Review Article

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

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Abstract: Graphene is one of most exceptional type of nanocarbon. It is a two-dimensional, one atom thick, nanosheet of sp² 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

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 sp² 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 sp² 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.

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-responsive polymers revealed chain movements at the transition temperature ($T_{\text{trans}}$), 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 $T_{\text{trans}}$ (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 $T_{\text{trans}}$ (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).

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
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 $T_{\text{trans}}$, 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 sp² hybridized hexagonally arranged carbon atoms in a single layer (77,78). The two-dimensional graphene layers stack together through van der
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 \(200,000 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}\) and \(3,000–5,000 \text{ W}\cdot\text{mK}^{-1}\), respectively \((83,84)\). Graphene also has high tensile strength and Young’s modulus of \(130 \text{ GPa}\) and \(1 \text{ TPa}\), 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, \(0.005–0.5 \text{ wt}\%\) 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 thermost, 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 \(1.5 \text{ wt}\%\) graphene contents enhanced the \(T_g\) of the nanocomposites by \(40^\circ\text{C}\), 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 \(<1 \text{ wt}\%\) revealed fine shape recovery in response to the electric voltage of \(<10 \text{ V}\). Figure 5 shows the shape recovery through the joule heating effect. The application of voltage of \(9 \text{ V}\) for \(1 \text{ min}\) increased the temperature to \(58^\circ\text{C}\) 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...
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 cm². 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
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. The polyurethane was prepared through the condensation of 1,3-butanediol, polypropylene glycol, and 4,4′-methylene diphényl 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-Dimethylfor- mamide 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. Sofía et al. (105) prepared the thermo-responsive and electroactive shape-memory polyurethane/graphene nanocomposites. The polyurethane was prepared using the polycaprolactone diol, hexamethylene disocyanate (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 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.](image)

![Figure 8: Thermomechanical cyclic behavior of polyurethane/graphene 2.5 phr (103). N – number of cycles. Reproduced with permission from Wiley.](image)
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 memory 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 polyethylene elastomer were also improved with the octadecylamine-modified GO (115). The modified GO loading of the 0.25–1.0 wt% considerably enhanced the shape memory

![Figure 9: Thermo-mechanical cyclic behavior of polyurethane and polyurethane/graphene nanocomposites (105). Reproduced with permission from Elsevier.](image1)

![Figure 10: TEM image of polyurethane/graphene nanoplatelet 1.5 wt% nanocomposite (106). Reproduced with permission from Wiley.](image2)

| 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                                      |

Table 1: Shape memory properties of polyurethane and polyurethane/graphene nanocomposites (105). Reproduced with permission from Elsevier
The properties of the nanocomposites due to the hydrogen bonding between the polymer/graphene interfaces have been developed. The shape memory polyacrylonitrile/graphene nanocomposites have been developed. The cross-linking in the nanocomposite constituents improved the shape recovery properties of the polyacrylonitrile/graphene nanocomposites. 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. 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. developed the shape memory polyamide having triple-shape memory behavior. The $T_g$ and $T_{trans}$ of the polymer were found at $\sim$125°C and $\geq$200°C, respectively. The shape recovery rate of the polyamide was found to be $\sim$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. 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. Ma et al. 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. The thermo-responsive and electro-active shape memory behavior have been observed in PS. Shape memory PS/graphene nanocomposites have also been focused. The PS has been chemically cross-linked with the nanofillers. Li et al. 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 $9.2 \times 10^{-6}$ 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. The shape memory lignin-poly(N-methylaniline)/graphene nanocomposites have been designed using in situ polymerization. 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 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.

