Review Article

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Shape memory polymer/graphene nanocomposites: State-of-the-art

Abstract: Graphene is one of most exceptional type of nanocarbon. It is a two-dimensional, one atom thick, nanosheet of sp^2 hybridized carbon atoms. Graphene has been employed as nanofiller for shape memory polymeric nanocomposites due to outstanding electrical conductivity, mechanical strength, flexibility, and thermal stability characteristics. Consequently, graphene nanostructures have been reinforced in the polymer matrices to attain superior structural, physical, and shape recovery properties. This review basically addresses the important class of shape memory polymer (SMP)/graphene nanocomposites. This assessment is revolutionary to portray the scientific development and advancement in the field of polymer and graphene-based shape memory nanocomposites. In SMP/graphene nanocomposites, polymer shape has been fixed at above transition temperature and then converted to memorized shape through desired external stimuli. Presence of graphene has caused fast switching of temporary shape to original shape in polymer/graphene nanocomposites. In this regard, better graphene dispersion, interactions between matrix-nanofiller, and well-matched interface formation leading to high performance stimuli-responsive graphene derived nanocomposites, have been described. Incidentally, the fabrication, properties, actuation ways, and relevance of the SMP/graphene nanocomposite have been discussed here. The potential applications of these materials have been perceived for the aerospace/automotive components, self-healing nanocomposites, textiles, civil engineering, and biomaterials.

Keywords: stimuli-responsive, graphene, nanocomposite, actuation, application

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1 Introduction

Shape memory polymers (SMPs) form a continuously evolving class of smart materials (1). The SMPs possess propensity of shape recovery effect (2,3). Characteristically, the SMPs display shape change in response to heat, light, electricity, pH, moisture, and other external stimuli. SMPs retain two or three shapes, and the transition between the shapes is induced by the temperature (4,5). Besides the temperature change, the shape change in SMPs can also be triggered by an electric or magnetic field, light, or solution media. The shape memory effect depends on the structural units constituting the polymers. Efficient SMPs based on the physically/covalently cross-linked polymeric materials have been developed. Both the thermoplastic and thermosetting polymers have been used in SMPs. Among polymers, the epoxy (6), segmented polyurethane (7), polyester (8), polystyrene (PS) (9), and natural polymers (10) have the capability of shape recovery. Consequently, the SMPs show thermo-responsive (11), electro-active (12), photo-active (13), magnetic-active (14), water/moisture-active (15), pH-sensitive (16), ion-sensitive (17), and other effects (18). The SMPs have found applications in aerospace, automotive, engineering structures, electronics, and biomedical fields (19–22). Among all the SMPs, the thermo-responsive and electro-active effects have been most extensively considered in literature (23). To develop the stimuli-responsive nanocomposites, the SMPs have been reinforced with various nanoparticles such as graphene (24), carbon nanotube (25), nanodiamond (26), and several metal and inorganic nanoparticles (27). Graphene is an important two-dimensional nanocarbon nanofiller employed for the stimuli-responsive nanocomposites (28). Graphene is one atom thick nanosheet of sp^2 hybridized carbon atoms (29,30). Initially, the single-layer graphene was theoretically studied by Wallace in 1947 (31). It has been pondered as the thinnest material on Earth. The sp^2 hybridized carbon atoms are hexagonally packed in the honeycomb crystal lattice structure. Graphene possesses outstanding optical transparency, electrical conductivity, thermal stability, mechanical strength, and thermal conductivity

properties. The word "graphene" is derived from graphite with the suffix "-ene". The graphene nanosheets stack together via weak van der Waals forces. High performance SMP/graphene nanocomposites have been attained due to the large specific surface area, and exceptional physical properties of graphene (32). Inclusion of graphene not only endorses the shape memory actuation, but also improves the mechanical properties, thermal stability, glass transition temperature, electrical properties, and thermo-mechanical properties of the nanocomposites.

In this review, the imperative class of SMP/graphene nanocomposites has been discussed. Essential aspects of the SMPs, nanocomposites, polymer/graphene nanocomposites, and relevant solicitations have been sightseen (Figure 1). Hence, this is an all-inclusive and up-to-date review on the SMP/graphene nanocomposites portraying essential aspects on the synthesis/properties-to-technical potential. To the best of knowledge, the polymer/graphene nanocomposites have been scarcely reviewed comprehensively in literature. Therefore, the review article is a groundbreaking contribution in the field of shape memory graphene-based nanomaterials. Subsequently, the forthcoming progressions in the field of SMP/graphene nanocomposites are not possible for the researchers before getting the prior knowledge of accumulated literature on these nanomaterials.

responsive polymers revealed chain movements at the transition temperature (T_{trans}), i.e., usually above the glass transition temperature of the polymer (T_g) (36). The temporary shape of the sample is fixed by heating, molding, and cooling at low temperature (37,38). The original shape of the sample is recovered by heating the temporary shape at T_{trans} (39). Figure 2 reveals important steps involved in the shape memory effect.

The polymer shape is fixed at temperature above T_g, i.e., shape fixity process (40). Subsequently, the fixed shape returns to the memorized shape through heating at T_{trans} (41). The segmented polymers have been considered as the most successfully used polymers for shape memory. During the shape memory, usually polymer network is formed between the polymer chains to form the switchable segments (42). Polyurethane is a significant type of segmented SMP (43). Polyurethanes possess the thermo-elastic phase transformation at their T_g (44). Various other polymers have also been used as the SMPs such as the epoxies, polyesters, polyamide, PS, etc., (45,46). The SMPs have found potential applications in electronics, motors, aerospace, civil engineering (47), packaging, textiles, biomedical, and other technical relevant fields (48).

2 SMPs

SMPs are a type of stimuli-responsive or smart polymer (33). Initially, the SMPs have been recognized for the shape recovery from the temporary shape to the permanent shape upon the application of an external stimuli of heat, light, electricity, magnetic field, pH, moisture, etc. (34). Conventional SMPs have been studied for the shape change in response to heat (35). Such SMPs are referred as thermally induced or thermo-responsive polymers. The thermo-

3 Stimuli responsive polymeric nanocomposites

Significant thermoplastic SMPs recognized are polyurethane and PS (49,50). High-performance epoxy-derived SMPs have also been stated (51,52). These polymers are thermo-responsive (53), electro-active (54), light-active (55), pH sensitive (56), and moisture sensitive (57). The stable shape memory network is formed in the polymers to recover the original shape (58,59). The SMPs possess the optimal
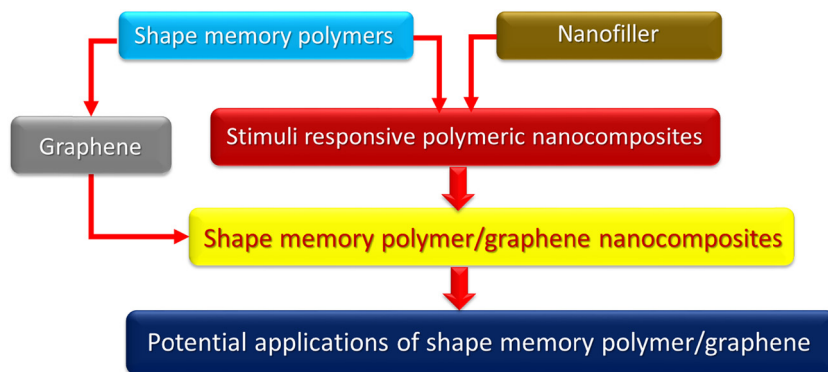

