Experimental investigation of shape memory polymer hybrid nanocomposites modified by carbon fiber reinforced multi-walled carbon nanotube (MWCNT)

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Abstract
This paper presents the effect of the variations of multi-walled carbon nanotube (MWCNT) modification in shape memory polymer hybrid composites concerning their mechanical, thermomechanical, and shape memory characterizations. The process of fabrication includes preparation of the MWCNT/epoxy hybrid nanocomposites by shear mixing, ultrasonication, magnetic stirring, and subsequent molding by hand layup method. The appropriate post-processing was performed for the curing and cutting to prepare the samples for the mechanical and thermomechanical characterizations as per the ASTM standards. An enhancement in the thermomechanical properties was noticed due to the incorporation of the MWCNT. These observations were also validated with improvement in the interfacial bonding between the carbon fiber and the modified matrix, as shown in the morphological fractography. The tensile strengths were improved by 18%, 39%, and 26% with the incorporation of 0.4%, 0.6%, and 0.8% modified MWCNT nanocomposites as compared to pure unmodified SMPC. However, the shape recovery of all the configurations of the shape memory polymer hybrid composites was not compromised on polymer-modified remaining almost unchanged at 94%.

1. Introduction

Smart materials are one whose properties can be altered in a controlled fashion by some internal or external excitation, which may be pH, temperature, magnetic field, moisture, light or voltage [1–3]. Chameleons, squid, octopus and mimosa pudica are the few examples from the animal and plant kingdom which change their shape, size or colour based on the respective stimuli. These live examples have presented a pathway for discovery of smart materials, such as temperature sensitive shape memory polymers (SMP) in the 1930s [4]. Shape memory polymer and fiber reinforced shape memory polymer composites (SMPC) have increased attention in recent years, because of their reusable capability (which saves time, money, manpower, efficiency) [5, 6]. SMP and shape memory alloy (SMA) wires are the two material which have been intensively utilised as smart materials because of their highly efficient shape memory capabilities. SMPs can be thermosoftening or thermosetting polymers which can store upto three dissimilar contours in their shape memory [7]. These polymers hold their temporary shape till some external stimulation, primarily temperature, then to undergo change permanent shape. SMP have the salient features of low cost, easy availability, recyclability and can handle large deformation produced in mechanical structures [8]. But because of their low strength, low load carrying capacity and brittleness, these factors create restrictions in many real life applications. Thus composites prepared from SMP have gained wide attention [9–11]. SMPC are particularly useful in space antennas, aircraft blades, and construction and industrial fields due to their improved strength and stiffness [10, 11]. SMPCs are two phase composite materials, which are prepared by incorporating fibers into the SMPs and can also actuated by external stimulation media, but offer enhanced stiffness, rigidity, strength and mechanical properties [12].
Various methods are available for manufacturing the fiber reinforced polymer composites and shape memory polymer composites which includes hand lay-up method (for production a extensive range of composites samples from very small to very large) [13], filament winding (used generally for making pipes and tanks to handle chemicals) [13–18], autoclave forming (for making complex shapes with low void content) [13, 19], resin transfer molding (implemented in auto industry where necessity of short production runs) [13, 20], vacuum infusion process (for large or small product with less time with cleaner production but have complicated set-up) [13, 21], Pultrusion process (for complex objects with less energy) [13, 22, 23], 3D printing (is an additive manufacturing and have revolutionary benefits like Print on demand, flexible design etc but have size and material constraints) [13, 24]. Gemi et al [14–17] and Li et al [18] examined effect of low velocity impact over filament wound hybrid pipes subjected to internal pressure, and concluded the improved range in progressive damage and impact response, with increased internal pressure. Along with that, three stratifications relative work, delamination and damage developments and stacking sequence effect on damage and impact response were studied in [25]. Pultrusion process used in the production of FRP profiles using oriented fibers [22, 23]. Advantages like ability of production of complex shapes, decreasing cost and requirement of less energy for polymer production as compared to metallic parts/profile, the process is adopted [22, 23, 26–29] for GFRP composite preparation. Also the also the impact of different process parameters like pulling speed, raw material type and proportion, temperature, resin viscosity etc analyzed in several studies [30–32]. Matsuzaki et al [33], Zeng et al [34], Yu et al [35] impregnated long carbon fiber reinforced polymer composites to fabricate improved tensile strength additively manufactured composites. Uslu et al [36], Erdal et al [37] carried out production and determination of two-phase PMCs using reinforcement of PAN, DMF, and PVAc polymers by electrospinning technique.

