Abstract: polymers change their shape by changing their

ABSTRACT: Shape memory polymers are versatile classes of polymers which provide form different shapes upon exposure to an appropriate trigger. Shapes are often dual in nature, where one shape is controllably deformed and the other shape is recovered by the trigger. Even though, these polymers were not recently discovered, their applications are still being researched due to their property-tunable nature. Some of the tunable properties include type of trigger used, chemical structure, mechanical properties and biological properties. Their application are numerous for the same reason. In this report, a brief introduction and their mechanisms of changing shapes will be given. This will be followed by some of the recent developments done with these class of polymers in both aerospace and non-aerospace industries. More importantly this report focuses on how these developments aid for commercial and future applications.

Keywords: Shape memory polymers, tunable, trigger, aerospace, property.

INTRODUCTIONShape memory polymers are a class of polymers (abbreviated as SMPs) termed under Smart materials. As their name suggests, they are able to remember and transform to the shape they were produced in (before subsequent deformations and strains) by various triggers like heat, light and to a lesser extent (by indirectly usage of primary triggers like heat) electric fields, alternating magnetic fields, IR irradiation, water immersion etc 1.

These triggers can be enabled for the specific application. These polymers are not supposed to be confused with shape changing polymers which return to the shape they were produced, upon removal of this trigger. The shape memory property termed as “ Shape memory effect” (abbreviated as SME), is not dependant on the polymer properties themselves, but rather its functionalization which is influenced by both its morphology and processing technique. Thus, the polymers change their shape by changing their macroscopic properties only.

This effect comes for the fact that these polymer morphologies are able to store strain energy in the temporary form rather than relax elastically. Their return to the original shape is only facilitated by recrystallization facilitated by an external stimulus 4. Hence, the type of monomers can be changed according to our application, which gives the designers complete control over the mechanical properties of the resulting polymer.

The SME can also be incorporated in alloys, composites (by using specific reinforcements into the SMPs for a specific property) and ceramics, which provides a broad range of applications. Some of them include: smart fabrics, heat-shrinkable tubes for electronics or films for packaging, self-deployable sun sails in spacecraft, self-disassembling mobile phones, intelligent medical devices, or implants for minimally invasive surgery 1. SMPs are preferred over the other shape memory materials due to the high strains they can endure, their low weight and cost 2. This is especially useful for aeronautical and aerospace application. Furthermore, their biodegradability can be tweaked based on chemical structure of their respective monomers and thus, biomedical applications become numerous. SHAPE MEMORY EFFECTThe shape memory effect involves various dynamic thermal and mechanical process that occurs macroscopically in the polymer.

This is illustrated in the figure-1 as a 3D plot of elongation vs the applied stress and the temperature. The general structure of the SMP consists of two types of domains corresponding to the two shapes that can be produced: a temporary/deformed shape and a permanent shape. They are: molecular switches, which determine the former, and netpoints which determine the latter. As one may intuitively guess, there are obviously, two thermal transitions associated with such polymers: Tperm, associated with the netpoints and Ttrans, associated with the switches. The shape memory effect can thus, be described as follows: Firstly, the switches are opened by heating atleast 30 degrees above Ttrans2, and strain is applied on the polymer to achieve the desired shape (given by process-1 in diagram).

Secondly, the polymer is cooled below this temperature to close the switches (given by process-2). Thirdly, the stress is gradually removed to fix the shape (given by process-3). All the above processes collectively, are called “ programming” of the polymer 1.

Lastly, the polymer is heated to the same temperature that was present in the beginning to open the molecular switches again and the original/permanent effect is achieved (given by process-4). A detailed study on the characterization of these polymers based on their thermomechanical effects is done by Yiping et al. and Brent et al. Biomedical application typically employ this shape memory effects directly biodegradable sutures which gradually close the wound as well as degrade owing to the body temperature and degrading atmosphere. TYPES OF SMPs Based on the mechanism of the fixing and the original shape produced by the polymers, SMPs can be classified into 4 categories: Type-1: Type-1 SMPs consist of thermoset networks which are cross-linked with covalent bonds forming an amorphous structure. These type of polymers usually have a sharp Tg above which the cross-links promptly form.

The thermoset networks are obviously, permanent cross-links which offer an excellent degree of shape recovery. Also, the capacity of working can be tweaked easily by changing the amount of cross-links during the recovery phase. However, these polymers have the same disadvantage as conventional thermoset polymers: Reshapability. Examples of these polymers consist of vinylidene monomers compiled as random co-polymers. Another type of polymers that belong to this category are polymers with very high molecular weight (ultra-high-molecular weight) and having a Tg higher than room temperature.

The chemical cross-links in these polymers are replaced with high numbers of entanglements. An example of this type is: Polynorbornene. Type-2: Type-2 SMPs consist of polymers which have formed a semi-crystalline structure cross-linked with covalent bonds. In these types of polymers the temporary shape is constrained and formed by recrystallisation rather than vitrification like in Type-1. Since, their semi-crystalline, they have two transition temperature which can be utilised for shape changes. The change of shape across Tg is sharper in this type since, they undergo only first order transitions.

