University Of Technology- Iraq
Department of Materials Engineering
General Materials Branch
Fourth class

Smart Materials

Lecture 9 : Biomimteic Materials and Shape Memroy Polymer

Class Code on Google Classroom :2shhens

Biomimetic Materials

- **Biomimetic materials** are materials developed using inspiration from nature. This may be useful in the design of composite materials. Natural structures have inspired and innovated human creations.
- Notable examples of these natural structures include: honeycomb structure of the beehive, strength of spider silks, bird flight mechanics, and shark skin water repellency.
- The etymological roots of the neologism "biomimetic" derive from Greek, since *bios* means "life" and *mimetikos* means "imitative".

Biomimetic Materials

- *Bio-inspired materials engineering*: **applying biological principles** to synthetize new materials
  Bio-mediated materials engineering: take advantages of **biological materials properties** by incorporation into another system
- *Biomimicry* : new science that **studies nature's models and then imitates or takes inspiration** from these designs and processes to solve human problems

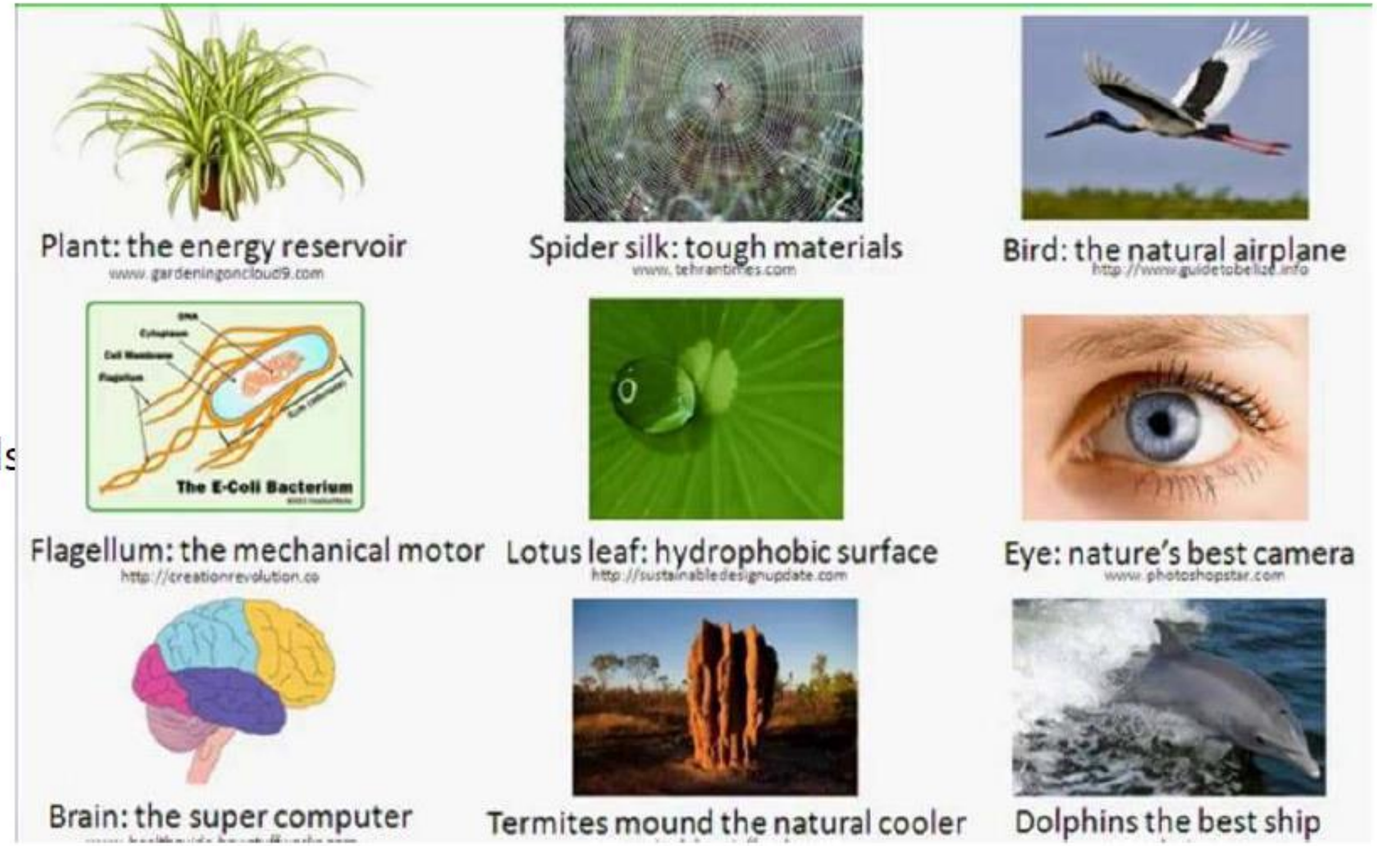
Biomimetic materials

- Nature synthetize its materials under mild conditions:

➢ Ambient temperature
➢ Ambient pressure
➢ Near-neutral pH

- The idea behind the biomimetics are:

➢ Understand the parameters which **control** biological **self-assembly** and **mineralization**
➢ Understand both the **synthesis-structure** and **structure-property** relationship of biological materials
➢ Developing of next-generation **high performance** multifunctional **materials**



Nacre-inspired materials

- **Bio-materials**, such as mammalian bones, crustacean shells and reptile skins have unique properties that are intimately associated to their structure




- **Associated properties** are often the result of a **combination** of two distinct components: a '**hard' component**, and a **'soft' component**, consisting of organic matter, such as collagen, elastin or cellulose.