Observation has shown that however, the improvement in thermo-mechanical properties like elastic or storage modulus, strength etc are still low with fortification by particles or short fibers, and it would be irrational to use them as a structural material [38]. SMPs have low stiffness and strength, but addition of fibers into it offers improvement in these properties which eventually effect the shape memory properties of the shape memory polymer composites [39].

Sun et al [40] demonstrated the enhancement in mechanical properties of SMP with the utilization of elastic fiber reinforcements in the SMP. Azzawi et al [41] suggested that, as compared to neat SMP, 1.75 and 2.35 times improvement in storage modulus below glass transition temperature ($T_g$) were obtained with 20% and 25% glass fiber reinforcement in SMP. Moreover, marginal increments in $T_g$ were also observed with the incorporation of glass fibers into the polymer matrix. Fejos et al [42] reported significant improvement in the recovery stress of SMPC also shape memory characteristic differentiation were presented between SMP and glass fiber SMPC. Okhı et al [43] showed a 140% improvement was noted in the failure stress with the utilization of 50% weight fraction of glass fiber.

To utilise the fiber reinforced polymer composites (FRP) in aviation, structural, auto industry, defence, and sports applications, it is required to enhance the mechanical properties of the FRP through the addition of nanofillers in the matrix to form multi-phase composite material [44]. In FRP, matrix exhibit two main purposes: (i) binding the fibers together even during loading and (ii) during the actual stress application effective transfer of the load from matrix to the fiber. The matrix is an isotropic material which has relatively lesser elastic modulus than the reinforced fiber. Due to the low strength matrix, many times before positive the load transfer, it cracks/fail under the application of higher magnitude stresses. In order to overcome this drawback and improve overall properties, nanofillers like single-walled carbon nanotube (SWCNT), multi-walled carbon nanotube (MWCNT), nanofibers, graphene etc are incorporated into the matrix to fabricate multi-phase or hybrid composites [45, 46]. Teng and co-authors [47, 48] observed the performance of TPI/HDPE hybrid matrix under dynamic vulcanization process, which results inadequate improvement in mechanical properties of SMPC. So in their further work [49, 50] introduced hybrid matrix with the use of TPI/HDPE/nan-fillers in SMPC and observed satisfactory improvement in mechanical and thermal properties. The multi-phase composites help to improve its various properties such as toughness, strength and electrical conductivity [51, 52]. Addition of nanoparticles provide high aspect ratio as well as improve mechanical properties of structural adhesives [53], which will help in the smooth load transmission into two phase matrix and hence into nanofillers. Unique multi-functionality of CNT (SWCNT/MWCNT) find its application as reinforcement/filler into matrix or adhesives for the formation of exceptional composite materials [54]. The present study focuses on CNT’s ability to enhance the mechanical, thermomechanical and shape memory properties of the carbon fiber reinforced polymer (CFRP) hybrid composites.

CNT nanofillers provides a high surface area and larger aspect ratio, however it possess intermolecular attractive force which generate the tendency of agglomeration of CNTs into matrix [55]. Further, agglomerated CNTs may act as an inclusion into the matrix which act as an impurity and hamper the overall performance of the material during its application. To overcome this drawback, various methods are adopted for the proper dispersion of CNT in the matrix for instance sonication, magnetic stirring or calendering [56, 57]. Keeping this
fact in consideration, in the present study, concentration of CNTs are taken as 0.4, 0.6 and 0.8 wt%. Some significant work dealing with CNT based composites are presented for the sake of completion. Rathore et al.\textsuperscript{[38]} have reported 11.5% and 32.8% improvement in modulus and bending strength of fibrous composite with the 0.1% addition of MWCNT in the hybrid composite. Liu and Chen\textsuperscript{[59]} showed that with addition of 2% and 5% CNTs in the matrix, the stiffness of the hybrid composite improved by about 0.7 and 9.7 times. Saboori et al.\textsuperscript{[60]} presented that, instead of using only unmodified CFRP, hybrid CFRP with 0.5% CNT increased the fracture toughness of the composite structure by 19.5%, whereas, as per Gojny et al.\textsuperscript{[61]}, it raised by 43% with the use of MWCNT in the hybrid composite. Yang et al.\textsuperscript{[62]} observed that with the addition of 0.6% MWCNT into the polymer matrix, improvement of 22% and 29% in bending modulus and strength as compared to neat CFRP.

