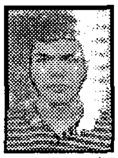
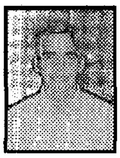
Shape Memory Polymers

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Abstract

Shape memory is the ability of a material to remember its original shape after deformation and return to its original shape upon activation of the shape memory effect by the application of an external stimulus.

Shape-memory polymers (SMPs) are an emerging class of active polymers that have dual-shape capability and belong to the group of 'actively moving' polymers. They can actively change from a shape A to a shape B. SMPs are unique class of polymers which soften and harden quickly and repetitively on demand. This feature provides the ability to temporarily soften, change shape, and harden back to a solid structural state. They have applications as environmental tracking sensors, valves, healable vehicle impact devices, smart textiles, pressure sensors and biomedical devices.

1. Introduction

Shape-memory polymers are stimuli-responsive materials. Upon application of an external stimulus they have the ability to change their shape. The shape-memory effect results from the polymer's structure, that is, its morphology in combination with a certain processing and programming technology. The basis of the shape memory polymer concept is the glass transition temperature. The temperature at which the transition of a polymer from hard glassy state to soft rubbery state takes place is called the glass transition temperature. The first materials to show such a property were shape memory metal alloys. The advantage of shape memory polymers over metal alloys is that the polymers can be easily manufactured, programmed and are also far cheaper. Also, these polymers showed far better recovery properties1.The applications of shape memory polymers include environmental tracking, valves, healable vehicle impact devices, biomedical devices like stents, pressure sensors and smart textiles.

2. Mechanism of shape memory effect

Shape memory effect can be achieved by using different stimuli. Examples of stimuli which may be employed are: change in temperature, irradiation with light, change in pH, treatment with ultrasound, change in ion concentration, and subjection to magnetic fields[1].

2.1 Heat

Shape memory polymers are elastomers consisting of segment chains that are connected by netpoints. The netpoints can be formed by entanglements of the polymer chains or intermolecular interaction of certain polymer blocks. These cross-links are called physical netpoints. Cross-links in the form of covalent bonds form chemical netpoints. An elastomer exhibits a shape-memory functionality if the material can be stabilized in the deformed state in a temperature range that is relevant for the particular application. This can be achieved by using the network chains as a kind of molecular switch. There are two types of segments present, the hard segment and the switching segment. The segments have thermal transition temperatures T_{trans}. Above T_{trans} the chain segments are flexible whereas below this temperature the flexibility of the segments is restricted. The transition temperature can be the melting temperature T_m or it can be the glass transition temperature T_g. The hard segment provides the mechanical support as its transistion temperature is high whereas the switching segment is the one which undergoes the change with change in temperature as it has a much lower transition temperature. The molecular mechanism of the shape-memory effect is illustrated for the thermally induced shape-memory effect in Fig. 1and Fig 1.

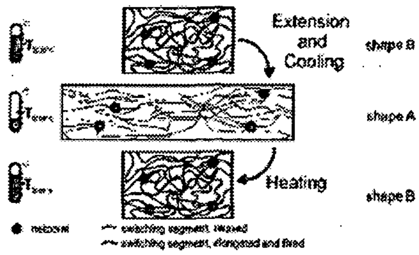

Fig. 1 Molecular mechanism of the thermally induced shape-memory effect T_{trans} = thermal transition temperature related to the switching phase.

Fig 1.

An example of shape memory polymers with physical netpoints is polyurethane with poly(ε-caprolactone) switching segment. The polyurethanes with a hard segment determining block of 4,4_-methylenebis(phenylisocyanate) (MDI) and 1,4-butanediol are prepared by the prepolymer method, they have a T_{trans} between 200 to 240°C. Poly(ε-caprolactone) of high molecular weight form the switching segments as their T_{trans} is between 44 and 55°C. In chemically crosslinked shape memory networks the permanent shape is stabilized by the covalent netpoints. The temporary shape of these shape memory polymers can be fixed either by crystallizable segment chains or by a glass transition of the segment chains that is in the temperature range of interest. An example of these type of shape memory polymers is "heat shrinkable" polyethylene. The polyethylene is covalently crosslinked by ionizing radiation. The permanent shape is fixed by covalent crosslinks whereas the switching process is controlled by the melting temperature of the polyethylene crystallites[1].