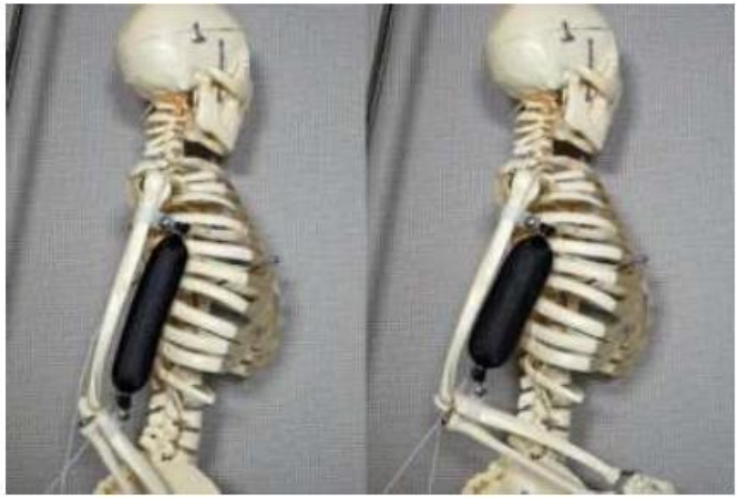
- **Nacre** consists **of 95 wt% of aragonite**, which is a crystalline form of $CaCO_3$ and **5 wt% organic materials**, which are proteins and polysaccharides

Biomimetic artificial muscles

Artificial muscles are materials or devices that **mimic natural muscles** and can reversibly contract, expand, or rotate within one component due to an external stimulus (such as voltage, current, pressure or temperature)

Artificial muscles are divided in three major groups based on the actuation mechanism

- **Electric actuation –** Electroactive polymers (EAPs)
- **Pneumatic actuation** (PAMs)
- **Thermal actuation** – Shape memory alloy (SMA) – Shape memory polymers (SMPs)

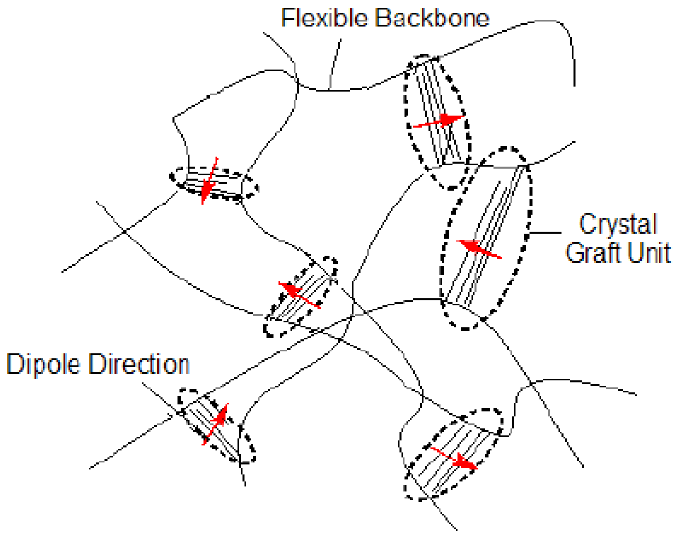


Pneumatic Artificial Muscles

Electroactive polymers (EPAs)

EPAs = polymers that exhibit a **change in size or shape** when stimulated by an electric field

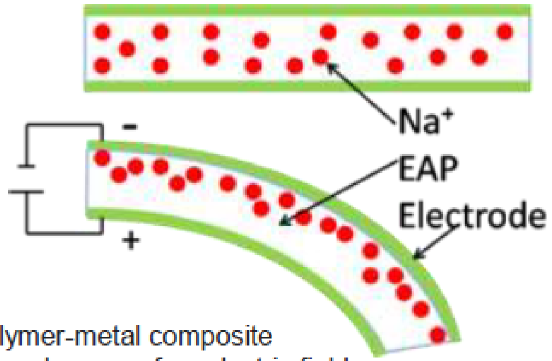
Large deformation when a large force is applied over time



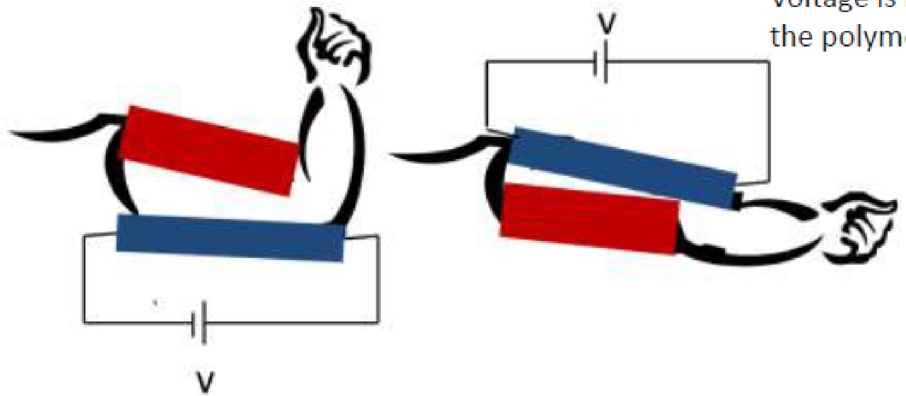
EPAs are divided in two main groups: Dielectric and Ionic

- **Dielectric** = electrostatic forces between two electrodes squeeze the polymer. It is required high voltage to produce high electric fields.

- **Ionic** = the response is related by the displacement of the ions inside the polymers (e.g conductive polymers)



The cations in the ionic polymer-metal composite are randomly oriented in the absence of an electric field. Once a field is applied the cations gather to the side of the polymer causing the polymer to bend.