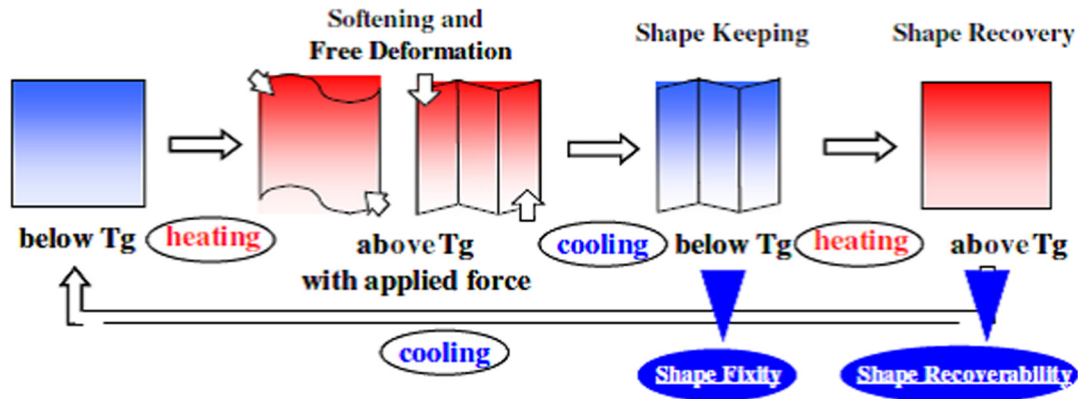**Figure 1:** Schematic of the overview of shape memory polymer/graphene nanocomposites.

Figure 2: Shape memory steps: (1) memorized shape after molding and cooling; (2) free deformation due to rubber elasticity of amorphous portion by heating over T_g under an applied force; (3) shape fixity by cooling below T_g; and (4) shape recovery by heating over T_g (40). Reproduced with permission from Elsevier.

melting transition temperature, glass transition temperature, crystallization temperature, and liquid crystal transitions (60). In addition to the SMPs, the shape recovery nanocomposites have also been focused. Diverse fillers and nanofillers have been used with the SMPs to form the composites and nanocomposites (61). Figure 3 shows the thermo-mechanical cycle of a thermo-responsive SMP. The important steps involved are the formation of sample original shape, heating above T_{trans}, deformation through an external force, shape fixing, and heating for the original shape recovery. Figure 4 shows shape memory process of the bisphenol A diglycidyl ether epoxy and epoxy matrix composite filled with the glass fiber filler. Inclusion of 50 wt% glass fiber in the epoxy matrix led to the high shape recovery rate (41).

A notable way of improving the shape memory effect of the polymers is the incorporation of nanoparticles like carbon nanotube, graphene, nanoclay, and inorganic nanoparticles. The carbon nanoparticles have been used to supplement the electro-active and thermo-responsive effects (62). In this regard, the homogeneous nanofiller dispersion is a challenging factor to develop the high-performance shape memory materials. The solution mixing, melt blending, and other processing techniques have been used to form these nanocomposites (63). The nanocarbon functionalization improves the compatibility between the SMPs and the nanoparticles (64). The nanocarbon functionalization processes have been used to improve the shape memory effect through improved cross-linking reactions (65). Increase in the nanofiller contents also enriches the shape memory effect of the materials (66). Among nanocarbons, carbon nanotube has promoted the dispersion and prevented the aggregation or coagulation in the shape memory matrices. Carbon nanotube has been efficiently reinforced in the epoxy-based nanocomposites to enhance the stress relaxation at T_g (67). The poly(vinyl alcohol)/carbon nanotube nanocomposites have also been prepared and studied for the thermo-responsive and electro-active effects (62,68). In the polymer/nanocarbon nanocomposites, the traditional shape memory can be triggered by the direct heating (69), electro-active effect (70), light-active response (71), water/moisture actuation (72), and pH sensitive effect (73). The SMP/nanocarbon nanocomposites have found applications in the aerospace, energy devices, civil structures, and biomedical devices (74–76).

4 Graphene

Graphene is an exclusive type of nanocarbon nanostructure. Graphene is made up of sp^2 hybridized hexagonally arranged carbon atoms in a single layer (77,78). The two-dimensional graphene layers stack together through van der
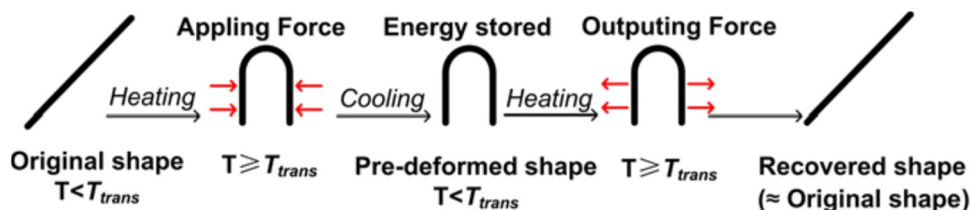

Figure 3: Schematic of shape memory effect during typical thermo-mechanical cycle (41). Reproduced with permission from Elsevier.
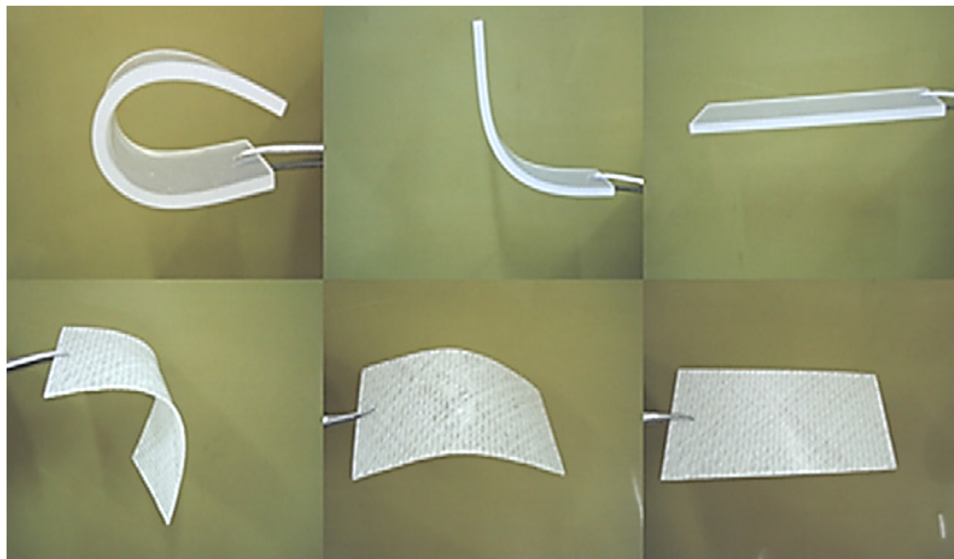
Figure 4: Shape recovery of neat polymer (top row) and reinforced shape memory composite (bottom row) (41). Reproduced with permission from Elsevier.