2.2 Light

Application of heat stimulated SMPs is limited to those cases where the surrounding temperature is close to the glass transition temperature of the polymer. The need for a shape memory polymer that can be activated by means other than heat is especially felt in areas where heating material above ambient temperatures can be dangerous such as biomedical applications or where raising the temperature of the SMP above Tg requires large amount of energy such as with space vehicles and aircrafts. Hence there is a need for a SMP which can be activated by light or other form of electromagnetic energy. Light-induced stimulation of shape-memory polymers has been realized through the incorporation of reversible photoreactive molecular switches. Light stimulated SMPs are formed by monomers which contain reversible photo crosslinkable groups in addition to primary polymerizable groups. The reaction mixture includes a photo reactive monomer comprising a photoreactive group and a polymerizable group. A second monomer which is preferably a mixture of monomers which are acrylate based, preferably a mixture of methyl methacrylate and butyl acrylate added in proportion to fine tune the materials Tg as needed, a multifunctional cross linking agent like 1,6-hexanediol diacrylate and a free radical initiator. The crosslinking between the photoreactive groups is reversible by irradiation with a different wavelength. The mechanism is based on the fact that Tg of a thermosetting polymer is proportional to its crosslinking density. Thus depending on the crosslinking density achieved during exposure to the proper wavelength of light the Tg can be varied and tailored to meet the specific requirement. Example of photoreactive monomer is 3-(2-benzothiaazolyl)-7-(diethylamino)coumarin[3].

2.3 Electricity

Another method of raising the temperature of the sample above its transition temperature is by incorporating a certain level of conductivity by employing carbon nanotubes in shape-memory polyurethanes. Upon application of an electrical current, the sample temperature is increased as a result of the high ohmic resistance of the composite. Due to rise in temperature of the polymer above its T_{trans} the net points break thus, returning the polymer to its original

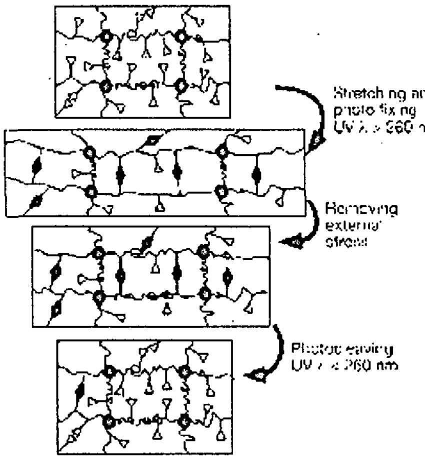

Fig.2 Molecular mechanism responsible for the light-induced shape-memory effect in a grafted polymer network. Chromophores (open triangles) are grafted onto the permanent polymer network (filled circles, permanent cross-links). Photoreversible cross-links (filled diamonds) are formed during fixation of the temporary shape by ultraviolet (UV) light irradiation of a suitable wavelength. Recovery is realized by UV irradiation at a second wavelength.

shape. This effect has been used to trigger the shape-memory effect in an indirect fashion.

2.4 Magnetic field

A novel method of bringing about the shape memory effect is by incorporation of magnetic nanoparticles consisting of Fe(III)oxide cores in a silica matrix into shape-memory thermoplastics enabling remote actuation of the thermally induced shape-memory effect using magnetic fields. Here, the sample temperature is increased by inductive heating of the nanoparticles in an alternating magnetic field. Two different thermoplastic materials have been used as the matrix. The first material was an aliphatic polyetherurethane (TFX) from methylene bis(p-cyclohexyl isocyanate), butanediol and polytetrahydrofuran, while the other was a biodegradable multiblock copolymer (PDC) with poly(p-dioxanone) as the hard segment and poly(ε-caprolactone) as the switching segment. While TFX has an amorphous switching phase, PDC has a crystallizable switching segment. Indirect magnetic actuation has also been realized by the incorporation of Ni-Zn ferrite particles into a commercial ester based thermoset polyurethane[4].