### 6 Combination polymers and graphene dispersion in shape memory nanocomposites

Various polymers have been employed to form the shape memory graphene-based nanocomposites. Among frequently used thermosetting and thermoplastic polymers are epoxies, polyurethanes, PMMA, polyamides, and PS.
| 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 | | |
| Epoxy  | Graphene  | Electro-active | Joule heating effect; 9 V; shape recovery in 60 s | (95) |
| Epoxy  | Graphene oxide | Electro-active | Shape recovery 6 V; 5 s | (96) |
| Hydro-epoxy | Graphene | Thermo-responsive | Shape recovery in 72 s | (98) |
| Polyurethane (1,3-butandiol, polypropylene glycol, 4,4′-methylene diphenyl diisocyanate) | Graphene | Electro-active | Shape recovery of 96% | (99) |
| Polyurethane (polycaprolactone diol, HDI, and 1,4-butandiol) | Graphene nanoplatelet | Thermo-responsive | 100% shape recovery | (101) |
| Polyurethane (poly(ε-caprolactone)diol, castor oil, and HDI) | Graphene nanoplatelet | Thermo-responsive | Shape fixity of ~96% | (105) |
| Polyurethane | Graphene nanoplatelet | Microwave irradiation | Shape memory increase 1–2 wt% loading | (102) |
| PMMA   | Graphene  | Thermo-responsive | Shape recovery of 97% at 100°C | (103) |
| PMMA   | Reduced graphene oxide | UV-curing | Storage modulus at ~30–140°C | (104) |
| Poly(lactic acid) | Graphene nanoplatelet | Thermo-responsive | Shape fixity of ~94%; shape recovery of 91% at 60–70°C | (105) |
| Poly(lactic acid) | Graphene nanoplatelet | Thermo-responsive | Shape fixity of ~88.7%; shape recovery of 91% at 70°C | (106) |
| 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% | (107) |
| Modified polydimethylsiloxane | Graphene oxide | Thermo-responsive | Self-healing capability of ~90% | (108) |
| Polyacrylonitrile | Graphene | Microwave/IR irradiation | Shape recovery time of 40 s | (109) |
| Polyamide | Graphene | Thermo-responsive | Shape recovery rate ~82% | (110) |
| Polyamide | Graphene | Thermo-responsive | Shape recovery time of 68 s; shape recovery rate of ~98–99.5% | (111) |
| Cross-linked epoxy resin | Graphene oxide | Thermo-responsive | Shape recovery of 97.8%; recovery temperature of 87.5°C | (112) |
| Polyamide | Graphene oxide | Photoelectrical response | — | (113) |
| Polystyrene | Nanofiller | Thermo-responsive | Shape recovery time of 12 s; shape recovery rate of ~90% | (114) |
| Lignin-poly(N-methylaniline) | Graphene oxide | Moisture-active | Methylene blue adsorption 201.7 mg g⁻¹; Pb²⁺ ion 753.5 mg g⁻¹ | (115) |
| Hydroxyethyl cellulose | Graphene oxide | Moisture-active | Recovery time 14 s | (116) |
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 effect (137,138). Among the thermoplastic polymers, polyurethane, PMMA, polycrylonitrile, 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 $T_{\text{trans}}$ (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
The 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 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.
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, electroactive, 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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References

(1) Yang X, Wang J, Guo H, Liu L, Xu W, Duan G. Structural design toward functional materials by electrospinning: a review. e-Polymers. 2020;20(1):682–712.

(2) Li Z, Pan Y, Zhang P, Zheng Z, Ding X, Peng Y. A novel shape memory polymer based on composites. e-Polymers. 2009;9(1):1–8.

(3) Wischke C, Lendlein A. Shape-memory polymers as drug carriers- a multifunctional system. Pharmaceut Res. 2010;27(4):527–9.

(4) Huang W, Ding Z, Wang C, Wei J, Zhao Y, Purnawali H. Shape memory materials. Mater Today. 2010;13(7–8):54–61.

(5) Xie T. Tunable polymer multi-shape memory effect. Nature. 2010;464(7286):267–70.

(6) Li J, Liu T, Xia S, Pan Y, Zheng Z, Ding X, et al. A versatile approach to achieve quintuple-shape memory effect by semi-interpenetrating polymer networks containing broadened glass transition and crystalline segments. J Mater Chem. 2011;21(33):12213–7.

(7) Gao Y, Lv J, Liu L, Yu Y. Effect of diacylhydrazine as chain extender on microphase separation and performance of energetic polyurethane elastomer. e-Polymers. 2020;20(1):469–81.

(8) Zhou J, Schmidt AM, Ritter H. Bicomponent transparent polyester networks with shape memory effect. Macromolecules. 2010;43(2):939–42.

(9) Cox LM, Killgore JP, Li Z, Long R, Sanders AW, Xiao J, et al. Influences of substrate adhesion and particle size on the shape memory effect of polystyrene particles. Langmuir. 2016;32(15):3691–8.

(10) Liu C, Qin H, Mather PT. Review of progress in shape-memory polymers. J Mater Chem. 2007;17(16):1543–58.

(11) Chen L, Wei X, Wang F, Jian S, Yang W, Ma C, et al. In-situ polymerization for mechanical strong composite actuators based on anisotropic wood and thermoresponsive polymer. Chinese Chem Lett. 2021. doi: 10.1016/j.ccl.2021.09.075.

(12) Liu Y, Lv H, Lan X, Leng J, Du S. Review of electro-active shape-memory polymer composite. Compos Sci Technol. 2009;69(13):2064–8.

(13) Jian S, Tian Z, Hu J, Zhang K, Zhang L, Duan G, et al. Enhanced visible light photocatalytic efficiency of La-doped ZnO nanofibers via electrospinning-calcination technology. Adv Powd Mater. 2021. doi: 10.1016/j.apmate.2021.09.004.

(14) Sheikholeslami M, Zia QM, Ellahi R. Influence of induced magnetic field on free convection of nanofluid considering Koo-Kleinstreuer-Li (KPL) correlation. Appl Sci. 2016;6(11):324.

(15) Agarwal S, Jiang S, Chen Y. Progress in the field of water- and/or temperature-triggered polymer actuators. Macromol. Mater Engineer. 2019;304(2):1800548.

(16) Han XJ, Deng ZQ, Fan MM, Liu Y, Li JH, Wang YF, et al. pH-induced shape-memory polymers. Macromol Rapid Commun. 2012;33(12):1055–60.

