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COMPETENCE OF CARBONACEOUS FIBERS/NANOFILLERS (GRAPHENE, CARBON NANOTUBE) REINFORCED SHAPE MEMORY COMPOSITES/NANOCOMPOSITES TOWARDS AEROSPACE—EXISTENT STATUS AND EXPANSIONS

ABSTRACT

Shape memory or stimuli responsive polymers have established a unique grouping of smart materials. The technical merit of these polymers has been evaluated in aerospace sector, since last few decades. Particularly, the stimuli responsive polymers render inherent competences to recuperate the structural damages in exterior/interior space architectures. In this context, both the thermoplastics as well as thermosetting polymers depicted essential stimuli responsive behaviour. As interpreted in this state-of-the-art review, the carbonaceous reinforcement like carbon fibers and nano-reinforcements including nanocarbons (graphene, carbon nanotube) have been employed in the shape recovering matrices. The performance of ensuing shape retrieving aerospace materials was seemed to be reliant on the polymer chain crosslinking effects, filler/nanofiller dispersal/alignment, microstructural specs, interfacial contour and interactions, and processing techniques used. Consequently, the shape actuations of polymer/carbon fiber composites were found to be instigated and upgraded through the inclusion of nanocarbon nano-additives. The ensuing high-tech shape memory composites/nanocomposites have anomalous significance for various aero-structural units (fuselage, wings, antennas, engines, etc.) due to prevention of possible thermal/shock/impact damages. Future implications of carbonaceous shape memory composites/nanocomposites in aerospace demands minimizing the structure-property-performance challenges and large scale fabrication for industrial scale utilizations. In this way, deployment of carbonaceous nanofiller/filler based composites revealed enormous worth due to low density, anti-fatigue/wear, anti-corrosion, non-flammability, self-healing, and extended durability and long life operations. However, there are certain challenges associated with the use of nanocarbons and ensuing nanocomposites in this field markedly the adoption of appropriate carbon fiber coating technique, aggregation aptitude of nanocarbons, additional processing steps/cost, nanoparticle initiated invisible defects/voids, difficulty in machinability operations due to presence of nanoparticles, and corrosion risk of composite structures in contact with metal surfaces. By overcoming these hinderances, nanoparticles modified carbon fiber based composites can be promising towards a new look of upcoming modernized aerospace industry.

Keywords: *shape memory; carbon fiber, graphene, thermoset; nanocomposite; interactions; damage*

INTRODUCTION

Carbonaceous reinforcements and nano-reinforcements in aerospace materials depicted enormous technological worth [1]. The significant carbon fillers are carbon fibers, while numerous nanocarbon nano-additives have also been reported [2]. An important type of smart polymers is the shape memory or stimuli responsive polymers [3]. Owing to property-performance benefits, the shape memory polymers have been found functional for myriad of technological arenas including the aerospace/automotive, electronics, charge storing devices, environmental, and biomedical systems [4]. Most importantly, an exceptional application of

shape memory polymers has been observed in aeronautics [5-7]. Moreover, improvement in shape recovering proficiency of polymers was observed through the inclusion of nanoparticles [8]. Carbonaceous fillers like carbon fiber and nanocarbon nano-additives have been filled in matrices to see the effect on the shape memory performance [9]. The shape switching was found reliant on the physical or chemical associations between the polymer chains, interactions in matrix-filler, interfacial contour, and microstructural features [10-12]. Subsequently, the stimuli responsive materials have been employed for the advanced interior or exterior space related structural designs, engines, and several technical components [13, 14]. Here, epoxy matrices have been used to form carbon fiber reinforced polymeric materials for load bearing, strength, and heat resilience of airframes in flight operations and variety of primary/secondary space structural parts (antenna dishes, motor castings, gears, vertical/horizontal stabilizers, etc.) [15]. For example, Williams et al. [16] inspected self-healing competence of epoxy based carbon fibre reinforced polymer to recover impact damage and strength recovery by about 90%. The effect was credited to the homogeneously aligned fibers with epoxy in aerospace structural laminates developing specific interfaces. Understanding the shape memory phenomenon has been perceived indispensable to attain the high-tech final product [17, 18].

Henceforth, this article overviews the current state of shape memory polymeric composites and nanocomposites with carbonaceous reinforcing/nano-reinforcing agents having aerospace. Consequently, various facile and effective fabrication procedures have been applied to develop the shape memory carbon based materials/nanomaterials. Among the shape memory materials, major categories of carbon fiber, graphene, carbon nanotube, carbon fiber-graphene, and carbon fiber-carbon nanotube filled aerospace matrices have been surveyed. The shape memory performance of these materials was reliant upon the reinforcement type, amount, functionality, interaction with matrices, dispersal/alignment, microstructure, and processing tactics. Accordingly, the shape memory mechanisms have been explored for the aerospace related high performance shape changing systems. To the best of knowledge, this overview is structured to throw a novel vista on carbon fiber or nanocarbon modified carbon fiber derived shape memory composites for aerospace structural applications. Although, literature reports on the carbon fiber composites for aerospace, however no recent comprehensive article seen so far on the targeted shape memory carbon fiber composites or carbon fiber/nanocarbon nanocomposites. For this purpose, manuscript is systematically frame worked keeping in view the novelty of outline covering stimuli responsive polymeric composites with carbon fiber, carbonaceous nanofillers and carbon fibers, as well as structural applications towards advanced aeronautical solicitations. Such a literature collection and beneficial state-of-the-art deliberations on shape memory aerospace materials will be definitely advantageous for the field engineers/scientists struggling for new design innovations and space-age performance.

STATE OF THE ART: STIMULI RESPONSIVE POLYMERIC COMPOSITES WITH CARBON FIBER REINFORCEMENT FOR AEROSPACE

In aeronautical sector, the stimuli responsive or shape memory polymer composites have attained noteworthy value [19, 20]. Shape recovering materials/composites own intrinsic capacity to overcome the external shock/damages [21]. Particularly, carbon fiber filled composites have been practiced for the space related shape recovery processes and structures [22, 23]. For space related carbon fiber composites, numerous thermoplastics and thermosetting matrices have been practiced [24]. In simple words, thermoplastics have reversible molding

behavior upon the application of heat. On the other hand, thermosets cannot be remolded upon heating, once cured. Another category of plastics is thermosetting plastics consisting of long macromolecular chains viable to remolding upon heating. Stimuli responsive polymers can be thermoplastic, thermosets, or thermosetting plastics, depending upon their aptitude of shape fixation and actuation towards external stimuli. In addition to the conventional structural processing approaches, the advanced shape memory composites have been designed using the sophisticated three dimensional or four dimensional printing techniques [25, 26]. Wang and scientists [27] reported on the carbon fiber filled stimuli responsive composites with poly(lactic acid) matrix through four dimensional printing method for aerospace application. The materials paraded electrical/thermal driven shape recovery behavior (Fig. 1A&B). To monitor the shape memory behavior, high-tech photographic techniques were used. The electrothermally induced shape deformation, fixation, and recovering processes were investigated. The temperature dissemination in the samples were also monitored through an efficient infrared thermal imager. The shape memory composites were scrutinized for simulated effective temperature zone ratio/stress studies (Fig. 1C).

