**PlastControl**). Hydraulic cylinders in this system allow the non-return lock to be opened and closed in a controlled way.

The active actuation (lock immediately after dosing) safely prevents any leakage flow. The result is more precise cavity filling and thus less waste and rejects.

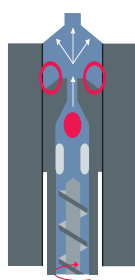
Furthermore, this system provides for a better flushing of the injection piston area. This efficiently prevents deposits to build up during production or compound change.



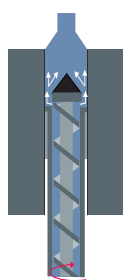
PlastControl



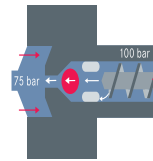
Conventional non-return lock



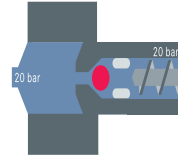
PlastControl non-return lock



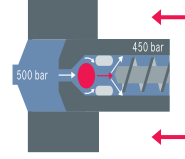
1. Plasticizing



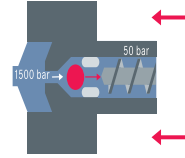
2. End of plasticizing



3. Start of injection leakage flow



4. After approx. 0.5 sec injection time



5.2.4 NON-RETURN VALVE

In the plasticization process, the compound must be able to flow with lowest possible resistance from the screw cylinder into the injection cylinder. Since up to 3,500 bars are built up in the injection cylinder during the subsequent injection phase, a very solid lock is required here to prevent the compound from flowing back towards the screw.

Conventional injection units use passive non-return valves for this purpose. This means that the locking element (ball, taper, or ring) is moved only by the mass flow. At first, the valve therefore remains open after the dosing / plasticization phase. It is only after the beginning of the injection phase that the increasing pressure in the injection cylinder presses the locking element against the sealing seat. Until the valve is closed completely, a part of the dosed compound can flow back into the screw cylinder (leakage flow).

This is a problem, in particular, during liquid silicone processing. Since the mixing and dosing units that are used here are only designed for a maximum pressure of 200 bars, they can easily be damaged by the high return flow pressure. Furthermore, temperature and batch variations in this system always lead to changing locking times and thus inaccurate injection volume.

5.2.5 CLEANING / COMPOUND CHANGE

The employed compounds vary very much. Certain deposits on the walls can therefore not be avoided, even with optimized flushing effects. Such a waste material layer, which is very thin to start with, can heavily grow in the course of time. The channel cross section is increasingly narrowed, which causes the flow rate to rise. As a result, particles can be torn off the layer which frequently embrittles rapidly. The injection compound then „drags“ these particles into the mould cavity (contamination with old rubber).

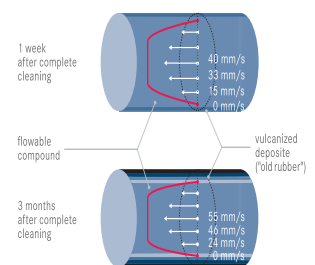
Although old rubber inclusions can mostly not be detected from the outside, they can lead to product failure!

The most efficient and safe **countermeasure** is therefore a preventive cleaning of the steel surfaces. This should be done with the injection unit and, if necessary, also with the cold runner block. Depending on compound and temperatures, the following process should be performed every 3 to 6 months:

1. **Complete full curing** of the compound inside the injection unit (including the cold runner block, if necessary)
2. Pull / press out the vulcanized material including deposits

In **conventional injection units** with passive non-return lock, you must also remove injection piston and non-return lock when you clean the screw cylinder. To be able to press the vulcanized material (using the new compound) out of injection cylinder and nozzle, you must also remove the nozzle tip. A visual inspection of the steel surfaces is thus not possible.

CAUSE OF WALL DEPOSITS WITHIN NOZZLE AND CRB AREA (flow speeds in tube)





The **PlastControl** technique significantly reduces the effort:

1. Hydraulically retract the screw cylinder.

Due to the strong undercut at the injection piston, the entire vulcanized material is pulled out of injection cylinder and nozzle. The nozzle tip can therefore remain installed.

2. Start plasticization

The screw automatically delivers the vulcanized material from the screw flights (feeding new compound is therefore not necessary).

3. Finished

□ □ For the first time, all surfaces can be checked directly (with visual inspection)!

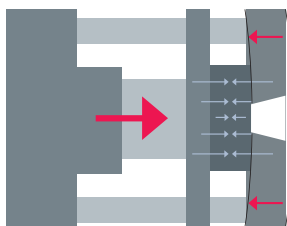


Vulcanized material pulled out of the **PlastControl** injection unit (nozzle, injection and screw cylinder)



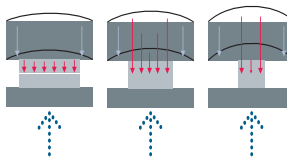
If absolute cleanliness is required, the entire screw can be screwed out from the front for inspection and cleaning.

Plasticizing new compound directly proves sufficient in most cases. Loose old material in the screw area (fibrous material, crumbs) are flushed out without any problems.



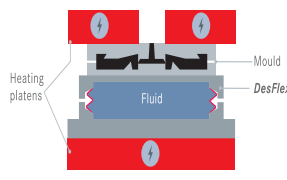
For changing mould sizes, however, not even clamping units in column design guarantee an absolutely homogenous pressure distribution in the split lines of the mould.

Basic problems with mould clamping

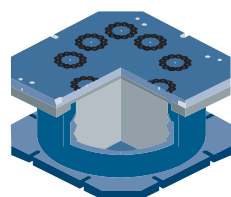


In particular the clamping force, the width and height of the mould, the material of the mould plates, and the position of the split lines have a significant influence on the transmission of the force.

Pressure distribution with different mould width



The patented auxiliary equipment **DesFlex** permits to achieve optimized force transmission for a wide range of applications. Its operating principle generates a uniform distribution of the pressure, even under changing conditions (for example with different moulds or changed clamping force).



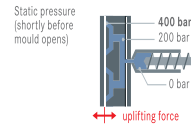
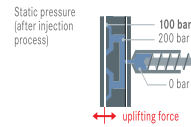
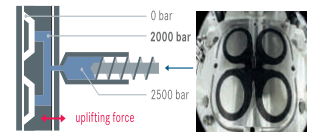
In contrast to conventional measures, **DesFlex** can adjust to the currently prevailing conditions. It thus provides the best conditions to produce permanently articles that do not require any reworking (i.e. articles without visible burr or overmoulding).

5.3 CLAMPING UNIT

Tasks:

- Accommodating the injection mould
- **Transferring the clamping force uniformly on the mould**
- Opening and closing the mould, moving mould parts (e.g. intermediate plates), positioning to certain stroke points
- Protection of mould against damage
- Uniform heating of the mould

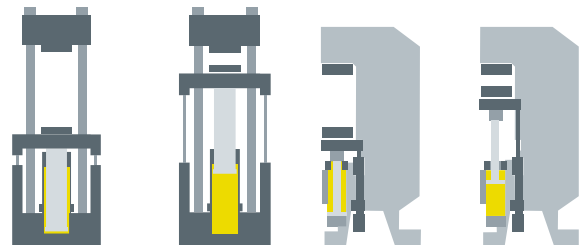
PRESSURES AND UPLIFT DURING INJECTION



5.3.1 CLAMPING

A sufficiently large and **equally distributed surface pressure** (pressure distribution) in the split lines is necessary to avoid overmoulding (burr, flash) at runner and article.