(17) Yasin A, Li H, Lu Z, ur Rehman S, Siddiq M, Yang H. A shape memory hydrogel induced by the interactions between metal ions and phosphate. Soft Matter. 2014;10(7):972–7.

(18) Leng L, Hu L, Liu Y, Huang WM, Du S. Shape-memory polymers—a class of novel smart materials. MRS Bull. 2009;34(11):848–55.

(19) Li F, Liu Y, Leng J. Progress of shape memory polymers and their composites in aerospace applications. Smart Mater Struct. 2019;28:103003.

(20) Ward Small I, Singhal P, Wilson TS, Maitland DJ. Biomedical applications of thermally activated shape memory polymers. J Mater Chem. 2010;20(7):3356–66.

(21) Zarek M, Layani M, Cooperstein I, Sachyani E, Cohn D, Magdassi S. 3D printing of shape memory polymers for flexible electronic devices. Adv Mater. 2016;28(22):4449–54.

(22) Barikani M, Zia KM, Bhatti IA, Zubair M, Bhatti VN. Molecular engineering and properties of chitin based shape memory polyurethanes. Carbohydr Polym. 2008;74(3):621–6.

(23) Sun L, Huang WM, Ding Z, Zhao Y, Wang CC, Purnawali H, et al. Stimulus-responsive shape memory materials: a review. Mater Des. 2012;33:577–640.
(24) Yooessi M, Shi Y, Scheiman DA, Lebron-Colon M, Tigelaaar DM, Weiss R, et al. Graphene polyimide nanocomposites: thermal, mechanical, and high-temperature shape memory effects. ACS nano. 2012;6(9):7644–55.
(25) Yu K, Liu Y, Leng J. Shape memory polymer/CNT composites and their microwave induced shape memory behaviors. RSC Adv. 2014;4(6):2961–8.
(26) Kausar A. Nanodiamond tethered epoxy/polyurethane interpenetrating network nanocomposites: physical properties and thermoresponsive shape-memory behavior. Int J Polym Anal Charactizat. 2016;21(4):348–58.
(27) Bae C, Park J, Kim E, Kang Y, Kim B. Organic–inorganic nanocomposite bilayers with triple shape memory effect. J Mater Chem. 2011;21(30):11288–95.
(28) Nakanishi W, Minami K, Shrestha LK, Ji Q, Hill JP, Ariga K. Bioactive carbon nanomaterials: nanoarchitectonics and applications. Nano Today. 2014;9(3):378–94.
(29) Grigorenko AN, Polini M, Novoselov K. Graphene plasmonics. Nat Photon. 2012;6(11):749–58.
(30) Lui CH, Liu L, Mak KT, Flynn GW, Heinz TF. Ultraflat graphene. Nature. 2009;462(7271):339–41.
(31) Wallace PR. The band theory of graphite. Phys Rev. 1947;79(1):622.
(32) Han S, Chun BC. Preparation of polyurethane nanocomposites via covalent incorporation of functionalized graphene and its shape memory effect. Compos A: Appl Sci Manuf. 2014;58:65–72.
(33) Lee HY, An J, Chua CK. Two-way 4D printing: a review on the reversibility of 3D-printed shape memory materials. Engineering. 2017;3(5):663–74.
(34) Wu DY, Meure S, Solomon D. Self-healing polymeric materials: a review of recent developments. Prog Polym Sci. 2008;33(5):479–522.
(35) Prathumrat P, Tiptipakorn S, Rimdusit S. Multiple-shape memory polymers from benzoxazine–urethane copolymers. Smart Mater. 2017;26(6):065025.
(36) Mitchell A, Lafont U, Holyńska M, Semprimoschnig C. Additive manufacturing—A review of 4D printing and future applications. Addit Manufact. 2018;24:606–26.
(37) Firouzeh A, Salerno M, Paik J. Stiffness control with shape memory polymer in underactuated robotic origamis. IEEE Transact Robot. 2017;33:765–77.
(38) Scalet G. Two-way and multiple-shape memory polymers for soft robotics: an overview. Actuators. 2020;9(1):1–10.
(39) Du H, Liu L, Zhang F, Leng J, Liu Y. Triple-shape memory effect in a styrene-based shape memory polymer: characterization, theory and application. Compos B: Engineer. 2019;173:106905.
(40) Ni Q-Q, Zhang C-S, Fu Y, Dai G, Kimura T. Shape memory effect and mechanical properties of carbon nanotube/shape memory polymer nanocomposites. Compos Struct. 2007;81(2):176–84.
(41) Leng J, Lan X, Liu Y, Du S. Shape-memory polymers and their composites: stimulus methods and applications. Prog Masc Sci. 2011;56(7):1077–135.
(42) Liu Y, Du H, Liu L, Leng J. Shape memory polymers and their composites in aerospace applications: a review. Smart Mascr Structur. 2014;23(2):023001.
(43) Xie T. Recent advances in polymer shape memory. Polymer. 2011;52(22):4985–5000.