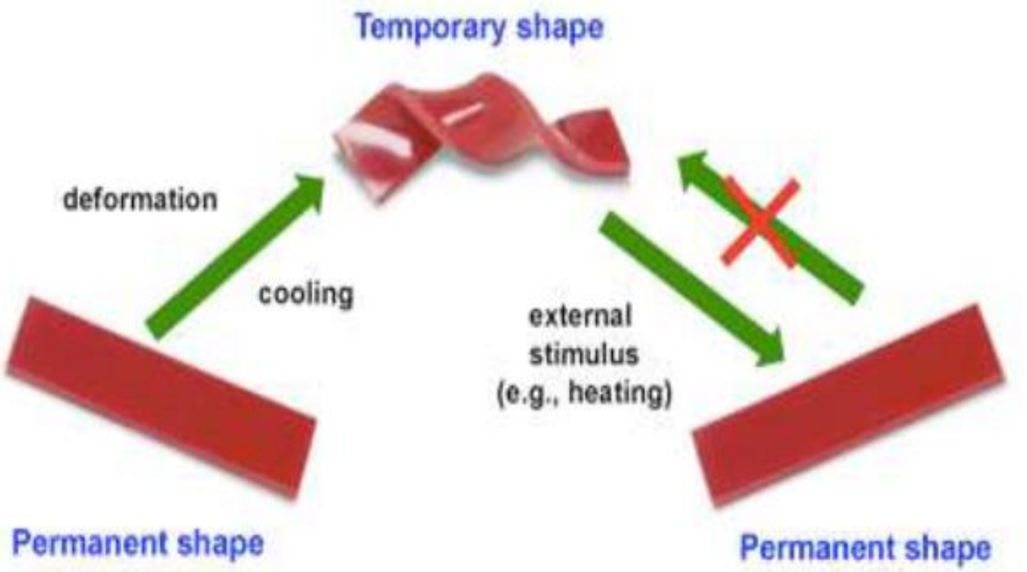


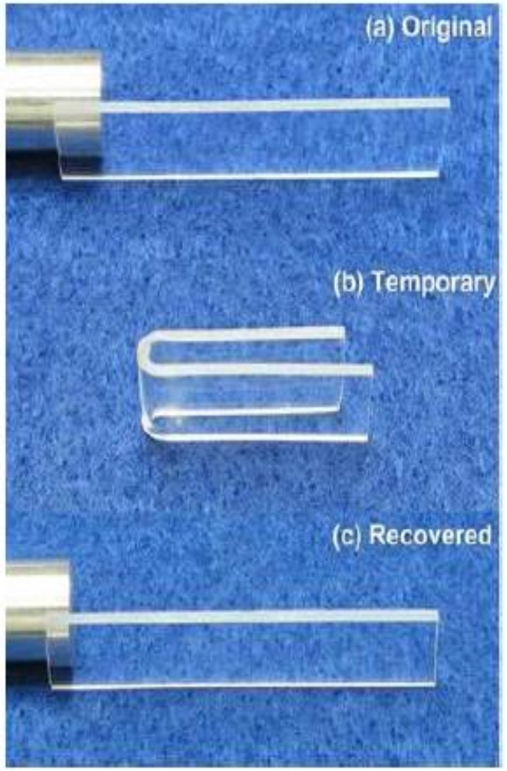
Voltage is removed (red muscles) the polymer returns to original state.

Applied voltage = polymer expand (blue)

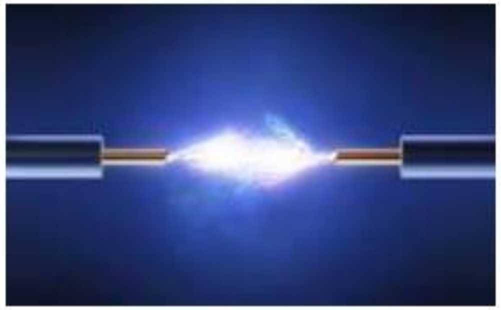
Shape Memory Polymers (SMPs)

- *Polymers with ability to return from a deformed state (**temporary shape**) to their original (**permanent**) shape*
- *induced by an **external stimulus** (trigger)* heat
- The classifications of SMP have been discussed widely. SMP have been reported to be thermally induced, light-induced, electro-active, water/moisture/solvent-induced, pH-sensitive and magnetic-sensitive based on their external stimulus






heat


electric


magnetic


light


chemical

Shape Memory Polymers (SMPs)

- **Physical** cross-linked polymers
- **Chemical** cross-linked polymers

- The *thermal-induced* SMPs as the most researched SMPs, can change their shape in a predefined way under the stimulus of heat

- *Electric-induced* SMPs
- *Magnetic-induced* SMPs

→ indirect thermal-induced SMPs → electricity or magnetism are transformed to heating

- *Photo-induced* SMPs → form or destroy the networks in polymers under different wavelength