Due to their symmetric design, clamping units in **column design** combined with a fully hydraulic clamping cylinder satisfy best the requirement „best uniform force application possible“:



For the priority „best possible mould accessibility“, **tie-bar-less clamping units** are used:

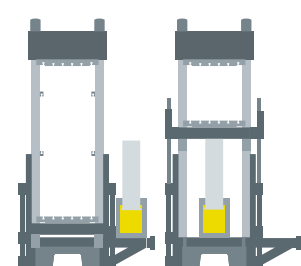
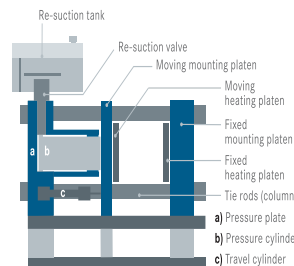
5.3.2 CURRENT DESMA DESIGNS

Fully hydraulic clamping unit

- Perfectly suitable for all horizontal machines
- Suitable for vertical machines up to a maximum of 4,000 kN
- **disadvantage: working height**

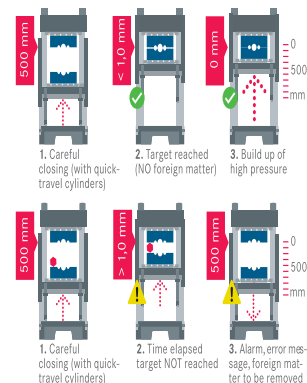
BENCHMARK clamping unit

- Perfectly suitable for vertical machines $\geq 4,000$ kN
- **Advantage: low working height**



5.3.3. PROTECTIVE CLOSING FUNCTION/ MOULD PROTECTION

Since elastomer injection moulding requires frequently inserts to be fed into the mould (such as plastic or metal inserts), there is always a high risk of damage for the injection mould. Modern clamping units are therefore able to detect incorrectly inserted parts, and can thus prevent serious mould damage. This is achieved by a force / time limit in conjunction with a specified target point when closing the mould.



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RCB - Recovered Carbon Black

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SH - 665	15 kg



Granular Grades		
1	SS - 330	25 kg
2	SS - 550	25 kg
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*Also available in Jumbo Bag packaging



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Heat Resistance of Rubbers

Indian Rubber Manufacturers Research Association

Suchismita Sahoo, Dr. K. Rajkumar

1. Introduction

Rubber is a special class of polymer with exceptionally high elasto – mechanical properties. The high elastic memory, high ultimate elongation, low elastic modulus and viscoelastic nature are used for applications requiring continuous deformation and regaining of shape. Compared to other engineering polymers rubber is recommended for wide range of unique applications. However, their limited ability to high temperature resistance restricts their opportunities to be used in multiple applications viz. seals and gaskets for engines. The upper temperature limit for commonly available elastomers is maximum up to 200 °C. The general purpose elastomers like natural rubber (NR), styrene butadiene rubber (SBR), ethylene propylene diene rubber (EPDM), polychloroprene (CR) are mostly restricted to the upper temperature limit of upto 120°C or lesser than that. Few elastomers like fluorine containing polymers and silicone polymers can sustain temperature up to 200°C due to their inherent chemical composition.

Multiple efforts have been made by different research groups to enhance the heat resistance of rubbers to widen the window of opportunities and application for rubber material which is the current topic of interest.

2. Theory of Heat Resistance of Rubber⁸

Heat resistance roots from the chemical nature of the base rubber. Table 1 shows the list of energy associated with different bonds. In [chemistry](#), **bond energy** (E) is the measure of [bond strength](#) in a [chemical bond](#). It is the heat required to break one [mole](#) of molecules into their individual atoms. For example, the [carbon-hydrogen](#) bond energy in [methane](#) ($E(C-H)$) is the [enthalpy](#) change involved with breaking up one molecule of methane into a carbon atom and 4 hydrogen [radicals](#) divided by 4. Bond energy (E) should not be confused with [bond-dissociation energy](#). It is a roughly [transferable property](#), and [enthalpy of formation](#) can typically be roughly approximated by simply adding tabulated values for bond energies for all bonds in a molecule, with an error of sometimes just a few percent. However, to get a better approximation is much more difficult.

	ΔH°		ΔH°		ΔH°
H-H	104.2	B-F	150	C=C	146
C-C	83	B-O	125	N=N	109
N-N	38.4	C-N	73	O=O	119
O-O	35	N-CO	86	C=N	147
F-F	36.6	C-O	85.5	C=O (CO ₂)	192
Si-Si	52	O-CO	110	C=O (aldehyde)	177
P-P	50	C-S	65	C=O (ketone)	178
S-S	54	C-F	116	C=O (ester)	179
Cl-Cl	58	C-Cl	81	C=O (amide)	179
Br-Br	46	C-Br	68	C=O (halide)	177
I-I	36	C-I	51	C=S (CS ₂)	138
H-C	99	C-B	90	N=O (HONO)	143
H-N	93	C-Si	76	P=O (POCl ₃)	110
H-O	111	C-P	70	P-S (PSCl ₃)	70
H-F	135	N-O	55	S=O (SO ₂)	128
H-Cl	103	S-O	87	S=O (DMSO)	93
H-Br	87.5	Si-F	135	P=P	84
H-I	71	Si-Cl	90	P≡P	117
H-B	90	Si-O	110	C≡O	258
H-S	81	P-Cl	79	C≡C	200
H-Si	75	P-Br	65	N≡N	226
H-P	77	P-O	90	C≡N	213

Bond Dissociation Energies									
atom or group	methyl	ethyl	i-propyl	t-butyl	phenyl	benzyl	allyl	acetyl	vinyl
H	103	98	95	93	110	85	88	87	112
F	110	110	109		124	94		119	
Cl	85	82	81	80	95	68	70	82	90
Br	71	70	69	66	79	55	56	68	80
I	57	54	54	51	64	40	42	51	
OH	93	94	92	91	111	79	82	107	
NH ₂	87	87	86	85	104	72	75	95	
CN	116	114	112		128	100			128
CH ₃	88	85	84	81	101	73	75	81	98
C ₂ H ₅	85	82	81	78	99	71	72	78	95
(CH ₃) ₂ CH	84	81	79	74	97	70	71	76	93
(CH ₃) ₃ C	81	78	74	68	94	67	67		89
C ₆ H ₅	101	99	97	94	110	83	87	93	108
C ₆ H ₅ CH ₂	73	71	70	67	83	59	59	63	81

Rubber molecules are primarily composed of carbon and hydrogen with smaller amounts of nitrogen, oxygen in few classes with the exception of silicone rubber which comprises of a backbone consisting of $-\text{Si}-\text{O}-$ which attributes the high temperature resistance to this class of elastomer. Similarly the fluoroelastomers are classified as the highest heat resistant elastomers attributed to the high bond energy associated with $-\text{C}-\text{F}-$ bond.

1. MECHANISM OF THERMAL DEGRADATION VIA OXIDATION

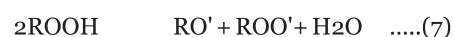
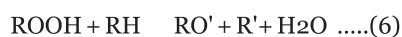
High temperature causes bond dissociation leading to generation of free radicals which in turn react with the atmospheric oxygen causing unwanted change in various physical and mechanical properties. The ease of bond dissociation depends on the polymer structure, lesser the bond dissociation energy lower the temperature required to cause the bond cleavage. Branching and unsaturation possessing lower bond energies are more susceptible to degradation. The thermal degradation causes hardening of some classes of synthetic rubbers like SBR and NBR due to oxidative crosslinking and some rubbers like natural rubber, IIR and IR softens due to chain scission.