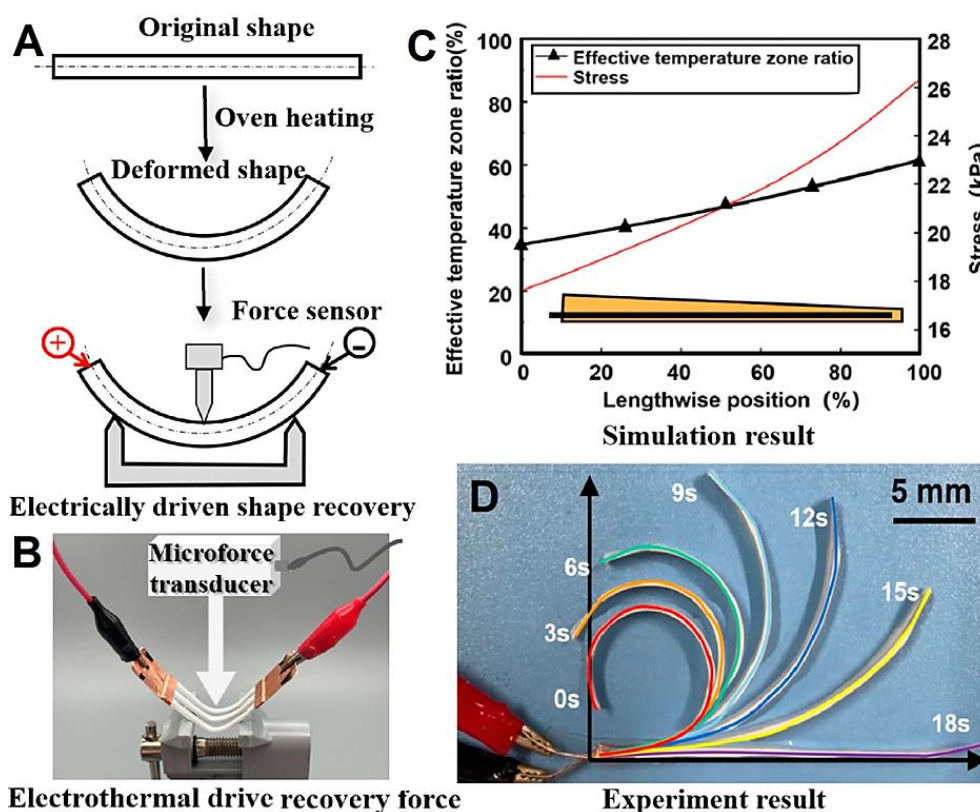


Fig. 1. (A) Recovery force test device during electrically driven shape memory recovery; (B) Photograph of electrically driven shape memory test fixture; (C) Simulated effective temperature zone ratio and stress along the lengthwise position for the carbon fiber reinforced shape memory composite gradient structure; and (D) Experimental results of the recovery process of the carbon fiber reinforced shape memory composites gradient structure [27]. Reproduced with permission from MDPI

Accordingly, the shape memory poly(lactic acid)/carbon fiber depicted steady increase in storage stress (energy stored in crosslinked polymer network during deformation caused by entropy decline) and effective temperature area with the decreasing structure thickness, in maximum axial stress distribution explorations. This effect was attributed to enhancements in the fiber volume contents with the declining structural thickness, so increasing the storage stress

on deformation. Consequently, the stimuli responses of carbon fiber filled composite gradient structures were recorded (Fig. 1D). The electro-actuation was studied at 6V and shape recovery was found within 18s. It was observed that the high fiber content areas undergo high curvature variations, compared with the low regional fiber volume content zones. On the other hand, the areas with higher poly(lactic acid) contents revealed slower shape deformation/recovering processes. Hence, the thermally electroactive shape memory in carbon fiber composites was reliant upon the fiber rich areas and the heterogenous temperature fields applied. Akhoundi et. al. [28] developed an equivalent system on poly(lactic acid) filled with nickel-chromium wires through melt impregnation and printing methods. The electroactive shape memory behavior was studied at 40 V. The resulting shape recovering time was 20-30 s. The results revealed that incorporation of metal wires were found less efficient in enhancing the shape memory properties of the poly(lactic acid) matrix, compared with the carbon fiber filler.

Among thermosets, variety of polymers have been applied to see the stimuli responses with carbon fibers such as epoxy, polyurethane, polyurea, formaldehyde, etc., for space structures [29, 30]. Quadri and colleagues [31] worked on the shape memory sandwich structures of thermosetting polyurethane foam core filled with the polyurea/formaldehyde microcapsules. Here, dicyclopentadiene was loaded in the microcapsules to initiate the self-healing effects in these sandwich structures. The in situ and compression molding techniques have been adopted for the formation/dispersion of microcapsules and fabrication of sandwiched laminates.

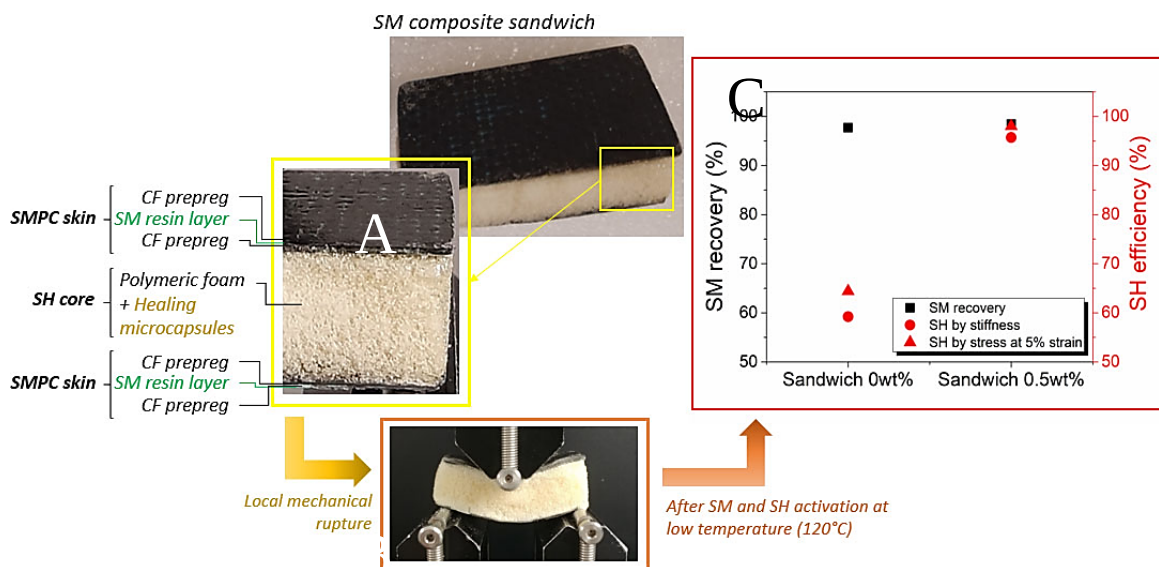


Fig. 2. (A) The designed shape memory (SM) sandwich structure with carbon fiber (CF); (B) photograph of compression and bending test; and (C) shape recovery and self healing (SH) analysis of sandwich structures [31]. SMPC = shape memory polymer composite. Reproduced with permission from MDPI

Fig. 2A illustrates the stimuli responsive sandwich structure having the carbon fiber composite based skin and the microcapsules loaded polyurethane foam core with $100 \times 30 \text{ mm}^2$ dimensions. Compression/bending test was applied for deforming the polyurethane foam core structure and to analyze the self-healing aptitude, the (Fig. 2B). The thermal activation temperature of 120°C was observed for both the shape recovery and self-healing processes. The synergistic effects of the shape memory carbon fiber composite skin and the self-healing agent containing polyurethane core yielded the shape recovering of about 98-99% (Fig. 2C).

Inclusion of nanoparticles to epoxies creates one nano-phase rendering the resulting composites materials as nanocomposites. Jang and group [32] surveyed the carbon fiber filled epoxy composites for space structures. For studying the stimuli responsiveness of these materials, ultraviolet (UV) irradiation and ultra-high vacuum systems were utilized. The UV

irradiation was used to generate the crosslinking effects in epoxy/carbon fiber composites to initiate efficient shape recovery processes. The vacuum based ultraviolet environmental chamber used is displayed in Fig. 3A. The sample heating was regulated with the temperature controller and high vacuum of 10^{-6} torr was maintained. For the vacuum/ultraviolet irradiated composites, storage moduli were measured (Fig. 3B). According to dynamic mechanical analysis, the storage moduli curves were superimposed with the increasing UV intensity. In addition, the storage moduli of the vacuum/ultraviolet irradiated carbon fiber composites were monitored at varying temperatures. The storage moduli seemed to be constant with the increasing temperature values. The overall superior mechanical and stimuli responsive features of the epoxy/carbon fiber composites were accredited to the UV induced crosslinking and chain relaxation effects. Essentially, these shape recovering composites revealed effectiveness towards the aerospace coating materials [33].