Published papers often contain the result based on particular properties: mechanical or physical, thermomechanical and some literatures also covered the effect of nanofillers addition either on polymer or fiber composites. This research presented mechanical and physical properties of different hybrid multiphase composites manufactured and tested in the same conditions. Thus, the readers can examine and compare the influence of weight fraction variation of MWCNT. However, the heat activation shape memory bending tests of the shape memory hybrid multiphase composites under the dynamic temperature variation with mechanical and thermomechanical characterization are scarcely available. Bisphenol with aliphatic amine epoxy with high purity MWCNT used for the preparation of hybrid multiphase matrix. The micro-structural morphology and the tensile behavior of the hybrid composite are studied to present the microscopic study of the variation of nanofillers on the interfacial bonding between the fiber the modified matrix. The study also covers the analytical evaluation of the mechanical and thermomechanical properties of the multi-phase shape memory hybrid composites along with its experimental comparison.

### 2. Experimental details

#### 2.1. Materials

Bisphenol-A based epoxy resin (LY 556) with aliphatic amine (HY 951), for the fabrication of epoxy-based nanocomposites, were procured from Huntsman International (India). High purity multiwalled carbon nanotubes (MWCNT) with the external diameter of 10–15 nm and length of 5 μm were supplied by Ad-Nano Technologies Private Ltd (India). The carbon fiber used in this study was the product of Formosa Plastics Corp. (India), with 12 K filaments reel (specification: TC35–12 K). The material properties of epoxy, carbon fiber and MWCNT are summarized in Table 1, with the data taken from Lal and Markad\textsuperscript{[63]} and Tas and Soykok\textsuperscript{[64]}.

#### 2.2. Evaluation of the effective material properties

The modelling of the material properties was essential for the simulation of the experimental and its applications in our numerical study. The present study utilized the Halpin-Tsai approach for the determination of the effective material properties of the three phase laminated composite (matrix, MWCNT, and carbon fiber) sample as shown in Figure 1.

The elastic modulus of the MWCNTs can be evaluated from equation (1) as per Lal and Markad\textsuperscript{[36]}. The equation facilitates the evaluation of the modulus for the required number of concentric cylindrical tubes of MWCNTs.

| Table 1. Mechanical properties of the epoxy, carbon fiber and CNT. |
|----------------------|---------|-------|--------------|---|
| Material prop.       | Symbol  | Value | Unit         |
| Young’s modulus (E)  | E_f    | 230   | GPa          |
| Poisson’s ratio (ν)  | ν_f    | 0.25  | —            |
| Shear’s modulus (G)  | G_f    | 98.3  | GPa          |
| Young’s modulus (E)  | E_m    | 3.30  | GPa          |
| Poisson’s ratio (ν)  | ν_m    | 0.40  | —            |
| Shear’s modulus (G)  | G_m    | 1.18  | GPa          |
| Young’s modulus (E)  | E_{sw} | 1.0   | TPa          |
| Poisson’s ratio (ν)  | ν_{sw} | 0.28  | —            |
| Number of walls of   | W_{sw} | 3     | —            |
| MWCNT                |         |       |              |
| CNT volume fraction  | V_{sw}  | 0.4%,0.6%,0.8% | —  |
$E_{\text{eq}} = \left( \frac{E_m}{E_m^c} - 1 \right) E_m + \frac{E_m^c}{E_m} \frac{E_m^c}{E_m^c + G_T} V_{\text{cnt}}$

Here, the SWCNT thickness $t_{\text{cnt}}$ was taken as 1.5 nm and $h_{\text{nt}}$ is the MWCNT wall spacing ($h_{\text{nt}} = 1.5 t_{\text{cnt}}$). The equivalent modulus ($E_{\text{eq}}$) of the CNT was evaluated as per Tas and Soykok [64],

$$E_{\text{eq}} = \left( 2 * t_{\text{cnt}} * E_{\text{cnt}}^m \right) / t_{\text{cnt}}$$

where $E_{\text{cnt}}^m$, $t_{\text{cnt}}$, and $r_{\text{cnt}}$ are Young's modulus of MWCNT, nanotube wall thickness and radius of nanotube respectively. Assuming randomly oriented MWCNT reinforcement in the Bisphenol-A based epoxy resin, its Young's modulus, shear modulus and Poisson's ratio were calculated as per the Halpin-Tsai approach which is shown in equations (3)–(5), as reported by Tas and Soykok [64]

$$E_m^c = \frac{3}{8} \left[ \frac{E_m}{E_m^c} - 1 \right] E_m + \frac{E_m^c}{E_m^c + G_T} V_{\text{cnt}}$$

$$G_m^c = \frac{1}{8} \left[ \frac{E_m}{E_m^c} - 1 \right] E_m + \frac{E_m^c}{E_m^c + G_T} V_{\text{cnt}}$$

