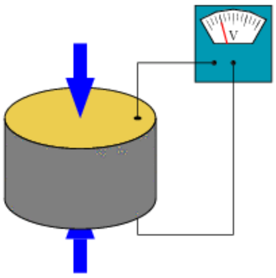
# UNIT 5: SMART MATERIALS AND LUBRICANTS

## Introduction

**Smart materials**:

- Smart materials are those in which properties can be significantly changed in a controlled fashion and reversible by external stimuli, such as stress, moisture, electric or magnetic fields, light temperature, pH, chemical or biological components.
- These materials are also called intelligent or responsive materials.

1. **Piezoelectric materials:** The materials that produce a voltage when stress is applied are called piezoelectric materials. Since this effect also applies in the reverse manner, a voltage across the sample will produce stress within the sample. Suitably designed structures made from these materials can therefore be made that bend, expand or contract when a voltage is applied.
   **Example:** Quartz, $BaTiO_3$, $GaPO_4$



**Applications:**
In lighters or portable sparkers with a piezofuze a sudden and strong pressure is used to produce a voltage. The spark then ignites the gas.



2. **Magnetostrictive materials:** Magneto striction is a property of ferromagnetic materials that causes them to change their shape or dimensions during the process of magnetization.
   Ex: Fe, Co, Terfenol–D (US transducers, sonar, sound bug)

3. **Electrostrictive materials:** In the presence of electric field, these materials experience a strain (mechanical change) which is proportional to strength of

electric field.

Eg: Lead Lanthanum Zirconate Titanate (PLZT), Lead Magnesium Niobate (PMN)

4. **Thermoelectric materials:** These materials when subjected to any temperature difference; they produce change in voltage and vice versa

5. **Rheological materials:** Materials which can change state instantly through the application of an electric or magnetic charge/field.

   Eg: Silicates, Food additives etc.;

6. **Chromic materials:** These materials have very excellent property to change their color when subjected toexternal impetus (temperature, lights, electric field).

   Eg: A variety of dyes, pigments, oxides, organic molecules, conjugated conducting polymers etc; show chromic phenomenon.

   Types: Photochromic, Thermochromic; Electrochromic, Magnetochromic, piezochromic etc.

7. **pH sensitive materials:** This kind of smart materials have properties to change their color when their willbe the change in the acidity of the liquid. This kind of smart materials can be used to indicates the corrosionby mixing it with the paint.

| TYPE OF SMARTMATERIAL | INPUT | OUTPUT |
|---|---|---|
| **Piezoelectric** | **Bending** | **Potential difference** |
| **Electrostrictive** | **Potential difference** | **Deformation** |
| **Magnetostrictive** | **Magnetic field** | **Deformation** |
| **Thermoelectric** | **Temperature** | **Potential difference** |
| **Shape memory alloys** | **Temperature** | **Deformation** |

| | | |
|---|---|---|
| **Chromic materials** | **Radiation** | **Color change** |
| **Rheological materials** | **Electric or magnetic field** | **Physical state change** |
| **pH sensitive materials** | **pH** | **Color change** |

### Applications of smart materials:

Some major field of application of smart materials are:


## Shape memory alloys:

- Shape memory alloys and shape memory polymers are responsive materials where deformation can be induced and recovered through temperature changes.
- Example: NiTi (Nickel Titanium) alloy that “remembers” its original, cold- forged shape By heating it returns back to their deformed shape.
- SMAs are materials which can revert back to original shape & size on cooling by undergoing phase transformations.
- Examples: NiTiNOL (thermal), NiMnGa, Fe-Pd, Terfenol-D (Magnetic)


**Applications:**

- Aircraft and Spacecraft (to minimize the vibrations of the body)
- Valves (for making actuating valves)
- Bio-engineered robots (for memory based movements)
- Civil Structures (to identify the damages)
- Medicine (orthopedic surgery, dental braces, capsule endoscopy, etc.)
- Optometry (Eyeglass frames)

## Poly Lactic Acid (PLA):

Shape memory materials are a unique class of smart materials that can return to their original shape after being deformed. These materials have the potential to revolutionize various industries, including healthcare, automotive, aerospace, and robotics. One such shape memory material is Poly Lactic Acid (PLA).

i) PLA is a biodegradable and biocompatible polymer

ii) One of the most intriguing properties of PLA is its shape memory effect. When the material is heated, it softens and can be easily moulded into a new shape. Once it cools down, it retains its new shape until it is reheated to its original shape.

iii) This shape memory effect is due to the molecular structure of the polymer, which allows it to switch between two different states – crystalline and amorphous – based on changes in temperature.