(44) Liu J, Wang Z, Li S, Sun X. A novel graphene oxide/trans-1, 4-polyisoprene (GO/TPI) shape memory polymer nanocomposite and its multifunctional properties. Nanotechnology. 2019;30(25):255706.
(45) Kuranska M, Prociak A. Porous polyurethane composites with natural fibres. Compos Sci Technol. 2012;72(2):299–304.
(46) Nam ND, Tuan VA, Yen NH, Van Lap D, Khanh PM. A study of phase transformation in shape memory alloy. J Mech Engineer Res Develop. 2019;42(2):72–5.
(47) Cladera A, Weber B, Leinebach C, Czaderski C, Shahverdi M, Motavalli M. Iron-based shape memory alloys for civil engineering structures: an overview. Construct Build Mater. 2014;63:281–93.
(48) Sahoo NG, Rana S, Cho JW, Li L, Chan SH. Polymer nano-composites based on functionalized carbon nanotubes. Prog Polym Sci. 2010;35:837–67.
(49) Liu X, Chakraborty A, Luo C. Fabrication of micropatterns on the sidewalls of a thermal shape memory polystyrene block. J Micromech Microeng. 2010;20(9):095025.
(50) Sarwate P, Chakraborty A, Garg V, Luo C. Controllable strain recovery of shape memory polystyrene to achieve super-hydrophobicity with tunable adhesion. J Micromech Microeng. 2014;24(11):115006.
(51) Kumar KS, Biju R, Nair CR. Progress in shape memory epoxy resins. React Funct Polym. 2013;73(2):421–30.
(52) Xie T, Rodak DE, Rodgers WR. Shape memory epoxy polymers. Google Patents. USA: US8618328B2; 2013.
(53) Truong TT, Thai SH, Nguyen HT, Nguyen TH, Nguyen L-TT. Poly (ε-caprolactone) networks with tunable thermoresponsive shape memory via a facile photo-initiated thiol–ene pathway. J Mater Sci. 2018;53(3):2236–52.
(54) Zhao X, Dong R, Guo B, Ma PX. Dopamine–incorporated dual bioactive electroactive shape memory polystyrene elas- tomers with physiological shape recovery temperature, high stretchability, and enhanced C2C12 myogenic differentiation. ACS Appl Mater Interf. 2017;9(35):29595–611.
(55) Yu K, Ritchie A, Mao Y, Dunn ML, Qi HJ. Controlled sequential shape changing components by 3D printing of shape memory polymer multilayers. Procedia Lutam. 2015;12(1):193–203.
(56) Guo W, Lu CH, Orbach R, Wang F, Qi XJ, Ceconello A, et al. pH-stimulated DNA hydrogels exhibiting shape-memory properties. Adv Mater. 2015;27(1):73–8.
(57) Wu T, Friedych M, O’Kelly K, Chen B. Poly (glycerol sebacate urethane)–cellulose nanocomposites with water-active shape-memory effects. Biomacromolecules. 2014;15(7):2663–71.
(58) Lewis CL, Dell EM. A review of shape memory polymers bearing reversible binding groups. J Polym Sci B: Polym Phys. 2016;54(14):1340–64.
(59) Luo F, Yan P, Qian Q, Li H, Huang B, Chen Q, et al. Highly thermally conductive phase change composites for thermal energy storage featuring shape memory. Compos A: Appl Sci Manuf. 2020;129:105706.
(60) Burke KA, Rousseau IA, Mather PT. Reversible actuation in main-chain liquid crystalline elastomers with varying cross-link densities. Polymer. 2014;55(23):5897–907.
(61) Rahman A, Ali I, Al Zahrani SM, Eleithy RH. A review of the applications of nanocarbon polymer composite. Nano. 2011;6(3):185–203.
Hamid SBA, Tan TL, Lai CW, Samsudin EM. Multiwalled carbon nanotubes in bi-component biodegradable polyester blend for rapid electroactive shape memory performance. Compos Sci Technol. 2016;125:38–46.

Jiang X, Li R, Feng C, Lu G, Huang X. Triple-stimuli-responsive ferrocene-containing homopolymers by RAFT polymerization. Polym Chem. 2017;8(8):2773–84.

Heinz H, Pramanik C, Heinz O, Ding Y, Mishra RK, Marchon D, et al. Nanoparticle decoration with surfactants: molecular interactions, assembly, and applications. Surf Sci Rep. 2017;72(1):1–58.

Alagi P, Choi YJ, Hong SC. Preparation of vegetable oil-based polyols with controlled hydroxyl functionalities for thermoplastic polyurethane. Eur Polym J. 2016;78:46–60.

Wang G, Dong Y, Islam MZ, Yu L, Liu F, Chen S, et al. Effect of graphene oxide-carbon nanotube hybrid filler on the mechanical property and thermal response speed of shape memory epoxy composites. Compos Sci Technol. 2019;169:209–16.

Nurliy H, Yan Q, Song B, Shi Y. Effect of carbon nanotubes reinforcement on the polynvinyl alcohol–polyethylene glycol double-network hydrogel composites: a general approach to shape memory and printability. Eur Polym J. 2019;110:114–22.