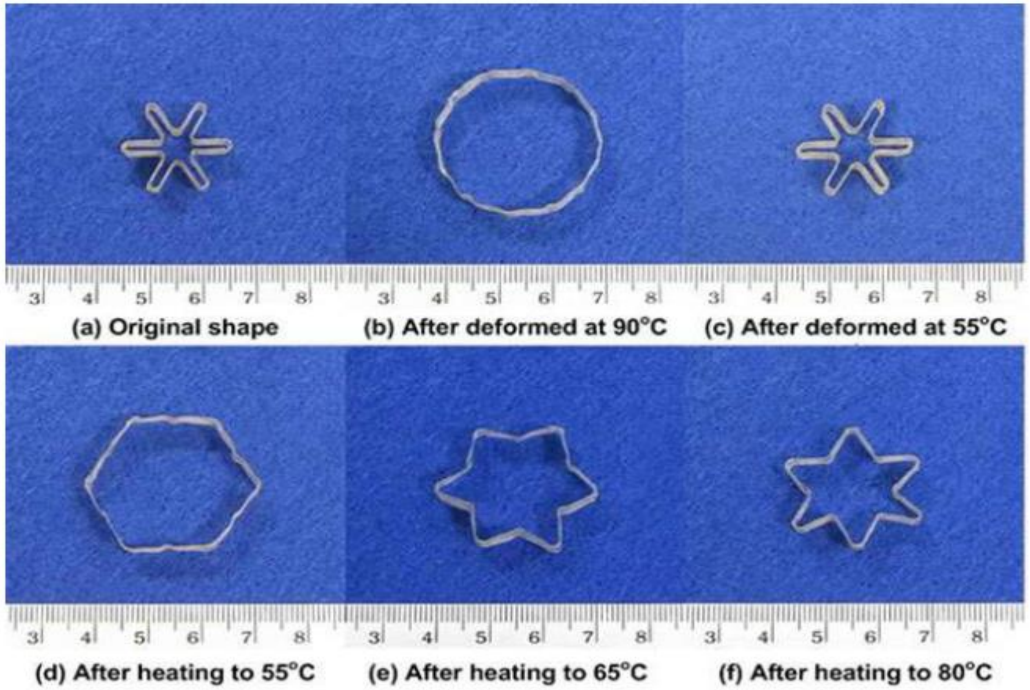
- *Chemical-induced* SMPs → water induced, solvent-induced, pH-induced

Shape Memory Polymers (SMPs)

Traditional SMPs – **Dual** SMPs
- Temporary shape
- Permanent shape

Triple SMPs
- 2 Temporary shapes
- Permanent shape

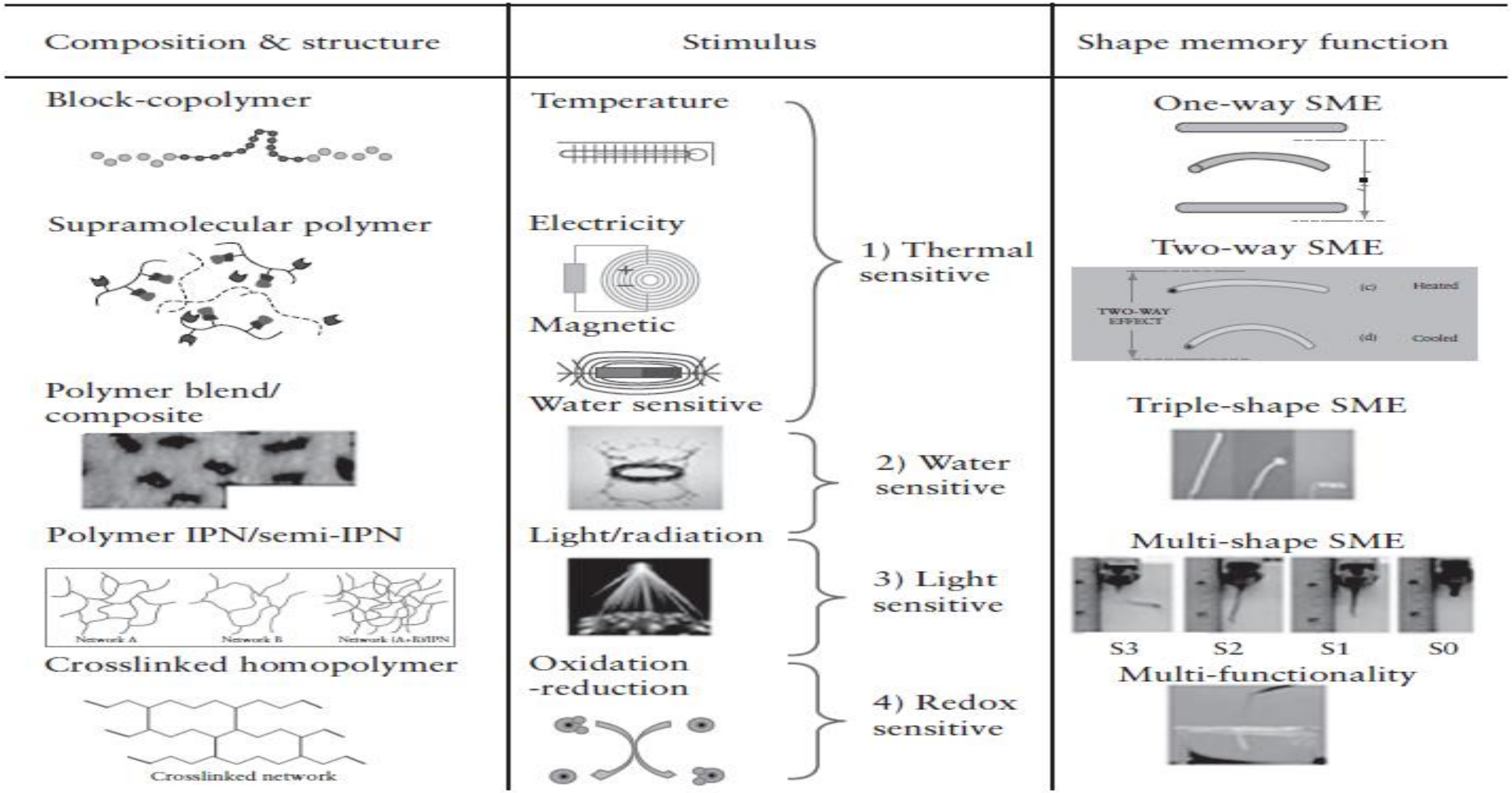
Quadruple SMPs
- 3 Temporary shapes
- Permanent shape



