UNIT - V: Engineering Materials

Cement: Portland cement, its composition, setting and hardening.

Smart materials and their engineering applications

Shape memory materials- Poly L- Lactic acid. Thermo response materials- Poly acryl amides and Poly vinyl amides

Lubricants: Classification of lubricants with examples-characteristics of a good lubricant - mechanism of lubrication (thick film, thin film and extreme pressure)- properties of lubricants: viscosity, cloud point, pour point, flash point and fire point.

Cement is a binding substance which possesses adhesive and cohesive properties and used for binding the building blocks, bricks, stones.

Cement is classified into 4 types based on chemical composition.

(1) Natural cement
(2) Pozzolana cement
(3) Slag cement
(4) Portland cement

The essential constituents of cement, compounds of **Calcium (Calcarious)** and **Al+Si (argillaceous)** materials.

Portland cement

Portland cement is made by calcination of calculated amounts of **clay and lime** followed by **gypsum.** It is a mixture of calcium silicate and aluminium silicate with small amount of gypsum. It is hydraulic in nature i.e. property of setting and hardening in presence of water.

Chemical Composition of Portland cement:

Portland cement contains finely powdered mixture of silica (SiO_2), lime (CaO) and alumina (Al_2O_3).

Compound	Percentage range by mass
Calcium oide or lime (CaO)	60-70
silica (SiO_2)	20-24
alumina (Al_2O_3)	5-7.5
Magnesia (MgO)	2-3
Iron oxide (Fe_2O_3)	1-2.5

The basic chemical compounds in the Portland cement

Name	Chemical formula	Abbreviation
Tricalcium silicate	$3CaO. SiO_2$	C_3S
Dicalcium silicate	$2CaO. SiO_2$	C_2S
Tricalcium aluminate	$3CaO. Al_2O_3$	C_3A
Tetracalcium alumino ferrite	$4CaO. Al_2O_3. Fe_2O_3$	C_4AF

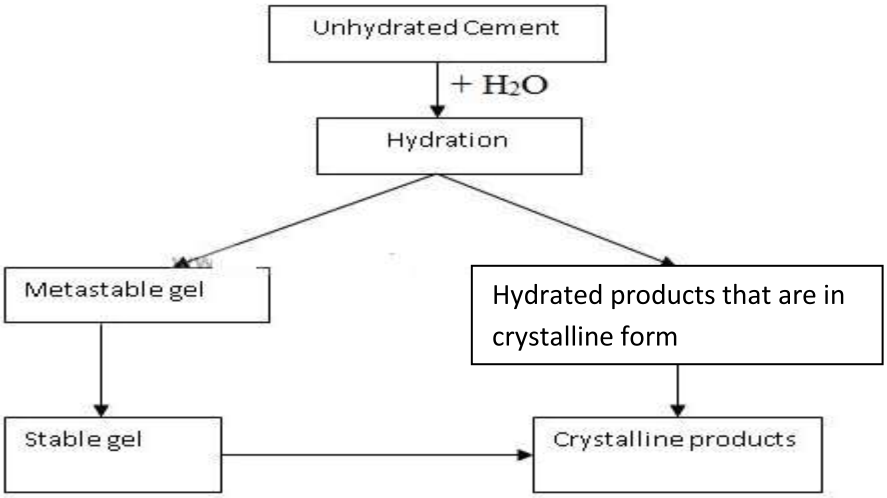
Setting and hardening

Cement is mixed with water to produce a plastic paste. The past is subjected to hydration and gelation and finally crystalline products are formed.

Setting: Due to the formation of gel, cement paste stiffens which refers to setting.

Hardening: Due to crystallization, the cement develops strength.

Physical changes occurring in the setting and hardening of cement may be summarized in a flow cart as follows.



a) Hydration of C_3A and C_4AF

Initial setting of cement involves hydration of tricalcium aluminate (C_3A). Within 40min when cement mixed with water, C_3A interact with water and forms C_3A crystals.