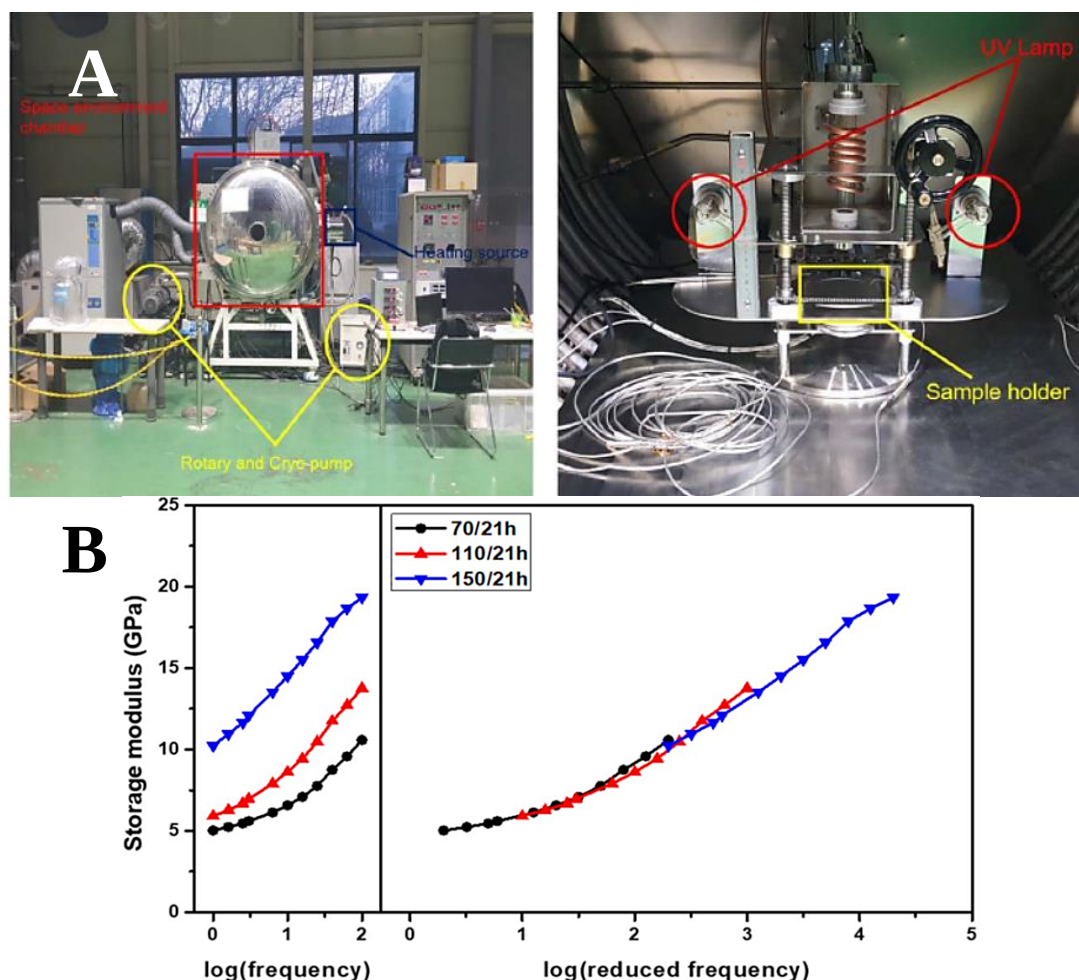


Fig. 3. (A) Vacuum and ultraviolet environmental chamber: (left) graphic diagram of built-in chamber; (right) UV lamp and sample holder; (B) thermomechanical behavior of vacuum and ultraviolet exposed shape memory composite i.e., storage moduli measured vs. frequency at a reference temperature of 70°C by dynamic mechanical analysis [32]. Reproduced with permission from IOP Publishing

Hence, aerospace related carbon fiber reinforced shape memory composites have been developed using both the thermoplastic and thermosetting matrices like poly(lactic acid), epoxies, polyurethanes, etc. These materials have found to parade heat active, electro responsive, or photo actuation behaviors. In most of the cases, the potential materials have been tested for the mechanical and thermal damage recovery. Conventional fabrication techniques like autoclave, compression molding, injection molding, vacuum bagging, and number of other

approaches have been frequently applied to develop the space structures [34]. However, these techniques generally are time consuming and resulting products have disadvantages of structural voids viable to meager strength, dimensional or thermo-dimensional fragility. Consequently, to attain radical design precision and end performance, aerospace research is turning towards the advanced three dimensional printing strategies [35]. Moreover, the use of high performance epoxy matrices have been found to outperform the thermoplastic matrices in carbon fiber based aerospace structures.

SHAPE MEMORY NANOCOMPOSITES WITH CARBONACEOUS NANOFILLERS AND FIBERS FOR AERONAUTICS

Epoxy resins are usually among the most frequently employed thermosets for the stimuli responsive materials revealing shape recovery towards the heat, voltage, light, moisture, etc. [36, 37]. Consequently, the epoxies have been reported for the remarkable shape switching transitions [38]. For these polymers, shape changing phenomenon has been perceived owing to the glass transition, melting, crystallization, or liquid crystal transition temperatures [39]. In consequence, the shape retrieving epoxies have worth for the space industry [40]. Conversion of epoxies to nanocomposites was initially practiced in 2000 [41]. Correspondingly, the nanocarbon reinforced shape memory epoxy nanomaterials have been noticed [42-44]. Like epoxies, these nanomaterials show shape recovering responses towards range of stimuli owing to reversible physical interactions and interfacial associations [45-47]. Here, the inherent shape recovery or self-healing effects have become obvious in the nano-derived epoxy systems for aeronautics [48, 49]. Accordingly, the shape memory epoxy nanocomposites have been analyzed for the engines, fuselage, and engineered space structures [50].

In epoxy matrices, graphene nano-additives have been known to instigate effectual stimuli responses [51]. For example, graphene inclusion in vitrimer epoxy has revealed shape recovery for aerospace purposes [52]. These systems possess exchangeable physical associations causing swift shape changes [53]. The shape memory epoxy nanocomposites reinforced with graphene foam have been industrialized for space related strengthened structures (interior/exterior), antennas, morphing wings, wearable sensors, etc. [54]. Idowu and scientists [55] developed the stimuli responsive systems based on the epoxy and three dimensional graphene foam. The molecular-level stimuli responsiveness was proposed including the heating above the room temperature (T_1) to the shape memory actuation temperature (T_2) and then the sample deformation at T_2 , i.e., the temperature higher than the glass transition temperature (T_g) (Fig. 4A). The entire process will cause energy storage in the deformed epoxy rigid phase, due to the elastic deformation of Neopentyl glycol diglycidyl ether chains. At varying actuation temperatures, the shape recovery rate of the nanocomposites was measured (Fig. 4B). The graphene foam loaded nanocomposite revealed higher recovery rate than the neat shape memory epoxy matrix. The reason was seemed to be the facilitated phonon transference through the epoxy/graphene foam base interlinked structures. The biomimetic shape memory epoxy/graphene foam nanocomposite bird shaped structure was formed to see the crack healing process (Fig. 4C). In heat simulation, the self-healing process was found advantageous to close the crack in the bird wing. The shape recovery was attributed to the multiple structural/dynamic aspects of the graphene foam filled epoxy nanomaterials. Furthermore, the formation of consistent three-dimensional graphene network was found to trigger and cause the dual shape recovery effect. In this concern, adding 0.13 wt.% graphene foam contents enhanced the glass transition temperature by 19%. At 70°C, a 57% upsurge in the heat conduction was observed

(0.3 W mK⁻¹). Such shape memory nanocomposites were remarkably competent for employment in the rigid atmosphere sustaining space components.