Multi-stimuli SMPs → polymers can recover shape under more than one stimuli

Multi-functional SMPs → possess not only shape memory properties but also other stimuli-responsive function, such as healing, drug delivery

Classification of Shape-memory Polymers



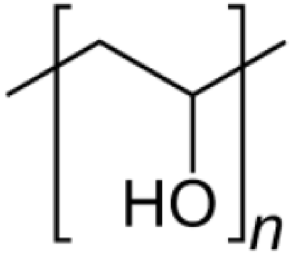
Examples of SMPs

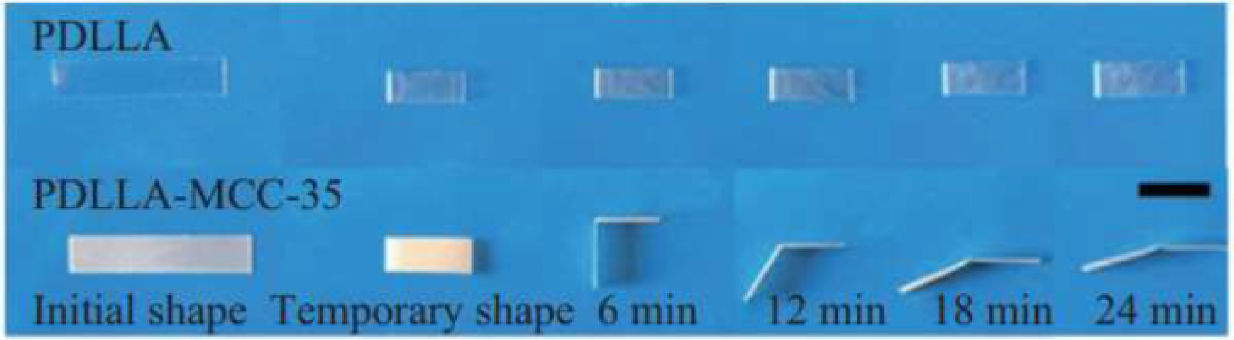
Water-induced SMPs

- The absorbed water can be divided into
  - *free water* = cannot affect the properties of the SMPs = no changes of shape
  - *bounded water* = affect the shape = weaken the hydrogen bonds in polymer networks to increase the flexibility of the macromolecular chains

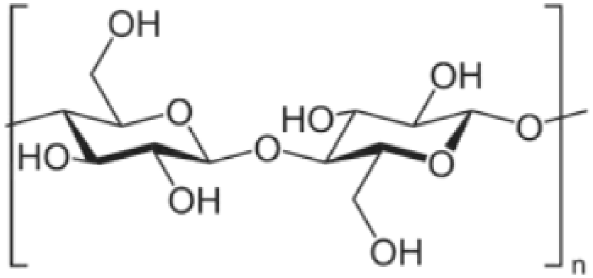
Poly(vinyl alcohol) (PVA)

- nontoxic nature and biocompatible material
- both the chemically and physically crosslinked networks
- good water induced shape memory effect