$3CaO.Al_2O_3$ + $6H_2O$ $\rightarrow$ $3CaO.Al_2O_3.6H_2O$
(Tricalcium aluminate) (Crystalline)

Formed C_3A crystals has tendency to become stiff materials immediately. Therefore, to prolong the setting time gypsum is added

In the first day C_4AF hydrated to form gels and crystals.

$4CaO.Al_2O_3.Fe_2O_3$ + $7H_2O$ $\rightarrow$ $3CaO.Al_2O_3.6H_2O$ + $CaO.Fe_2O_3.H_2O$
(Tetracalcium alumino ferrite) (Crystalline) (Gel)

b) Second step of the reaction involves gelation in which tobermonite gel is formed. It also produces calcium hydroxide.

$2(2CaO.SiO_2)$ + $4H_2O$ $\rightarrow$ $3CaO.2SiO_2.3H_2O$ + $Ca(OH)_2$
Dicalcium silicate Gel (Tobermonite) calcium hydroxide Crystalline

c) Finally, tricalcium silicate (C_3S) undergoes hydrolysis to produce tobermonite gel.

$2(3CaO.SiO_2)$ +	$6H_2O$	$\rightarrow$	$3CaO.2SiO_2.3H_2O$	+ $3Ca(OH)_2$
(tricalcium silicate)			Gel (Tobermonite)	calcium hydroxide Crystalline

During the setting and hardening of Portland cement, some amount t of heat is liberated due to hydration and hydrolysis reactions. Approximately 28days are required for setting and hardening of cement.

Sequence of chemical reactions during setting & hardening:-

Cement + Water paste	1 day ------------>	hydration of C_3A and C_4AF	7 days ----------->	gelation of C_3S	28 days ------------->	gelation of C_2S & C_3S

Lubricants

"Any substance introduced between two moving surfaces to reduce the frictional resistance known as Lubricant". The process of reducing frictional resistance between moving surfaces by application of lubricant in between them called Lubrication.

Classification of lubricants with examples

Lubricants are classified into three types. They are

1. Liquid lubricants 2. Semi-solid lubricants 3. Solid lubricants

Liquid lubricants

Liquid lubricant is a continuous fluid film inserted in between the rubbing surfaces to reduce friction between them.

It includes animal oils, vegetable oils, petroleum oils, synthetic lubricants.

Animal oils: tallow oil, whale oil etc.

Vegetable oils: olive oil, castor oil, palm oil etc

Petroleum oils: petroleum fractions

Synthetic lubricants: polyglycol, silicones etc.

Semi-solid lubricants (Grease)

Semi-solid lubricants contain high viscosity than the liquid lubricants and are used where liquid lubricant (like oil) cannot remain in place.

Greases are classified on the basis of the soap used in their manufacture as soda-based greases, lithium based greases etc.

Solid lubricants

Graphite, Teflon, mica, molybdenum disulphide (MoS_2), boron nitride $(BN)_x$ are predominantly used as a solid lubricants. They are used under high temperature and high load (pressure).

The grain particles present in solid lubricants may damage delicate machine parts. Hence, solid lubricants are used in special cases only.

Characteristics of a good lubricant

A good lubricant must have the following functions.

1. It helps in reducing frictional forces between two sliding surfaces.
2. Must possess a medium viscosity.
3. Thermal or heat stability. It reduces loss of heat energy there by increasing the efficiency of engine.
4. A high boiling point and low freezing point
5. It acts as seal in internal combustion engines and prevents the leakage of gases.
6. It prevents rust formation and corrosion and hence reduces the running cost of machinery.
7. High oxidation resistance
8. It reduces surface deformation
9. Act as coolant. Lubricants when placed between two surfaces, helps in absorbing the released heat. Therefore lubricant acts as a Coolant.
10. Should not react chemically with the metals being used.

Properties of lubricants:

Viscosity: Viscosity is the property of a liquid which offers resistance to its own flow. It is an indicator of flow ability of lubricating oil. The lower viscosity greater will be the flow ability. If temperature increases viscosity of the lubricating oil decreases and pressure increases viscosity of lubricating oil increases. In short we can say that good lubricating oil is that whose viscosity does not change with temperature.

