# Study on Electro Active Shape Memory Polymeric Composites and

# **Its Applications**

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## Abstract:

Shapememory polymers (SMPs) are of great interest in basic research and technological innovation. SMPs are typically only powered by external heat. As a result, electroactivate SMP has been discovered, and its significance will grow in the coming years.

The advancement of electro-activate SMP composites is the focus of this paper. The various types of fillers used in the preparation of composites and their applications are highlighted in particular.

As a result of the early stage work, the electroactivate SMP has matured. This paper continues the recent development of shapememory polymer in undergoing e lectroinduced shape recovery, and it summarises the growth of electro-activate shapememory polymer research.

Key words: Shape memory polymers, Composites, Electro active composites.

# Introduction:

Shape memory materials are a type of material that can recover its original shape after deformation. They can retain a permanent or temporary shape when the right combination of mechanical strain and stimulus is applied [1-5]. This is known as the shape memory effect (SME). Shape memory polymers exhibit shape memory effect when deformed and heated to a temperature higher than the switching temperature. In general, this can be accomplished by directly heating the polymer. When exposed to an appropriate stimulus, several polymers can be distorted and fixed into a new shape that can afterward be returned to the initial. Polymers with this shape memory effect (SME) have promising utility in biology and medicine, soft robotic systems, and astronautics. They have been investigated for use as auto stents, identity wound sutures, systems for drug delivery, transportable devices, thermal packaging films, smart fabrics, stepper motors, and other goods. They

prevent chain sliding while the system is distorted, which is needed for the SME. These tie linkages d o not always have to be permanent, such as irrevocable cross links. Reversible bonds can also be used to achieve efficient SME as long as they can sustain their original shape .

By applying stress, the polymer is heated above its Tg and deformed into a desired shape. After that, the temporary shape is fixed by lowering the temperature until the polymer network freezes. Finally, shape recovery is aided by raising the temperature above the Tg, giving the polymer chains enough energy to move and rearrange according to their maximum conformational entropy. (1,5) The tie links in the polymer network play an important role here. They keep the chain from slipping as the system is deformed, which is required to achieve the SME. These tie linkages do not have to be permanent, like irreversible covalent bonds. Reversible bonds can also be used to achieve efficient SME.

SMPs are mechanically functional smart materials that have recently attracted much interest for biomedical applications, such as sutures [5], catheters [6], the repair of cardiac valves [7], as well as for drug delivery [8,9] and cardiovascular [10,11], orthodontic, and surgical applications [12-13]. .Temperature variation has been used for activation stimulus because of the intrinsic thermal phase transition occurred in polymers the required properties of the SMPs can be achieved by an electric or magnetic field, by light or by using solution [6-8].There are different types of SMPs like e thermoplastic and thermoset, stable to biodegradable, soft , hard, and from elastic to rigid, which depends on their structural units. These materials can store up to three different shapes in their memory and their recoverable strains of above 800%

Infinite possibilities can be created when shape memory structures are built-in electronics. Going to support techniques for the selffolding origami energy harvesting system, for example, are maturing.One of the most important applications of SMPCs was thought to be selffolding. Traditional folding hinges, however, were designed to be too 1 arge due to the lower output force of SMPCs, resulting in large deadweight losses, limiting their commercial applications.

SMPs have been used in various biomedical applications, like sutures, fixing cardiac valves, in drug delivery [8,9] and cardiovascular ,orthodontic, and surgical applications

[10-12].different external stimuli like electrical, light, and electromagnetic fields have been reported

When electrical conductive materials are added into thermal- active SMPs, the current passing through them can induce Joule heating and trigger shape recovery.

Shape memory polymers have various advantages, such as large deformation, low cost, light weight, adjustable glass transition temperature [7–10].

Due to the low dimensionality and high electrical conductivity, graphene is a very attractive alternative for the preparation of shape memory composites [11-12].