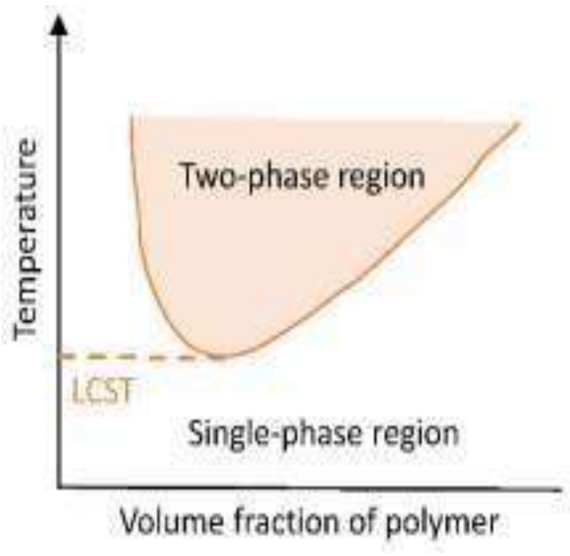
V) However, PLA also has some drawbacks that limit its widespread use. It has poor mechanical properties compared to other polymers, which can affect its performance in certain applications. Additionally, its slow degradation rate can be a disadvantage for medical applications, where a faster degradation rate is desired.

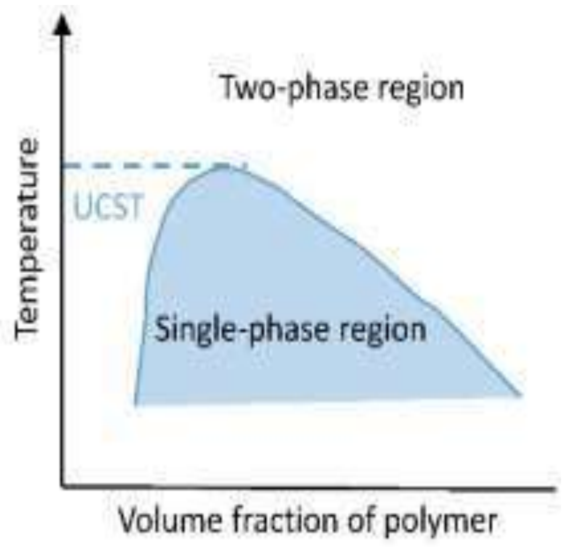
**Applications:**

It is extensively researched for medical applications such as drug delivery, tissue engineering, and wound healing. It is also used in various industrial applications, including packaging, textiles, and composites.

## Thermoresponsive polymers (Temperature-responsive)

- The polymers which exhibit drastic and discontinuous changes in their physical properties with temperature are called thermoresponsive polymers
- These are contrast to temperature – sensitive materials which change their properties continuously with environmental conditions.
- Usually, the temperature responsive term is concerned with solubility property in a given solvent, but not only limited to solubility.
- Based on miscibility gap of the polymers in the phase diagram, polymers can have either lower critical solution temperature (LCST) or upper critical solution temperature (UCST).
- The polymers which are miscible (Single phase) below the phase transition temperature and immiscible (two phases) above the phase transition temperature come under LCST type.
- The polymers which are immiscible (two phases) below the phase transition temperature and miscible (Single phase) above the phase transition temperature come under UCST type.

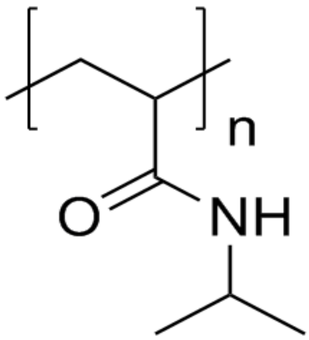



**POLY ACRYLAMIDE:**

- The most commonly studied and first reported thermoresponsive polymer in aqueous solution is Poly (N-isopropyl acryl amide) (PNIPAM).
- PNIPAM is considered to be the gold standard of thermoresponisve polymers, especially for biomedical applications.

**Structure:**



Poly(N-isopropyl acryl amide)

**Preparation:**

- Free radical polymerization of N-isopropyl acryl amide monomers using radical initiator (azo bis-isobuytronitrile)

**Advantages:**

- LCST lies between body and room temperature i.e., ~32°C, suitable for biological applications.
- Robust phase behaviour.
- LCST of PNIPAM does not depend on chain length or Environmental such as $P^H$.