Oxidation of polymers can lead to chain scission, crosslinking or formation of oxygen containing functional groups in the polymer or its degradation products.

Initiation



Propagation



Chain transfer



Termination



Scheme1: An outline of the oxidation process

RH = polymer molecule or portion thereof, AH = antioxidant, A' = antioxidant radical, RO_2' = polymer peroxy radical, and ROOH = polymer peroxide. According to Arrhenius principle with every 10°C rise in temperature doubles the rate of reaction.

2. TYPES OF RUBBERS AND THERE HEAT RESISTANCE RANKING

Rubber can be broadly classified into natural and synthetic. Natural rubber is extracted from the tree *Hevea Brasiliensis* and synthetic rubbers has base from the petroleum sources. Increasing demands of rubber usage lead to the invention of various types of synthetic rubbers.

Subjective ranking of heat resistance of different rubbers is as below:

FKM (Best) > VMQ > Fluorosilicone > ACM > AEM > EPDM > CO/ECO \approx CM > CSM \approx NBR > CR > IIR \approx NBR/PVC > SBR > NR

Information of Upcoming Rubber Events / Exhibitions



National Rubber Conference 2018

National Rubber Conference 2018 Technology adoption and market expansion during 1-2 October, 2018 at Sahara Star, Domestic Airport, Mumbai.



Rubber 2018 Istanbul

10th Rubber 2018 Istanbul Rubber Industry Fair at Tuyup Fair Convention & Congress Centre, Istanbul during 24-25-26-27 October, 2018.



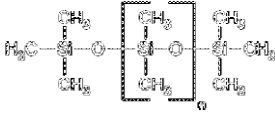
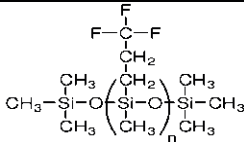
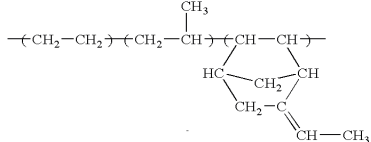
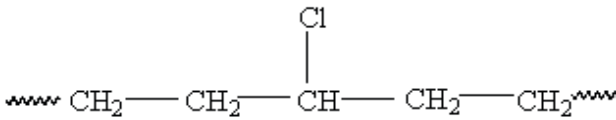
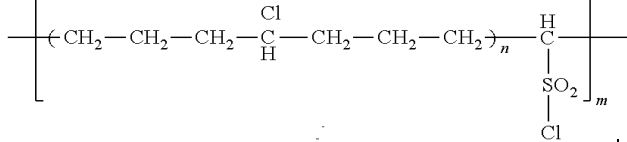
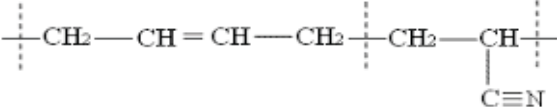
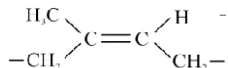
Africa Rubber Expo & Summit 2018

Meeting Points for Rubber, Latex and Tyre Industries at Johannesburg South Africa during 20-21 November, 2018.



India Rubber Expo 2019

"INDIA RUBBER EXPO - 2019" is in its 10th Edition and the Marquee event is being held from 17th to 19th January 2019 at the Nesco Complex - Goregaon(E) Mumbai.

IUFAC NAME	Description	Chemical Structure
FKM		$-(\text{CH}_2-\text{CF}_2)_l-(\text{CF}_2-\overset{\text{CF}_3}{\underset{ }{\text{CF}}})_m-$
VMQ	S	
FMQ		
ACM	P	$\left[-\text{CH}_2-\overset{\text{R}'}{\underset{\text{COOR}}{\text{C}}} - \right]_n$
AEM	V	$\begin{array}{cccc} \text{C} & \text{C} & \text{C} & \text{C} \\ & & & \\ \text{C} & & & \\ & & & \\ \text{C} & & & \end{array}$
EPDM		
CO/ECO	C/	$\left[-\text{CH}_2-\underset{\text{CH}_2\text{Cl}}{\text{CH}}-\text{O}- \right]_n \left[-\text{CH}_2-\text{CH}_2- \right]_m$
CM	Chlorinated Polyethylene	
CSM	Chlorosulfonated polyethylene	
NBR	Acrylonitrile butadiene rubber	
NR	Natural rubber	

1. MATERIALS AND TECHNOLOGIES FOR HIGH HEAT RESISTANT RUBBER

1.1 Rubber with bound antioxidants

Numerous studies done on improvement in rubber properties by binding the antioxidants to the main polymer chain. The primary intention of binding the antioxidant is to prevent the leaching and loss of antioxidant thereby extending useful life and heat aging resistance of rubber. Most of the studies used amino type antioxidants and showed an improvement over the conventional antioxidants in aging resistance. However due to manufacturing complexity versus the incremental advantage, there are no commercial grades of rubber with bound antioxidants.

1.2 Hydrogenated Rubbers

Hydrogenation is a well-known technique to improve the heat aging and resistance to oxidation. Hydrogenated nitrile rubber is widely used for improved heat and ozone resistance. Lanxess and Zeon Chemicals are the leading manufacturers of hydrogenated nitrile rubber (HNBR). HNBR has improved mechanical properties, heat and ozone resistance compared to the NBR. Higher the level of unsaturation better is the heat resistance.

1.3 BIMS⁹

Polyisobutylene with brominated p-methylstyrene as cure site based compounds may have better heat aging properties than a conventional halobutyl rubber compound under more severe temperatures such as 125°C to 150°C.

1.4 Metal Rubber⁶

NanoSonic's Metal rubber is a highly electrically conductive and highly flexible elastomer. It can be mechanically strained to greater than 1000 percent of its original dimensions while remaining electrically conductive. As Metal Rubber can carry data and electrical power and is environmentally rugged, it opens up a new world of applications requiring robust, flexible and stretchable electrical conductors in the aerospace/defense, electronics and bioengineering markets. Metal Rubber sheets are available in two sizes: 6" x 6" and 12" x 12" sheets. Metal Rubber is made through a modified molecular-level self-assembly production process using precursors NanoSonic produces in-house. Materials are manufactured in a variety of sizes and

geometries. Applications include but are not limited to: Metal Rubber Cables - Replace heavy data and power cables - Flexible Metal Rubber conductors, Metal Rubber fabrics and CNTs - Lightweight, improved EMI shielding - Related production of novel cylindrical tubing and hoses.

2 EXPERIMENTAL METHODS TO IMPROVE THE HEAT RESISTANCE

2.1 Metal powders as filler to improve the

conductivity and heat resistance

Aluminum powder has been studied in the matrix of natural rubber other metals like silver and copper has also potential but silver is expensive and copper act as a pro-oxidant to natural rubber². A bonding agent like hexamethylenetetramine or similar can be used to improve the adhesion between the metal and rubber particles and improve the physical and mechanical properties. The incorporation of aluminum powder along with conventional rubber filler positively impacts the heat build up in rubber compounds but negatively impacts the mechanical properties and abrasion. The incorporation of aluminum powder also helps improving the compression set values due to improved crosslinking because of better heat conductivity.