Waals forces (79). Graphene has been prepared by top-down and bottom-up methods including graphite exfoliation, graphite mechanical cleavage, chemical vapor deposition, and organic synthesis routes (80,81). Graphene owns the range of fascinating structural and physical features. Graphene is transparent in nature (82). Graphene has high electron mobility and thermal conductivity of 200,000 $cm^2 \cdot V^{-1} \cdot s^{-1}$ and 3,000–5,000 $W \cdot mK^{-1}$, respectively (83,84). Graphene also has high tensile strength and Young's modulus of 130 GPa and 1 TPa, respectively (85). Graphene oxide (GO) is an important modified form of graphene with epoxide, hydroxyl, carbonyl, and carboxyl surface functionalities. Graphene has been used in significant electronics, energy devices, and composite related applications. Nanofillers have been used to progress the electrical conductivity, thermal conductivity, thermal stability, and mechanical properties of the polymers (86). The polymer/graphene nanocomposites have found applications in the electronics (87), energy devices (88), and sensors (89).

5 Stimuli responsive polymer/graphene nanocomposites

Graphene has been incorporated in the polymers to augment the shape memory and self-healing properties of the nanocomposite (90). In high performance polymer/graphene nanocomposites, 0.005–0.5 wt% graphene nanofillers have been reinforced. The shape memory performance of the nanocomposites depends on the chemical composition of the polymers, nanocomposites, and macroscopic properties of the nanocomposites (91). The formation of the interlinked network in the polymer/graphene interface plays an important role in the shape recovery properties. Epoxy, a thermoset, has been used as an excellent SMP due to ideal thermo-mechanical properties (92). Lu et al. (93) developed the epoxy nanocomposite with graphene nanofiller. The carbon fiber was covalently grafted with the graphene nanosheets to form the modified reinforcement (94). The graphene related carbon fiber filler was capable of forming the interfacial bonding with the epoxy matrix. Martin-Gallego et al. (95) prepared the epoxy materials with the functional graphene nanosheets and cured using cationic photo-polymerization. Inclusion of the 1.5 wt% graphene contents enhanced the T_g of the nanocomposites by 40°C, relative to the neat epoxy. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study the fine dispersion state of the graphene nanofillers in the matrix. D'Elia et al. (96) designed the shape memory epoxy/graphene nanocomposites. The sample was heated through the Joule heating effect. The epoxy/graphene nanocomposite with <1 wt% revealed fine shape recovery in response to the electric voltage of <10 V. Figure 5 shows the shape recovery through the joule heating effect. The application of voltage of 9 V for 1 min increased the temperature to 58°C and caused the shape recovery. The shape memory behavior has credited to the formation of graphene network in the epoxy matrix (97). The sample was developed in a tight ring shape and
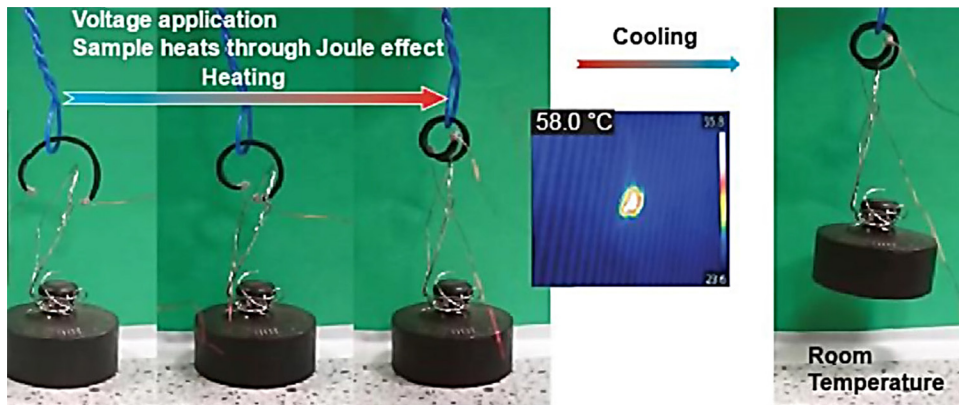
Figure 5: Infographic showing the behavior of epoxy nanocomposite subject to potential of 9 V. The composite coils back to pre-set shape after 60 s of Joule heating. The increase in temperature of sample to 58°C activated shape-memory effect (96). Reproduced with permission from Elsevier.

fixed in an open ring shape. The original tight ring shape was attained under few seconds of joule heating effect. The recovery of original shape also strengthened the ring shape to lift a heavy object. The flexural modulus of the sample was increased to 2.8 ± 0.1 GPa. Wang et al. (98) developed electro-active epoxy/reduced GO-derived shape memory nanocomposite. The applied voltage was found to boost the shape recovery effect. Figure 6 shows the shape memory behavior of epoxy/reduced GO nanocomposite. The sample was bent to 'U' shape at 113°C. The epoxy/reduced GO paper had thickness of 0.1 cm and surface area of 6.5 cm^2. The shape recovery of the epoxy/reduced GO paper was obtained in 5 s at a voltage of 6 V and temperature of 240°C.

Yang et al. (99) fabricated thermo-responsive shape memory graphene filled vitrimer epoxy nanocomposite. The vitrimer/graphene nanocomposites revealed superior shape retrieval properties with the graphene loading. The shape recovery was attained in 80 s for 1 wt% graphene loaded nanocomposite. The graphene loading also enhanced the yield strength and breaking strain of the nanocomposites to 23 MPa and 44%, respectively. The high mechanical and thermo-responsive shape memory properties were credited to the interactions between the nanocomposite constituents (100). Wang et al. (101) studied the electro-actuation in the hydro-epoxy/graphene nanocomposites. The nanofiller loading promoted the processability and shape recovery of the nanocomposite. The original shape was rapidly recovered within 72 s for the 3 wt% graphene loaded nanocomposite, relative to the 2 wt% loaded nanocomposite (90 s).

Polyurethane is a multi-purpose engineering material. The segmented polyurethanes have been usually developed using the polyol, isocyanate, and chain extender. Park et al. (102) produced the shape memory polyurethane/graphene nanocomposites. The shape recovery effect was improved through the nanofiller loading. Kim et al. (103) prepared
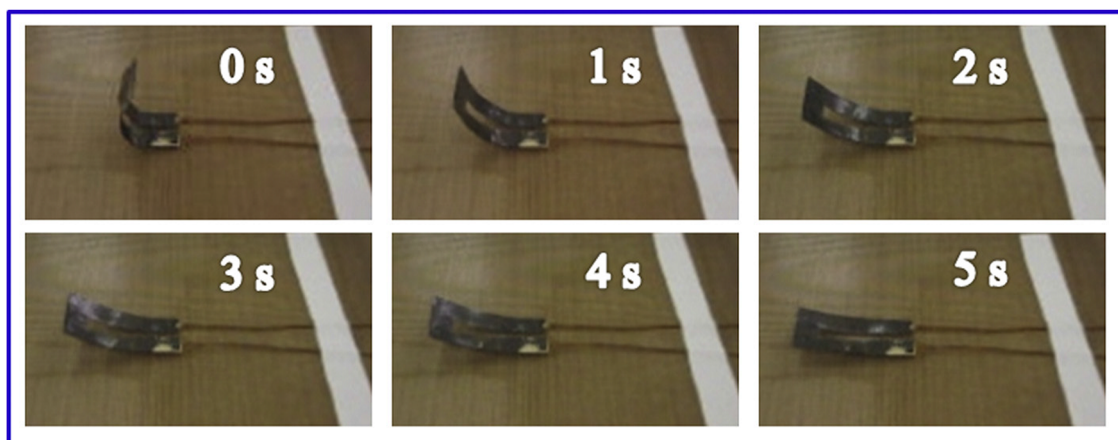