On the other hand addition of chopped fibreglass, Kevlar fiber and woven fiber glass on thermoplastic shape memory polyurethane (SMPU) exhibited that fibers can significantly raise the strength and stiffness of the composites [12-13], along with these categories, the SMP nano composites whose SME is induced by joule heating using electricity have been at the front position In contrast to the direct heating methods, joule heating method has various benefits, such as convenient, consistent heating and remotely convenient, which is particularly useful for applications where direct heating is not possible (e.g., in self-deployable aerospace structures, actuators, and biomedical devices). For joule heating, shape memory polymeric materials must be electrically conductive. Consequently, the polymers were packed with adequate electrical conductive nanofillers. The conductive nanofillers that have been expansively reported in the literature include carbon nanotubes (CNTs), metallic powders, conducting polymers, and carbon fibers. In which CNTs and functionalized CNTs with some organic groups such as carboxylic, amine and hydroxyl groups have approach more and more into the centre of attention in recent years [14-15]. on the other hand, metals such as Ag, Cu, and Pt decorated CNTs have also involved important attention for their better electrical and thermal properties, which have leading position to make the fast actuation easy in SMP nanocomposite induced by electrically resistive heating. Recently, it was reported the polymer nanocomposite of polyurethane (PU) and Ag and Cu decorated CNTs and the electrically resistive heating-driven shape-memory end product of the PU/M-CNTs nanocomposite system.

In their research, they found that Ag and Cu decorated CNTs reinforced polyurethane (PU) nanocomposite showed extraordinary recoverability of its shape at lower applied dc voltages because of a significant enhancement in the thermal and electrical conductivity of the PU/M-CNTs nanocomposite. [16], [17]. It has been reported that carbon fiber reinforced epoxy laminates are proficient in rising the stiffness of epoxy SMP resins [18], [19].

In a paper the effect of graphene concentration on the shape memory composites was studied and their mechanical, dynamic mechanical analysis (DMA), electrical properties, and thermoelectric responsive shape memory test reported. The results show that when graphene concentration was 2 wt %, the bend strength of the composite enhanced by about 47% with a storage modulus higher than other composites.[20].

For applications of SMP, the ideal driving methods must be selected according to physiological environment. In human body, physiological pH is variational in different regions. In addition, different from physiological environment, pH changes usually occur in the whole biological systems.

This paper describes the different types of fillers for development of shape memory polymeric composites and explores their current and potential applications.

#### SMP prepared by using conductive fillers

Graphite, due to its exceptional electrical mechanical and optical properties, has been gaining substantial attention as one of the most capable industrial materials. Different techniques have been used to improve graphite's dispersion, like chemical exfoliation [22] which significantly decrease its electrical conductivity. If graphite oxide (GO) is reduced, then the reduced graphite oxide (RGO) is still less conductive than pure graphite[20-22]. In addition, the high conductivity of graphite is also mainly compromised by the inter-sheet contact resistance. The three-dimensional (3D) graphite structure was deemed to lessen the aforesaid problems presently hindering the performance of graphite composites. The 3D graphite system is continuous and exhibits higher conductivity due to increasing inter-sheet junctions.

Despite their superior performance, thermoset shape memory polymers are limited in their application due to their low mechanical strength and shape recovery stress.To address this issue, researchers filled SMPs with high modulus inorganic or organic fillers to improve their mechanical properties. Carbon materials, such as carbon black, carbon fibre, carbon nanotubes, carbon nanopapers, graphene, and their combined nanofillers, are the most commonly used fillers it was reported that carbon fillers have found numerous applications in polymer materials, resulting in a variety of fascinating multifunctional composite materials. Electrical properties are one of the many material properties of composite materials reinforced with carbonaceous material. Carbon fibres are also known to have excellent electrical conductivity and mechanical properties. Doping carbon fibres into SMPs thus improves not only the mechanical properties of SMPs, but also their conductivity. Electroactive SMPs can be made from S MPs with high conductivity. Electrical response is a very convenient stimulus, particularly in applications where direct heating is inconvenient or difficult to achieve.

### SMP prepared by using carbon nanotubes

chemically surface-modified multi-walled carbon nanotubes (MWNTs) in a mixed solvent of nitric acid and sulfuric acid were employed to prepare electro-activate SMP and for the enhancement of interfacial bonding between polymers and conductive fillers [23]. The electrical conductivity of composite films, calculated by the four point probe method, was in the range of 10<sup>-3</sup> S cm for samples having 5 wt.% modified MWNT concentration. It was reported that with the rise in the quantity of modified MWNT concentration, the electrical conductivity also increased which is due to the increased defects in the lattice configuration of carbon–carbon bonds .

The electrical conductivity of composite films measured using the four point probe method was in the order of  $10^3$  S cm for samples containing 5% modified MWNT. The electrical conductivity increased as the amount of modified MWNT content increased. Furthermore, surface modified MWNT had a significant effect on electrical conductance. At the same filler content, the electrical conductivity of this surface-modified MWNT composite was lower than that of untreated MWNT composites. This is due to the acid treatment's increased defects in the lattice structure of carbon-carbon bonds formed on the nanotube surface

In practise, the severe modification of the nanotubes reduced their electrical conductivity significantly. As a result, both mechanical and electrical properties were improved.