$$\nu_m = \frac{E_{\text{cnt}}^m}{2G_m^c} - 1$$

where $V_{\text{cnt}}$ is the volume fraction of the carbon nanotubes, $G_T = \frac{2 * l}{d}$ and $G_T = 2$ with $l = 5000$ nm and $d = 15$ nm being the length and diameter of the nanotube. The equivalent material properties of the MWCNT reinforced fiber composites were evaluated by using the following relations, Lal and Markad [63].
Where, $V_f$ and $V_m$ are carbon fiber and matrix volume fraction respectively. Young’s modulus of unidirectional lamina in longitudinal and transverse direction are represented by $E_{11}$, $E_{22}$. Poisson’s ratio $\nu_{12}$ were evaluated by rule of mixture. $G_{12}$, $G_{23}$ are the shear modulus evaluated by using mixture rule. Remaining parameters like $E_{12}$, $E_{13}$, $E_{23}$, $G_{13}$ defined in table 1.

### 2.3. Preparation of carbon fiber reinforced epoxy samples

The specimens were fabricated through the hand layup technique of required size. The unidirectional tows of the carbon fibers were laid in a mold with the dimensions of 250 mm $\times$ 250 mm and the epoxy resin was applied on the fibers. The mixing ratio of the epoxy resin and the hardener was maintained at 100:10 (as per the guidelines of manufacturer). The excessive resin was removed with a roller applied in the direction of the fiber layup. In order to eliminate the resin regions and voids in the specimen, uniform pressure was applied on the mold and the layered specimen was allowed to cure for 24 h at room temperature. The post curing was performed to remove any remaining air traps in the specimen by placing it in an oven (LABLINE microwave oven, India) at 80 °C for 6 h, as suggested by the supplier and available literature. The volume fraction of the carbon fiber was maintained at 22% to ensure wetting of fibers and subsequently observe the influence of MWCNT on the interfacial bond between the fiber and the epoxy matrix and its effect on the shape memory behavior of the nanocomposites.

### 2.4. Preparation of carbon fiber reinforced MWCNT modified epoxy nanocomposites

The MWCNT, used in the preparation of the samples were used in received condition from the manufacturer. The required MWCNT were dispersed in 100 ml of acetone and stirred for 1 h in a magnetic stirrer and then sonicated for 10 min by a probe sonicator for de-agglomeration of the MWCNT nanoparticles. During the sonication, the temperature raises to an undesirable temperature, which may rupture the inherent cylindrical orientation of the MWCNT. Thus, during the entire procedure of stirring and sonication, the specimen beakers were placed in an ice bath. The mixture of acetone and MWCNT were added to the epoxy resin and stirred at 2000 rpm at 80 °C, till the acetone was evaporated from the suspension. The remaining MWCNT and epoxy resin were sonicated for 1 h for uniform distribution of the MWCNT.
Air bubbles were formed in the process of stirring and sonication of suspension, which may lead to the creation of voids in the samples; therefore, to remove the air bubbles, the MWCNT/epoxy mixture was placed in a vacuum chamber (BHF2020 SS vacuum chamber, India) for 24 h. Then the required amount of hardener was added in the MWCNT/epoxy mixture and stirred for 10 min. The five layered specimens were hand layup in the mold and were allowed to cure and post cure as described previously. The entire process of fabrication is schematically described in figure 2. The samples with 0.4 wt.%, 0.6 wt.% and 0.8 wt.% with respect to the epoxy’s weight were chosen, with the MWCNT contents verified with the resin burn off test below. After the preparation of 250 mm × 250 mm sample plates with the thickness of 2.0 ± 0.1 mm considering uniform thickness of all layers, specimens were machined to the required dimensions by an abrasive water jet machine (R V Industries, Surat, GJ, India) for the burn off test, tensile test and dynamic mechanical analysis (DMA).

2.5. Material characterization
The fiber volume fraction and voids in the samples were determined by the resin burn off test, as per ASTM D 3171–99. In this process, the specimen of dimension 25 mm × 25 mm were weighed to measure the initial mass. Then it was held in a muffle furnace at 625 °C for 5 h, during which the epoxy and the trapped air degraded off and the weight of remaining content of fiber and the MWCNT were measured.

Uniaxial tensile experiments were performed to determine the longitudinal properties of the nanocomposites as per ASTM D3039 on the samples with the dimensions: 250 mm × 15 mm × 2 mm. These tests were carried out on an Instron UTM 5582 (ARAI, Pune, India) with load cell capacity of ± 100 kN at the test speed of 5 mm min⁻¹.

The dynamic mechanical properties of rectangular specimens with the dimensions of 40 mm × 10 mm × 2 mm, were characterized by a DMA 8000 (Perkin Elmer-MNIT, Jaipur, India) through 3-point bending tests as per ASTM D7028–07. The temperature was increased from room temperature to 150 °C at the heating rate of 3 °C under 1 Hz frequency.