Figure 6: Shape recovery process of epoxy/reduced graphene oxide paper-based shape memory nanocomposite under applied voltage of 6 V (98). Reproduced with permission from Elsevier.
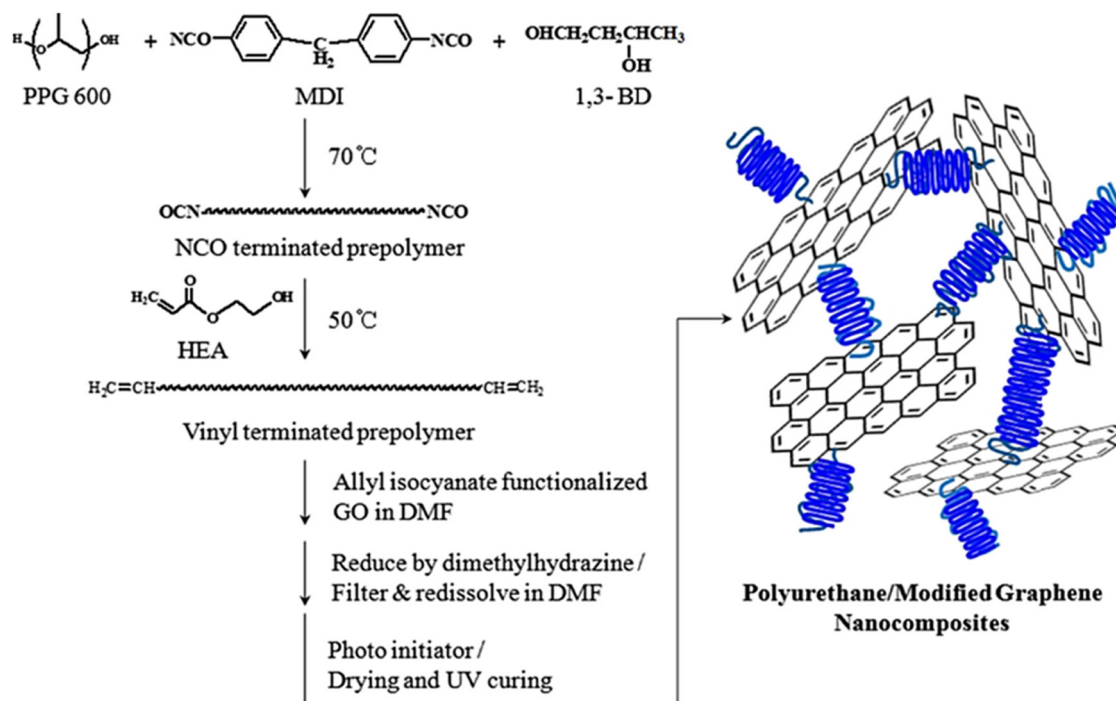
Figure 7: Scheme for preparation of polyurethane/graphene nanocomposite (103). HEA – hydroxyethylacrylate; DMF – *N,N*-dimethylformamide; GO – graphene oxide; 1,3-BD – 1,3-butanediol; PPG – polypropylene glycol; MDI – 4,4′-methylene diphenyl diisocyanate. Reproduced with permission from Wiley.

the allyl isocyanate modified graphene and filled in the polyurethane matrix. The allyl isocyanate-modified graphene formed better compatibility with the polyurethane matrix to enhance the mechanical and shape memory properties of the nanocomposites (104). The polyurethane was prepared through the condensation of 1,3-butanediol, polypropylene glycol, and 4,4′-methylene diphenyl diisocyanate. The modified graphene nanofillers was loaded in the 0–2.5 phr. Figure 7 shows the preparation process for the polyurethane/graphene nanocomposite. *N,N*-Dimethylformamide was used as solvent. Figure 8 shows the thermomechanical cyclic behavior of polyurethane/graphene with the 2.5 phr nanofiller loading.

The polyurethane nanocomposite revealed the shape fixity and shape recovery of 96% for the first cycle. The shape fixity and shape recovery were maintained >90%, even after the fourth cycle. The modified nanofiller acted as cross-linker for the polyurethane chains and caused reinforcing effect. Sofla et al. (105) prepared the thermo-responsive and electroactive shape-memory polyurethane/graphene nanocomposites. The polyurethane was prepared using the polycaprolactone diol, hexamethylene diisocyanate (HDI), and 1,4-butanediol through the solution method. The shape memory properties and the thermo-mechanical cyclic behavior of polyurethane and polyurethane/graphene nanocomposites have been studied. The cyclic behavior of

the polyurethane and polyurethane/graphene nanocomposites is given in Figure 9. The results of the shape memory behavior are given in Table 1.

The polyurethane/graphene nanocomposite with 3 wt% nanofiller loading showed 100% shape recovery during the thermo-responsive and electro-active actuations. The
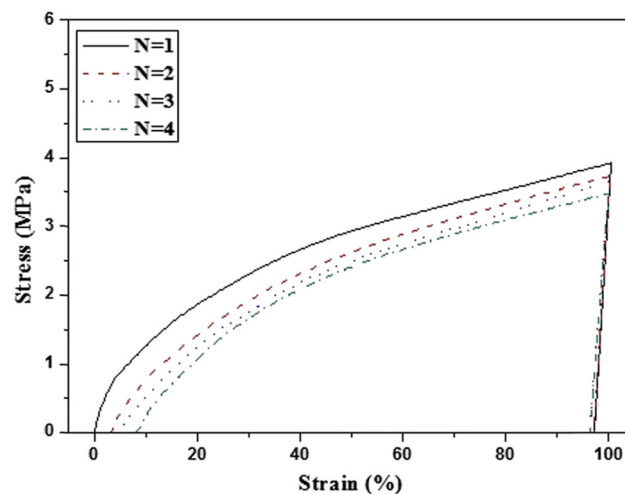

Figure 8: Thermomechanical cyclic behavior of polyurethane/graphene 2.5 phr (103). *N* – number of cycles. Reproduced with permission from Wiley.
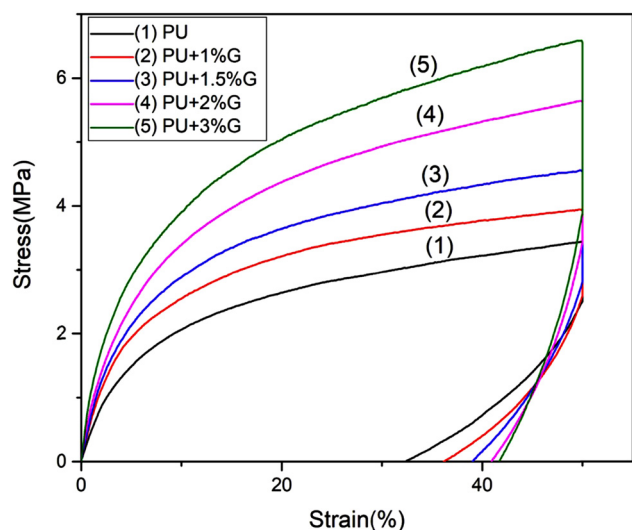
Figure 9: Thermo-mechanical cyclic behavior of polyurethane and polyurethane/graphene nanocomposites (105). Reproduced with permission from Elsevier.