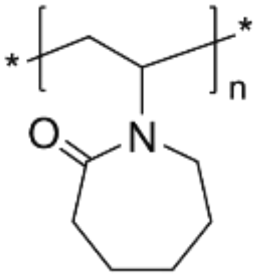
**Disadvantages:**

- Very high glass transition temperature (~140°C to 150°C) may lead to vitrification of high concentrated polymers.

**POLYVINYL AMIDE:**

- This class of thermo-responsive polymers are second most explored polymer
- Poly N-Vinyl caprolactum (PVCL) is the best example of this category.

**Structure of Poly N-Vinyl caprolactum:**



- It can be prepared by free radical polymerisation of N-Vinyl caprolactum by using azo bis-isobutyronitrile as free radical initiator,

**Advantages:**

- Low critical solution temperature (LCST) of this polymer lies in between body and room temperature (~31°C).
- LCST of Caprolactum does not depend on chain length or Environmental such as $P^H$.

**Disadadvantages:**

- Very high glass transition temperature (~130$^O$C to 140$^O$C) may lead to vitrification of high concentrated polymers.

**Applications of thermoreponsive polymers:**

- Drug delivery
- Tissue engineering
- Liquid chromatography
- Bio separation

# LUBRICANTS

In all types of machines, the surfaces of moving or sliding or rolling parts rub against each other. Due to the mutual rubbing of one part against another, a resistance is offered to their movement. This resistance is known as friction. It causes a lot of wear and tear of surfaces ofmoving parts. Any substance introduced between two moving/sliding surfaces with a view to reduce the friction (or frictional resistance) between them, is known as a lubricant. The main purpose of a lubricant is to keep the moving/sliding surfaces apart, so that friction andconsequent destruction of material is minimized. The process of reducing friction between moving/sliding surfaces, by the introduction of lubricants in between them, are called lubrication.

## Function of Lubricants:

- It reduces wear and tear of the surfaces by avoiding direct metal to metal contact

- Between the rubbing surfaces, i.e. by introducing lubricants between the two surfaces
- It reduces expansion of metal due to frictional heat and destruction of material
- It acts as coolant of metal due to heat transfer media
- It avoids unsmooth relative motion
- It reduces maintenance cost
- It also reduces power loss in internal combustion engines

## Classification of Lubricants:

Lubricants are classified on the basis of their physical state, as follows;

Liquid lubricants or Lubricating Oils,

Semi-solid lubricants or Greases and

Solid lubricants.

**(a) Liquid lubricants or Lubricating oils:**

Lubricating oils also known as liquid lubricants and further classified into four categories;

(i) Animal and Vegetables oils, (ii) Mineral or Petroleum oils, (iii) blended oils and (iv) Synthetic Lubricants

**i. Animal and Vegetables oils:**

- Animal oils are extracted from the crude fat and vegetables oils such as cotton seed oil and caster oils.
- These oils possess good oiliness and hence they can stick on metal surfaces effectively even under elevated temperatures and heavy loads.
- But they suffer from the disadvantages that they are costly, undergo easy oxidation to give gummy products and hydrolyze easily on contact with moist air or water.
- Hence, they are only rarely used these days for lubrication. But they are still used as blending agents in petroleum-based lubricants to get improved oiliness.

**ii. Mineral or Petroleum oils:**

- These are basically lower molecular weight hydrocarbons with about 12 to 50 carbon atoms.
- As they are cheap, available in abundance and stable under service conditions, hence they are widely used.
- But the oiliness of mineral oils is less, so the addition of higher molecular weight compounds like oleic acid and stearic acid increases the oiliness of mineral oil.

**iii. Blended oils:**

- No single oil possesses all the properties required for a good lubricant and hence addition ofproper additives is essential to make them perform well.
- Such additives added lubricating oils are called blended oils.
  Examples: The addition of higher molecular weight compounds like oleic acid, stearic acid, palmetic acid, etc or vegetables oil like coconut oil, castor oil, etc increases the oiliness of mineral oil.

**iv. Synthetic oils:**

- Mineral oils cannot be used effectively as they tend to get oxidized at very high temperature while wax separation will occur at very low temperature. So, synthetic lubricants have been developed, which can meet the severe operating conditions such as in Aircrafts.
- The same lubricants may have to be in the temperature range of -50 $^0$C to 250 $^0$C.
- Polyglycol ethers, fluoro and chloro hydrocarbons, organophosphates and silicones are currently used as synthetic lubricants.