Yang J, Zhang Z, Men X, Xu X, Zhu X. Thermo-responsive surface wettability on a pristine carbon nanotube film. Carbon. 2011;49(1):19–23.

Salinas-Torres D, Huerta F, Montilla F, Morallón E. Study on electroactive and electrocatalytic surfaces of single walled carbon nanotube-modified electrodes. Electrochim Acta. 2011;56(5):2464–70.

Hamid SBA, Tan TL, Lai CW, Samsudin EM. Multiwalled carbon nanotube/Thio2 nanocomposite as a highly active photocatalyst for photodegradation of Reactive Black 5 dye. Chinese J Catal. 2014;35(12):2014–9.

He S, Chen P, Qiu L, Wang B, Sun X, Xu Y, et al. A mechanically actuating carbon-nanotube fiber in response to water and moisture. Angew Chem Int Ed. 2015;54(49):14880–4.

Xing Z, Liu Q, Xing W, Asiri AM, Sun X. Interconnected co-entrapped, N-doped carbon nanotube film as active hydrogen evolution cathode over the whole pH range. ChemSusChem. 2015;8(11):1850–5.

Bacakova L, Pajorova J, Tomkova M, Matejka R, Broz A, Stepanovska J, et al. Applications of nanocellulose/nano-carbon composites: focus on biotechnology and medicine. Nanomaterials. 2020;10(2):196.

von Gratosvsky S, Kolevod V, Orlov A, Nesoloven A, Smolovich A, Lega P, et al. Application of mechanical bottom-up nanointegration for CNT based functional nanostructures creation for spintronics and caloritronics. J Radio Electron. 2020;168(4):1719.

Ren D, Chen Y, Li H, Rehman HU, Cai Y, Liu H. High-efficiency dual-responsive shape memory assisted self-healing of carbon nanotubes enhanced polycaprolactone/thermoplastic polyurethane composites. Coll Surf A: physicochem Engineer Asp. 2019;580:123731.

Novoselov KS, Fal V, Colombo L, Gellert P, Schwab M, Kim K. A roadmap for graphene. Nature. 2012;490(7419):192–200.

Huang PY, Ruiz-Vargas CS, Van Der Zande AM, Whitney WS, Levendov MP, Kevek JW, et al. Grains and grain boundaries in single-layer graphene atomic patchwork quilts. Nature. 2011;469(7330):389–92.

Zhou Q, Xia G, Du M, Lu Y, Xu H. Scotch-tape-like exfoliation effect of graphene quantum dots for efficient preparation of graphene nanosheets in water. Appl Surf Sci. 2019;483:52–9.

Wei C, Negishi R, Ogawa Y, Akabori M, Taniyasu Y, Kobayashi Y. Turbostratic multilayer graphene synthesis on CVD graphene template toward improving electrical performance. Japanese J Appl Phys. 2019;58(S1):SILB04.

Cabrero-Vilatel A, Weatherup RS, Braeuninger-Weimer P, Caneva S, Hofmann S. Towards a general growth model for graphene CVD on transition metal catalysts. Nanoscale. 2016;8(4):2149–58.

Narayanan PK, Botcha GD, Ghosh M, Major SS. Growth and photocatalytic behaviour of transparent reduced GO-ZnO nanocomposite sheets. Nanotechnology. 2019;30:485601.

Kausar A. Potential of polymer/graphene nanocomposite in electronics. Am J Nanosci Nanotechnol Res. 2018;6(1):55–63.

Hu K, Kulkarni DD, Choi I, Tuskruk VV. Graphene-polymer nanocomposites for structural and functional applications. Prog Polym Sci. 2014;39(11):1934–72.

Zandiatashbar A, Lee G-H, An SJ, Lee S, Mathew N, Terrones M, et al. Effect of defects on the intrinsic strength and stiffness of graphene. Nat Commun. 2014;5:3186.

Kong W, Kum H, Bae SH, Shim J, Kim H, Kong L, et al. Path towards graphene commercialization from lab to market. Nat Nanotechnol. 2019;14(10):927–38.

Han JT, Jang JI, Cho JY, Hwang JY, Woo JS, Jeong HJ, et al. Synthesis of nanobelt-like 1-dimensional silver/nanocarbon hybrid materials for flexible and wearable electronics. Sci Rep. 2017;7(1):1–9.

Tang C, Titirici M-M, Zhang Q. A review of nanocarbons in energy electrocatalysis: multifunctional substrates and highly active sites. J Ener Chem. 2017;26(6):1077–93.

Freund P, Senkovska I, Kaskel S. Switchable conductive MOF–nanocarbon composite coatings as threshold sensing architectures. ACS Appl Mater Interf. 2017;9(50):43782–9.

Hornat CC, Urban MW. Shape memory effects in self-healing polymers. Prog Polym Sci. 2020;102:101208.

Wu X, Liu Y, Leng J. Investigation of mechanical behavior of epoxy shape memory polymers. Int Soc Opt Photon. 2009;7289:72890Z.