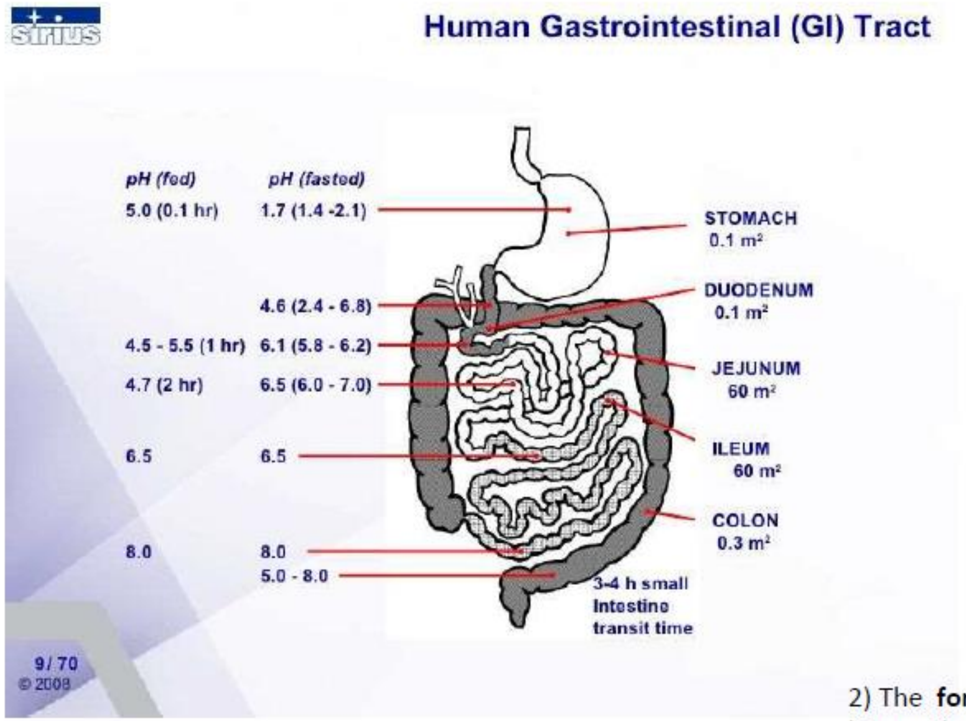
MCC = microscristalline cellulose



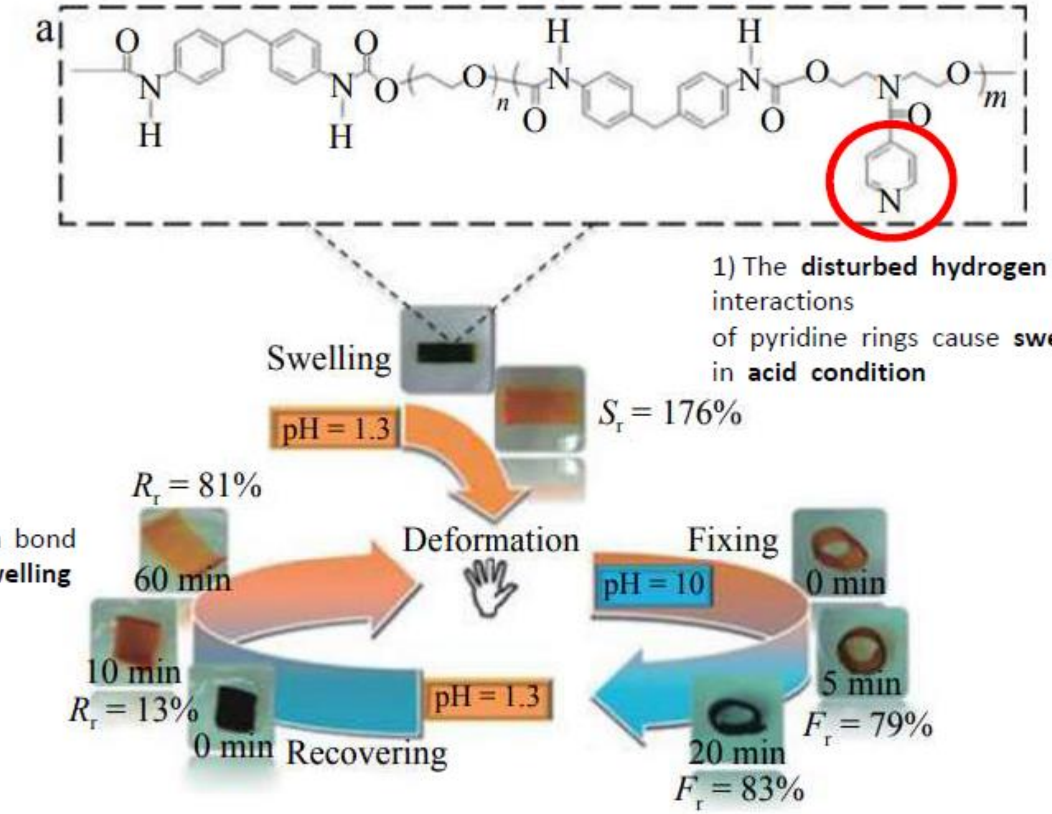
Cellulose

pH-induced SMPs

- ➢ Body compartments have variations in physiological pH values
- ➢ In pathological conditions the pH is some body compartments can be different than in healthy conditions



- pH induced shape memory effect is achieved through **switching** effect of **hydrogen bond interactions** of pH sensitive groups in polymer



1) The **disturbed hydrogen bond** interactions of pyridine rings cause **swelling** in **acid condition**

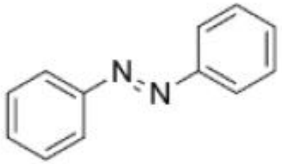
2) The **formed hydrogen** bond interactions lead to **de-swelling** in **base condition**

The pH-sensitive memory effect of **polyurethane with pyridine rings**

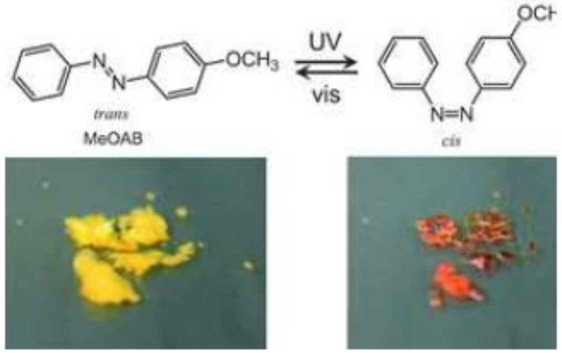
- pH sensitive groups
  - ➢ amino
  - ➢ carboxyl
  - ➢ sulfonic