Viscosity of lubricating oil should be moderate, because if it is too low unable to withstand between two moving surfaces and if it is too high excessive friction will result.

Viscosity Index:

The rate at which the viscosity of oil changes with temperature is measured by an empirical number known as the viscosity index. A relatively small change in viscosity with temperature is indicated by high viscosity index. Whereas a low viscosity index shows a relatively large change in viscosity with temperature.

Cloud point

"The **temperature at which** the impurities begin to separate from the solution and lubricating oil **becomes cloudy or hazy** in appearance is called cloud point"

Pour point

When oil cooled slowly, the **temperature at which** the oil **ceases to flow and pour** is called pour point.

It indicates the suitability of lubricants used in cold condition. Good lubricant should possess low pour point.

Cloud point and pour points indicate the stability of lubricants in cold conditions. Machines working with low temperatures like refrigerator plants, air craft engines, lubricants with low cloud point and pour points are preferred.

Flash point

"Flash point is defined as the minimum temperature at which the lubricating oil gives off its vapours that ignite for a moment, when a flame is brought near it.

The Pensky–Martens closed-cup flash-point test is a test for the determination of the flash point of flammable liquids.

Fire point

Fire point is the lowest temperature at which the vapours of lubricating oil burn continually for at least 5 seconds, when flame is brought near it.

In most of the cases, the fire point of an oil is about 5-40 ^{0}C higher than the flash point. These two properties are important when the oil is used at very high temperatures.

A good lubricant should have flash and fire points higher than the operating temperature of the machine.

Mechanism of lubrication

The following 3 mechanisms have been proposed to explain the action of lubricants:

(1) Thin film or boundary lubrication

(2) Thick film or Fluid film or hydrodynamic lubrication

(3) Extreme pressure lubrication

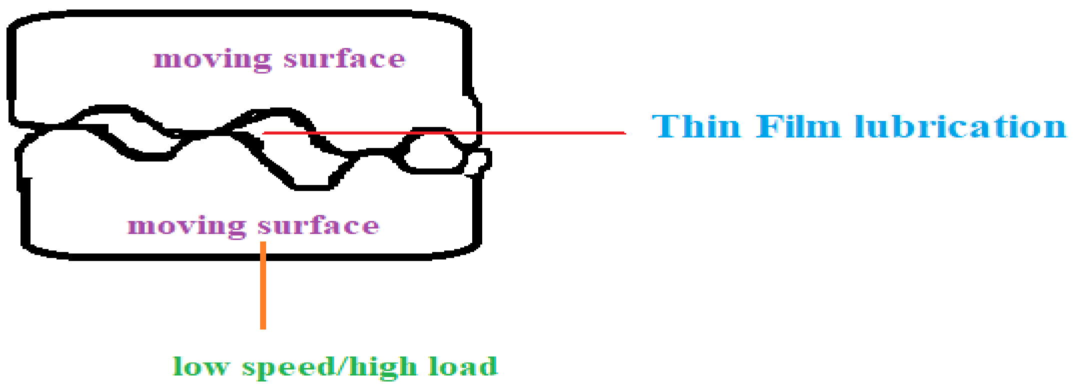
Thin film or boundary lubrication:

It is carried out with semi-solid (grease) and solid (graphite and molybdenum disulphide) lubricants.

In this type of lubrication, thin film of lubricant is adsorbed on the surface and held by van der waal's forces due to which friction is reduced.