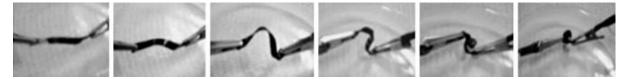


Fig. 1. Electro-activate shape recovery behaviour of PU-MWNT composites. Sample undergoes the transition from impermanent shape to lasting in 10 s when a steady voltage of 40 V was applied.

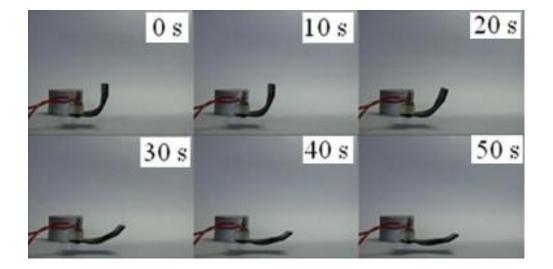
# SMP prepared by using conductive carbon nanofiber

A conductive carbon nanofiber (CNF) paper was used for the actuation of shape recovery of a shapememory polymer (SMP) prepared by electrically resistive Joule heating. The CNF paper was prepared by using physical vapor deposition method it was reported that the electrical properties of CNF paper with the proper weight concentration was suitable for SMP actuation by electrical resistive heating with a low electrical voltage [24].

The electrically induced shapememory effect is exemplified in Fig. 2 for SMP filled with 5 wt.% CB and 2 wt.% SCF, in which a change in shape from momentary

flexural form to permanent plane stripe shape occurs within 50 s when a constant voltage of 24 V is imposed. [25]

The rate of shape recovery was hugely affected by the amplitude of the applied voltage as well as the electrical resistivity of the SMPC.[25]



## SMP filled with electromagnetic filler

It was reported that on addition of surface-modified super-paramagnetic nanoparticles into shapememory polymer matrices, remote

actuation of complex shape transitions by electromagnetic fields is possible. The thermosetting composite prepared by using oligo (e-caprolactone)dimethacrylate/butyl acrylate having 2 and 12 wt.% magnetite nanoparticles served as nano-antennas by

magnetic field heating. When ferromagnetic fillers are added in SMPs, magnetic- active SME can also be obtained by inducing heat through magnetic field. Water molecules can be employed to decrease the switch temperature of the SMPs to bring shape recovery of deformed SMPs. Light absorbed by distorted SMPs can also raise SMP temperature to the switch transition temperature, to generate shape recovery [22].

# SMP prepared by using Nickel

Magnetic particles when added into SMP, then they formed chains by applying magnetic field in the cured process. Electrical resistance is considerably decreased in this method. SEM images showed that single chains start to be formed at 1 volume fraction percent of Ni. On increasing Ni concentration, bundles were formed, and finally no clear apparent Ni chain was found [26].

#### **Applications:**

SMPs with indirect heating can be developed in different routes and have numerous applications in various fields. The thermo responsive shape recovery of SMPs is induced by straight heating the polymer to a temperature higher than the switching temperature.

Electrical conductivity can be increased when a fixed amount of electrical conductive materials are added in to thermally- active SMPs. When a current passes through the arrangement of conductive materials within the SMPs, the induced Joule heating may enhance the internal temperature over the switch transition temperature of the polymer, and activate shape recovery.

SMPs can be employed in numerous applications like healthcare and in the stitches [19], in robotics, actuators for synthetic muscles

Internal joule heating is one more process to induce shape changes on applying a current. In which an electrically conductive material, such as, carbon-based additives have been used to produce electrically-responsive shape-memory composites [10-20]. The standard way of getting the percolation threshold high electrical conductivities includes the systematic homogenisation of the filler in the polymers. [14]. furthermore, these materials often show poor mechanical properties, with strengths of a few MPa to kPa and their electrical conductivities remain limited (lower than a few S/m).Hence , high voltages (that can be above 90 V) are required for actuation [21–23] graphene gaining attraction for the fabrication of shape memory composites due to its low dimensionality and high electrical conductivity.

SMP composites are now used as vibration control materials; as they absorb vibration energy capably by shape deformation at its glass transition temperature ( $T_g$ ).

Fabrication of biocompatible and biodegradable SMPs medical devices is of immense interest due to their crucial impact on human health. This involves scaffolds for tissue engineering, implants for minimally invasive surgery procedures, self-retractable and removable stents, drug delivery systems. Shape memory polymeric composites have wide applications in the production of smart materials and structures manufactured by three-dimensional technique (3D printing) which is an extra striking choice for the near future. The deviation in their structural properties by external stimuli gave the

appearance of novel '4D printing' process. This led the production of actuators for soft robotics, selfevolving structures, anti-counterfeiting system, 4D bio-printing materials [27].