**(b) Semi-solid Lubricants or Grease:**

- A semi-solid lubricant obtained by combining lubricating oil with thickening agents is termed as grease.
- The thickeners consist primarily of special soaps of Li, Na, Ca, Ba, Al, etc. Non-soap thickeners Include carbon black, silica gel, polyureas and other synthetic polymers, clays, etc.
- Grease can support much heavier load at lower speed. Internal resistance of grease is much higher than that of lubricating oils; therefore it is better to use oil instead of grease. Compared to lubricating oils, grease cannot effectively dissipate heat from the bearings, so work at relatively lower temp.

**(c) Solid lubricants:**

These are preferred where (1) the operating conditions are such that a lubricating film cannot be secured by the use of lubricating oils or grease (2) contamination (by the entry of dust particles) of lubricating oils or grease is unacceptable (3) the operating temperature or load is too high, even for grease to remain in position and (4) combustible lubricants must be avoided.

They are used either in the dry powder form or with binders to make them stick firmly to the metal surfaces while in use. They are available as dispersions in non-volatile carriers like soaps, fats, waxes, etc and as soft metal films.

The most common solid lubricants are graphite, molybdenum disulphide, tungsten disulphide and zinc oxide. They can withstand temperature upto 650° C and can be applied in continuously operating situations.They are also used as additives to mineral oils and greases in order to increase the load carrying capacity of the lubricant. Other solid lubricants in use are soapstone (talc) and mica.

Graphite:

It is the most widely used of all the solid lubricants and can be used either in the powderedform or in suspension. It is soapy to touch; non-inflammable and stable up to a Temperatureof 375 °C. Graphite has a flat plate like structure and the layers of graphite sheets are arranged one above the other and held together by weak van Der Waal's forces. These parallel layers which can easily slide one over other make graphite an effective lubricant. Also the layer of graphite has a tendency to absorb oil and to be wetted of it.

Molybdenum Disulphide:

It has a sandwich- like structure with a layer of molybdenum atoms in between two layers of sulphur atoms. Poor interlaminar attraction helps these layers to Slide over one another easily. It is stable up to a temperature of 400 °C.

### Characteristic of good lubricating oils:

- high boiling point,
- low freezing point,
- adequate viscosity for proper functioning in service,
- high resistance to oxidation and heat,
- non-corrosive properties and Stability to decomposition at the operating temperatures.
- A good lubricant must have low cloud and pour points.

## Mechanism of Lubrication:

The phenomenon of lubrication can be explained with the help of the following mechanism;

(a) Thick-Film lubrication (Fluid-Film or hydrodynamic lubrication) (b) Thin Filmlubrication (Boundary lubrication) and (c) Extreme Pressure lubrication.

**(a) Thick-Film lubrication:**

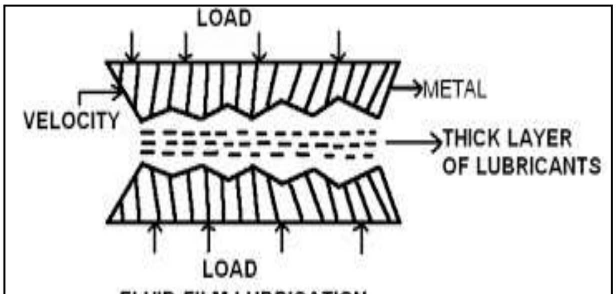
In this, moving/sliding surfaces are separated from each other by a thick film of fluid (at least 1000 $A^{\circ}$ thick), so that direct surface to surface contact and wearing of junctions rarely occurs.

The lubricant film covers/fills the irregularities of moving/sliding surfaces and forms a thick layer between them, so that there is no direct contact between the material surfaces. This consequently reduces friction.

The lubricant chosen should have the minimum viscosity (to reduce the internal resistance between the particles of the lubricant) under working conditions and at the same time, it should remain in place and separate the surfaces.

Hydrocarbon oils (mineral oils which are lower molecular weight hydrocarbons with about 12 to 50 carbon atoms) are considered to be satisfactory lubricants for thick-film lubrication.

In order to maintain the viscosity of the oil in all seasons of year, ordinary hydrocarbon lubricants are blended with selected long chain polymers.



FLUID-FILM LUBRICATION

**(b) Thin Film lubrication:**

This type of lubrication is preferred where a continuous film of lubricant cannot persist.