Thin film lubrication is applied when

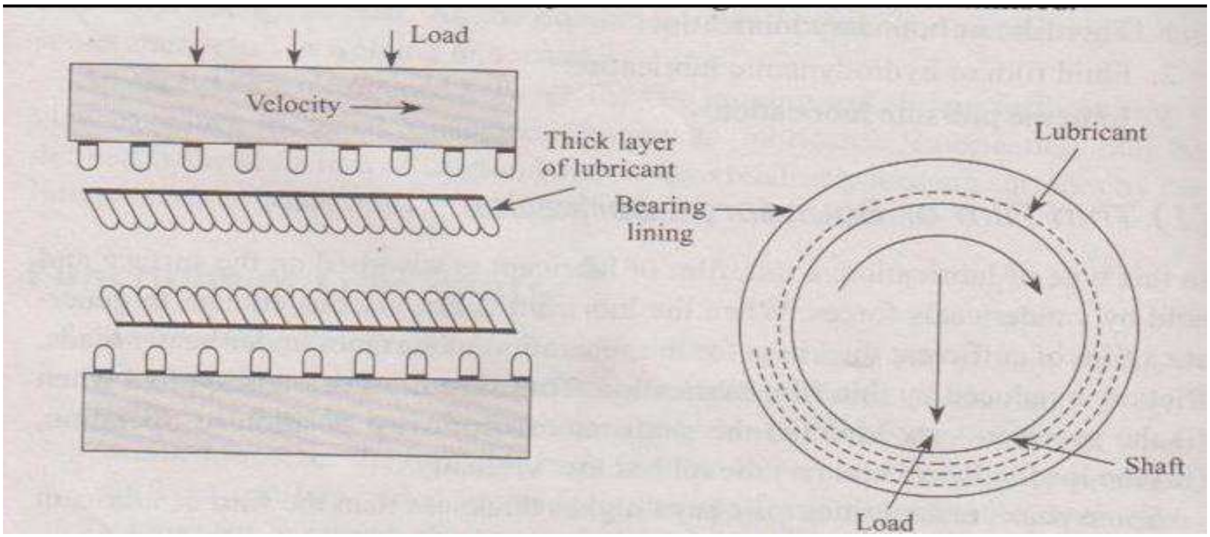
(a) The speed is very low. (b) The load is high. (c) The oil has low viscosity.



During this process, a thin film of lubricant is absorbed on both the metallic surfaces due to physical or chemical forces. This absorbed layers help to avoid direct metal to metal contact between the rubbing surfaces. The coefficient of friction in boundary lubrication varies from 0.05 to 0.15.

Thick film or Fluid film or hydrodynamic lubrication

It is carried out with the help of liquid lubricants. In this mechanism, two moving and sliding surfaces are separated by thick film of lubricant fluid of about 1000A°, applied to prevent direct surface to surface contact and consequently reduce wearing and tearing of metals. Therefore it is known as thick film or fluid film lubrication or hydrodynamic (hydro meaning liquid and dynamic meaning relative motion) lubrication. In this case fluid is formed by mixing of hydrocarbon oils and anti-oxidants with long chain polymer so as to maintain viscosity. Fluid film lubrication is useful in delicate and light machines like watches, clocks, guns, scientific equipment's.



Extreme pressure lubrication

Under heavy load and high speed conditions, high local temperature is generated. Due to this temperature liquid film may not stick, it may decompose and vaporize. Under these conditions special additives called extreme pressure additives are used.

Extreme pressure additives are blended with lubricating oils to form more durable film to withstand high temperature and pressure.

Examples: Chlorinated esters, sulfurised oils and tricresyl phosphates.

These metallic compounds possess high melting points and serve as good lubricants under extreme temperatures and pressures.

Smart materials and their engineering applications

Smart Materials are also known as advanced materials or intelligent materials or responsive materials. A smart material can be defined as the material which can change their behaviour or their properties as per change in the atmosphere or in the response of external stimuli and these stimuli could be anything i.e. pressure, force, temperature, stress, moisture, electrical or magnetic fields, pH, or chemical compounds..

This ability to respond to stimuli and adopt their properties makes them highly useful in various applications.

Aerospace industry
Smart materials are used in construction of aircraft, satellites and other aerospace applications.

Automotive industry
In automotive industries smart materials can be used to improve safety and performance.
Ex: smart sensors can detect changes in tyre pressure and adjust the vehicles handling accordingly.

Medical industry
Smart materials have numerous applications in the medical industry such as drug delivery, tissue engineering, implantable medical devices etc.

Construction industry
Smart materials can be used to enhance the performance of buildings and infrastructure
Ex: self-healing concrete can repair cracks and damage caused by weather.

Textile industry
Smart materials used to create clothing and accessories that change colour, shape or temperature in response to changes in the wearer's environment or body.
Ex: smart clothing can adjust to the user's body temperature to keep them comfortable in varying conditions.