In general, the metals like copper, manganese, nickel, or cobalt should be avoided in rubber compounds. These transition elements can function as pro-oxidants and promote the degradation of the vulcanizate.

2.2 FILLERS

2.2.1 Graphite⁷

Addition of nano graphite to improves the thermal aging resistance. The graphite platelet restricts the movement of polymer chains. For NBR compounds an improvement of 10°C in the maximum degradation temperature was reported in the study done by Rajkumar et.al and a retention of tensile strength by 59 % compared to the non-graphite vulcanizate which retained tensile strength by 23%.

2.2.2 Nanoclay

Nanoclay has been studied in rubber matrices like NR, SBR to improve the barrier properties. Because of the layered structure nanoclay can improve the overall

performance of rubber.

2.2.3 Nanoalumina

Effect of nano alumina has been studied by Thomas et. al which shows a positive impact on the mechanical properties in presence of maleic anhydride as a compatibilizer³.

2.2.4 Silica

Consider using precipitated silica in a rubber compound where an improvement in heat aging resistance is needed. RT: Chapter 13, "Precipitated Silica and Non-black Fillers," W. Waddell, L. Evans, p. 331

2.2.5 Talc

It has been reported that substituting 40% of the carbon black in an EPDM hose compound with talc resulted in an improvement in heat aging resistance. Certain grades of talc may show a significant advantage over treated and untreated clay as well. GEN: O. Noel, unpublished draft, "Talc Synergy with Carbon Black in Sulfur Donor Cured EPDM," June, 2003; H. Bertram, "Influence of Light Colored Fillers on the Aging Behavior of NBR Vulcanizate," Bayer TIB 17. RP: O. Noel.

2.3 Blending with polymers with high heat

resistance

2.3.1 EPDM/Silicone Blend

Using compounds based on silicone-EPDM in place of straight EPDM compounds can enable heat resistance up to 204°C (399°F). GEN:

2.3.2 EPDM/NBR Blend with nanoclay

Nitrile rubber will provide oil resistance and nanoclay will impart mechanical strength and heat resistance.

2.4 PTFE as a filler Rubber

Poly tetrafluoro ethylene (PTFE) possess excellent heat resistance combined tribological properties. The extremely low friction properties of PTFE are well known. There has been multiple efforts to combine the PTFE with elastomer, PTFE because of its hydrophobicity and low wetting properties has limited interaction with the rubber matrix limiting its application as a filler for improving the properties.

Literatures have been published on improving the mechanical properties (tensile strength, elastic modulus) for EPDM and silicone rubber by effective fibrillation of PTFE powder. In the case of rubbers such as nitrile, 2 – 6 wt % of PTFE improves the vulcanizate strength and modulus. A formation of entangled fibers during high shearing mixing results in the improvement of properties. The granulate PTFE can be etched to enhance interaction with rubber matrix.

Bonding of PTFE needs physical or chemical surface treatment to impart an improvement in mechanical properties.

3 LAB TEST METHOD TO DETERMINE THE HEAT AGING RESISTANCE

Retention of mechanical properties after being exposed to elevated temperature for the desired number of hours provides a measure of the resistance at the test temperature. ASTM D573, ASTM D 865, test temperature and duration is decided based on the application requirement. The change in hardness, tensile strength and elongation at break provides an insight of the material behavior when exposed to the said temperature during application.

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RMWA Activities & News

Discount to Members in IRE 2019

Special Discount for RMWA Members in "India Rubber Expo 2019".

Our association has negotiated a special discount to our members of Rs. 2800/- per sqmt for booking stalls in Gujarat Pavilion, by participation in IRE 2019 being organized on 17th, 18th, 19th, January 2019 at Nesco Complex, Goregaon(E), Mumbai.

We are also negotiating small size stalls of 2m x 3m for our MSME members in the same.

As an added benefit, we propose to grant "Past Participant" discount in our own IIRS 2019/2020 to be held at Ahmedabad/ Gandhinagar for any member who avails this offer for IRE 2019.

Annual General Meeting :

RMWA Annual General Meeting was organized on 3rd August, 2018 at Ahmedabad Management Association for the year 2017-2018.

Last AGM's Minutes were read out by Jt. Secy, Mr. Snehal Shah and unanimously approved by all. Meeting commenced with National Anthem and two minutes silence in the remembrance of departed souls.

Financial Statements were read out by Treasurer, Mr. Samir Shah and approved by all and a presentations of last years activities was done by Secy, Mr. Yashodhar Kahate.

With the Permission of President Mr. Dipak Doshi the new Membership fee structure from 1st September, 2018 was discussed and approved by all the members present.

Mr. Doshi, President shared his experiences as a president in the association on the termination of his tenure for the same.

New Trustees for 2018-2019 were selected.

Light was thrown on upcoming future activities mostly IIRS 2019/2020.

Meeting was concluded by vote of thank by V.P. Mr. Piyush Shah.

Meeting was carried out successfully by the presence of forty members.

Tour to Rubber Tech China:

Association has planed for group tour of four nights and five days to Rubber Tech China, The 18th International Exhibition on Rubber Technology during 19-21 September, 2018 at Shanghai New International Expo Centre, Pudong, Shanghai, China.

Minutes of First Board of Trustees Meeting scheduled at RMWA on 31/08/18"

***Managing Trustee ***

Mr. Mukesh Desai's name proposed by Mr. Yashodhar Kahate and seconded by Mr. Snehal Shah and accepted unanimously.

***President ***

Mr. Dipak Doshi's name proposed by Mr. Snehal Shah and seconded by Mr. Piyush Shah and accepted unanimously .

***Secretary ***

Mr. Yashodhar Kahate's name proposed by Mr. Arpit Karbhari and seconded by Mr. Samir Shah and accepted unanimously .

Treasurer

Mr. Samir Shah's name proposed by Mr. Dinesh Chauhan and seconded by Mr. Yashodhar Kahate and accepted unanimously .

Selection of Executive Committee

***Mr. Piyush Shah Sr. Vice President**
***Mr. Arpit Karbhari Jt. Treasurer**

***Mr. Rupen Soni Vice President**
*** Mr. Rajesh Kothari Past President**

***Mr. Snehal Shah Jt. Secretary**
***Mr. Rajendra Shah Trustee**

Selection of working Committee

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***Mr. Jignesh Sanghavi**

***Mr. Janak Shukla**
***Mr. Nilesh Parikh**

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Dynamic Properties of Polymers

Materials and their Measurements

Kartik Srinivas

Principal Engineer

Advanced Scientific and Engineering Services (AdvanSES)

1.1 Polymers

Polymer materials in their basic form exhibit a range of characteristics and behavior from elastic solid to a viscous liquid. These behavior and properties depend on the temperature, frequency and time scale at which the material or the engineering component is analyzed. The viscous liquid polymer is defined as by having no definite shape and flow deformation under the effect of applied load is irreversible. Elastic materials such as steels and aluminium deform instantaneously under the application of load and return to the original state upon the removal of load, provided the applied load is within the yield or plastic limits of the material. An elastic solid polymer is characterized by having a definite shape that deforms under external forces, storing this deformation energy and giving it back upon the removal of applied load. Material behavior which combines both viscous liquid and solid like features is termed as Viscoelasticity. These viscoelastic materials exhibit a time-dependent behavior where the applied load does not cause an instantaneous deformation, but there is a time lag between the application of load and the resulting deformation. We also observe that in polymeric materials the resultant deformation also depends upon the speed of the applied load.