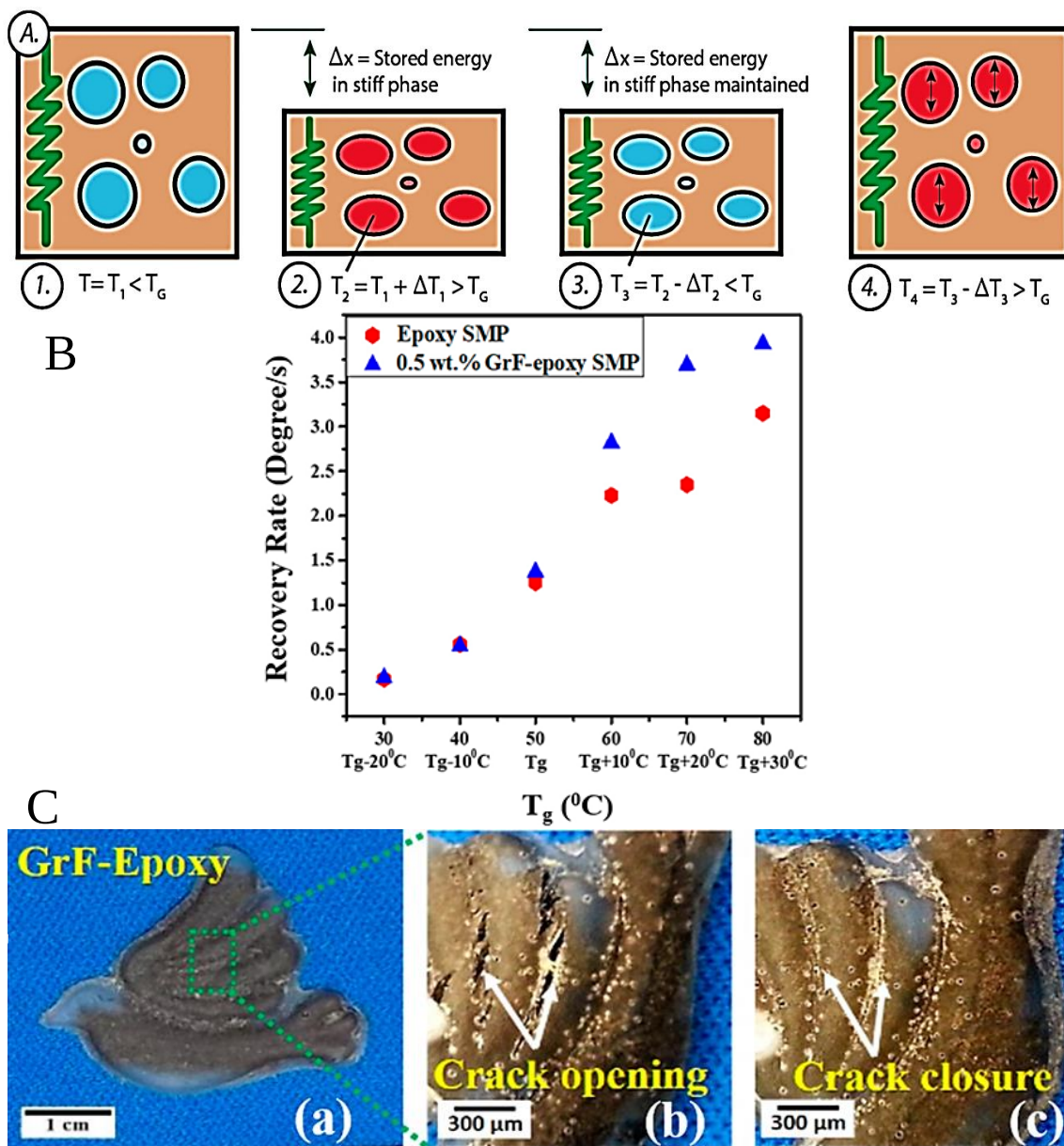


Fig. 4. (A) Illustration of the dual-component mechanism (DCM) in shape memory polymer (SMP) epoxy; (B) shape recovery rate of SMP epoxy and SMP epoxy-0.5 wt.% graphene foam (GrF) as a function of switching temperatures; (C) (a&b) image of a cracked-open wing of biomimetic graphene-foam-epoxy SMP bird after 15th T-M cyclic deformation; and (c) images of the crack-closed wing of graphene-foam-epoxy SMP bird [55]. Reproduced with permission from MDPI

Yoonessi and scientists [56] manufactured the imide functional graphene nanocomposite. N-Methyl-2-pyrrolidone solvent was used for graphene scattering and association towards the nanocarbon (Fig. 5A). The mechanism of stimuli responsive process is illustrated in Fig. 5B. At temperature higher than the glass transition, a transitory shape was formed and subsequently fixed by lowering the temperature below T_g . Again, the pristine shape was recovered by heating the sample above T_g . 100% shape recovering was perceived. The thermal stability of the graphene and imidized graphene is given in Fig. 5C. Considerably high decomposition

temperature for the modified graphene was detected (about 663°C). The heat stable imide functionalities were accountable for the elevated thermal profiles and shape recovery effects of these aerospace intended structural nanomaterials.

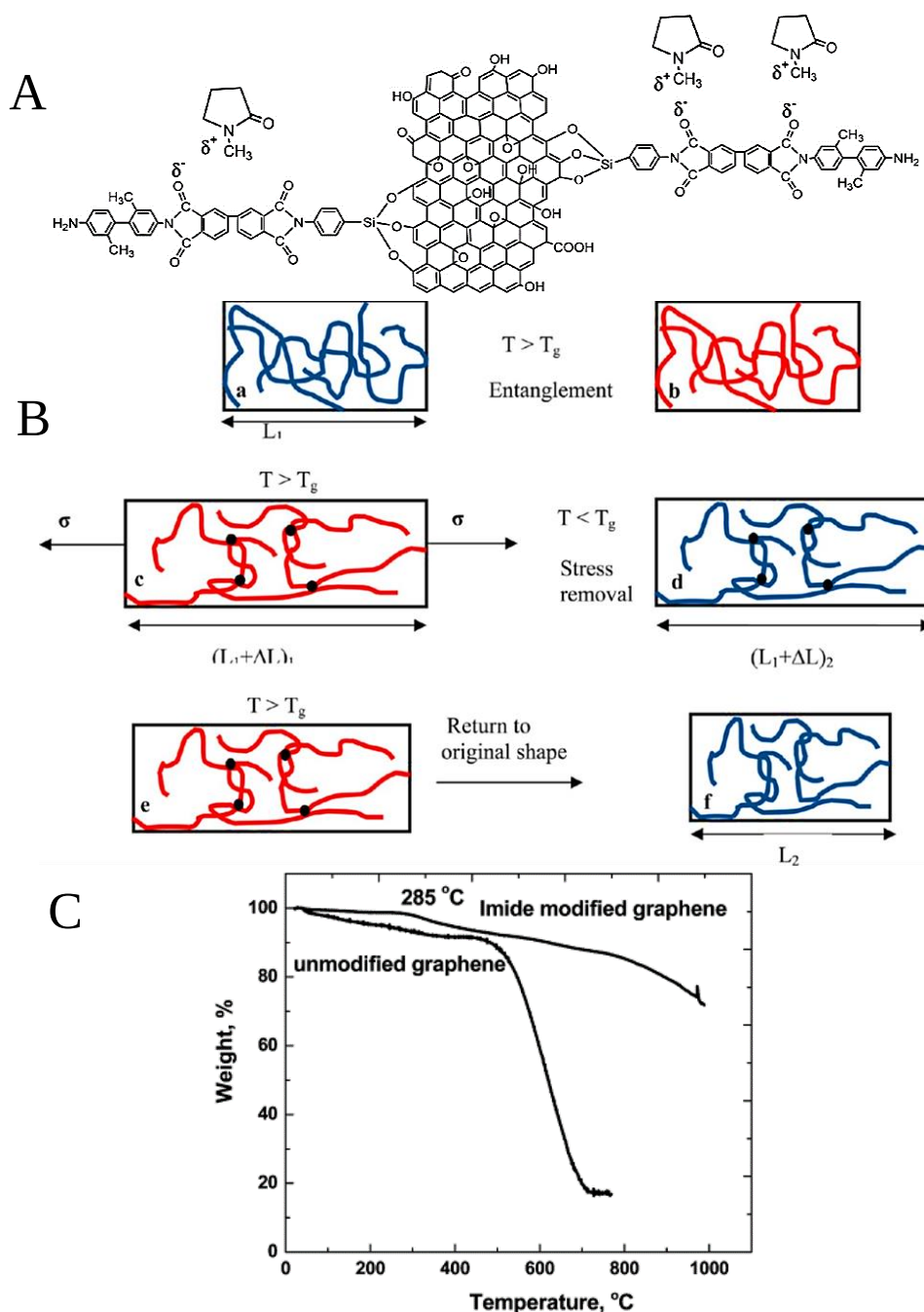


Fig. 5. (A) Dispersion of imidized graphene in N-Methyl-2-pyrrolidone solvent; (B) diagrams of shape memory behavior with glass transition temperature (T_g) as a switching temperature (polymeric composite 100% recovery); and (C) thermogravimetric analysis of pristine graphene and imide-modified graphene [56]. Reproduced with permission from ACS

Krishnakumar and group [57] researched the graphene oxide reinforced epoxy nanomaterials for space structures. The stimuli responsive epoxy/vitrimer nanomaterials depicted shape change at 60°C (5 min). Here, the shape recovery was 88% for the nanocomposite (Fig. 6a). The stress-strain studies (prior to/after healing) were performed on the unfilled and up to 1 wt.% graphene oxide filled epoxy nanomaterials (Fig. 6b). Enhancing the nanoparticle contents upsurge the mechanical features of the nanomaterials. The flexural

modulus variations were detected with the graphene oxide nanofiller additions (Fig. 6c). These features were merely affected with healing cycles owing to efficient chain alterations and recoveries upon heat stimuli.