They also have superior mechanical propertie sowing to their crystalline nature. An example of these types of polymers are semi-crystalline and liquid crystal rubbers. Type-3: Type-3 SMPs are essentially the same as Type-

1 but they have physical cross-links instead of covalent bonds. Owing to this, they have a broader Tg distribution, and thus, have a slight downside to their recovery of shape. This is compensated by their reshapability and properties close to Type-1 polymers. In this type of polymers, both crystalline and amorphous regions can serve as domains for physical cross-linking. There are two temperature transitions for this type.

The lower one is used to fix a temporary shape while the higher one is used to reshape. The two temperature transitions can be the melting point or the Tg of both the segments (hard segment has higher transitions, vice-versa for soft segments). Thus, they have four different temperature where fixing and recovery can be done. Furthermore, hydrogen bonds can be incorporated to adjust the strength of the cross-links.

An example of this type of polymers are blends with Polyurethane which are miscible. Type-4: Type-4 SMPs are the same as Type-2 polymers but again, with physical cross-links. In these polymers, the segment which is soft, crystallises rather than flows at Tg.

Thus, the melting point is used for the shape-recovery mechanism while at Tg, the material automatically fixes its shape by crystallisation. An example of this type of polymer is Polyurethane block PEO polymer, where the Polyurethane serves as the hard segment. Type-4 polymer are the most widely used due to their versatility in fixing and recovering the shapes. DEVELOPMENTS IN RECENT TIMES (NON-AEROSPACE)Developments of SMPs can be broadly classified into 7 categories based on current research being conducted at the topic. Stress recovery: When the SMPs are fixed to their temporary shape, they have stored energy in the form of strain energy.

Recent research was conducted to recover this strain energy and use it for some other purpose. This was done by constraining the SMP before recovery, such that it releases the stored energy during shape-fixing in the form of work. By heating this constrained SMP, we can recover the stored energy completely as work. However, the energy is released in two forms: A useful recovery stress and a non-useful viscous stress. Thus, research is focused on mainly maximizing the recovery stress released, which remains a challenge. Some of the innovations which were tried were: Increasing the modulus of rubber by reinforcement with nano-fillers, by synthesising the material with high cross-linking densities.

For example, reinforcing with carbon nano-tubes (abbreviated as CNTs), increases the factor of recovery stress released by 1. 5. Self-healing: Self-healing of SMPs can be carried out by exploiting the “ Reversible plasticity shape memory effect” 13 (abbreviated as RP-SME). This is essentially the shape recovery of the SMP by heating it, after it has been plastically deformed.

This is done by deforming it in the beginning without an elevated temperature application. This effect can be used for passive self-healing of the polymers, by application of suitable temperatures to the surfaces after a dent or an impact takes place. Note that, this effect cannot heal permanent fractures like cracks and deep dents.

However, when these SMPs are made miscible with free-flowing polymers, then typical self-healing effect can be brought about, where even permanent fractures can be healed. Another approach would be to reinforce the SMPs with highly layered-graphene particles, such that fractures don’t form in the first place. SMPs with small strains: Although, one may imagine the capability of SMPs to deform much higher than shape memory alloys (abbreviated as SMAs) and ceramics to be good, commercially speaking, there are hardly any application which require very large deformations. Also, the mechanical properties offered by SMAs is much higher than SMPs making their use much more economical.

Nevertheless, SMPs are advantageous in-terms of their better processability. SMPs with small strains have found their way in applications like adhesives and colour changing SMPs. For example, a bilayer adhesive can be made by having a SMP backing layer on a sticky elastomer layer. Due to the thermal mismatch between the layers, the adhesive is curved when placed on a substrate.

The adhesive can be deformed to achieve adhesions as high as 200N/cm2 and can be removed from adhesion by providing heat. Thus, the adhesive provides a very versatile form of adhesion provided it has a small strain effect. Shape memory effect on surface: This effect has the same phenomenon expressed in the shape memory effect, but the deformation and the recovery phases are on the surface rather than on the bulk. This accounts for faster shape-recovery. This effect is utilised on photo-lithography and micro-contact printing owing to its “ rewritable” nature. An example of this would be in the creation of localised wrinkle structures to capture any macroscopic object. Typically, a localised indentation is done on an SMP surface, followed by a coating of a thin-metallic strip on top of this surface.

When recovery of the SMP surface is done via heating, wrinkles are formed where the indentation took place which correspond to certain wavelengths of visible light. Thus, the indentation can be clearly seen and quantified. Two-way shape memory effect: Typically, SMPs have no directional control in their mechanism. That is, going from the permanent shape to the deformed shape always requires a precalculated deformation. Two-way shape memory polymers, typically are Liquid crystal elastomers (abbreviated as LCEs) and hydrogels which are typically used in LCDs. One of the drawbacks of these types of polymers is their complicated chemistry during processing.