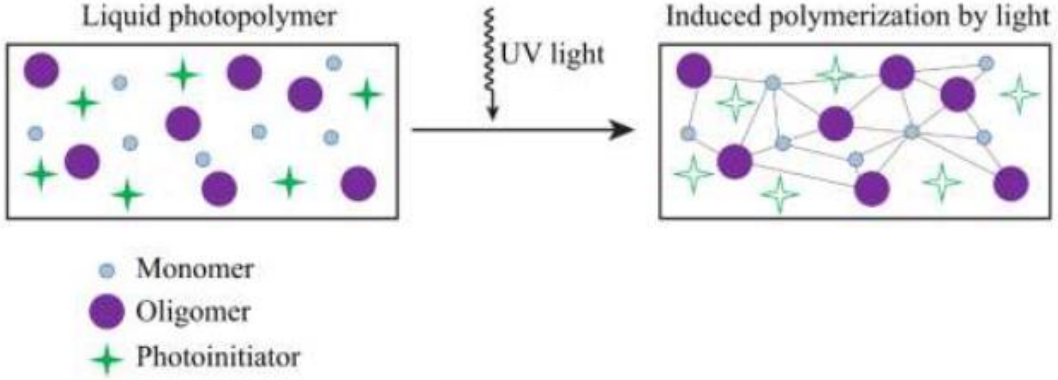
Light induce SMPs

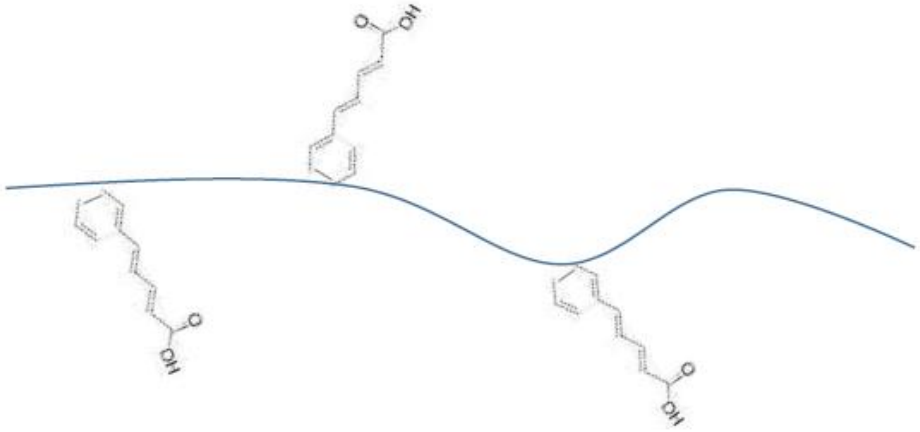
- Photosensitive functional group



e.g azobenzenes





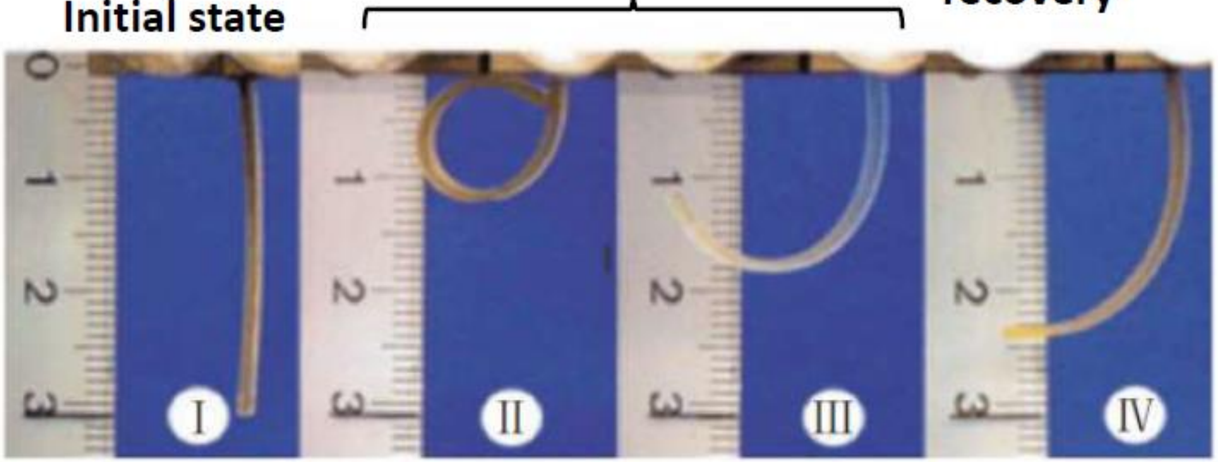


cinnamylidene acetic acid

100% elongation Initial state

λ > 300 nm for 35 min deformation

λ = 254 nm for 120 min recovery

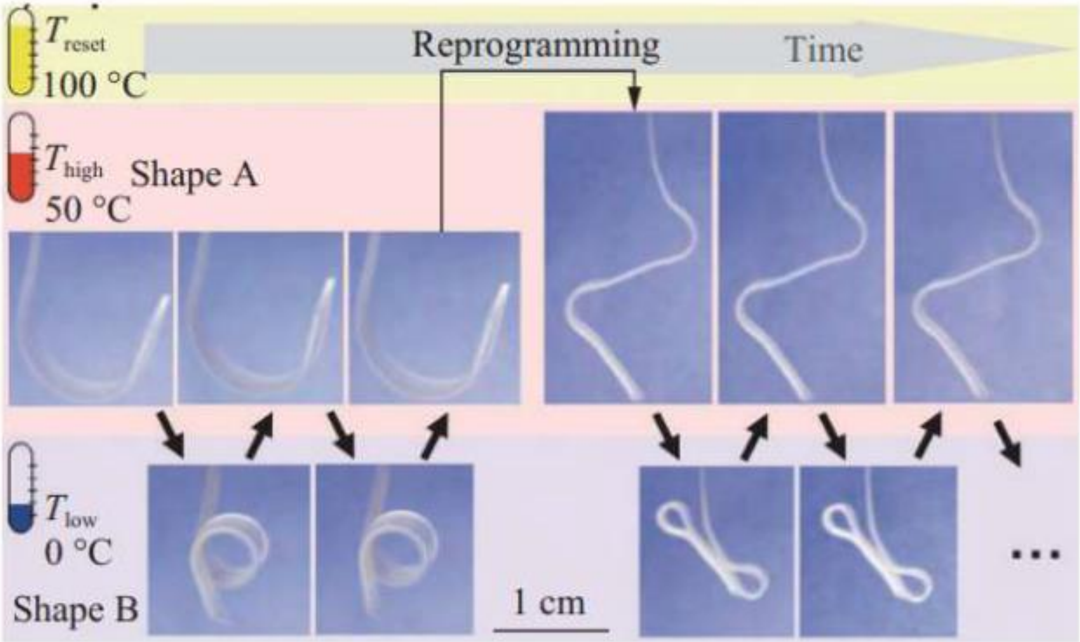


Interpenetrating polymer network (IPN polymer) containing cinnamylidene acetic acid terminal group.