Figure 10: TEM image of polyurethane/graphene nanoplatelet 1.5 wt% nanocomposite (106). Reproduced with permission from Wiley.

polyurethane nanocomposite with the 3 wt% graphene showed shape recovery in 60 s. Whereas, the neat polyurethane had no shape memory behavior. The thermo-responsive effect was observed at 60°C, although the electro-active effect was observed at 75 V. Abbasi et al. (106) prepared the polyurethane/graphene nanoplatelet nanocomposites. The polyurethane was formed using poly(ε-caprolactone)diol, castor oil, and HDI through the *in situ* polymerization. Figure 10 portrays the TEM image of the polyurethane/graphene nanoplatelet nanocomposite with 1.5 wt% nanofiller. The graphene nanoplatelet was found consistently dispersed in the polyurethane matrix. Figure 11 designates the stress-strain curves of the polyurethane and polyurethane/graphene nanoplatelet nanocomposites. The nanofiller addition augmented the tensile stress of the nanocomposites due to the matrix-nanoparticle connections. However, the strain was decreased with the graphene nanoplatelet inclusion due to the stiffness of the polymer chains. The inclusion of the graphene nanoplatelet-based nanocomposites revealed the high shape fixity of ~96% and shape recovery of ~99%. Patel and Purohit (107) developed the shape m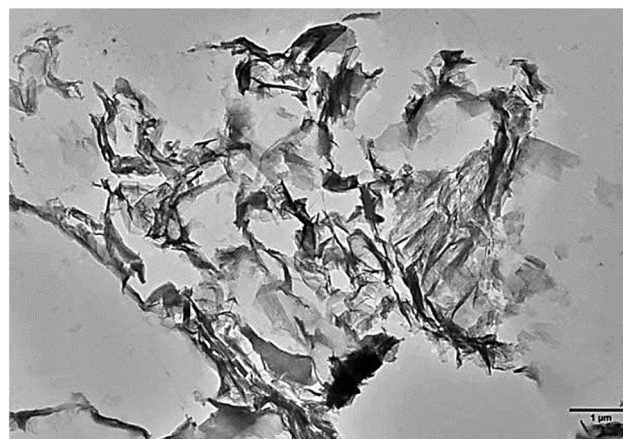emory polyurethane/graphene nanoplatelet nanocomposites by the melt mixing. The graphene nanoplatelet was loaded in the range of 0–2 phr. The shape memory was induced using the microwave irradiation technique. The shape recovery of the nanocomposites relies on the microwave frequency and nanofillers content.

Among other shape memory matrices, poly(methyl methacrylate) (PMMA) has been used with graphene. PMMA is an important thermoplastic polymer with fine chemical, weathering, and corrosion resistance features (108,109). Eshkaftaki and Ghasemi (110) reported the thermo-responsive PMMA/graphene nanocomposite obtained from the melt mixing method. The heating was performed in the range of 65–100°C. The shape recovery of 97% was attained at 100°C. Ji et al. (111) formed the PMMA/thermally reduced GO-based nanocomposite using solution method. The shape recovery was experiential using UV-curing method. The storage modulus of the nanocomposite was found at ~30–140°C. Shape memory poly(lactic acid) has been filled with the graphene nanofiller (112). The nanofiller was uniformly dispersed in the poly(lactic acid) matrix to enhance the crystallization ability and shape memory properties of the polymer (113,114). The shape memory properties of the poly-ethylene elastomer were also improved with the octadecyl-amine-modified GO (115). The modified GO loading of the 0.25–1.0 wt% considerably enhanced the shape memory

Table 1: Shape memory properties of polyurethane and polyurethane/graphene nanocomposites (105). Reproduced with permission from Elsevier

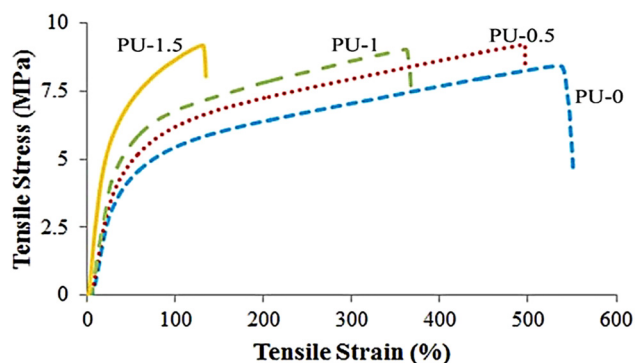| Sample	Shape fixity (%)	Shape recovery (%) (thermal 60°C)	Shape recovery (%) (electrical 75 V; 60 s)
Polyurethane	65 ± 2	90 ± 2	Not recovered
Polyurethane/graphene 1 wt%	71 ± 3	94 ± 2	Not recovered
Polyurethane/graphene 1.5 wt%	78 ± 2	94 ± 3	Not recovered
Polyurethane/graphene 2 wt%	82 ± 4	98 ± 2	95
Polyurethane/graphene 3 wt%	83 ± 1	100	100

Figure 11: Typical tensile stress-strain curves of polyurethane/graphene nanoplatelet nanocomposites (106). PU – polyurethane. Reproduced with permission from Wiley.

properties of the nanocomposites due to the hydrogen bonding between the polymer/graphene interfaces (116). The shape memory polyacrylonitrile/graphene nanocomposites have been developed (117). The cross-linking in the nanocomposite constituents improved the shape recovery properties of the polyacrylonitrile/graphene nanocomposites (117). Hence, the effects of the graphene nanofillers on the shape memory properties of the polymeric nanocomposites have been established in literature. The most commonly studied polymers with the graphene nanofillers are epoxy, polyurethane, and PMMA. The commonly observed shape memory effects include, Joule heating effect, electro-activity, thermal response, and radiation triggered actuation. Table 2 displays the specifications of the stimuli-responsive polymer/graphene nanocomposites discovered so far.

Shape memory polyamide matrices have been reported (118). The hydrogen bonding associations between the polymer chains and crystallization have led to the optimum switching/transition temperature and toughness of the shape memory polyamides. Li et al. (119) developed the shape memory polyamide having triple-shape memory behavior. The T_g and T_{trans} of the polymer were found at ~125°C and ≥200°C, respectively. The shape recovery rate of the polyamide was found to be ~82%. Figure 12 reveals the steps involved in the multi-step shape memory process. The torsion tests were applied to cause the strains and stresses in the rectangular bar sample. Consequently, the shape deformation, fixation, and recovery steps in the shape memory have been studied. Figure 13 shows the semicrystalline, crystalline, and covalent cross-links in the polymer structure. The overall semicrystalline structure has caused the feasible switching during the shape memory effect.