Leng J, Wu X, Liu Y. Effect of a linear monomer on the thermomechanical properties of epoxy shape-memory polymer. Smart Mater Struct. 2009;18(9):095031.

Lu H, Yao Y, Huang WM, Hui D. Noncovalently functionalized carbon fiber by grafted self-assembled graphene oxide and the synergistic effect on polymeric shape memory nanocomposites. Compos B: Engineer. 2014;67:290–5.
(95) Martin-Gallego M, Verdejo R, López-Manchado MA, Sangermano M. Epoxy-graphene UV-cured nanocomposites. Polymer. 2011;52(21):4664–9.

(96) D’Elia E, Ahmed HS, Fiehler E, Saiz E. Electrically-responsive graphene-based shape-memory composites. Appl Mater Today. 2019;35:185–91.

(97) Zaman I, Phan TT, Kuan H-C, Meng Q, La LTB, Luong L, et al. Epoxy/graphene platelets nanocomposites with two levels of interface strength. Polymer. 2011;52(7):163–1.

(98) Wang W, Liu D, Liu Y, Leng J, Bhattacharyya D. Electrical actuation properties of reduced graphene oxide paper/epoxy-based shape memory composites. Compos Sci Technol. 2015;106:20–40.

(99) Yang Z, Wang Q, Wang T. Dual-triggered and thermally reconfigurable shape memory graphene-vitrimer composites. ACS Appl Mater Interf. 2016;8(33):21691–99.

(100) Ponnamma D, El-Gawady YM, Rajan M, Goutham S, Rao KV, Al-Maadeed MAA. Shape memory behavior of conducting polymer nanocomposites. Smart Polymer Nanocomposites. Cham: Springer; 2017. p. 321–43.

(101) Wang Y, Tian W, Xie J, Liu Y. Thermoelectric responsive shape memory graphene/hydro-epoxy composites for actuators. Micromachines. 2013;6(8):145.

(102) Park J, Dao T, Lee H-J, Jeong H, Kim B. Properties of graphene/shape memory thermoplastic polyurethane composites actuating by various methods. Materials. 2014;7(3):1520–38.

(103) Kim J, Kim B, Kim E, Park H, Jeong H. Synthesis and shape memory performance of polyurethane/graphene nanocomposites. React Funct Polym. 2014;74:16–21.

(104) Lendlein A, Gould OE. Reprogrammable recovery and actuation behaviour of shape-memory polymers. Nat Rev Mater. 2019;4(2):116–33.

(105) Sofia RLM, Rezaei M, Babaie A, Nasiri M. Preparation of electroactive shape memory polyurethane/graphene nanocomposites and investigation of relationship between rheology, morphology and electrical properties. Compos B: Engineer. 2019;175:107090.

(106) Abbasi A, Mir Mohamad Sadeghi G, Ghasemi I, Shahrousvand M. Shape memory performance of green in situ polymerized nanocomposites based on polyurethane/graphene nanoplatelets: synthesis, properties, and cell behavior. Polym Compos. 2018;39(11):4020–33.

(107) Patel KK, Purohit R. Improved shape memory and mechanical properties of microwave-induced thermoplastic polyurethane/graphene nanoplatelets composites. Sens Actuat A: Phys. 2019;285:17–24.

(108) Kausar A. Nanodiamond integrating poly(methyl methacrylate) nanocomposites intending for technological innovations. Materials Research Innovations. 2021;25:310–9.

(109) Barker LM, Hollenbach R. Shock-wave studies of PMMA, fused silica, and sapphire. J Appl Phys. 1970;41(10):4208–26.

(110) Eskhaftaki FJ, Ghasemi I. Multiple shape memory behavior of nanocomposite based on polymethylmethacrylate/poly(lactic acid)/graphene nanoplatelets (PMMA/PLA/GNP). Polym Bull. 2018;75(9):4073–84.

(111) Ji W-F, Chang K-C, Lai M-C, Li C-W, Hsu S-C, Chuang T-L, et al. Preparation and comparison of the physical properties of PMMA/thermally reduced graphene oxides composites with different carboxylic group content of thermally reduced graphene oxides. Compos A: Appl Sci Manuf. 2014;65:308–14.

(112) Keramati M, Ghasemi I, Karrabi M, Azizi H, Sabzi M. Incorporation of surface modified graphene nanoplatelets for development of shape memory PLA nanocomposite. Fiber Polym. 2016;17:1062–8.

(113) Piekarśka K, Sowiński P, Piorkowska E, Haque MM-U, Pracella M. Structure and properties of hybrid PLA nanocomposites with inorganic nanofillers and cellulose fibers. Compos A: Appl Sci Manuf. 2016;82:34–41.

(114) Keramati M, Ghasemi I, Karrabi M, Azizi H, Sabzi M. Dispersion of graphene nanoplatelets in polyacrylic acid with the aid of a zwitterionic surfactant: evaluation of the shape memory behavior. Polym-Plast Technol Engineer. 2016;55:1039–47.