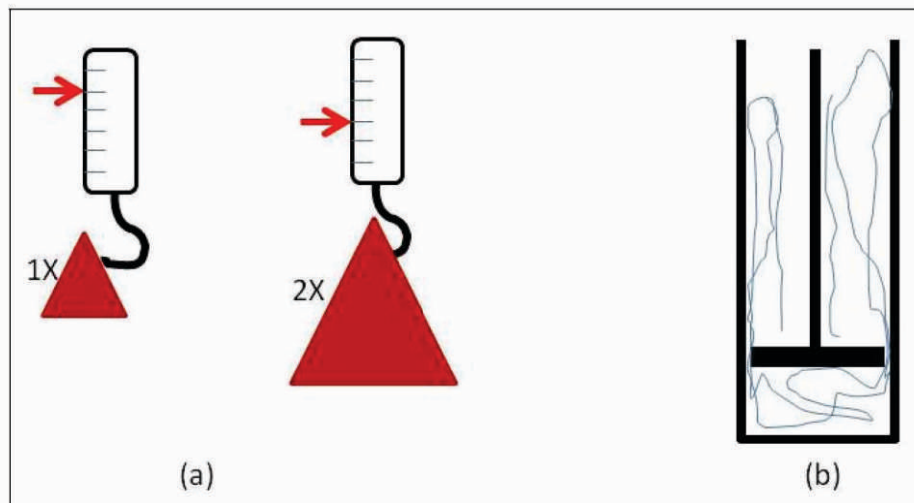


Figure 1.1: Linear Elastic and Non-linear Viscous Materials

Consider a spring based weighing scale as shown in Figure (1.1). If we put a fixed load on the scale such as a weigh bar we get a fixed amount of deflection and the needle points to point 2. Using an exactly double weight the needle moves twice as far upto point 4 and comes to rest. When we remove the weights the needle returns back to 0 position or the no-load position. The energy we put into the spring based weighing scale to cause deflection is equal to the energy the spring fully gives up when the needle moves back to 0. This concept gives the spring perfectly linear properties and 100% efficiency. If we are to consider a situation where if we were to put our weight on the scale slowly such that it takes ten minutes before the needle comes to the 2 point mark, and if we did the same action in thirty seconds, one minute, and five minutes? The needle would still come to rest at the 2 point mark. This shows that when we double the load, the needle pointer moves twice as far as originally meaning the response of the weighing scale is linear. We can also observe that the weighing scale takes the same time or the deformation rate remains the same even if we apply the weight at different times. This shows that the deformation is independent of the rate of the loading. The weighing scale thus obeys Hooke's laws and is a perfect Hookean spring. The deformation energy is always stored as elastic energy and is fully given up upon removal of the load.

Consider a tall cylindrical jar filled with 5W40 engine oil as shown in Figure (1.1b) . At the bottom of the jar is a round disc. The disc is slightly smaller than the inside of the jar so that the oil can move around this disc. Applying an X amount of force we can see that it takes 2 minute to extract the disc from the jar. To decrease the time taken by the disc to extract from the jar by 1 minute we see that we need to apply a higher force and to extract the disc in 30 seconds we need to apply an even higher force.

If the disc is moved from the bottom of the center of the jar to the center of the jar and let it rest, it remains in the same spot and after some time under the force of gravity it starts sinking to the bottom. We can feel that by moving the disc through the engine oil we are applying force or putting work into the oil system by shearing it between the disc and the wall of the jar. The faster we try to move the disc, higher the force required. Unlike the independent nature of the force in the weight scale, the amount of force required for the oil system now becomes rate dependent. e.g. It now depends upon how fast or slow we want to move the disc. The amount of force is not always proportional to the speed and now this becomes a non-linear relationship.

When we moved the disc from the bottom of the center of the jar, it stayed there and did not sink immediately to the bottom of the barrel. We put energy into the system but none of it was given back. All energy put into a viscous oil system is lost. The ideal viscous material is sometimes referred to as a Newtonian system.

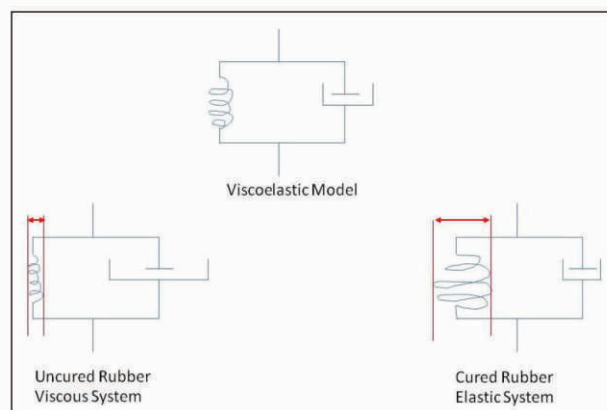


Figure 1.2: Viscous and Elastic Phases making up the Kelvin-Voigt Viscoelastic System

To summarize the response of the phases; The elastic response is linear and all the work input into the system is given up upon removal of applied load. The viscous response on the other hand is non-linear with the force and the deformation dependent upon the rate of the loading and the time. Joining the two phases; we now have a visco-elastic material that is graphically represented by a Hookean spring in parallel with a Newtonian dashpot, defined as the Kelvin-Voigt model as shown in Figure(1.2). When the viscous and elastic components are joined, we can simultaneously put energy into both of them, but the response of each phase is almost on opposites. In uncured rubber, the viscous phase dominates as evidenced by the flow of the material in the mold. As the rubber is cured during vulcanization the elastic phase slowly begins to emerge and starts dominating the deformation characteristics.

Hookes law for an elastic solid states that stress is linearly related to strain,

$$\sigma(t) = E\varepsilon(t); \quad (1.1)$$

or

$$\frac{d\sigma}{dt} = E \frac{d\varepsilon(t)}{dt} \quad (1.2)$$

Newtons law for a viscous liquid states that;

$$\sigma(t) = \eta \frac{d\varepsilon(t)}{dt}; \quad (1.3)$$

Combining equations (1.1 and 1.3), we get the Kelvin-Voigt model for a linear viscoelastic material;

$$\sigma(t) = E\varepsilon(t) + \eta \frac{d\varepsilon(t)}{dt}; \quad (1.4)$$

1.2 Viscoelastic Properties

Figure 1.3 shows the regimes of a typical polymer material from the glassy to liquid state. The material is in the glassy state below the glass transition temperature, and the modulus of the material as high as 3 GPa. The material practically behaves as a hard elastic material in this state. As the temperature increases the regime changes to glass transition state and the material modulus decreases from 3 GPa to approximately 10 MPa. Subsequently, the