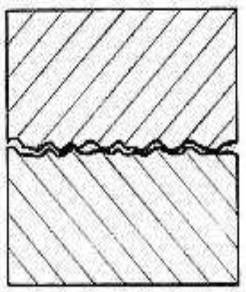


Figure 1: Boundary Lubrication

In such cases, the clearance space between the moving/sliding surfaces is lubricated by such a material which can get adsorbed on both the metallic surfaces by either physical orchemical forces.

This adsorbed film helps to keep the metal surfaces away from each other at least up to the height of the peaks present on the surface.

Vegetable and animal oils and their soaps can be used in this type of lubrication because they can get either physically adsorbed or chemically react in to the metal surface to form a thin film of metallic soap which can act as lubricant.

Although these oils have good oiliness, they suffer from the disadvantage that they will break down at high temperatures. On the other hand, mineral oils are thermally stable and the addition of vegetable/animal oils to mineral oils, their oiliness can also be brought up. Graphite and molybdenum disulphide are also suitable for thin film lubrication.

**(c) Extreme Pressure lubrication:**

When the moving/sliding surfaces are under very high pressure and speed, a high local temperature is attained under such conditions, liquid lubricants fail to stick and may decompose and even vaporize.

To meet these extreme pressure conditions, special additivesare added to minerals oils. These are called extreme pressure additives. These additives formmore durable films (capable of withstanding very high loads and high temperatures) on metal surfaces. Important additives are organic compounds having active radicals or groups such as chlorine (as in chlorinated esters), sulphur (as in sulphurized oils) or phosphorus (asin tricresyl phosphate). These compounds react with metallic surfaces, at existing high temperatures, to form metallic chlorides, sulphides or phosphides

## Properties of Lubricants:

### Viscosity:

It is the property of liquid by virtue of which it offers resistance to its own flow (the resistance to flow of liquid is known as viscosity). The unit of viscosity is poise. It is the most important single property of any lubricating oil, because it is the main determinant of the operating characteristics of the lubricant. If the viscosity of the oil is too low, a liquid oil film cannot be maintained between two moving/sliding surfaces. On the other hand, if the viscosity of the oil is too high, excessive friction will result.

Effect of temperature on viscosity: Viscosity of liquids decreases with increasing temperature and, consequently, the lubricating oil becomes thinner as the operating temperature increases. Hence, viscosity of good lubricating oil should not change much with change in Temperature, so that it can be used continuously, under varying conditions of temperature.The rate at which the viscosity of lubricating oil changes with temperature is measured by an arbitrary scale, known as Viscosity Index (V. I). If the viscosity of lubricating oil falls rapidlyas the temperature is raised, it has a low viscosity index. On the other hand, if the viscosity of lubricating oil is only slightly affected on raising the temperature, its viscosity index is high.

Significance:

Viscosity helps in the selection of good lubricating oil. Viscosity helps in the selection of good lubricating oil. Light oils have low densities and easy flow abilities and are used on parts moving a high speed. Heavy oils are used on parts moving at slow speed under heavy loads.

### Flash Point and Fire Point:

Flash point is the lowest temperature at which the lubricant oil gives off enough vapours that ignite for a moment, when a tiny flame is brought near it; while Fire point is the lowesttemperature at which the vapours of the lubricant oil burn continuously for at least five seconds, when a tiny flame is brought near it. In most cases, the fire points are 5° C to 40° Chigher than the flash points. The flash and fire do not have any bearing with lubricating property of the oil, but these are important when oil is exposed to high Temperature service. A good lubricant should have flash point at least above the temperature at which it is to be used. This safeguards against risk if fire, during the use of lubricant.

Significance:

A good lubricant must have higher flash point than working temperature of a machine.

The knowledge of flash point and fire point helps in selecting the suitable oil and maintaining necessary conditions to prevent fire accidents while storing or transportation.

## Cloud Point and Pour Point:

When the lubricant oil is cooled slowly, the temperature at which it becomes cloudy or hazyin appearance, is called its cloud point; while the temperature at which the lubricant oil ceaseto flow or pour, is called its pour point. Cloud and pour points indicate the suitability of lubricant oil in cold conditions. Lubricant oil used in a machine working at low temperaturesshould possess low pour point; otherwise solidification of lubricant oil will cause jamming ofmachine. It has been found that presence of waxes in the lubricant oil raise pour point.

Significance:

Cloud point and pour point are due to presence of impurities.

These two help in deciding the suitability of a lubricant to the machines working at low temperatures.