Field electron scanning electron microscopy was carried by a Nova Nano FE-SEM 450 (FEI- MNIT, Jaipur, India) to image the surface morphology of the fractured samples. This was utilized to visualize the distribution of the MWCNT in the matrix and the interfacial bonds between the carbon fibers and the modified matrix (MWCNT + matrix).

2.6. Shape memory behavior
The shape memory capabilities of the prepared samples were estimated by heat activated bending test of the specimen bent at 90°. In this test, the rectangular beam with the dimension of 40 mm × 5 mm × 2 mm were heated above T_g of the material and then bent to a desired angle and cooled gradually in a mold. The specimen was then heated above T_g and time lapse recovery of the sample shape was recorded by a high definition camera during the transition from the angles of 90° and 0°. Recording of the shape recovery were studied at the
temperatures of $T_g + 10 \, ^\circ C$ for each sample with different functional groups to ensure and accuracy and repeatability of the results [9], as described in section 3.5.

3. Results and discussion

3.1. Void and carbon fiber content

The void content and volume fraction of the reinforcements are indicated in figures 3(a), (b), as per the ASTM D 3171–99.

The void content in the carbon fiber reinforced polymer composite (CFRP) was 0.8% which increased with the incorporation of MWCNT in the shape memory epoxy matrix. The volume fractions of void content in the shape memory polymer nanocomposites with 0.4%, 0.6% and 0.8% MWCNT were 1.2%, 1.7% and 1.4% respectively. These voids may be formed after the degasification of the sonicated epoxy resin modified with MWCNT in the vacuum chamber, where some bubbles may have been trapped in the matrix [65]. For all the composites samples as shown in figure 3(b), the volume fraction of the carbon fiber remained approximately constant which was 23%.

3.2. Tensile characteristics

The tensile properties of the carbon fiber reinforced MWCNT modified nanocomposites is shown in figures 4(a), (b) for the different MWCNT content.

Figure 4(a) represent the force-displacement plot for samples with various MWCNT at environmental temperature. The result clearly shows, the load carrying capacity of prepared shape memory polymer MWCNT samples increased as compared to pure CFRP samples. The tensile stress-strain plots for samples with various MWCNT are shown in figure 4(b). An increment of the slope was observed with the incorporation of MWCNT as indicated by the slope in the elastic region of the stress-strain trajectory. Figure 5 shows the increase of modulus of elasticity from 54.4 GPa for the unmodified CFRP to 56 GPa and 58.8 GPa for the nanocomposites with MWCNT content of 0.4% and 0.6% respectively. This would be due to restriction in the cross-links in the epoxy matrix and viscoelastic distortion at the interface between the epoxy and MWCNT.

Moreover, the tensile strength was improved by 18%, 39% and 26% for the modified nanocomposites with 0.4%, 0.6% and 0.8% MWCNT as compared to pure CFRP, as shown in figure 6(a). Other tensile properties enhancement with respect to maximum force (figure 6(b)), Poisson’s ratio (figure 6(c)) and percentage elongation at maximum force (figure 6(d)) were also observed which were similar to the observed in [66] and [67].

The interface plays a significant role in the stress transfer between the carbon nanotube (CNT) and the polymer matrix which consequently improve the tensile properties. Chemical bonding between the CNT and the matrix improves interfacial interaction through ionic or covalent bond that enables an efficient stress transfer. The surface roughness of the carbon fiber increased tremendously after the incorporation of the 3D orientated CNTs, increasing the interfacial surface area of the carbon fiber with the matrix. The presence of the large interfacial area at the MWCNT-epoxy interphase reduces the stress concentration which results in the enhancement of the mechanical properties. Considering carbon nanotubes, this effect is caused by a large surface area and covalent bond formation between polymer chains. These attributes were even noticed in the SEM of the fractured samples, discussed in section 3.4.

A drop in the tensile strength was noticed for the sample with 0.8% MWCNT as compared to the one with 0.6% MWCNT, which was in contradiction to the increased interfacial area between the CNT and matrix. The
primary reason for this we suggest was the occurrence of agglomeration of the MWCNT in the matrix [67]. MWCNT agglomerates to reduce the high surface energy among MWCNT and enhance its stability. Thus, MWCNT should not be added above a particular concentration to avoid agglomeration of the MWCNT. The
The mathematical simulation of the tensile behavior is presented and discussed in the following section prior to discussion of the thermomechanical properties of the nanocomposites.