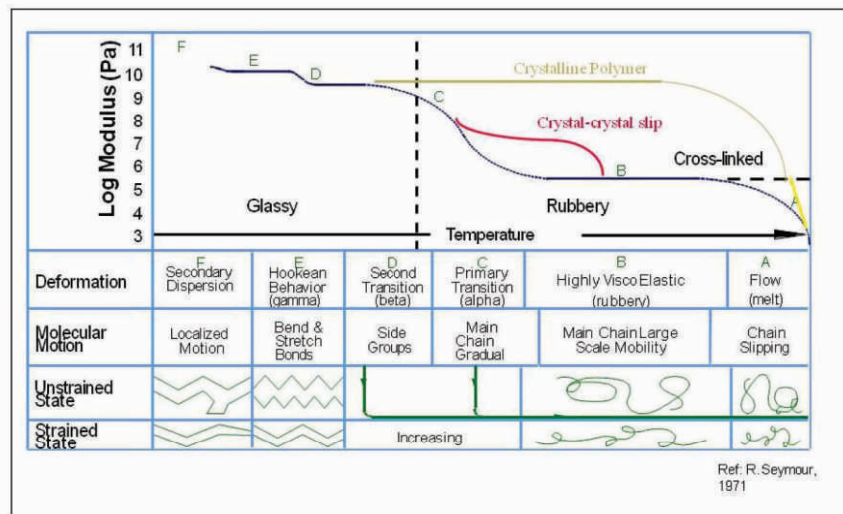


Figure 1.3: Different States and Modulus Regimes in Polymer Materials

material enters the rubber regime or rubbery plateau and is effectively at room temperature. Most of our applications of polymer materials to engineering components fall within this plateau regime. Below the rubbery plateau is the viscous regime where the modulus of the material further decreases causing the material to flow like a liquid. Processing of plastic or rubber materials in a compression-transfer mold or injection mold takes place in this regime. Below the viscous regime in the region of decomposition and complete breakdown of the polymer material and its ingredients.

Polymer materials by their very nature exhibit linear and nonlinear viscoelasticity. Linear viscoelastic behavior is exhibited by a material that is subjected to a deformation that is either very small or very slow on the application time scale. It can be said that the nature of the deformation can be predicted using a linear theoretical expression. While the application of polymers to a rapid rate of flow and deformation or sudden temperature cycling to the extremes results in deformation patterns that cannot be predicted by linear expressions, and the behavior is said to exhibit nonlinearity.

1.3 Dynamic Properties

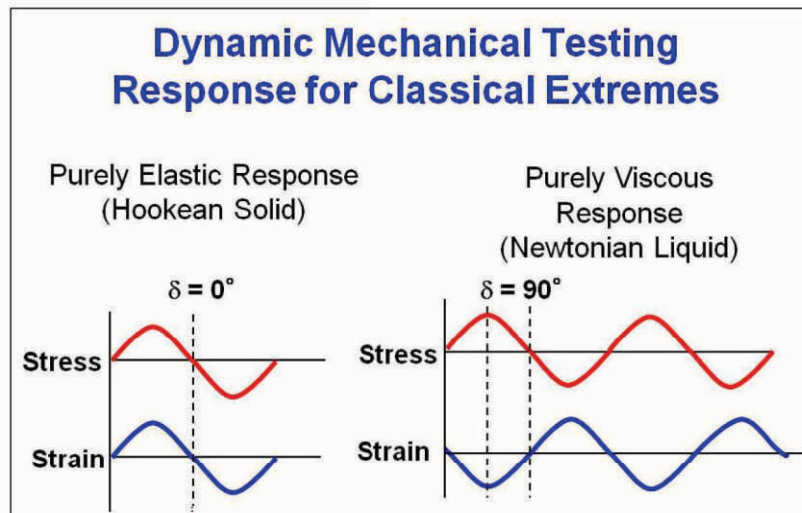


Figure 1.4: Purely Elastic and Purely Viscous Responses of Materials

Characterization of dynamic properties play an important part in comparing mechanical properties of different polymers for quality, failure analysis and new material qualification. Figures 1.4 and 1.5 show the responses of purely elastic, purely viscous and of a viscoelastic material. In the case of purely elastic, the stress and the strain (force and resultant deformation) are in perfect sync with each other, resulting in a phase angle of 0. For a purely viscous response the input and resultant deformation are out of phase by 90° . For a viscoelastic material the phase angle lies between 0 and 90° . Generally the measurements of viscoelastic materials are rerepresented as a complex modulus E^* to capture both viscous and elastic behavior of the material. The stress is the sum of an in-phase response and out-of-phase responses.

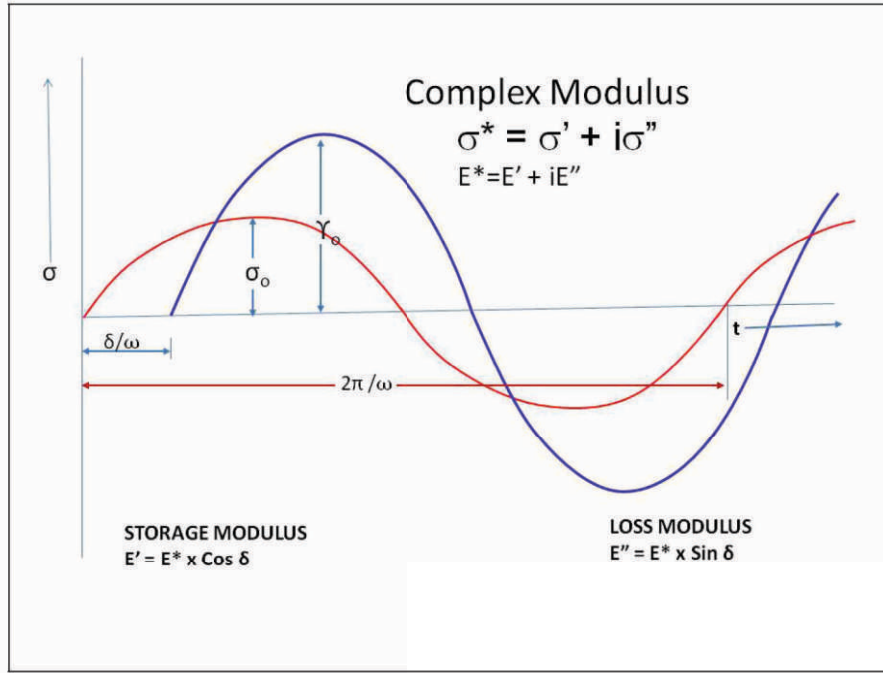


Figure 1.5: Viscoelastic Response of a Polymer Material

Figure 1.5 shows that the resultant strain lags the applied stress and can be written as,

$$\varepsilon(t) = \varepsilon_o \sin \omega t \quad (1.5)$$

and the stress can be written as

$$\sigma(t) = \sigma_o \sin(\omega t + \delta) \quad (1.6)$$

where σ_o is the stress amplitude and ω is the angular frequency. Expanding the equation, it can be expressed as

$$\sigma(t) = \sigma_o \cos \delta \sin \omega t + \sigma_o \sin \delta \cos \omega t \quad (1.7)$$

The $\sigma_o \cos \delta$ term is in phase with the strain, while the term $\sigma_o \sin \delta$ is out of phase with the applied strain. The modulus E' is in phase with strain while, E'' is out of phase with the strain. The E' is termed as storage modulus, and E'' is termed as the loss modulus.

$$E' = \frac{\sigma_o}{\gamma_o} \cos \delta$$

$$E'' = \frac{\sigma_o}{\gamma_o} \sin \delta$$

$$E' = \frac{\text{In-phase stress}}{\text{Maximum strain}} = \text{Storage Modulus}$$

The storage modulus deals with the elastic modulus part, where the deformations are fully recoverable at the end of the displacement cycle.

$$E'' = \frac{\text{Out of phase stress}}{\text{Maximum strain}} = \text{Loss Modulus}$$

The in-phase stress and strain results in completely recoverable elastic energy while the out-of-phase stress and strain results in the dissipated energy termed as loss. Both the storage modulus and the loss modulus are functions of the applied frequency ω .