Triple shape memory effect: SMPs typically have only two shape memories (a temporary shape given by a deformation and a permanent recoverable shape based on heating). However, SMPs can be tuned and synthesised in such a way that they possess two or more temporary shapes and one permanent shape. For example, this can be done by cross-linking a semi-crystalline polymer and distributing the transition temperatures in such a way that three or more shapes can be formed.

Due to this, a wide number of applications can be created. Shape memory by other triggers: In most applications, heat cannot be supplied directly to the SMPs to activate their recovery process. Thus, SMPs must be synthesised in such a way that another actuation/trigger produces the necessary effect or the actuation enables the application of heat. These include triggers by IR radiation, magnetic induction heating which indirectly/remotely apply heat. Another type of these polymers is light induced SMPs which are actuated by supplying a specific wavelength of light.

Water-immersion of the SMPs can also be used as a trigger for shape recovery. The SMP can be chemically modified in-such a way that immersion in water causes a decrease in the Tg thus, favouring the shape memory mechanism. This is especially useful in biomedical applications where, an aqueous atmosphere is prevalent. SMPs CHANGING THE SHAPE OF FUTURE AEROSPACE TECHNOLOGIESThe capability of SMPs to have lesser weight, cost and better shock resistance to deployment have enabled their entry into aerospace structures.

Also, changing atmospheric conditions which needs to be taken into consideration during flight is the primary reason, SMPs have started gaining popularity in aeronautical structures as well. Morever, SMPs can be reinforced with specific fillers to withstand the harsh environments of space and flight atmospheres which is cost-effective. Some of the research conducted in this respect is given below: SMP composite hinges: In deployment structures of space, usually the shock encountered during deployment is large. The hinges usually serve as the main navigation of the deployment. They transfer the loads from the deployable structures to the main body of the spacecraft.

Thus, they suffer high shocks and almost always have a delay in precision. Using, SMP composite hinges would reduce the amount of mechanical complexity needed to construct the hinge and would provide precise landingsSMPC booms: The booms in deployable structures serve as the main load-bearing components in the spacecraft. Metallic booms are thus, complex in their design, control and are very heavy. Thus, SMPC booms are being researched as alternative designs. These new types of booms can be divided into three types STEM booms, Coilable truss booms and foldable truss booms. STEM booms are expanded storable tubular extendible member booms. As their name suggests, they have a bigger cross-sectional area and simpler structures compared to other types of booms, however, their development is still in the prototype stages.

Coilable truss booms are coiled and incur a huge strain energy in their components during deployment. However, it has the lowest weight among the three types of booms and moderately simple structure. The foldable truss booms are the commercially used booms. A three semi-cylindrical shaped EMC longerons packed into a ‘ z’ shape was used for the Falconsat-3 mission. However, movement and fastening of these types of trusses still remains a problem. Solar arrays and deployable panels: Solar arrays are used to provide energy from the Sun to the spacecraft/deployable structure. The arrays are however, not used before launch for drag related reasons and thus, need to be deployed after orbit.

This requires the SME and thus, usage of SMPCs. The SMPCs are primarily used as hinges and supports for these arrays to provide quick, reliable, cost-effective and lighter deployment. SMPC reflector antennas: These antennas are used for traditional antenna functions.

They are signal transmitters and receivers. Their deployment mainly depends on the antenna thickness and precision. To satisfy both these criteria, SMPCs are the only option to prevent a complex design. Morever, before deployment, the weight and space occupied by the antennas are also important motivations to an SMP inspired structure. Morphing structures: Morphing structures are being developed not only for spacecrafts but for, UAVs as well.

The motivation behind using morphing structures is the capability of using different shapes for structures under different environmental conditions as it is the most effective way to reduce damage and weight considerations in aircrafts and spacecrafts. Several prototypes have been developed for morphing structures mainly in the fields of ‘ morphing wings’. For example, one of the wings developed by NASA, is expected to have a 300% increase in wing area based on the flight conditions 2. Expandable lunar habitats: In spacecrafts, there is always a definite shelf life for the spacecraft to operate in orbits.

This is due to the harsh environments (mostly due to UV and gamma rays) present in space. Thus, the spacecrafts are usually fitted with shelter-like structures to increase this shelf-life. Thus, SMPCs find their way into these structures as they maximise this area better than conventional structures whilst also adding lesser weight.

CONCLUSIONSMPs have several advantages that incur their use in various applications. These include lesser weight, lesser complexity in design, capability to form shapes with respect to the given environment in flight, lower cost and capacity to tailor its properties based on the manufacturer’s given interest. Their development is expected to increase much more in the near future, especially in aerospace applications.

Furthermore, the ability of the SMPs to perform complex movements by themselves, and their ability to be triggered to perform these movements based on several types of triggers, enables their usage in biomedical and commercial applications as well. However, the fact that there are limited numbers of temperature resistant SMPCs that can be used in the space environment and their subsequent commercialisation for biomedical applications remains a problem for their use.