Yan et al. (120) formed the solution processed rapidly responsive shape memory polyamide. The responsive time was found around 6–8 s and the recovery rate was 99.5%. Consequently, the shape memory polyamide/graphene

nanocomposites have been produced (121). Ma et al. (122) developed the polyamide and graphene-based nanocomposites through the *in situ* chemical polymerization. The polyamide/graphene nanocomposites own photo-electrical responsive shape memory effect.

PS is an aromatic thermoplastic polymer used for the shape memory materials (123). The thermo-responsive and electro-active shape memory behavior have been observed in PS. Shape memory PS/graphene nanocomposites have also been focused (124). The PS has been chemically cross-linked with the nanofillers. Li et al. (125) prepared the electro-active PS/graphene oxide-octadecylamine (PS/GO−ODA) nanocomposites. The SEM and TEM analysis depicted the homogeneous dispersion of GO−ODA in PS, while the pristine GO has revealed aggregated morphology (Figure 14). The electro-active shape memory effect was perceived due to the high electrical conductivity of the PS/GO−ODA nanocomposite. Figure 15 shows higher electrical conductivity of 9.2×10^{-4} S·m^{-1}, for the GO−ODA nanocomposite. The fine nanofillers distribution and interface formation with the matrix produced the superior electrical conductivity and electro-actuation features.

The bio-based polymers such as lignin, cellulose, and lyocell fibers form an important category of the natural polymers (126−128). The shape memory lignin-poly (*N*-methylaniline)/graphene oxide nanocomposites have been designed using *in situ* polymerization (129). The three dimensional self-assembled lignin-poly(*N*-methylaniline)/GO hydrogel revealed the dye and ion adsorption capacities. The lignin−PNMA−rGO had high adsorption capacity for methylene blue and Pb^{2+} ion as 201.7 and 753.5 mg·g^{-1}, respectively. The new lignin-based adsorbent is low-cost, environmentally benign, and is an attractive adsorbent for the wastewater treatment. Bai and Chen (130) formed the shape memory hydroxyethyl cellulose and GO-based nanocomposites. The hydroxyethyl cellulose/GO nanocomposites showed moisture active behavior within 14 s. Such natural polymer-based shape memory materials have been applied in water responsive sensors, actuators, and biomedical devices (131,132).

6 Combination polymers and graphene dispersion in shape memory nanocomposites

Various polymers have been employed to form the shape memory graphene-based nanocomposites (133). Among frequently used thermosetting and thermoplastic polymers are epoxies, polyurethanes, PMMA, polyamides, and PS.

Table 2: Aspects of shape memory polymer/graphene nanocomposites

| Matrix	Nanofiller	Actuation	Properties	Ref.
Epoxy	Graphene	Joule heating effect	5.5 V DC voltage; shape recovery time of 80 s; shape recovery of 95%	(93)
Epoxy	Graphene	Thermo-responsive	T_g 40°C	(95)
Epoxy	Graphene	Electro-active	Joule heating effect; 9 V; shape recovery in 60 s	(96)
Epoxy	Graphene oxide	Electro-active	Shape recovery 6 V; 5 s	(98)
Vitrimer	Graphene	Thermo-responsive	Shape recovery in 80 s; yield strength 23 MPa; breaking strain 44%	(99)
Hydro-epoxy	Graphene	Electro-active	Shape recovery in 72 s	(101)
Polyurethane (1,3-butanediol, polypropylene glycol, 4,4'-methylene diphenyl diisocyanate)	Allyl isocyanate-modified graphene	Thermo-responsive	Shape recovery of 96%	(103)
Polyurethane (polycaprolactone diol, HDI, and 1,4-butanediol)	Graphene	Thermo-responsive	100% shape recovery	(105)
Polyurethane (poly(ε-caprolactone)diol, castor oil, and HDI)	Graphene nanoplatelet	Thermo-responsive	Shape fixity of ~96%	(106)
Polyurethane	Graphene nanoplatelet	Microwave irradiation	Shape memory increase 1–2 wt% loading	(107)
PMMA	Graphene	Thermo-responsive	Shape recovery of 97% at 100°C	(110)
PMMA	Reduced graphene oxide	UV-curing	Storage modulus at ~30–140°C	(111)
Poly(lactic acid)	Graphene nanoplatelet	Thermo-responsive	Shape fixity of ~94%; shape recovery of 91% at 60–70°C	(112)
Poly(lactic acid)	Graphene nanoplatelet	Thermo-responsive	Shape fixity of ~88.7%; shape recovery of 91% at 70°C	(114)
Polyolefin elastomer	Octadecylamine modified graphene	Sample fixed at 65°C; near infrared responsive shape memory	Shape fixity of ~91.2%; shape recovery of 99.6%	(115)
Modified polydimethylsiloxane	Graphene oxide	Thermo-responsive	Self-healing capability of ~90%	(116)
Polyacrylonitrile	Graphene	Microwave/IR irradiation	Shape recovery time of 40 s	(117)
Polyamide	Graphene	Thermo-responsive	Shape recovery rate ~82%	(118)
Polyamide	Graphene	Thermo-responsive	Shape recovery time of 68 s; shape recovery rate of ~98–99.5%	(120)
Cross-linked epoxy resin	Graphene oxide	Thermo-responsive	Shape recovery of 97.8%; recovery temperature of 87.5°C	(121)
Polyamide	Graphene oxide	Photoelectrical response	—	(122)
Polystyrene	Nanofiller	Thermo-responsive	Shape recovery time of 12 s; shape recovery rate of ~90%	(124)
Lignin-poly(N-methylaniline)	Graphene oxide	Moisture-active	Methylene blue adsorption 201.7 mg·g^{-1}; Pb^{2+} ion 753.5 mg·g^{-1}	(129)
Hydroxyethyl cellulose	Graphene oxide	Moisture-active	Recovery time 14 s	(130)
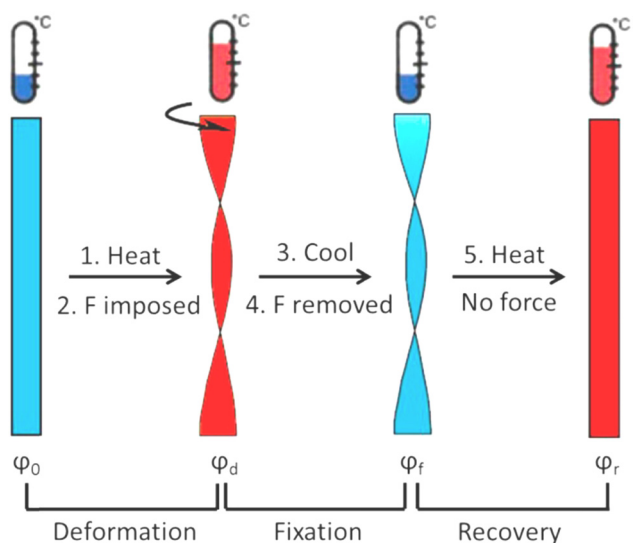
Figure 12: Illustration of shape deformation, fixation, and recovery cycle of multi-shape memory effect in torsion mode (119). Reproduced with permission from ACS.
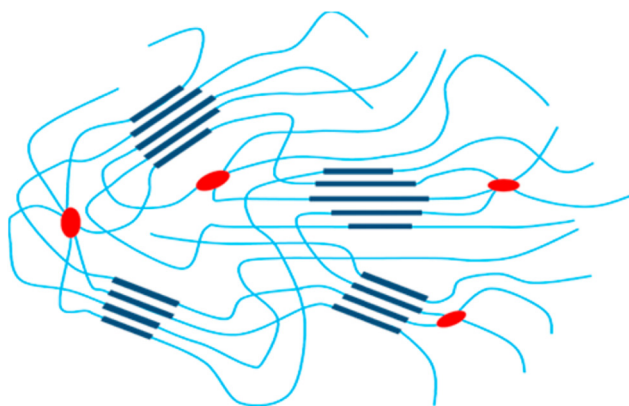

Figure 13: Molecular representation of the semicrystalline polyamide. Crystalline polymer (dark blue) is embedded in an amorphous matrix (light blue), and red dots represent covalent cross-link points (119). Reproduced with permission from ACS.