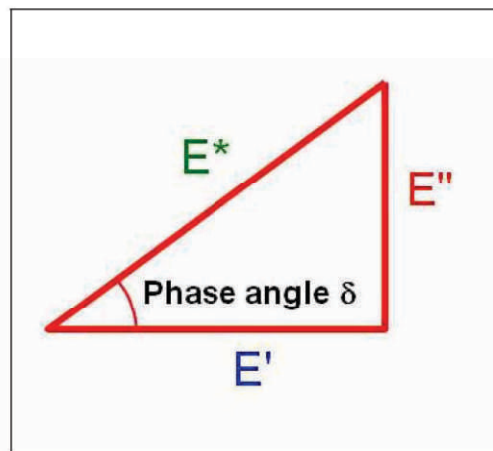


Figure 1.6: Concept of Complex, Loss and Storage Modulus

Figure 1.6 shows the graphical representation of the loss modulus, storage and complex modulus. The loss tangent or the damping coefficient is defined as

$$\tan\delta = \frac{E''}{E'} = \frac{\text{Loss.Modulus}}{\text{Storage.Modulus}} \quad (1.8)$$

Figure (1.7) shows the concept of loss and storage modulus from the example of a rubber ball. The ball when bounced off the ground from a height does not bounce to the level from where it was dropped but bounces only to a level lower. This loss of height can be defined as the energy that has been lost in energy dissipation due to deformation of the rubber.

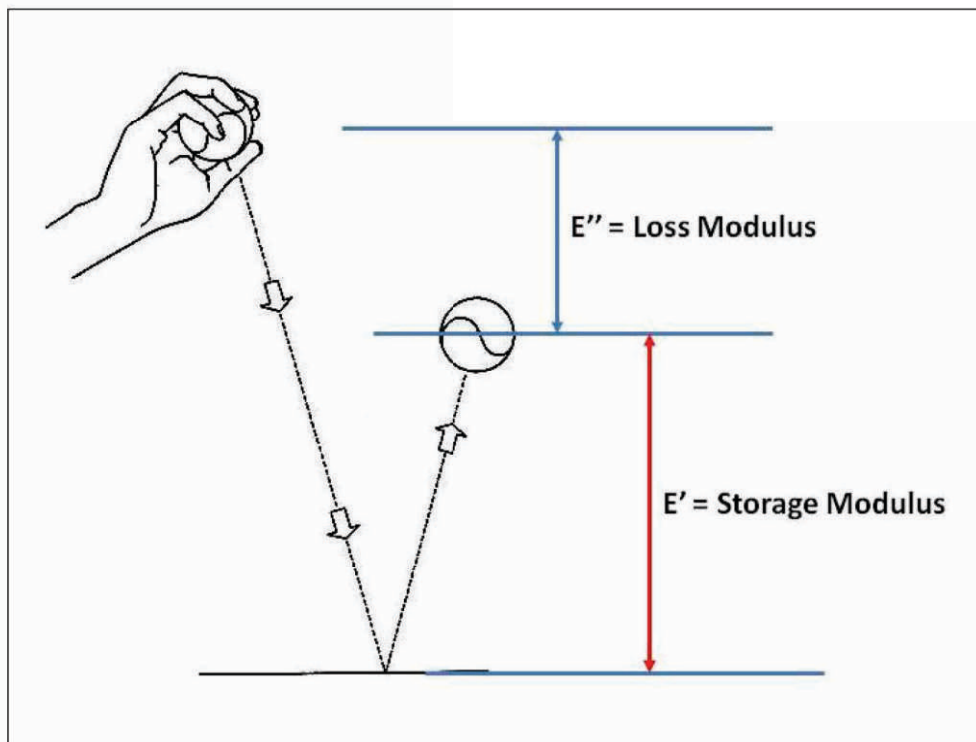


Figure 1.7: Loss and Storage Modulus in Elastomers

Polymer materials exhibit strong time and rate dependent properties. Studying these time and rate dependent properties is necessary to predict the performance of engineering components.

To accurately characterize the viscoelastic properties of polymers, the generally used technique is that the material is sinusoidally deformed and the resulting stress is recorded. The deformation can be applied in tension, compression or shear mode depending on the geometric design or the application condition of the engineering component.

1.4 Stress Relaxation

Stress relaxation is a viscoelastic property of an elastomeric material. In a stress relaxation experiment, the sample is rapidly stretched or compressed to a predefined strain and held constant. The stress is then recorded as a function of time. Creep experiments are carried out in a similar manner but instead of the application of a constant strain, a constant stress is applied and the deformations or the resultant strain is studied as a function of time. The stress relaxation modulus may be defined as

$$E_{rel.}(t) = \sigma(t)/\epsilon_0 \quad (1.9)$$

If there is no viscous flow in the material, the stress decays to a finite value for polymeric materials. For amorphous linear polymers at high temperatures, the stress may eventually decay to zero. For a linear viscoelastic solid, the instantaneous stress will be proportional to applied strain and will always decrease with time.

The molecular causes of stress relaxation and creep can be classified to be based on five different processes.

1. *Chain Scission* The decrease in the measured stress over time is shown in Figure(1.8) where 3 chains initially bear the load but subsequently one of the chains degrades and breaks.

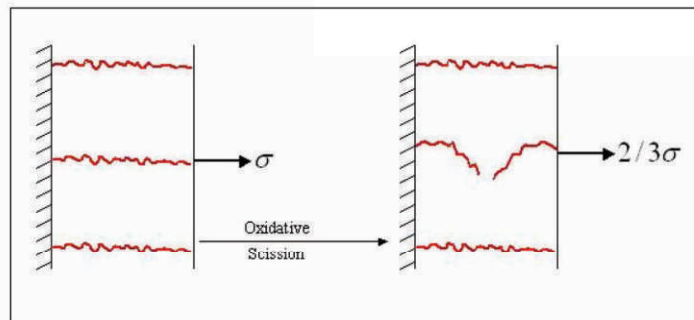


Figure 1.8: Chain Scission in an Elastomeric Material

2. *Bond Interchange* In this particular type of material degradation process, the chain

portions reorient themselves with respect to their partners causing a decrease in stress.

3. *Viscous Flow* This occurs basically due to the slipping of linear chains one over the other. It is particularly responsible for viscous flow in pipes and elongation flow under stress.
4. *Thirion Relaxation* This is a reversible relaxation of the physical crosslinks or the entanglements in elastomeric networks. Generally an elastomeric network will instantaneously relax by about 5% through this mechanism.
5. *Molecular Relaxation* Molecular relaxation occurs especially near T_g (Glass Transition Temperature). The molecular chains generally tend to relax near the T_g .