2.5 Mechanical Forces

For some applications it is desirable to have a material which displays a shape memory effect in response to the exertion of mechanical forces. The device comprises a first material which can memorize at least one shape (the permanent shape). This material, in the device, is present in the deformed, i.e. temporary shape. However, it is not required that the deformed state, i.e. the temporary shape is fixed by means of interactions within the material (for example by chemical or physical interactions of soft or switching segments of shape memory polymers) since the device comprises an additional second material fixing the deformed shape. Thus, it is required that the first material is elastic, in order to allow a recovery of the permanent shape after release of the fixation provided by the second material. The device fixes the deformed shape by an additional second material, which may for example be provided in the form of a coating, partially or completely covering the article made from the first material. This second material displays a sufficient mechanical strength and physical integrity so that the temporary shape is secured. However, the second material is selected so that the application of a suitable external stimulus leads to a decrease of the mechanical strength of the second material or to the removal, partially or completely of the second material, so that the deformed shape cannot be maintained anymore. Instead the first material, no longer fixed by the second material, recovers its initial permanent shape, i.e. the deformed shape is lost and the permanent shape is formed. As indicated above a suitable external stimulus in particular is a mechanical manipulation, such as a compression or a tensile stress. The first material must be elastic such as natural or synthetic rubber. A further alternative is the application of a solvent in which selectively only the second material may be dissolved or at least swollen, so that the mechanical fixation is removed. The polymers which can be used for this application are polyvinyl alcohol and polyethylene glycol[8].

2.6 Ion Exchange

The use of polyelectrolytes as soft segments in shape memory polymers has enabled us to use novel external stimuli such as change in pH or ionic strength for triggering the shape memory effect. The polyelectrolytes can be polyacidic like polyvinyl sulfonic acid or polybasic like polyvinyl amine or the polyelectrolytes can also have both acidic as well as basic groups, these are known as ampholytic segments. The temporary shape is fixed by chemical manipulation leading to strong ionic interaction between polyelectrolyte segments in the deformed state. Recovery to the permanent shape can be triggered by changing the chemical composition with respect to the polyelectrolyte segments such as by adding reagents which lead to change in pH or salt exchange reactions. In this way it is possible to replace the bridging divalent or trivalent cation by a monovalent one so that the bridging or crosslinking of different polyelectrolyte segments ceases to exist, due to this the segments have more freedom so that they can return to their original, permanent shape. The temporary shape can return by deforming the polymer and replacing the monovalent cations by di or trivalent cations to fix the temporary shape[1].

2.7 Ultrasound

Ultrasound is another important tool in triggering the shape memory effect. The polymer can be given its temporary deformed state and when ultrasound is applied it can break the interactions between the soft segments relieving the strain causing the object to return to its original shape. But the disadvantage with this method is that it can be used only once as it results in the cleavage of covalent bonds. Polymers responsive to ultrasound are those which have functional groups which can fragment to form stable radicals in response to ultrasound such as triphenylmethane and nitroso groups.

3. Applications

3.1. Environmental tracking

Shape memory polymers can be used as inexpensive humidity and temperature sensors which require no electrical power. These polymers are capable of monitoring both temperature and humidity by incorporating hydrophilic groups like polyethylene glycol (PEG) into the polymer structure. As the temperature rises above the glass transition temperature the polymer gains enough mobility to transport water molecules and by the mechanism discussed in the previous section they become responsive to water as well as temperature. An example of such a sensor is moisture sensitive shape memory polyurethane with PEG as the hydrophilic groups. An advantage of this type of device is that it can be reheated to remove the excess moisture and reset to its deformed position for it to be used again. This device can be used for monitoring food items, ammunition, fuel and other items whose exposure to heat and humidity need to be monitored[6].

3.2 Valves

Shape memory polymers can be used in valves (Fig 3). The valve comprises of a tube A with a pierced internal divider to allow flow. The downstream side of the divider has a plug B made up of shape memory polymer fixed to the circumference of the tube. Application of pressure through the divider causes the plug B to deform until the slit is forced open, thus allowing through flow, the loss of pressure causes the plug to revert back to its original shape in order to get a perfect seal. The advantage of this type of valve is that it is a one way valve with no mechanical moving parts that will open and close automatically under the application and loss of pressure respectively[5].

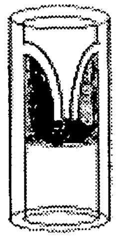

Fig.3

3.3. Healable vehicle impact devices

Shape memory devices are used in crash boxes (Fig 4) in smaller vehicles so that they can absorb low speed impacts and can be repaired simply by heating. The shape memory polymer is used in the form of springs, foams or rollers which absorb the energy of the impact to undergo a certain plastic deformation and these materials can be restored o their original shape by heating above their transition temperature[7].