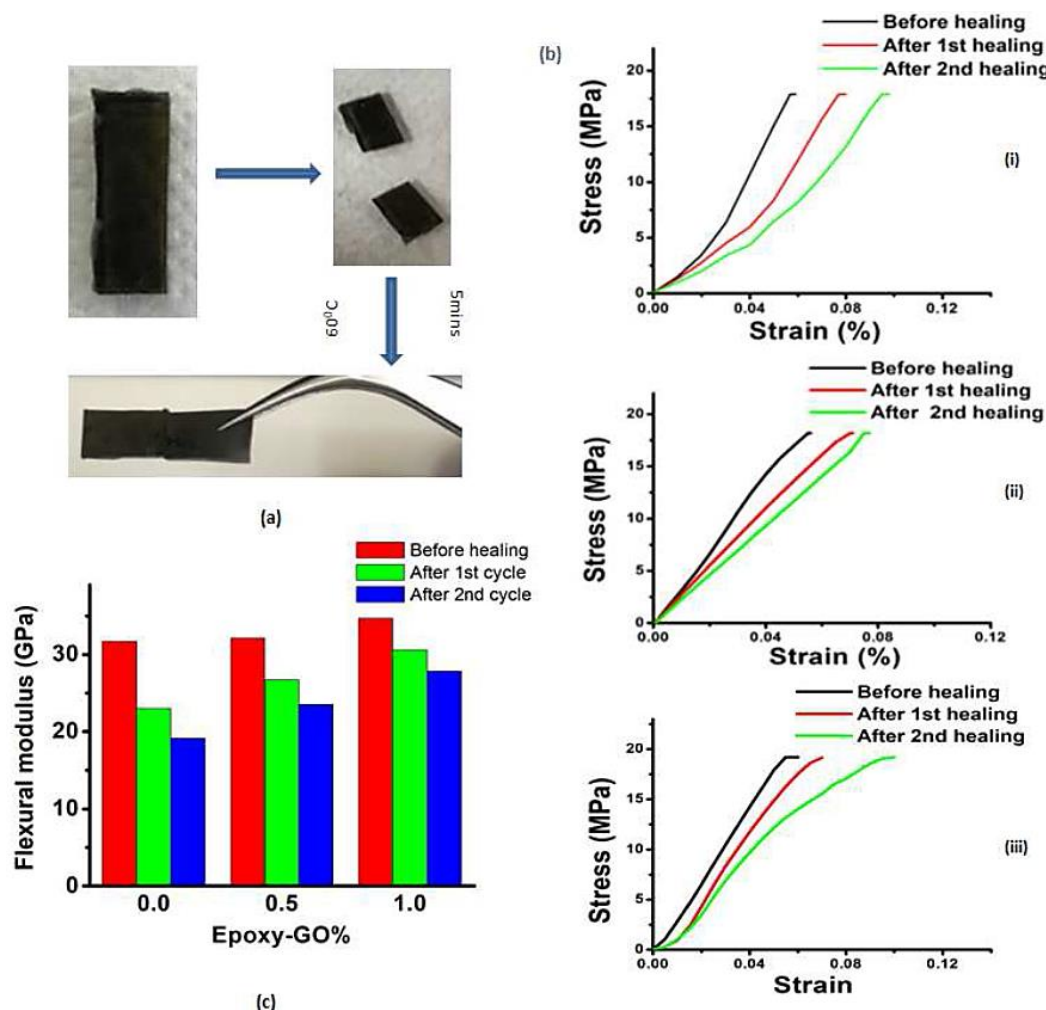


Fig. 6. (a) Optical images of uncured, cut, and healed epoxy 1 wt.% specimen; (b) healing represented stress-strain curves for (i) epoxy pristine, (ii) epoxy 0.5 wt.% graphene oxide (GO), and (iii) epoxy 1 wt.% GO; and (c) flexural modulus changes after healing cycles for different samples [57]. Reproduced with permission from Elsevier

In addition to graphene, carbon nanotube has also been utilized to develop the high performance materials for functional shape memory space architectures [58]. For active stimuli responsiveness, the carbon nanotubes have been found capable to develop the reversible hydrogen binding associations with the matrices [59]. Wang with colleagues [60] focused the fabrication of carbon fiber and carbon nanotube filled epoxy matrix for aerospace structures. The epoxy and carbon fiber based laminates were casted and influence of carbon nanotube inclusions on the microstructure and shape recovery were tested [61]. Slobodian and co-workers [62] designed a nanocomposite nanopaper based on the thermosetting epoxy and multi walled carbon nanotube nanofiller. According to microscopic studies, neat multi walled carbon nanotube based nanopaper had nanoporous microstructure (Fig. 7A&B). On the other hand, the epoxy/multi walled carbon nanotube nanocomposite nanopaper had nanostructure with nanotubes embedded in the matrix, along with some protrusions on surface. The temperature distribution in the nanotube filled nanocomposite was scrutinized using the thermographic image (Fig. 7C). Using a thermal camera, temperature was found to decline at edges owing to cooling in these areas. The time dependent stimuli responsiveness of nanocomposite nanopaper

was studied after Joule heating (Fig. 7D). Efficient Joule heating effect was noticed during bending and recovery of the sample within 20 s. Hence, the study reported on the curing of epoxy matrix through Joule heating effect. Subsequently, epoxy network was capable of shape regaining under the impact of joule heating. This effect enables the sample to rapidly attain the desired glass transition temperature within short time for shape changing. Upon cooling the desired shape is attained.

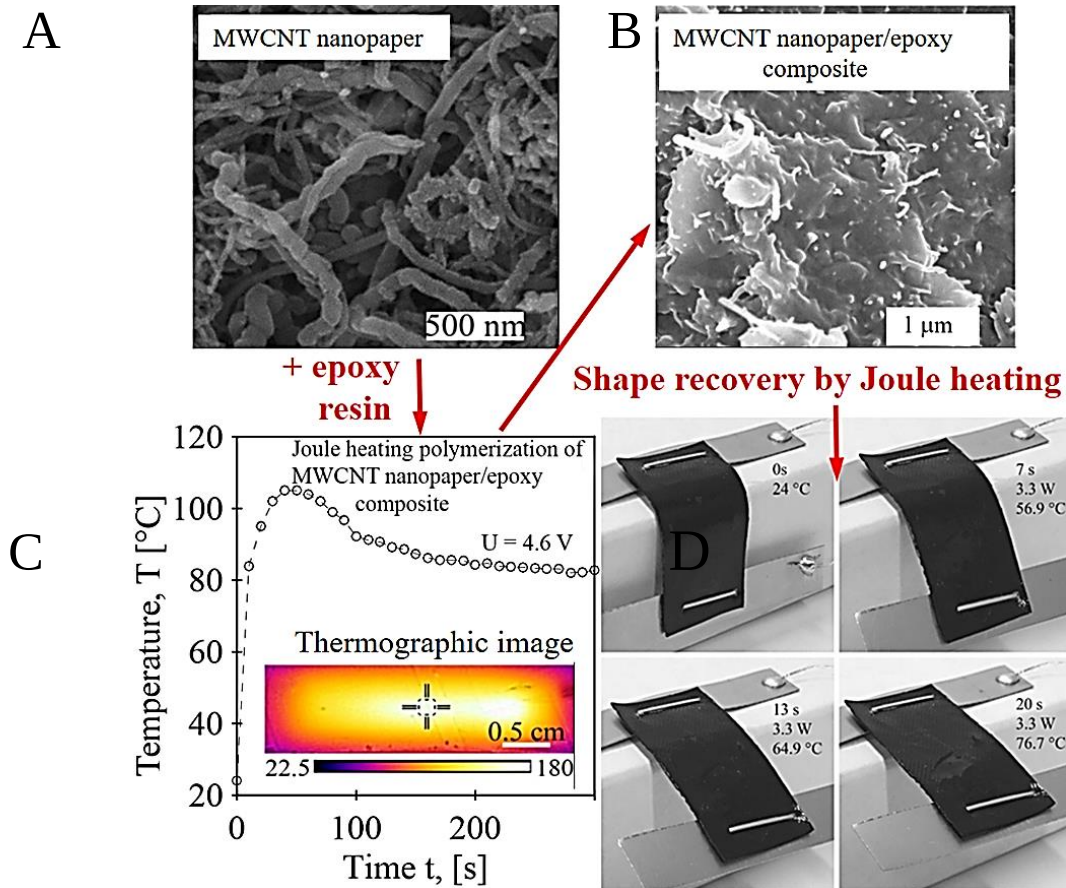


Fig. 7. (A) Transmission electron microscopy micrograph of pristine multi walled carbon nanotube (MWCNT) with visible lines of rolled graphene layers at distance of 0.35 nm; (B) scanning electron microscopy micrograph of epoxy/MWCNT surface; (C) thermographic image of temperature distribution in epoxy/MWCNT nanocomposite strip while temperature curing at 4.6 V (cross section temperature 173 °C); and (D) time dependent shape memory recovery of epoxy/MWCNT nanopaper/epoxy strip after Joule heating (77 °C, 3.3 W) [62]. Reproduced with permission from MDPI

Guadagno and researchers [63] fabricated the epoxy derived space nanocomposites having thymine and barbiturate functional carbon nanotube. Consequently, the matrix was hydrogen linked bonded to the amine, hydroxyl, and carbonyl groups on the nanotubes [64]. These linkages actually caused the effective shape deformation and rapid recovery during shape memory testing [65]. Same group [66] developed a shape memory epoxy resin based on 1,4-butanedioldiglycidylether, tetraglycidyl methylene dianiline epoxy functional carboxyl terminated butadiene acrylonitrile, and 4,4'-diaminodiphenyl sulfone. The multi walled carbon nanotube used was surface functionalized using the barbiturate. Afterwards, the addition of functional nanocarbon to epoxy blend matrix caused considerable shape recovery influence owing to mutual interactions. The nanocomposites were suggested beneficial for strengthened and robust space structures.