Reversible SMPs

- **one-way** SMEs — materials can remember and recover shape in **only one direction**

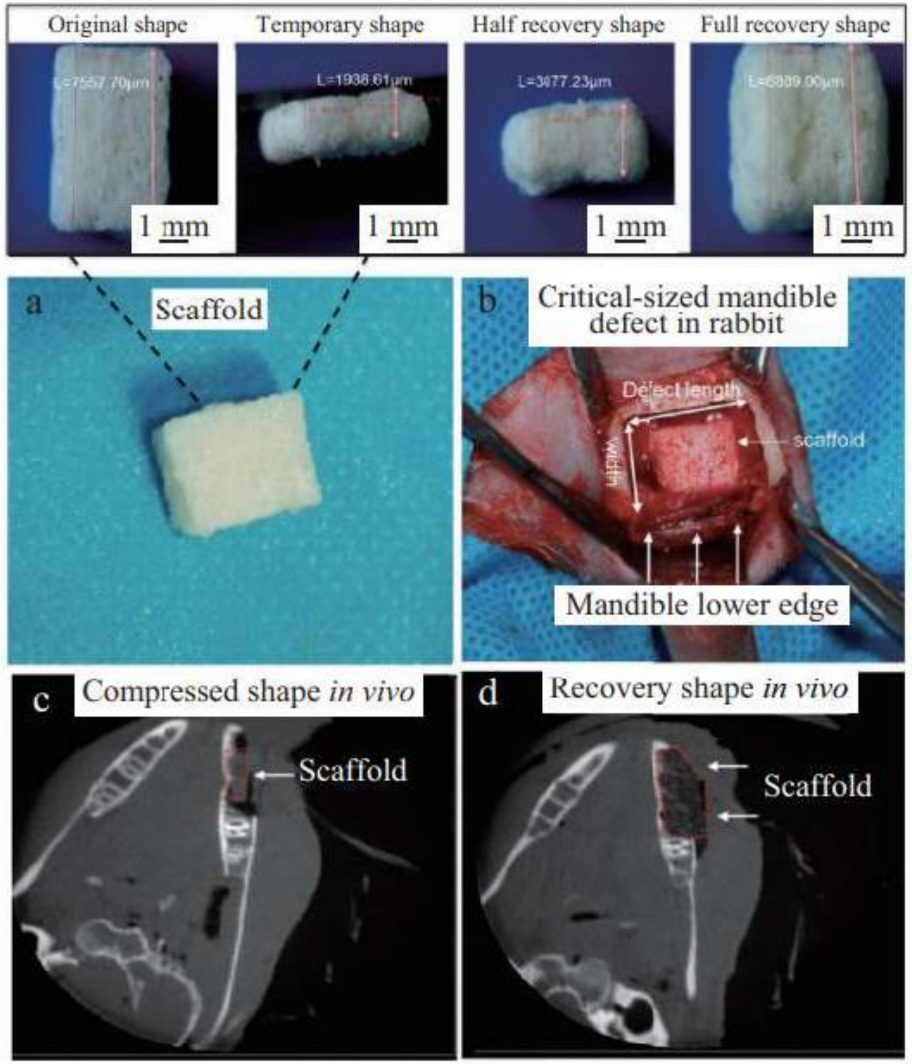
- **two-way** SMEs — the materials can reversibly **change** shapes between **temporary shape** and **permanent shape** under different external stimuli (reversible SME)



reversible bidirectional shape memory effect

Biomedical Applications

SMPs-based Biomaterials for Tissue Engineering



(a) compressed scaffold

(b) the scaffold implanted in the rabbit mandibular bone defect

(c) and (d) the scaffold cans recovery the original shape in vivo after 10 min of implantation

Physical properties ofshape memory polymers and metal alloys

Physical property	Polymers	Metal alloys
Density (g/cm^3)	0.9–1.1	6–8
Deformation (%)	250–800	6–7
Recovery temperature (°C)	25–90	– 10–100
Force required for deformation (kgf/cm^2)	10–30	500–2000
Recovery stress (kgf/cm^2)	10–30	1500–3000

Physical properties of shape memory polymers

Property	Poly-norbornene	*trans*-Polyisoprene	Styrene–butadiene copolymer
Deformation (%)	~ 200	~ 400	~ 400
Recovery temperature (°C)	38	60–90	60–90
Recovery stress (kgf/cm^2)	—	10–30	5–15
Tensile strength (kgf/cm^2)	350	250	100

Design criteria in Biomimetic Materials

1. Compensation for low reliability of various functions. This implies feedback, which is a dynamic way of providing high-quality performance; it also implies shielding against failure in various ways, leading to good damage control and toughness.
2. Varying properties and shapes over small distances thus giving rise to multifunctionality.
3. Merging of functions and morphology (which is another means of generating multifunctionality and hierarchy). This is a useful exercise in the later stages of a design, combining characteristics to see how they can supplement each other (the functionality of a mobile phone is an exemplar) and reduce the number of components. This is sometimes called trimming
4. Allow the material or structure to be more dynamic, relaxing the original design parameters so that the system can equilibrate to other energetic minima than may have been included in the original design.