(115) Kashif M, Chang Y-W. Supramolecular hydrogen-bonded polyolefin elastomer/modified graphene nanocomposites with near infrared responsive shape memory and healing properties. Eur Polym J. 2015;66:273–81.

(116) Wang C, Liu N, Allen R, Tok JBH, Wu Y, Zhang F, et al. A rapid and efficient self-healing thermo-reversible elastomer crosslinked with graphene oxide. Adv Mater. 2013;25(40):5785–90.

(117) Cai C, Zhang Y, Li M, Chen Y, Zhang R, Wang X, et al. Multiple-responsive shape memory polycyanonitrile/graphene nanocomposites with rapid self-healing and recycling properties. RSC Adv. 2018;8(3):1225–31.

(118) Woroch JC, Weems AC, Yu J, Arno MC, Wilks TR, Huckstepp RT, et al. Elastomeric polyanide biomaterials with stereochimically tunable mechanical properties and shape memory. Nat Commun. 2020;11(1):1–11.

(119) Li M, Guan Q, Dingemans TJ. High-temperature shape memory behavior of semicrystalline polamide thermosets. ACS Appl Mater Interf. 2018;10(22):19106–15.

(120) Yan G-M, Wang H, Li D-S, Lu H-R, Liu S-L, Yang J, et al. Design of recyclable, fast-responsive and high temperature shape memory semi-atheromatic polamide. Polymer. 2021;216:123427.

(121) Marotta A, Lama GC, Ambrogi V, Cerruti P, Giamberini M, Gentile G. Shape memory behavior of liquid-crystalline elastomer/graphene oxide nanocomposites. Compos Sci Technol. 2018;159:251–8.

(122) Ma L, Niu H, Cai J, Zhao P, Wang C, Lian Y, et al. Optical, electrochemical, photoelectrochemical and electrochemical properties of polypamide/graphene oxide with various feed ratios of polamide to graphite oxide. J Mater Chem C. 2014;2(12):2272–82.

(123) Kausar A. Shape memory polystyrene-based nanocomposite: present status and future opportunities. J Macromol Sci A. 2021;58(3):182–91.

(124) Xu B, Fu YQ, Ahmad M, Luo J, Huang WM, Kraft A, et al. Thermo-mechanical properties of polystyrene-based shape memory nanocomposites. J Mater Chem. 2010;20(17):3442–8.

(125) Li W, Tang X-Z, Zhang H-B, Jiang Z-G, Yu Z-Z, Du X-S, et al. Simultaneous surface functionalization and reduction of graphene oxide with octadecylamine for electrically conductive polystyrene composites. Carbon. 2011;49(14):4724–30.
(126) Thakur VK, Thakur MK, Raghavan P, Kessler MR. Progress in green polymer composites from lignin for multifunctional applications: a review. ACS Sustain Chem Eng. 2014;2(5):1072–92.

(127) Ralph J, Lapierre C, Boerjan W. Lignin structure and its engineering. Curr Opin Biotechnol. 2019;56:240–9.

(128) Joseph B, Sagarkia VK, Sabu C, Kalarikkal N, Thomas S. Cellulose nanofibrillates: fabrication and biomedical applications. J Bioresources Bioprod. 2020;5(4):223–37.

(129) Qian H, Wang J, Yan L. Synthesis of lignin-poly (N-methyl-lanilime)-reduced graphene oxide hydrogel for organic dye and lead ions removal. J Bioresources Bioprod. 2020;5(3):204–10.

(130) Bai Y, Chen X. A fast water-induced shape memory polymer based on hydroxyethyl cellulose/graphene oxide composites. Compos A: Appl Sci Manuf. 2017;103:9–16.

(131) Xia Z, Li J, Zhang J, Zhang X, Zheng X, Zhang J. Processing and valorization of cellulose, lignin and lignocellulose using ionic liquids. J Bioresources Bioprod. 2020;5(2):79–95.

(132) Jiang X, Bai Y, Chen X, Liu W. A review on raw materials, commercial production and properties of lyocell fiber. J Bioresources Bioprod. 2020;5(1):16–25.

(133) Pappas G, Ferrari S, Wan C. Recent advances in graphene-based materials for lithium batteries. Curr Org Chem. 2015;19(18):1838–49.

(134) Kullala T, Bhadra S, Yao D, Kim NH, Bose S, Lee JH. Recent advances in graphene based polymer composites. Prog Polym Sci. 2010;35(11):1350–75.

(135) Kim H, Abdala AA, Macosko CW. Graphene/polymer nanocomposites. Macromolecules. 2010;43(16):6515–30.

(136) Bellouard Y. Shape memory alloys for microsystems: a review from a material research perspective. Mater Sci Engineer: A. 2008;481:582–9.

(137) Nataraj S, Yang K, Aminabhavi T. Polyacrylonitrile-based nanofibers—a state-of-the-art review. Prog Polym Sci. 2012;37(3):487–513.

(138) Jadhav SA, Rane AV, Kanny K, Muple SS, Abitha VK, Thomas S. Application of blends and polyurethane interpenetrating polymer networks. Polyurethane Polymers. Netherlands: Elsevier; 2017. p. 359–75.