The choice of the polymer determines the rate of shape recovery and rapid response time. Graphene has thin nanosheet nanostructure and large specific surface area often leading to agglomeration. The poor dispersion and aggregation of graphene deteriorated the shape memory performance. Consequently, the graphene dispersion in various polymers is an important factor to determine the recovery properties and performance of the nanocomposites. Most importantly, the strength, toughness, and flexibility properties of the polymer/graphene nanocomposites have been affected due to the poor graphene dispersability. Moreover, the nanoparticle accumulation influenced the electrical properties of the electro-active polymer/graphene nanomaterials. The electron conduction through the system depends on the formation of the percolation network in the matrix, which was affected by the aggregation. The graphene dispersion techniques such as the ultrasonication and *in situ* method need to be adopted in this regard. In addition to the fine graphene dispersion, the interfacial links and miscibility with the polymers have been found as essential factors to improve the shape memory properties (134). The superior interfacial connections between the polymer and graphene have yielded high mechanical properties and electrical conductivity. Incidentally, the surface modification of graphene must be developed to prevent the nanoparticle masses and improve the dispersal in the polymer. The plasticizers have been applied for cross-linking between the graphene and polymers (135). Formation of graphene network in the matrix not only enhanced the microscopic properties, shape fixity, and shape recovery rate but also supported the technical performance of polymer/graphene nanocomposite. Hence, the choice of polymer, nanofiller content, nanofiller modification, dispersion, and processing technique contribute to the shape memory property increments in the technical polymer/graphene nanocomposites.

7 SMP/graphene nanocomposites: Potential applications

SMPs are smart materials having ability to return from the deformed shape to the original shape. SMPs have been used as the beneficial materials, compared with the shape memory alloys (136). The thermoplastic and thermoset polymers have the ability to reveal shape memory behavior. Among the thermoplastic polymers, polyurethane, PMMA, polyacrylonitrile, polylactic acid, PS, etc., have been used as SMPs (137,138). In thermosets, epoxies and polyesters reveal shape memory effect (139,140). The segmented polymers such as polyurethanes have switching segments in the backbone to display T_{trans} (141). The switching segments cause the recovery of the temporary shape to the original shape (142). An important factor here is the cross-linking of polymer chains and the formation of the switchable polymer-nanofiller network. The cross-linking allows the polymer chains to maintain the chemical and physical features, in addition to the shape recovery (143). The polymer chains can be physically or covalently associated to reveal the shape memory behavior (144). The crystallization, viscoelastic behavior, strain recovery, and
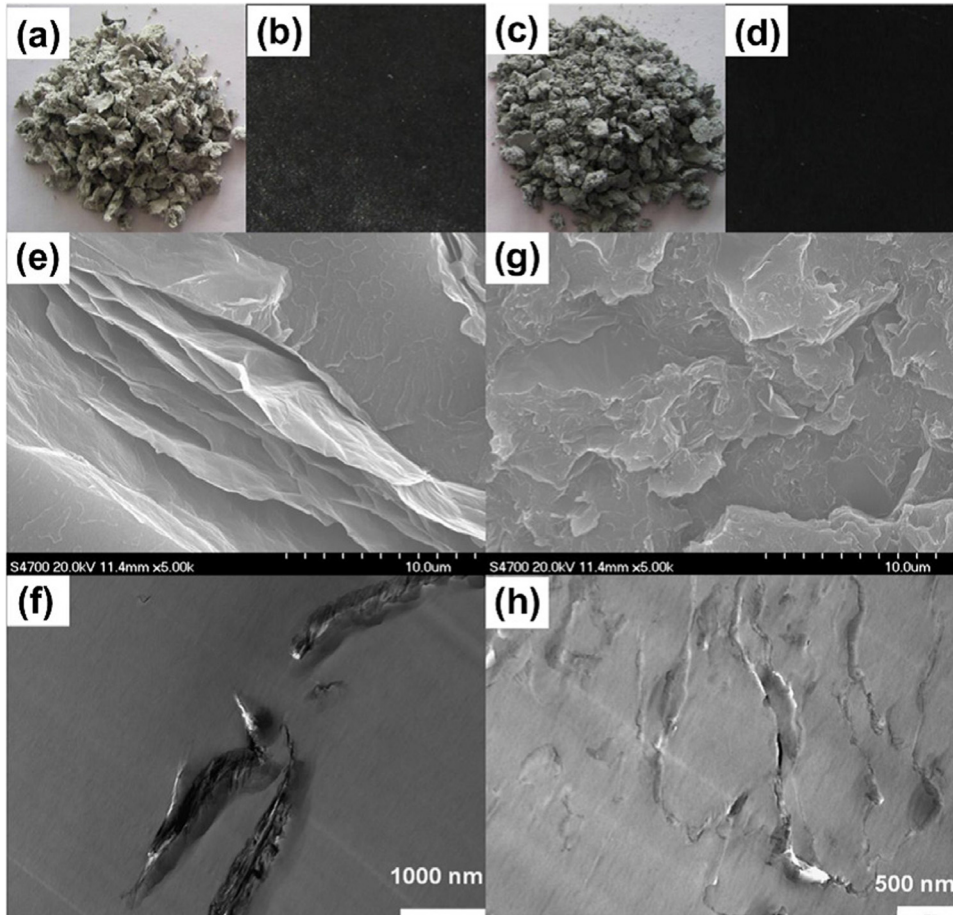
Figure 14: Digital photographs of (a and b) PS/3 wt% GO and (c and d) PS/3 wt% GO–ODA nanocomposites; SEM photographs of (e) PS/3 wt% GO and (g) PS/3 wt% GO–ODA nanocomposites; TEM photographs of (f) PS/4 wt% GO, and (h) PS/4 wt% GO–ODA nanocomposites (125). PS – polystyrene; GO–ODA – graphene oxide-octadecylamine. Reproduced with permission from Elsevier.
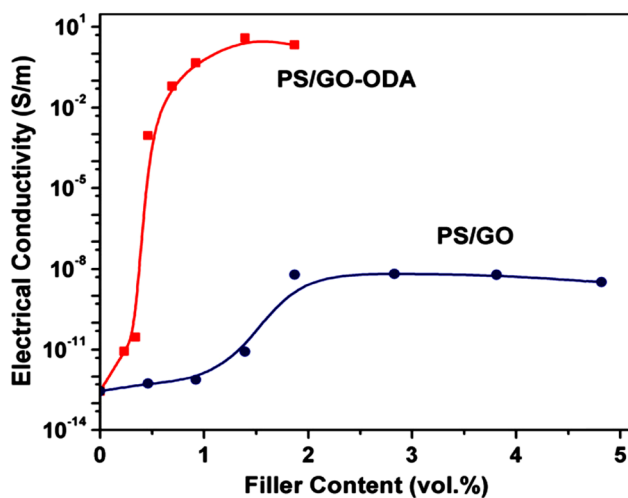

Figure 15: Electrical conductivity of polystyrene based nanocomposites as a function of filler content (125). PS/GO–ODA – polystyrene/graphene oxide-octadecylamine; PS/GO – polystyrene/graphene oxide. Reproduced with permission from Elsevier.

shape fixity of the SMPs can be altered using the fillers or nanofillers (145). Consequently, the polymer/graphene nanocomposites have been developed with tendency towards heat, electric, and radiation actuation. The SMP/graphene nanocomposites have found applications in aerospace and automobile components (145–147).