The comparison between the experimental tensile properties and the corresponding values calculated from the correlations discussed in section 2.2 are shown in Table 2. The difference between the results were minimal which indicates the appreciable quality of the fabricated samples. However, the deviation could be due to the presence of voids or agglomerated nanoparticle bundles in the matrix. Significant deviations were noticed in the composite with 0.8% CNT, which primarily existed due to the initiation of agglomerations resulting in a considerable decrease in the mechanical properties.

### 3.3. Dynamic mechanical analysis (DMA)

The relation of the storage modulus, Tan δ and loss modulus with respect to temperature in the range from 25 °C to 150 °C is presented in figures 7(a)–(c) respectively. The glass transition temperature (Tg) of the material can be determined either by selecting the midpoint of the dynamic region of the storage modulus graph or the peak point of Tan δ graph. In the present case, the peak point of Tan δ trajectory was selected as Tg (figure 7(d)). The incorporation of 23 wt.% of carbon fiber increased the Tg by 6.4 °C to 76.4 °C, as compared to the pure shape memory polymer [18]. A decline was observed in figure 7(d) when the MWCNT content increased from 0 to 0.6%. This occurred due to the enhancement of the viscosity of the MWCNT modified epoxy matrices which restricted the deformation of the nanocomposites [66].

The trajectories of the storage modulus followed the similar pattern as the one shown for tensile characteristics (figure 6(a)) up to 63.8 °C. Decreases of storage modulus and loss modulus were noticed beyond 63.8 °C, which indicates the initiation of the glass transition region of the modified epoxy matrix. The behaviour

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**Table 2. Comparison between experimental and modelling tensile properties.**

| Composite Configuration | Experimentation | Modelling |
|-------------------------|----------------|-----------|
|                         | $E$ (Pa)       | $\delta$  | $E$ (Pa)       | $\delta$  |
| CFRP                    | $54.5 \times 10^9$ | 0.32      | $56.6 \times 10^9$ | 0.29       |
| 0.4% MWCNT              | $56.5 \times 10^9$ | 0.33      | $58.9 \times 10^9$ | 0.33       |
| 0.6% MWCNT              | $58.8 \times 10^9$ | 0.34      | $59.9 \times 10^9$ | 0.34       |
| 0.8% MWCNT              | $61.6 \times 10^9$ | 0.34      | $62.8 \times 10^9$ | 0.35       |

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Figure 6. Variation in tensile characteristics for different %wt content of MWCNT (a) tensile strength (b) maximum force (c) Poisson’s ratio (d) elongation at maximum force.
of the shape memory polymers and its composites are regulated by the frozen and active phase in the glass transition region from the temperature $T_1$ (lower temperature utilised in study) to $T_2$ (highest temperature used in study) [68]. Frozen phase is dominant at temperature $T_1$ with the modulus $E_1$ prior to the onset of glass transition. The combination of active and frozen phases affects the behaviour at $T_g$ with the modulus $E_2$, whereas post the region active phase is dominant at $T_2$ with the modulus of $E_3$ [5].

An increment of the modulus of elasticity was also noticed with the reinforcement of MWCNT in the epoxy from 0.4 to 0.6 wt% (figure 7(a)). This would be due to restriction in the cross-links in the epoxy matrix and viscoelastic distortion at the interface between the epoxy and MWCNT [58]. However, the modulus decreased when the content of MWCNT was increased from 0.6 to 0.8 wt%. This could be due to agglomeration of the MWCNT in the modified matrix which reduced the restrictions in the cross-links, which also elevated the $T_g$ of the nanocomposite, as shown in figure 7(d). The loss modulus as shown in figure 7(c) denotes the amount of energy dissipated in the sample.

The results evaluated by DMA were simulated through the constitutive deformation model based on the curve-fitting technique employed in the user defined MATLAB program. Equations (11) and (12) present the relation between the modulus, $\tan\delta$, and the temperature in the glass transition region of the fabricated composites.

$$E = E_2 + \frac{(E_1 - E_2)}{1 + e^{\frac{(-T_1 - T_2)}{W_1}}} + \frac{(E_i - E_2)}{1 + e^{\frac{(-T - T_2)}{W_2}}}$$

$$\tan\delta = H + A \times \left[ \frac{1}{1 + e^{\frac{(-T - T_2)}{W_2}}} \right] \times \left[ 1 - \frac{1}{1 + e^{\frac{(-T - T_2 + W_3/2)}{W_3}}} \right]$$

where, $E_i$ (GPa) and $E_2$ (GPa) are the modulus of the composite prior and post the glass transition region respectively, $T_0$ (°C) is the reference temperature for the purpose of curve fitting, $m_i$ and $m_2$ are the exponentials and $H$ and $A$ are Gaussian coefficients, $W_1$, $W_2$, $W_3$ are the Gaussian exponential constants.