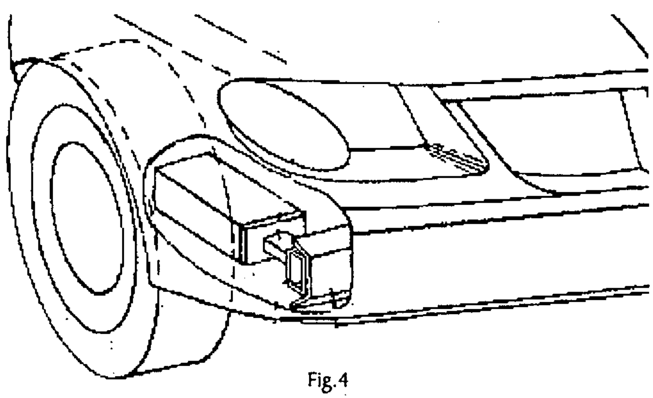

Fig.4

3.4. Biomedical

An attractive application area for shape-memory polymers is their use in active medical devices. First examples include a laser-activated device for the mechanical removal of blood clots (Fig 5). The device is inserted by minimally invasive surgery into the blood vessel and, upon laser activation, the shape-memory material coils into its permanent shape, enabling the mechanical removal of the thrombus (blood clot).

Another application of shape-memory polymers is in stents for the prevention of strokes[4]. Another preferred use is in the area of catheters, as they require high stiffness for insertion but are required to be soft and flexible once inserted. Hence, a polymer is selected which is rigid below body temperature but once it warms up to the body it becomes flexible thus reducing the patients discomfort and complications[9]. Shape memory polymers can also be used in biodegradable intragastric implants that inflate after a predetermined time thus giving the patient a feeling of satiety after less food has been eaten, hence, this can be used to curb the appetite of the obese. Polymers used for these applications are polyurethane based shape memory polymers which have biocompatibility[4].

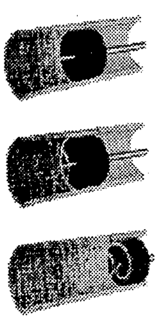

Fig.5

3.5. Biodegradable

The combination of shape-memory capability and biodegradability is an example of multi-functionality in a material. This type of multi-functionality is especially advantageous for medical devices used for minimally invasive surgery. The polymers allow the insertion of bulky implants in a compressed shape into the human body through a small incision. When stimulated within the body, they turn into their application relevant shape. Another example is a biodegradable shape-memory polymer as an intelligent suture for wound closure. Upon actuation of the shape-memory effect, the material is able to apply a defined stress to the wound lips. In both applications, removal of the implant in follow-up surgery is not necessary, as the implant degrades within a predefined time interval. Biodegradability of shape-memory polymers can be realized by the introduction of weak, hydrolysable bonds that cleave under physiological conditions. These hydrolysable bonds cleave to allow the polymer to return to its original shape. Example of the polymers used as biodegradable shape memory polymers is poly(e-caprolactone)dimethacrylate and PEG[4].

3.6. Release Catalysts, Reactants and Additives

Here the shape memory polymer encapsulates the catalyst, reactant or additive. Due to action of external stimulus the polymer releases the catalyst, reactant or additive. As a specific example, diesel fuel additives used to enhance the efficiency of the fuel are encapsulated in the shape memory polymer to ensure that the additive remains floating in the diesel and does not separate and also that it does not degrade. The shape memory polymer chosen for this use is temperature sensitive so at higher temperatures it releases the additive so that it can have the desired effect on the fuel. Care must be taken that the particle size is small enough so that it does not clog the engine[10].

3.7. Textiles

SMPs are finding an increasing use in such areas as clothing where they respond dynamically to changes in heat and moisture levels, ensuring greater comfort for the wearer[4].

3.8. Pressure Sensors

Shape memory polymers can be used as pressure sensors. They detect changes in pressure due to changes in mechanical forces and change their shape when a predetermined amount of pressure has been exerted on it. This can be used to warn us before a disastrous mechanical failure of our equipment occurs[8].

4. Conclusion

The field of actively moving polymers is progressing rapidly. Shape memory polymers play a key role within this field. Fundamental shape-memory research is focusing on the implementation of stimuli other than heat to actuate shape-memory polymers or to actuate them remotely. First examples include the light-induced stimulation of shape-memory polymers or the use of alternating magnetic fields for remote actuation. It is assumed that these methods of stimulation will open up new fields of application. An important application area for shape-memory polymers is in active medical devices and implants, and initial demonstrations have been presented. The application requirements can be complex in this area. Hence, polymers are introduced that can be multifunctional. Besides their dual-shape capability, these active materials are biofunctional or biodegradable.

5. References

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