Energy industry
Smart materials can be used to create more efficient solar panels and energy storage devices.

Classification of smart materials:
Smart materials are classified as

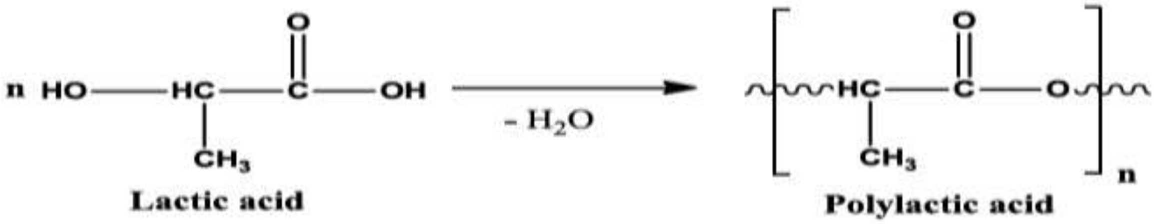
1. Piezo electric materials.
2. Shape memory alloys or materials.
3. Thermo responsive materials.
4. Electro rheological fluid
5. Magneto rheological materials.
6. Optical fibre.

Shape memory materials (SMMs)

Shape memory materials are a class of materials that can remember their original shape and returned to it after being deformed, usually through temperature or stress.
This unique behaviour is due to materials ability to undergo reversible phase transformation.

When a material is subjected to deformation at lower temperatures, it recovers to its original shape on heating the material.
Ex: PLA (Poly L- Lactic acid)

Poly L- Lactic acid.
Preparation
Poly lactic acid is a biodegradable thermoplastic polymer. It is synthesized by the condensation reaction of lactic acid.



Properties:

1. Biodegradable, Biocompatibility
2. super elasticity
3. It is a thermoplastic, meaning it will turn into a liquid in its melting point of 150-160 ^{o}C.
4. It is insoluble in water. But it is soluble in solvents, hot benzene, tetrahydrofuran, and dioxane.
5. PLA is a hydrophobic polymer due to the presence of $–CH_3$ side groups.
6. Good heat resistance.

Applications:

1. It is used in a number of biomedical applications such as sutures, stents, drug deliverydevices and dialysis media.

2. It is used as medical implants in the form of anchors, screws, plates, pins, rods, and as amesh.
3. It can be in the form of fibres and nonwoven textiles; potential uses: upholstery,disposable garments and diapers.
4. It is used in the preparation of bio-plastics for packing food and disposable tableware.
5. It is also used in paper coatings; pesticides and fertilizers release systems and compost bags.

Thermo response materials

Thermo responsive materials are materials that change their properties (Ex: Shape, size, solubility, conductivity) in responsive to changes in temperature.
Ex: Poly acryl amides, Poly vinyl amides

Poly acryl amides

Poly acryl amides are water soluble polymers. That can change their solubility in response to changes in temperature.

Preparation
It is obtained by the polymerisation of acryl amide.

Acrylamide Polyacrylamide

Properties
- Water soluble
- Thermally degrades between 175 to 300 ^{0}C
- Experiences photo degradation
- Bio-degradable

Applications
1. Used to produce paper and pulp
2. Used in agriculture, mining and to process food.
3. It is also used to treat waste water, for oil recovery, gel electrophoresis, DNA sequencing and medical treatment.
4. Used as carbon and nitrogen sources.

Poly vinyl amide

Poly vinyl amide is water soluble polymer. That can change their solubility and mechanical properties in response to temperature.

Preparation
It is obtained by the polymerisation of vinyl amide.

Properties

- water soluble
- insoluble in acetone and alcohols
- unstable in atmosphere
- bio-compatibility
- low toxicity

Applications

1. Used to produce paper and to treat waste water
2. cross linked poly vinyl amine is used as metal chelating resin
3. Poly vinyl amide hydrogels used to create sensors to detect environmental changes
4. Used in textiles. Those can respond to changes in temperature and humidity etc.
5. Used to create smart bandages that monitor wound healing.