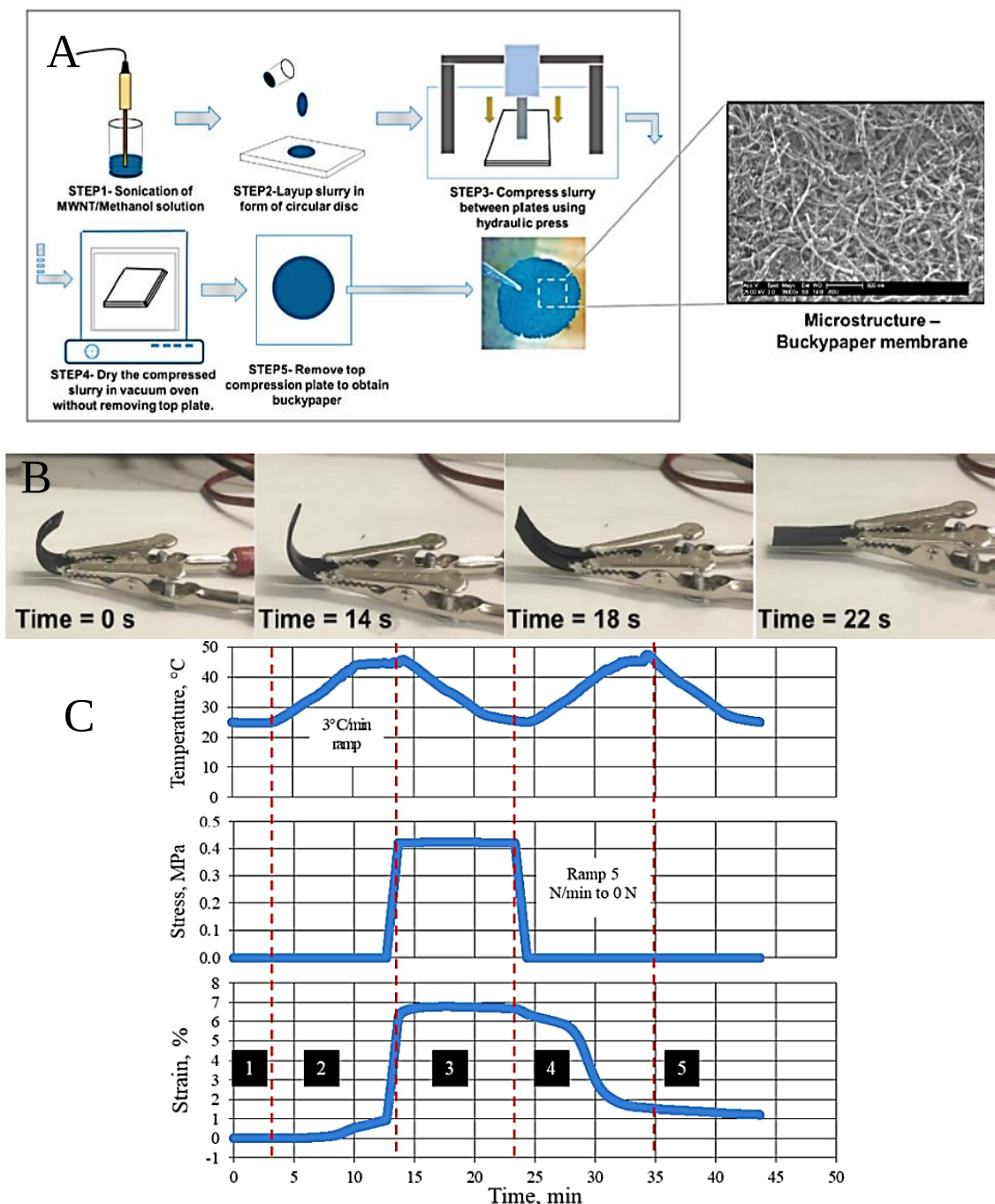


Fig. 8. (A) Buckypaper nanocomposite formation by slurry compression technique with scanning electron microscopy scan of nano-porous microstructure (scale bar: 500 nm); (B) shape recovery response of epoxy/carbon nanotube at 12 V DC stimulation; (C) tensile shape memory effect test showing the change in the temperature, stress, and strain over time for nanomaterial, plus temperature and stress are prescribed in the testing while the strain is measured: (1) isotherms at 25°C; (2) ramps the temperature to 45°C; (3) ramps the force to 5 N followed by lowering temperature to 25°C; (4) ramps the force to 0 N and heating specimen back to 45°C; (5) finally reducing temperature to 25°C for residual strain analysis [67]. Reproduced with permission from Elsevier.

Datta and scientists [67] intended the stimuli responsive carbon nanotube reinforced neopentyl glycol diglycidyl ether epoxy nanomaterials. The buckypaper nanocomposite membranes were designed using the resin compression method (Fig. 8A). In the electro-active shape memory studies at 12 V (DC), the sample was deformed at 180°C and recovered in 22 s (Fig. 8B). The shape memory programming and shape recovery features were studied with the stress, strain, and temperature responses with time (Fig. 8C). All these properties of bucky paper

nanocomposites were observed responsible for high performance shape recovering effects for space materials.

Liu and group [68] established the multi walled carbon nanotube reinforced diglycidyl ether of bisphenol A and methylhexahydrophthalic anhydride derived systems displaying heat responsiveness. In the blended matrix, carbon nano-additives were included in the range of 0.25 to 0.75 wt.%. The nanocomposite had glass transition around 65 to 140°C. The shape memory process was captured in photographs for the unfilled and multi walled carbon nanotube filled diglycidyl ether of bisphenol A/methylhexahydrophthalic anhydride nanocomposite (Fig. 9A). Furthermore, dynamic mechanical thermal tests were performed for stimuli responsiveness analysis (Fig. 9B). For the nanocomposite samples, the shape fixity and shape recovery of about 88 % and 97% were attained in the recovering time of 32 s.