The curve-fitting based simulation of the thermomechanical properties in terms of the storage modulus and $\tan\delta$ for different MWCNT contents are shown in figures 8(a)–(d). The magnitudes of the constants and curve fitting exponentials are compiled in table 3 for utilization in the simulations of storage modulus. These result in
an appreciable agreement of the theoretical results with experimentation. This modelling would aid future numerical analyses for more structural and thermomechanical studies.

3.4. Fracture surface analysis
Fractography of the samples fractured during the tensile tests were studied through SEM to analyze the influence of the MWCNT on the interfacial characteristics between the carbon and the SMP matrix. Figures 9(a)–(d) indicate the morphology of the samples with different wt.% of MWCNT in the modified matrix. The smooth interphase between the matrix and carbon fiber highlight the non-polar surface, chemical inertness, surface lipophobicty, smoothness and less adsorption, which lead to weaker bond with the matrix material [65, 69], as shown in figure 9(a). These observations were magnified in figure 10(a), where debonding and delamination of the matrix along the carbon fiber surface can be noticed [58]. Voids were observed in the composites which may have been formed due to the entrapment of air pockets during the degasification of the MWCNT modified epoxy resin to eliminate the air bubbles produced during the ultrasonication.

Incorporation of MWCNT in the SMP matrix played a vital role in the enhancement of interfacial bonds between the carbon fibers and the matrix which would improve the strength and toughness of the structure and restrict the failure of CFRP nanocomposites. Figures 9(b)–(d) and figures 10(b)–(d) indicate the morphology of the nanocomposites with the addition of MWCNT from 0.4 to 0.8 wt.%. The increased roughness at the interphase between the carbon fiber and modified matrix indicate the rise in the interfacial bonding. Figures 10(b)–(c) presents the improvement of the interface between the carbon fiber and MWCNT modified matrix which can also be validated by the observation of river line markings, fibers and rippled morphology on

Table 3. Values of constants to simulate temperature regulated storage modulus curve.

| Parameter | CFRP   | 0.4% CNT | 0.6% CNT | 0.8% CNT |
|-----------|--------|----------|----------|----------|
| $E_1$ (GPa) | 30.324 | 29.224   | 38.775   | 32.219   |
| $E_2$ (GPa) | 0.999  | 0.919    | 0.955    | 0.965    |
| $T_0$ (°C)  | 70     | 70       | 70       | 70       |
| $m_1$      | 1.9685 | 3.141    | 2.0109   | 2.345    |
| $m_2$      | 2.4452 | 3.111    | 1.963    | 2.028    |

Figure 8. Simulation of DMA for shape memory nanocomposites with different %wt content of MWCNT with respect to temperature (a) Pure CFRP (b) 0.4% MWCNT (c) 0.6% MWCNT (d) 0.8% MWCNT.
Figure 9. SEM images of fractured carbon fiber of the CFR nanocomposites with different MWCNT content (a) CFRP composite (b) 0.4% MWCNT (c) 0.6% MWCNT (d) 0.8% MWCNT (All scales are in μm).

Figure 10. SEM micrographs of the interfacial bonds in shape memory polymer nanocomposites with different MWCNT content (a) CFRP composite (b) 0.4% MWCNT (c) 0.6% MWCNT (d) 0.8% MWCNT (All scales are in μm).
the channels formed because of the debonded fiber on fractured morphology [66]. Figure 10(d) indicates the non-uniform spacing of the carbon fiber in the matrix which may be due to the increased viscosity because of the MWCNT agglomeration. This attribute the cause of lower tensile properties at 0.8 wt.% MWCNT modified epoxy nanocomposites.

The micrographs of the carbon fibres in the different composites are shown in figure 11. Smooth fiber removal from epoxy matrix were noticed in figure 11(a), which highlights the lesser restrictions because of the poor interfacial bonds in the fractured morphology of the composite during the tests. Matrix debonding and delamination without any indications of polymeric phase were also noticed which results in the inferior tensile properties as compared to MWCNT filled CFR nanocomposites. On the contrary, an improved interfacial adhesion between the fiber and modified matrix were noticed in figures 11(c)–(d), which is emboldened due to the presence of layer of the polymeric phase on the surface of the fibres. The surface roughness of the commercial carbon fiber increased significantly after the incorporation of CNTs, increasing the surface area of the carbon fiber. The incorporation of nanoparticles (MWCNT) alters the interphase characteristics as it introduces mechanical interlocking, increases interaction due to high surface energy, and increases the specific surface area [70].