In the motorized engineering, these nanocomposites can be applied in the outer body, seat assemblies, lenses, and interior components (148,149). The aerospace and automobile engineering desire further research to substitute the traditional structural materials for future advances (150). For the aerospace components, the polymer/graphene nanocomposites have been considered due to fine processability, chemical resistance, strength, non-flammability, electrical conductivity, heat stability, thermal conductivity, radiation shielding, and lightning strike resistance. Nevertheless, the future advancements have been needed to overcome the challenges related to the employment of the SMP/graphene nanocomposites in the automotive/aerospace vehicles (151).
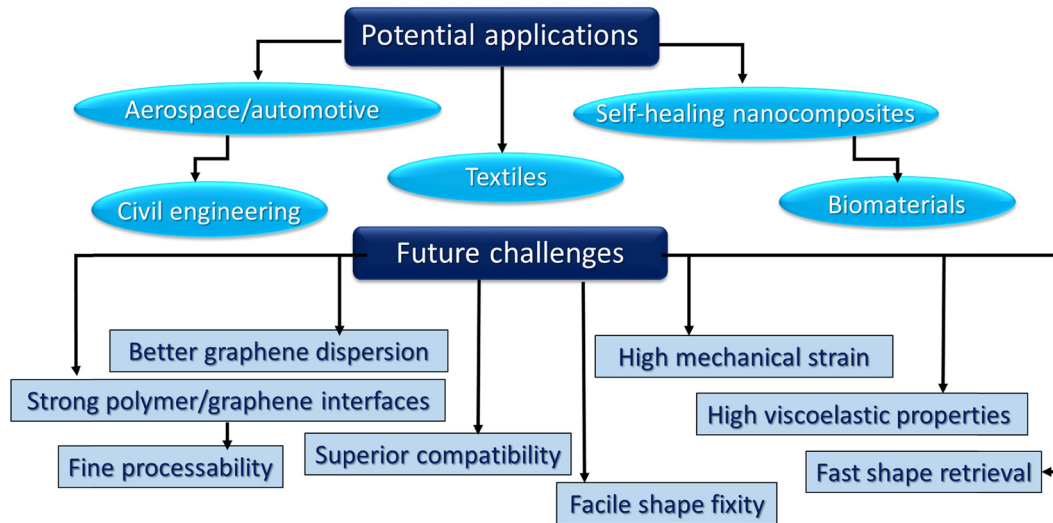
Figure 16: Schematic of the potentials and challenges of shape memory polymer/graphene nanocomposites.

The self-healing polymer/graphene nanocomposites have been developed (152). Usually very low graphene content has been reinforced in the polymers to gain the self-healing properties. The polymer is usually cross-linked with the modified graphene via hydrogen bonding to generate the self-healing properties. The shape memory and self-healing polymer/graphene nanocomposites have been studied for the sensors, actuators, and microelectronics, to some extent (153).

Besides, the graphene-filled shape memory nanocomposites have been employed in the smart textiles, fabrics, and spy garments (154). Novel self-healing effects render the textile material to reconcile its original properties. Moreover, such textiles have capability to sense the damaged place and recover the damaged fabric part.

Graphene has expanded the application of the SMPs to the civil engineering field (155). Thus, the civil engineering features of stimuli-responsive graphene-based nanomaterials have been focused (156). In this regard, the mechanically robust graphene-based actuation systems allow the instantaneous bending and fluctuation of the materials (157,158). For the civil engineering application, the polymer/graphene nanocomposites have large recoverable strains (159). The insertion of the graphene nanosheet in the SMPs has considerably increased the mechanical response, recovery, and other mechanical properties for the civil engineering structures (160).

The SMP/graphene nanocomposites also possess potential for the biomedical devices, actuated implants for human body, and drug delivery (161,162). The artificial implants (regenerative tissues, bones, skin, arteries, etc.) have been prepared by taking the advantage of the shape recovery properties of polymer/graphene nanomaterials. PMMA and polyurethanes have been used in the SMPs-based bio-implants. Precisely, the segmented polyurethane-based SMPs have been applied in the drug delivery systems owing to biocompatibility, *in situ* compatibility, and chemical interactions with the biological parts.

However, research in the aerospace, automotive, textile, electronic, and biomedical area need future explorations to establish the impact of the polymer/graphene nanocomposites (Figure 16). The future directions for progress in the field of shape memory graphene-based materials need to be focused. Advanced level research efforts must be carried out to encounter the challenges of stimuli-responsive nanocomposites towards various solicitations. The foremost challenges in the use of stimuli-responsive polymer/graphene nanocomposites involve the attainment of better graphene dispersion, fine polymer/graphene interfaces/compatibility, the nanocomposite processability, high mechanical strains, and viscoelastic properties required for the high-performance stimuli-responsive polymer/graphene nanocomposites. New research directions can be discovered using the modified polymers, the functional graphene nanofiller, and modified actuation approaches. The advancements in the shape memory effect in various technical fields depend on the various factors like optimum reinforcement content and matrix/nanoparticle miscibility. The graphene has been reinforced in the SMPs to improve the structural stability, thermal constancy, mechanical properties, storage modulus, shape fixity, shape retrieval, and other physical properties. Owing to the tendency of graphene aggregation, the homogeneous dispersal has been found essential to enhance the properties of the

SMPs. Better compatibilization between the polymer/graphene is essential to improve the crystallization, viscoelastic properties, and storage modulus of the nanocomposites.

8 Conclusion

In this review, initially a brief introduction to the SMP and nanocomposites has been presented. Afterwards, the SMP/graphene-based nanocomposites have been mainly studied. In this regard, the thermo-responsive, electro-active, photo-active, and strain-effect have been explored. Momentarily speaking, this review presents the significance of SMPs and the ensuing nanocomposites with graphene nanofiller. Various polymers have been reinforced with graphene to fabricate the high-performance nanocomposites. The polymer/graphene nanocomposites revealed the thermo-responsive, electro-active, and photo-sensitive behavior. Graphene dispersion and interface between the polymer/graphene have led to the advanced actuation performance. The polymeric nanocomposites have wide ranging potential applications in the aerospace, automobile, biomedical, and smart textile industries. Future advancements in the SMP-based nanocomposite may lead to the discovery of several concealed applications.

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