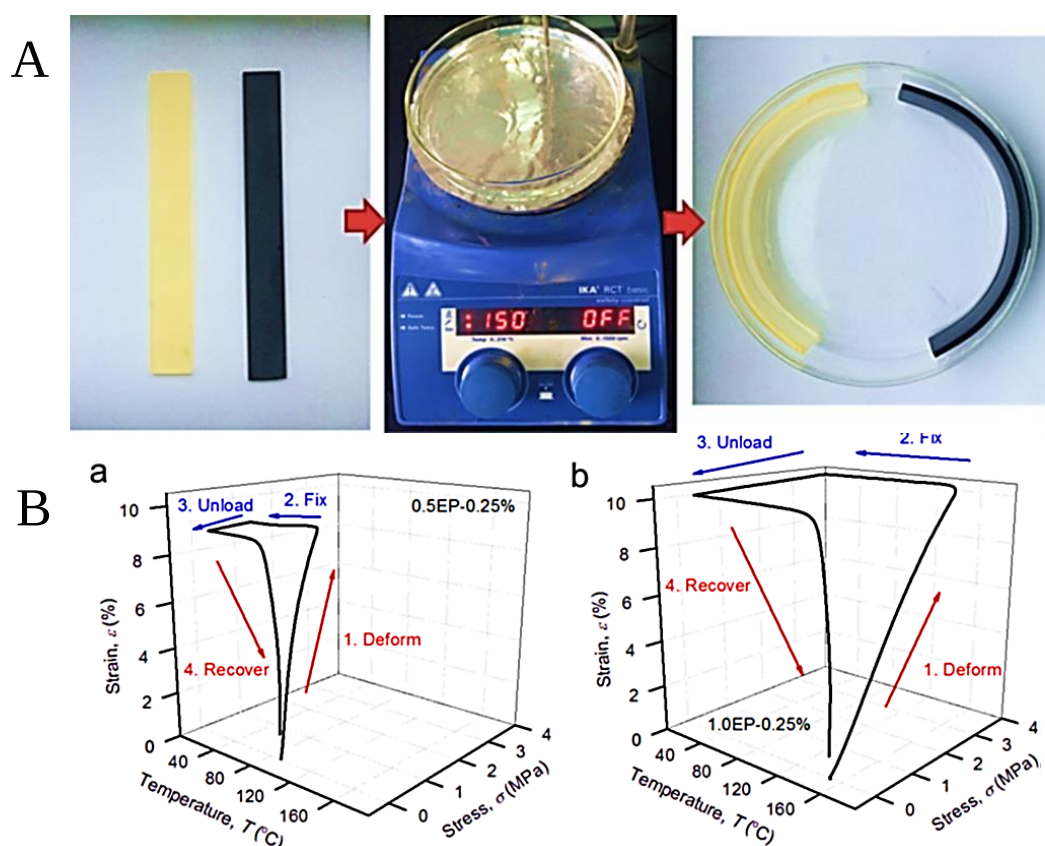


Fig. 9. (A) Photographs showing the fold-deploy shape memory test for neat shape memory sample (yellow) and shape memory nanocomposite sample (black): original shape (left), oil bath at 150 °C on an oven (middle), and temporary shape formed (right); and (B) shape memory cycle by dynamic mechanical thermal analysis of shape memory nanocomposite materials: (a) 0.5 DGEBA/MHHPA + 0.25% MWCNT; (b) 1.0 DGEBA/MHHPA + 0.25% MWCNT [68]. DGEBA/MHHPA = diglycidyl ether of bisphenol A/methylhexahydrophthalic anhydride; MWCNT = multi-walled carbon nanotube. Reproduced with permission from ACS

COMPETENCE OF SHAPE MEMORY NANOCOMPOSITES IN AEROSPACE SECTOR

In shock bearing space structures

Aeronautical structures are frequently prone to external shock effects including the lightening/speedy wind strikes, sound waves, collisions, and other worst environmental outrages [69-71]. In view of that, only the material having high shock waves confrontation and

any environmental turbulence resistance can be employed in the space structures [72]. Consequently, the stimuli responsive materials offer fine solutions for superior mechanical, thermal, radiation, or other shock endurences of space structures [73, 74]. Formerly, Fosness and colleagues [75] interpreted the low shock deployment systems based on the stimuli responsive materials for space purpose. Afterwards, Zhao and group [76] designed the shape actuating epoxy/carbon fiber composites. For exterior aerospace structural body, these materials have been reported for the impact based shock resistance [77]. Furthermore, the microstructure and compression strength of the shape memory epoxy/carbon fiber composites were analyzed. Zhang and scientists [78] examined the vibrational shock tolerance of the shape memory composites for aero-structures. The shock test analysis and theoretical/modeling investigations were executed for the high performance shape recovery aeronautical composites [79, 80]. Nonetheless, only counted attempts have been reported on the shock bearing shape memory composites for aero-structures. Therefore, all-inclusive inquiries seemed to be necessary to design high-impact stimuli responsive aerospace structure.

In morphing wings, antennas, booms

Steadfast aero-structures have been premeditated using the stimuli responsive advanced materials [81, 82]. Predominantly, composites/nanocomposites loaded with fibrous fillers have been preferred for this application [83, 84]. Important space parts such as morphing wings, antennas, and booms have been sightseen using some efficient shape changing polymers and composites [85]. Carbon fiber based composite laminates have been adopted for the construction of ultralight weight and fatigue resisting wings structures in Boeing 787 [86]. These smart materials have been found to visibly upsurge the resilience of hinges/truss booms [87-89]. In the space reflector antennas, polymeric composites with carbon fibers have been successfully practiced [90]. Consequently, these low density materials have been known to offer high shock resistance owing to superior recovery force involved [91, 92]. Incidentally, the carbon fiber reinforced epoxy composites have been applied for constructing the aerospace grade laminates for fabricating the high performance structural units [93-95]. For this purposes, the modern shape recovery materials must have high heat/fatigue/crack confronts [96]. Few attempts have also been noticed on the stimuli responsive carbon fiber and nanoparticles loaded hybrids for aeronautics [97]. Even so, further concentrated attempts seemed to be obligatory to develop and apply the aero-rank shape memory materials for antennas/hinges/truss booms.

In aeronautical fuselage

Similarly, aerospace fuselage has been modified using the lightweight composite structures instead of alloys or hybrid units [98]. Specifically, the fiber filled composites have been found worthy for fuselage structures [99]. Up till now, carbon/glass fiber reinforced composites have been practically utilized for the construction of fuselage in the Boeing 787 Dreamliner aircraft [86]. Composites based fuselage basically constitutes the frames, skin, and other space parts. Single piece barrel designs are usually adopted for pre-pregged carbon fiber composites using automated fiber placement method. Afterwards, the finally machined/finished fuselage parts are supplied to the relevant aerospace assembling unit. Owing to huge pressure difference among the atmospheric pressure and cabin environment, fuselage skin encounters huge pull out forces, pressure strains, and mechanical stresses [100]. Consequently, joint failure may occur due to the poor adhesive performance under extreme impact conditions [101]. Here, high-tech composites have been utilized to attain the required level adhesion and mechanical fastening of the fuselage skin and components [102]. These performance pleads have been fulfilled by employing the stimuli responsive materials in fuselage structures [103]. The derived shape memory structures own high sustainability and impact resistance to sustain or recover the impairments under extreme space conditions [104, 105]. In this context, the nanocomposite design of epoxy, carbon fiber, and carbon nanotube has been recommended for space fuselage

[106, 107]. Here, adding carbon nanotube not only initiated rapid shape recovery but also the impact damage recapture of 99 % [108, 109]. Future research on shape recovering nanocomposites may entirely swap the outmoded alloys in the aero fuselage skin and parts [110].

In space engines

Engines or aero-engines have generally metal or ceramic materials in their components and machineries [111]. Research has reported on the jet engines employing the polymer derived hybrid materials [112, 113]. Obviously, the composite materials for engines must have desirably superior heat stability [114]. In engine blades, impact/heat durable composite materials have been practiced [115, 116]. Consequently, the engine fan blades have been designed using the fiber based composites laminates having unvarying thickness and high performance. As ceramic matrix materials have been applied in the combustion chamber engine, therefore the advanced composites must have high heat stability of at least up to 1000°C or higher for this application [117]. In real world applications, the Airbus A350 XWB and Boeing 787 Dreamliner are found among foremost commercial examples of employing carbon fiber composites in aircraft engines [118]. Consequently, carbon fiber composites have been used to design complex, flexible, and large engine blades with reduced weight [119]. Origination of stimuli responsive nanomaterial designs with carbon fiber, carbon nanotube, and carbon black may fulfil the requirement of extreme conditions enduring engine components [120]. Nevertheless, systematic surveys on shape memory nanocomposites may reveal heat stable, strengthened, and pressure/corrosion/moisture resisting designs for space related combustion chambers [121-123].

CHALLENGES, FUTURE AND CONCLUSIONS

To meet the latest technological demands of aero structures, shape recovering hybrid materials have been recently focused [124]. Table 1 presents a quantitative outlook of different shape memory carbonaceous systems for aerospace, as surveyed in preceding sections of this review. The shape memory matrices with carbonaceous nanoparticles have shown competence of regaining heat, impact, and shock injuries of aero-structures [125]. In this context, the shape regaining mechanism have also been probed [126]. On molecular level, the shape memory phenomenon of polymers, composites, and nanocomposites usually relies upon the formation of molecular switches and net points within the structure [127]. The development of shape switching points have been defined by presence of secondary interactions between the polymer chains as well as matrix-nanofiller or filler [128, 129]. In the case of carbonaceous nanocomposites, nanoparticle dispersion has been found to efficiently develop interactions with matrix leading to net points/switches for shape flipping [130]. Ultimately, the shape memory mechanism or phenomenon occurs at molecular level guided by the nanostructural design including nanoparticle/matrix type and interfacial compatibility/interactions causing shape actuations [131-133].

To access the damages in the space structures, sophisticated damage sensing devices have been utilized [134]. Nevertheless, incorporation of shape memory materials in space structures faces numerous design and performance challenges. Amongst these fibers, carbon fibers, aramid fibers, and glass fibers have been mostly focused [135]. The thermosets like epoxies, polyurethanes, phenolics, etc., and some thermoplastics have been exploited as matrices [136]. Accordingly, the innovative aero structures based on carbon fiber composite laminates have been industrialized [137]. In addition, the carbonaceous nanoparticles like graphene and carbon nanotube have also gained significance for the space related shape memory composites. Consequently, the shape memory polymer/carbon fiber/nanocarbon nanocomposites have been reported. Carbon fibers as well as nanocarbons must be surface modified to enhance the system

compatibility and dispersal. For carbon fiber modification with carbon nanoparticles, various facile techniques have been developed namely chemical vapor deposition [138], electrophoretic deposition [139], electrospraying [140], and chemical means [141]. Among these, chemical vapor deposition has been found competent to uniformly coat the carbon fibers in the form of a thin layer coating. Moreover, it has vantages of precise parametric control and commercial scale processing. Owing to compatible interface formation, mechanical properties of the chemical vapor deposition modified carbon fibers have been enhanced. Nevertheless, this technique is expensive and demands sophisticated set-up and implications. Comparatively, electrophoretic and electrospraying methods are low cost and facilitate easy parametric control and uniformity of the applied coatings [142]. The finely nanocarbon coated carbon fibers have superior electrical features in addition to robustness, so has been found beneficial for micromachine components. However, aerospace trends have been seen towards adopting the chemical vapor deposition for carbon fiber coatings due to the desired structural precision.