(139) Zheng N, Fang G, Cao Z, Zhao Q, Xie T. High strain epoxy shape memory polymer. Chem Polym. 2015;6(16):3046–53.

(140) Jin H, Mangun CL, Stradley DS, Moore JS, Sottos NR, White SR. Self-healing thermost with encapsulated epoxy-amine healing chemistry. Polymer. 2012;53(2):581–7.

(141) Bellin I, Kelch S, Langer R, Lendlein A. Polymeric triple-shape materials. Proceed Nat Acad Sci. 2006;103(48):18043–7.

(142) Li Q, Zhou J, Vantakanh-Varnoosfaderani M, Nykypanchuk D, Gang O, Sheiko SS. Advancing reversible shape memory by tuning the polymer network architecture. Macromolecules. 2016;49(4):1383–91.

(143) Chung T, Romo-Uribe A, Mather PT. Two-way reversible shape memory in a semicrystalline network. Macromolecules. 2008;41(1):184–92.

(144) Jung D, Jeong H, Kim B. Organic–inorganic chemical hybrids having shape memory effect. J Mater Chem. 2010;20(17):3458–66.

(145) Ogunsone EO, Muthurai R, Ojogbo E, Valero O, Mekonnen TH. Engineered nanomaterials for antimicrobial applications: a review. Appl Mater Today. 2019;18:100473.

(146) Cao G, Lin H, Fraser S, Zheng X, Del Rosal B, Gan Z, et al. Resilient graphene ultrathin flat lens in aerospace, chemical, and biological harsh environments. ACS Appl Mater Interf. 2019;11(22):20298–303.

(147) Naghibi S, Kargar F, Wright D, Huang CYT, Mohammadzadeh A, Barani Z, et al. Noncuring graphene thermal interface materials for advanced electronics. Adv Electron Mater. 2020;6:1901303.

(148) Yadav R, Tirumali M, Wang X, Naeebe M, Kandasubramanian B. Polymer composite for antistatic application in aerospace. Defence Technol. 2020;16:107–18.

(149) Hasan SM, Harmon G, Zhou F, Raymond JE, Gustafson TP, Wilson TS, et al. Tungsten-loaded SMP foam nanocomposites with inherent radiopacity and tunable thermo-mechanical properties. Polym Adv Technol. 2016;27(2):195–203.

(150) Lu H, Gou J. Fabrication and electroactive responsive behavior of shape–memory nanocomposite incorporated with self-assembled multilayered carbon nanotube nanopaper. Polym Adv Technol. 2012;23(12):1529–35.

(151) Browne A, Johnson N. Morphable body moldings, rub strips, and bumpers. Google Patents. USA: US2005022248A1; 2005.

(152) Das R, Melchior C, Karumbakah K. Self-healing composites for aerospace applications. Advanced composite materials for aerospace engineering. Vol. 201. Netherlands: Elsevier; 2016. p. 333–64.

(153) Garces IT, Aslanzadeh S, Boluk Y, Ayranci C. Effect of moisture on shape memory polyurethane polymers for extrusion-based additive manufacturing. Materials. 2019;12(2):244.

(154) Dominique P, Crego P. Wearables, Smart Textiles & Smart Apparel. Netherlands: Elsevier; 2018.

(155) Krystek M, Pakulski D, Patroniak V, Gorski M, Szojda L, Ciesielski A, et al. High-performance graphene-based cementitious composites. Adv Sci. 2019;6(9):1801195.

(156) Shi K, Xu J, Jiang Z, Lu J, Lu Y. Mechanical properties of new composite wood-plant based composites with aluminium alloy frame. Advances in Civil Engineering. 2020;2020:8831999.

(157) Shariati M, Rafie S, Zandi Y, Fooladvar R, Gharahghei B, Mehrabi P, et al. Experimental investigation on the effect of cementitious materials on fresh and mechanical properties of self-consolidating concrete. Adv Concr Construct. 2019;8(3):225–37.

(158) Xiao J-Z, Li J-B, Zhang C. On relationships between the mechanical properties of recycled aggregate concrete: an overview. Mater Struct. 2006;39(6):655–64.

(159) Lin Y, Dong X, Liu S, Chen S, Wei Y, Liu L. Graphene–elastomer composites with segregated nanostructured network for liquid and strain sensing application. ACS Appl Mater Interf. 2016;8(36):24143–51.

(160) Luo S, Samad YA, Chan V, Liao K. Cellular graphene: fabrication, mechanical properties, and strain-sensing applications. Mater. 2019;1(5):1148–1202.

(161) Lendlein A, Behl M, Hiebl B, Wischke C. Shape-memory polymers as a technology platform for biomedical applications. Exp Rev Med Dev. 2010;7(3):357–79.

(162) Osman AF, Edwards GA, Schiller TL, Andriani Y, Jack KS, Morrow IC, et al. Structure–property relationships in biomedical thermoplastic polyurethane nanocomposites. Macromolecules. 2012;45(1):198–210.