In a paper Ag/CCF was created using an electroless plating method, and the silver coating appears to be uniformly deposited on the CCF. When the composite is doped with 7.2 wt% Ag/CCF, the thermal conductivity of the composite can reach 2.50 W/(mK), the surface resistivity can reach 6.19 102 cm, and the volume resistivity can reach 9.51 103.[26] The mechanical properties, storage modulus, and Tgs of the composites all increased as the Ag/CCF content was increased. When the Ag/CCF content exceeds 1.8 wt%, the composite have an excellent electroactive shape memory effect. The shape recovery rate of the composite increased with increasing applied voltage and Ag/CCF content; the shape recovery ratio exceeded 92%, and the shape fixation rate exceeded 95%.[26-28]

#### **Conclusions:**

Numerous studies have been conducted over the last decade on the mechanism,

shape recovery, and electrical properties of SMP filled with conductive filler, as well as the corresponding applications. The electroactivate SMP has matured as a result of the early stage work. This review of shapememory polymer continues its recent development in undergoing

electroinduced shape recovery, and it sums up the growth of electro-activate shape-

memory polymer research

As a stimulus, electricity enables resistive actuation of shapememory polymer filled with conductive f illers.External heating, which is unsuitable for many applications and is commonly used to stimulate conventional shapememory polymers, can thus be

avoided. Shapememory polymer composites' technological potential is expanded by electric triggering.

Some technological and design limitations remain still unexplained like : inadequate choice of polymer to be used, hybrid components fabrication, presence of micro structural defects. The design of self-cleaning, self-healing and self-adapting SMPs materials is gaining enlarged attention over the last few years due to environmental concerns. These materials are suitable for the amplification of load-bearing aircraft components, self-cleaning and light-guided windows, polymer solar cells, smart textiles, bionic robot, etc. The production of nano composites with multi-step responsive self-based capabilities and improved durability will further improve the performance in the field. However none of those polymer systems are commercially available at present and hence the development of new polymers and polymeric blends is needed.

In the industry, currently these materials find application in automobile engineering (seat and adaptive lens assemblies,

reconfigurable storage bins, airflow control devices, etc.), polymer solar cells, food packaging for thermal and light sensitive products, reflectors, smart textile such as life jacket, floating wheels. Despite their multi-functionality and large range of properties the direct transfer from the laboratory to industrial scale remains difficult. In this direction the main problems are the final SME complexity is mainly influenced by many parameters like programming steps and the triggering procedure parameters.

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#### References

[1] Lendlein A, Langer R. Biodegradable, elastic shape-memory polymers for potential biomedical applications. Science, 2002, 296 (5573): 1673–1676

[2]. Kratz K, Voigt U, Lendlein A. Temperature-memory effect of copolyesterurethanes and their application potential in minimally invasive medical technologies. Advanced Functional Materials, 2012, 22(14): 3057–3065

[3]. Enriquez-Sarano M, Schaff H V, Orszulak T A, Tajik A J, Bailey K R, Frye R L. Valve repair improves the outcome of surgery for mitral regurgitation: A multivariate analysis. Circulation, 1995, 91 (4): 1022–1028

[4]. Alarcón C D H, Pennadam S, Alexander C. Stimuli responsive polymers for biomedical applications. Chemical Society Reviews, 2005, 34(3): 276–285

[5]. Schmaljohann D. Thermo- and pH-responsive polymers in drug delivery. Advanced Drug Delivery Reviews, 2006, 58(15): 1655–1670

[6]. Xue L, Dai S, Li Z. Biodegradable shape-memory block copolymers for fast self-expandable stents. Biomaterials, 2010, 31 (32): 8132–8140

[7]. Yakacki C M, Shandas R, Lanning C, Rech B, Eckstein A, Gall K. Unconstrained recovery characterization of shape-memory polymer networks for cardiovascular applications. Biomaterials, 2007, 28(14): 2255–2263

[8]. Small W IV, Singhal P, Wilson T S, Maitland D J. Biomedical applications of thermally activated shape memory polymers. Journal of Materials Chemistry, 2010, 20(17): 3356–3366

[9]. Scott, T. F., Draughon, R. B. & Bowman, C. N. Actuation in crosslinked polymers via photoinduced stress relaxation. Adv. Mater. 18, 2128–2132 (2006).