Hence, limited successful shape memory aero designs have been reported so far and innovative high-tech nanocomposites need to be researched for durable and competent industrial level implication of these materials. Besides, the modern fabrication strategies like three dimensional or four dimensional printing techniques and lithographic methods need to be explored for precisely designed aero structures with minimal structural defects.

Although, nano-sized inclusions in shape memory carbon fiber composites (as fiber coatings or additives) have been found beneficial in enhancing the desired mechanical properties through efficient stress transfer at interfacial level, heat stability, and other engineering advantages. Nevertheless, there are certain drawbacks associated with including the nanomaterials in the carbon fiber aerospace composites. Firstly, owing to high specific surface are carbon nanoparticles own agglomeration tendency destressing the dispersion features causing weak interfacial adhesion and load transfer through the matrix [143]. In addition, nanoparticle aggregation can easily deteriorate the molecular weight of the matrix material, so causing decline in overall composite performance. Secondly, including nanoparticles in carbon fiber composites demand additional processing steps like particle synthesis, fiber coating, or dispersion, etc., which can be tedious, time consuming, as well as additional cost needs [144]. Thirdly, machinability operations (drilling, milling, cutting, crushing) used on carbon fiber laminates for structural applications have been found affected due to the presence of nanoparticles [145]. Mainly, surface fracturing, debonding, or delamination of the carbon fiber composites filled with nanoparticles and tool failure have been experienced during machining. Thus, challenges have been observed towards the large-scale aerospace applications of nanoparticle filled nanocomposite materials.

Numerous recompenses have been reported for the deployment of composite materials (relative to metals) in aerospace components including the weight, fatigue, corrosion, and flammability reduction attributes with extended life performance. However, two challenging aspects have been observed upon employing the carbon fiber composite in aerospace parts. Firstly, though composites are intrinsically resistant to corrosion events, yet erosion issues have been discovered for these materials when in contact with metal surfaces due to galvanic corrosion effects. Secondly, composite structures sometimes have invisible structural defects or voids which can be problematic in commercial level deployment of ensuing structures. Here, advanced damage monitoring approaches need to be utilized for the development of high-tech space architectures. Corrosion risks of composite structures can be minimized through the choice of appropriate metal or alloys for aerospace components which are usually erosion resistant. For example, using titanium, instead of aluminum, can resolve the corrosion issues faced by space fuselage.

Conclusively, this article elucidates the worth of stimuli responsive composites/nanocomposites for aeronautical structural components. In this regard, the

polymer/carbon fiber and polymer/carbon fiber/nanocarbon materials have been used as shape recovering space materials. The carbonaceous nanofillers mostly used are graphene and carbon nanotube. Ensuing shape changing nanomaterials have aptitude of recuperating the heat, impact, shock, erosion, and other detrimental space related damages. Consequently, the technological stance of high-tech stimuli responsive composites/nanocomposites have been surveyed for aero-structures, fuselage, engines, etc. It is important to state the current real-life application of carbonaceous or carbon fiber reinforced composites in aerospace. These composites have been found remarkably operative in the structural parts of Boeing 787 Air bus and Boeing 787 Dreamliner [146]. The carbon fiber reinforced composites have been engineered towards durable, sustainable, sturdier, and external force/environmental impact resistant materials. For aerospace structural parts, these composites have been processed through traditional techniques. Nevertheless latest attempts have shown the composite fabrication/exploration through three dimensional printing and three dimensional modeling techniques for Boeing 787-8 aircraft design [147]. Despite the factual progress of carbonaceous shape memory materials, there are several research gaps that need to be analyzed towards future progress of aerospace industry. For interested field scientists/engineers, this comprehensive review fundamentally points out the research lapses to evaluate the property enhancements, damage characteristics, and overall property influencing parameters of the space structures [148-150]. Of course, there is immense need of awareness regarding current research trends as well as challenges for developing high end shape memory or self-healing architectures. Focused research on understanding the mechanisms of shape memory can be helpful for sustainability of the space structures under extreme heat, stress, pressure, and wear environments. Hence, the current state of shape memory carbonaceous composites need calls for advanced fabrication strategies and characterization approaches to design, state-of-health monitoring, and damage assessments of the multifunctional aerospace structures.

Table 1. Specifications of carbonaceous fibres/nanofillers reinforced shape memory composites/nanocomposites

Matrix	Filler/nanofiller	Fabrication	Property/Application	Ref.
Poly(lactic acid)	Carbon fiber	Four-dimensional printing	Electrical/thermal driven shape recovery; electro-actuation 6V recovery time 18s. electrothermally induced shape fixation/ recovery; simulated effective temperature zone ratio/stress	[27]
Poly(lactic acid)	Nickel-chromium wires	Melt impregnation; printing methods	Electroactive shape memory behavior 40 V; shape recovery time 20-30 s	[28]
Thermosetting polyurethane foam	Carb. fiber; polyurea/formaldehyde microcapsules	In situ; compression molding techniques	Thermo-responsive shape recovery; thermal activation 120 °C; shape recovery 98-99%; self-healing	[31]
Epoxy	Carbon fiber	Ultraviolet irradiation; ultra-high vacuum systems	Photo-responsive; high vacuum of 10 ⁻⁶ torr; storage moduli; mechanical features	[32]
Neopentyl glycol diglycidyl ether epoxy	Three dimensional graphene foam; 0.13 wt. %	Melting; hand mixing; curing	Thermo-responsive shape recovery; glass transition temperature enhanced by 19 % relative to neat epoxy; 57% upsurge in thermal conductivity (0.3 W mK ⁻¹), relative to neat epoxy	[55]
Polyimide	Imide functional graphene	Solution technique; Thermal curing	Thermo-responsive; 100% shape recovery; high decomposition temperature	[56]

Epoxy vitrimer; 2-aminophenyl 16 disulfide	Graphene oxide	Solution; ultrasonication; curing	Thermo-responsive; shape recovery was 88 %; self-healing mechanical properties; flexural modulus	[57]
Epoxy	Multi-walled carbon nanotube	Mixing; curing	Thermo-responsive; Joule heating effect; temperature distribution by thermographic image; Shape recovery 20 s	[62]
Epoxy based on 1,4-butanedioldiglycidyl ether, tetraglycidyl methylene dianiline epoxy functional carboxyl terminated butadiene acrylonitrile, 4,4'-diaminodiphenyl sulfone	Barbiturate functional carbon nanotube	Curing	Thermo-responsive; robust structures	[66]
Neopentyl glycol diglycidyl ether epoxy	Carbon nanotube	Compression method	Electro-active shape memory 12 V (DC); Recovery time 22 s	[67]
Diglycidyl ether of bisphenol A; methylhexahydrophthalic anhydride	Multi-walled carbon nanotube	Heating; Thermal curing	Heat responsive; glass transition around 65-140 °C; shape fixity and shape recovery 88 % and 97%, respectively; recovering time 32 s	[68]
Epoxy	Carbon fiber	Impregnation/curing	Shock bearing space structures	[75, 76]
Epoxy	Carbon fiber	Impregnation/curing	Theoretical/modeling investigations; shock tolerance	[78]
Epoxy	Carbon fiber	Pre-pegged laminates	Boeing 787 wings; fatigue resistance; shock resistance	[86]
Epoxy	Carbon fiber	Pre-pegged laminates	Fuselage in the Boeing 787	[86]
Epoxy	Carbon fiber/carbon nanotube	Impregnation/curing	Recovery of impact damage recapture 99 %	[106, 107]
Epoxy	Carbon fiber/carbon nanotube	Impregnation/curing	Airbus A350 XWB and Boeing 787; engine blades; large/flexible; reduced weight	[118]
Epoxy	Carbon fiber/carbon nanotube/carbon black	Impregnation/curing	Engines; Resistant to extreme conditions	[120]

Conflicts of Interest

The author declared no competing conflicts of interest.

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