3.5. Shape memory characteristics

The thermal stimulated shape memory tests of the carbon fiber reinforced composites samples with different content of MWCNT were performed to calculate the shape memory parameters of shape fixity ($R_f$) and shape recovery ($R_r$). Shape fixity ($R_f$) describes the ability of the material to remain in its programmed shape on temporary deformation, whereas shape recovery ($R_r$) represents the ability to regain the original shape. These parameters were calculated by equations (13) and (14) [71].

$$R_f = \frac{|(\theta_f - \theta_0)|}{|(\theta_p - \theta_0)|}$$  \hspace{1cm} (13)

$$R_r = \frac{|(\theta_f - \theta_0)|}{|(\theta_f - \theta_0)|}$$  \hspace{1cm} (14)

where, $\theta_0$, $\theta_p$, $\theta_f$ and $\theta_r$ denote the original angle, programming angle, fixity angle and recovery angle.

Figure 12 shows the stages of shape memory cycle from the original shape to the programming stage and its corresponding phase wise recovery for each configuration of shape memory nanocomposites. The samples were
bent by 90° and during the recovery stage, they were subjected to the temperature of $T_g + 10$ °C. Image processing to measure the recovery angles at the interval of 2s for 10s was analysed in AutoCAD.

The shape fixity ($R_f$) of shape memory polymer composite without the incorporation of MWCNT was 98.8%, whereas with incorporation of MWCNT, a slight decline in its values were noticed. The values of $R_f$ was uniform for all the configurations of the nanocomposites with value of 97.2 ± 0.1%.

The phenomenon of shape recovery was initiated in the samples, as soon as it was at the elevated temperature above $T_g$. The recovery stage of the samples of the CFRP composite was completed in 9s, while those with the MWCNT modified matrix, took almost 6s which can be noticed in the analysis presented in figures 12 and 13.

The incorporation of MWCNT in the matrix enhanced the thermal response of the SMPC. As a result of which the time lag between the stress generation and release has been reduced. When the temperature exceeds the $T_g$ of the modified SMPC, the energy stored in the stationary phase and the reversible phase was gradually released, the molecular kinetic energy of the reversible phase molecular chain increases and the micro-Brownian motion intensifies, which drives the stationary phase to return to the entropy disorder state, thus realizing the shape recovery. Because of the increase of the content of vulcanizing agent, the degree of vulcanization increases gradually, but the crystalline region decreases. The increase of crosslinking structure leads to the increase of the content of the stationary phase, so the deformation decreases due to the increase of the limitation of the stationary phase, which finally results in the pertinent difference of the shape recovery degree and recovery rate near the $T_g$ of the two components. It can be inferred that the density of the crosslinked network formed by adding appropriate amount of MWCNT was moderate, and the strengthened cross-linked network stores more elastic recovery energy during external loading process. Therefore, The shape recovery ($R_s$) of the CFRP composite was 96.6% while those of the samples with the reinforcement of MWCNT were all 94.2 ± 0.1% as shown in figures 13(a), (b). The results inferred in this section are proposed to be of lucrative application for sophisticated smart structures such as smart space antennas, flexible electronics, robotics and biomedical applications.
4. Conclusions and future scope

The effective fabrication of the multiscale shape memory polymer hybrid composites has been performed in this study. The modification of epoxy matrix with the different wt.% of MWCNT nanoparticles considerably improved the tensile and thermomechanical properties of the hybrid composites.

1. The content of the MWCNT was varied from 0.4 wt.% to 0.8 wt.% in the study, which showed enhancement in the mechanical and thermomechanical characteristics as compared with simple CFRP. The tensile strengths were improved by 18%, 39% and 26% for the modified nanocomposites with 0.4%, 0.6% and 0.8% MWCNT respectively as compared to pure CFRP.

2. Morphological fractography indicated the improvement of the wettability and interfacial bonding between the modified matrix and carbon fiber due to the presence of the MWCNT in the matrix.

3. The incorporation of MWCNT in the modified matrix did not hamper the shape memory properties of the composites which were tested with the heat activation bending test.

4. Our comprehensive study presented an opportunity to focus on the effect of the variation of MWCNT in the smart matrix on the mechanical, thermomechanical and shape memory characteristics of the nanocomposites.

The corresponding simulation of the tensile properties and DMA were also presented briefly through micromechanical analysis and curve-fitting techniques which shows good agreement with experimental results that might be suitable for the extension through sophisticated numerical analysis in future. The results inferred in the study are proposed to be of lucrative application and would provide motivation for the implementation in sophisticated smart structures such as smart space antennas, biomedical application and flexible electronics.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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