[10].Yi, D. H., Yoo, H. J., Mahapatra, S. S., Kim, Y. A. & Cho, J. W. *The synergistic effect of the combined thin multi-walled carbon nanotubes and reduced graphene oxides on photothermally actuated shape memory polyurethane composites*. J. Col. Inter. Sci. **432**, 128–134 (2014).

[11]. Schmidt, A. M. Electromagnetic activation of shape memory polymer networks containing magnetic nanoparticles. Macromol. Rapid Commun. 27, 1168–1172 (2006)

[12]. Xiao, X. *et al.* Shape memory polymers with high and low temperature resistant properties. *Sci. Rep.* **5**, 14137; doi: 10.1038/srep14137 (2015).

[13] Yongkun Wang, <u>Wenchao Tian</u>, <u>Jianqiang Xie</u>, and Yan Liu Thermoelectric Responsive Shape Memory Graphene/Hydro-Epoxy Composites for Actuators <u>Micromachines (Basel)</u>. 2016 Aug; 7(8):
145. Published online 2016 Aug 22. doi: 10.3390/mi7080145

[14] Velasco-Santos C, Martinez-Hernandez AL, Fisher FT, Ruoff R, Castano VM. Improvement of thermal and mechanical properties of carbon nanotube composites through chemical functionalization. Chem Mater 2003;15(23):4470–5.

[15] Geng HZ, Rosen R, Zheng B, Shimoda H, Fleming L, Liu J, et al. Fabrication and properties of composites of poly(ethylene oxide) and functionalized carbon nanotubes. Adv Mater 2002;14(19):1387–90.

[16] W. Small, P. Singhal, T. Wilsona, D.J. Maitland, Biomedical applications of thermally activated shape memory polymers, J. Mater. Chem. 20 (2010) 3356–3366.

[17] A. Nakasima, J.R. Hu, M. Ichinose, H. Shimada, Potential application of shape memory plastic as elastic-material in clinical orthodontics, Eur. J. Orthod. 13 (1991) 179–186.

[18] Y.C. Jung, J.W. Cho, Application of shape memory polyurethane in orthodontic, J. Mater. Sci. Mater. Med. 21 (2010) 2881–2886.

[19] C.M. Yakacki, R. Shandas, D. Safranski, A.M. Ortega, K. Sassaman, K. Gall, Strong, tailored, biocompatible shape-memory polymer networks, Adv. Funct. Mater. 18 (2008) 2428–2435.

20. Raccichini, R., Varzi, A., Passerini, S. & Scrosati, B. The role of graphene for electrochemical energy storage. *Nat. Mater.* **14**, 271–279 (2015).

[21]. H.M. Chen, Y. Li, Y. Liu, T. Gong, L. Wang, S.B. Zhou, Highly pH-sensitive polyurethane exhibiting shape memory and drug release, Polym. Chem. 5 (2014)

[22] Schmidt AM. Electromagnetic activation of shape memory polymer networks containing magnetic nanoparticles. Macromol Rapid Commun 2006;27(14):1168–72.

[23] J.W. Cho, J.W. Kim, Y.C. Jung, N.S. GooElectroactive shape-memory polyurethane composites incorporating carbon nanotubes Macromol Rapid Commun, 26 (5) (2005), pp. 412-416

[24] Lv HB, Leng JS, Du SY. Electro-induced shape-memory polymer nanocomposite containing conductive particles and short fibers. In: Proceedings of 15<sup>th</sup> international symposia on smart structures and materials, vol. 6932. San Diego: SPIE; 2008.

[25] Lv HB, Leng JS, Du SY. Electro-induced shape-memory polymer nanocomposite containing conductive particles and short fibers. In: Proceedings of 15th international symposia on smart structures and materials, vol. 6932. San Diego: SPIE; 2008.

[26] Leng JS, Huang WM, Lan X, Liu YJ, Du SY. Significantly reducing electrical resistivity by forming conductive Ni chains in a polyurethane shape-memory polymer/carbon-black composite. Appl Phys Lett 2008;92:204101.

[27]. Wang Y, Chen Z, Niu J, Shi Y, Zhao J, Ye J, Tian W. Electrically responsive shape memory composites using silver plated chopped carbon fiber. Frontiers in Chemistry. 2020 May 8;8:322.

[28] Koerner H, Price G, Pearce N, Alexander M, Vaia RA. Remotely actuated polymer nanocomposites-stress-recovery of carbon-nanotube-filled thermoplastic elastomers. Nat Mater 2004;3(2):115–20.