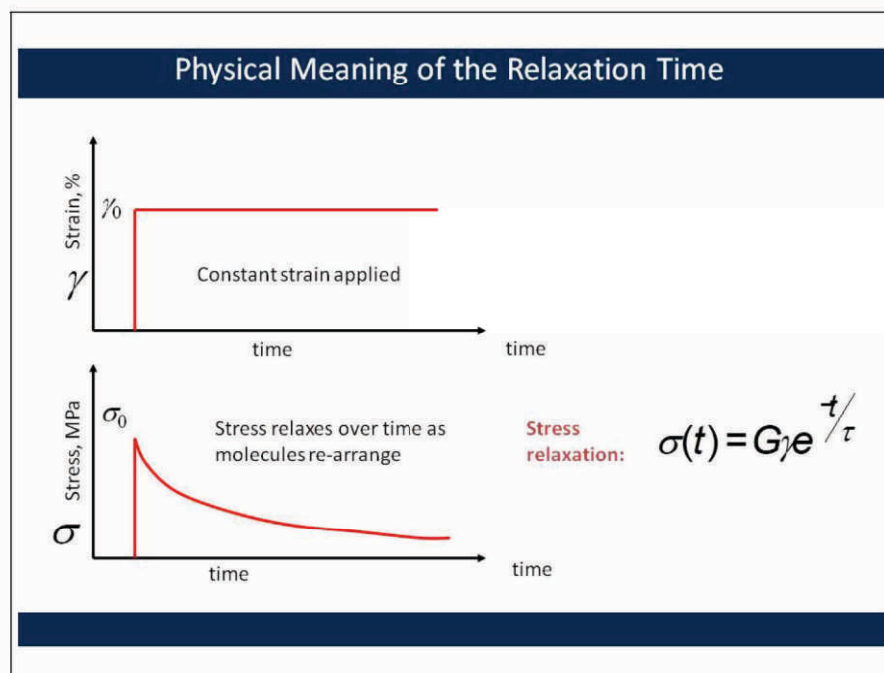


Figure 1.9: Physical Meaning of the Relaxation Time

The related effect of stress relaxation in sealing applications is the reduction in stress (i.e. sealing force) under constant strain (compression) conditions. In many applications when sealing force approaches zero, leakage is likely to occur as the seal geometry loses contact

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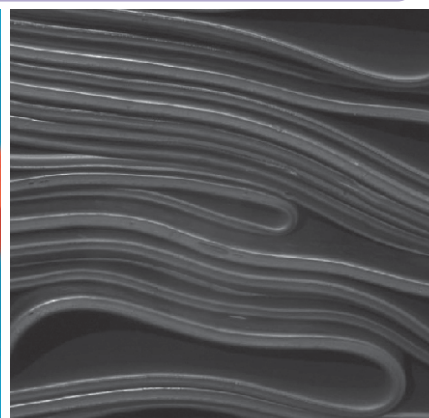
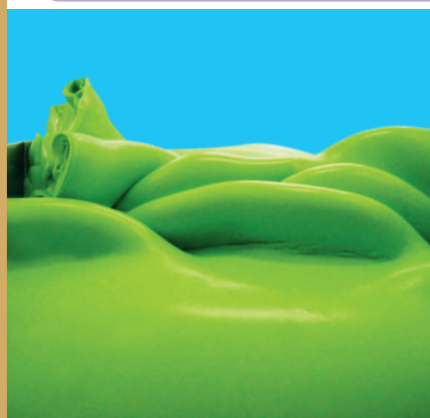
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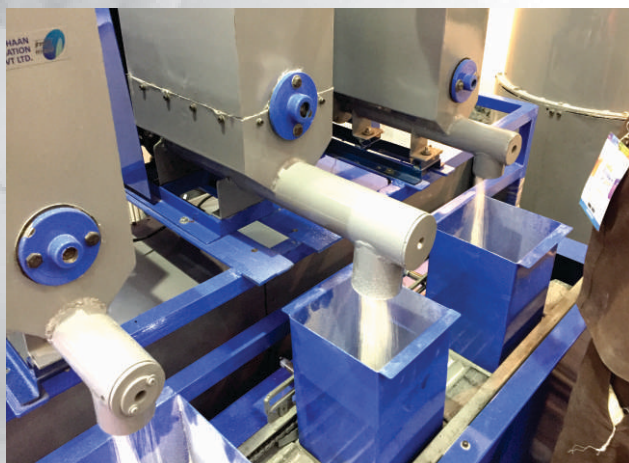


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Automatic Batching Systems



"Supply chain to rubber industries"

Dealers & Importer Natural Rubber, Synthetic Rubber,
Rubber Chemicals, Carbon Black, RPO Etc.

AVAILABLE READY STOCK :
NATURAL RUBBER, SYNTHETIC RUBBER,
RUBBER CHEMICALS, RPO, RECLAIM RUBBER

SYN. RUBBERS

NITRILE:

NT 3445 F, KNB 35L, JSR 230 SL, LG 6240,
OFF SPEC NBR, NBR POWDER

HIGH NITRILE:

JSR 220S, 220SH, 3965, 3945, KNB 41M

PVC NBR : JSR NIPOL 50:50, 70:30

SBR :

1502, 1712, 968, 568

PBR :

1220-GP, 01, 1220 IRAN

NEOPRENE:

B-30, A-90, Y-30-H, BAYPRENE 210,
BAY-100, DUPONT AD, DENKA A-100
A-400, G40S

SILICONE RUBBER:

DJ (CHINA) 40-50-60-70 80,
DOW CORNING TRANSPARENT 40-50-70,
DOW CORNING NPC 40-80

EPDM:

KEP 960, KEP 210, KEP 435,
ROYALINE 301T, VASTALON 7001, 5601,
8800, DOW NORDEL 4640, 4570, 3640

BUTYL :

BK 1675N, LANXESS 301,

BROMO BUTYL :

X2 PHARMA, 2030, RUSSIAN 232

CHLORO BUTYL:

EXOON 1066, RUSSIAN 139, LX 1240

HYPLON: TS 530

POLYISOPRENE :

SKI3S, NATSYN 2200

CARBON BLACK

HAF-330, FEF-550, GPF-660,
SRF-774, ISAF-220,

NATURAL RUBBERS

SVR3L (SELF IMPORT), ISNR3L, RSS1 X,
RSS4, RSS 5, RSS GOOD LOT, ISNR3L,
PLC 1X, ISNR 20, SKIM CREPE, ETC.

CHEMICALS

RUBBER CHEMICALS : LANXESS

MBTS, MBT, TMTD, TMT, TDQ, CBS,
ZDC 4020, PVI, ZDBC, ZDC, CBS, DCP-98,
DCP-40, NA-22, DIAK 3, STARIC ACID,
MGO, SULPHUR, DPTT, TETRON-A

RUBBER PROCESS OIL : GANDHAR

GANDHAR : FLEX P, FLEX A, FLEX N
HP : ELASTO 710, 245, 541

METAL OXIDE :

ZINC OXIDE (99.5% WHITE SEAL-'Ace
Chemie), TITANIUM DIOXIDE Dupont
Rutile 104, Anatase TTK,
LITHARGE - LEAD OXIDE, ACTIVE ZINC

RECLAIM RUBBER:

BUTYL RECLAIM, TUBE GRADE,
EPDM RECLAIM, WHITE RECLAIM,
HIGH TENSILE, WTR-SF HR-MEDIUM.

RESIN :

PF RESIN, CI RESIN,
HYDRO CARBON C9/C5, WOOD ROSIN

SILICONE EMULSIONS :

DOW CORNING, WACKERS

PLASTICIZER :

DOP, DBP, FH

WAX :

PARAFFIN WAX



Dealers :



Phillips Carbon
Black Limited



Jay Ashirwad Trading Co.

M : 98240 88289 RUSHABH KAMDAR

Add : 30, Janta Chamber, Saijpur Bogha, Naroda Road, Ahmedabad-382345.

E-mail : info@rubberrawmaterial.com, www.rubberrawmaterial.com

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IF COURIER NOT DELIVERED PLEASE RETURN TO :

RUBBER MANUFACTURERS' WELFARE ASSOCIATION, B/413, RUDRA ARCADE, NR. HELMET CIRCLE, MEMNAGAR, ABAD - 380052