Carbon nanotube/microcapsule/polyurethane nanocomposites for multi-stimuli responsive shape memory polymers

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ABSTRACT

The aim of this research is to incorporate the nanographite particle (NGP) modified microencapsulated phase change material (GPCM) and carbon nanotube (CNT) into shape memory materials (SMMs). The GPCM with paraffin in the core and NGP in the shell possesses characteristics such as high thermal capacity, rapid heat absorption, and reduced electrical resistance. Moreover, the thermal storage effect of this GPCM may enhance the shape fixity and shape recovery of the SMMs. Additionally, CNTs with high aspect ratios and exceptional electrical or thermal activation of SMMs. After adding these GPCM and CNT to the polyurethane (PU), the thermal conductivity increased to $0.60 \text{ W/m}\cdot\text{K}$, and the surface resistance decreased to $2.5 \times 10^2 \Omega/\text{sq}$. Upon thermal activation, the shape fixity and shape recovery of these SMMs can reach 98% and 99%, respectively. In addition, it was observed that the material could form a complete circuit under an AC voltage of 100V and successfully achieve the shape recovery effect. This indicates that the addition of GPCM and CNT can enable the SMMs to achieve shape recovery effects through heat, light, and electrical activation.

Keywords: Electrical activation, Nanographite, Phase change microcapsule, Shape memory.

1. INTRODUCTION

Shape memory materials (SMMs) have been considered as a class of smart materials capable of holding and returning to their initial shape from a temporary shape under external stimuli (Mather et al., 2009; Zhao et al., 2015). As responsive materials, the shape of SMMs can be reversibly programmed in one or multiple ways when external stimuli, such as temperature, electricity, magnetic field, or light, are applied. Several types of SMMs have been developed, including shape memory alloys (SMAs), shape memory polymers (SMPs), shape memory hybrids (SMHs), and shape memory ceramics (SMCs) (Sun et al., 2012). For instance, Kumar et al. (2020) developed a quarter-car model suspension system for a passenger car aimed at enhancing its performance. This was achieved by substituting the traditional spring with a SMA spring, resulting in reduced suspension travel. Due to the fact that polymer products can be prepared from a wide variety of structures, SMPs are critical components in advancing technologies such



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Shih et al., International Journal of Applied Science and Engineering, 21(4), 2024018

as aerospace devices (Liu et al., 2014), tissue engineering (Bao et al., 2014), self-reinforcing sutures (Zhao et al., 2019), wearable devices (Zarek et al., 2016), or 4D printing materials (Wan et al., 2022). The development of SMPs based on novel structure design and the presence of specific functional groups continues to attract enormous attention for desirable functional properties.

Generally, SMP materials exhibit a phase-separated morphology with at least two independent networks. One network is a stable network attributed to chemical or physical crosslinking, providing the permanent shape, while the other network is a temporary one consisting of crystalline, liquid crystalline, or amorphous domains responsible for shape deformation (Kim et al., 1996; Wu et al., 2015; Wu et al., 2017; Lendlein and Gould, 2019; Wu et al., 2020a; Zhang et al., 2022). By introducing various reinforcement materials such as nanoclay, silicon carbide, cellulose, or polyhedral oligomeric silsesquioxanes into the polymer matrix, the reinforcement bundles are bonded to merge the benefits of both original components, increasing the elastic moduli for shape memory polymer composites (SMPCs). The improved mechanical properties, responsible for fixing the permanent shape, result in high shape recovery ratios for SMPCs.

In addition, the use of responsive composites provides multiple functionalities for SMPCs. For example, incorporating conductive fibers like carbon nanotubes (CNTs) into thermoplastic polymers can create electroactive SMPCs (Xia et al., 2021). CNTs, characterized by a large specific surface area and enhanced electrical and thermal behaviors, are utilized in various optoelectronic fields owing to their outstanding electrical, mechanical, thermal, and optical properties (Kaliyannan et al., 2022). Yu et al. (2014) demonstrated microwave-active SMPCs through the study of the absorption capability ratio of external electromagnetic energy for SMPs filled with 5wt% CNTs. The increased thermal conductivity, along with the exposure to microwave radiation acting as node heating sources, leads to a SMPC with fast actuation. Moreover, the heat absorbance of SMPCs can be enhanced using CNTs as fillers (El Feninat et al., 2002; Koerner et al., 2004; Langer and Tirrell, 2004). However, as the CNT content increases, the uneven dispersion of CNTs in the matrix becomes significant due to the dissimilar chemical structures between the polymer and fillers. The presence of high filler loading can sometimes reduce polymer crystallinity, which is detrimental to the temporary network's domain for switching shape. Further research is necessary to design novel fillers for enhanced properties and functionalities of SMPCs, demonstrating outstanding shape memory performance.

The integration of phase change materials (PCMs) into a polymer matrix has proven to be feasible for triggering shape memory properties. PCM materials, such as paraffin, are known for their high latent heat energy switching within a narrow temperature range between storage and retrieval. Zhang and other researchers introduced various ratios of paraffin content in an olefin block copolymer (OBC) acting as a supporting material to create polyolefin-based PCMs (Zhang and Feng, 2013; Zhang et al., 2015). The addition of hexadecane strongly influenced the change of crystalline phase of the OBC, enabling the formation of PCM composites with good shape memory properties. Mineart et al. (2016) blended a commercial poly[styrene-b-(ethyleneco-butylene)-b-styrene] (SEBS) triblock copolymer with phase-change additives, which are crystallizable hydrocarbons with a linear structure, to produce SMP materials containing PCMs in the polymer matrix. Wu and other researchers prepared SMPs by introducing paraffin wax as a latent heat storage material and switching phase for melamine foam (Jing et al., 2019; Wu et al., 2019a; Wu et al., 2019b; Wu et al., 2020b). Although PCMs possess superior latent heat for high thermal energy storage density and exhibit a small temperature variation between storage and retrieval, their feasibility is limited by poor thermal conductivity and leakage during the phase transition process.

One attractive solution is the use of the microencapsulation process, which reduces the leakage problem of solid-liquid phase change and minimizes chemical interactions with the surrounding environment when creating PCMs (Hassan et al., 2016; Peng et al., 2020). Compared with organic shells, the organic-inorganic hybrid shell of the microcapsules not only possesses excellent dispersion in the polymer matrix but also exhibits thermophysical properties suitable for practical applications (Wang et al., 2017; Sun et al., 2020; Parvate et al., 2021). The incorporation of carbon-based materials such as graphite, graphene, and carbon nanotubes has been widely used to enhance the thermal and electrical conductivity of PCMs due to their quasi-metallic features (Chen et al., 2015; Su et al., 2017; Zhang et al., 2017). Zhang et al. (2017) synthesized microencapsulated PCMs (MEPCM) using graphene oxide-modified melamine-formaldehyde resin as the shell material for the core material of paraffin. The DSC test showed that the leakage rate decreased by 93.1% compared to those without the presence of graphene oxide. Additionally, Chen et al. (2015) demonstrated a novel type of graphene oxide-modified poly(melamine-formaldehyde) (PMF) microcapsule containing n-dodecanol as the core material through in-situ polymerization. Compared to neat PCMs, the thermal conductivity of PCMs with 4 wt% graphene oxide increased by 66.29%.

In a recently reported study by Wu et al. (2021) a new type of flexible composite PCM was created using the SEBS copolymer, paraffin, and expanded graphite (EG). The authors concluded that the SEBS-based composite PCM exhibited an excellent thermal shape memory effect in the temperature range of 50 to 80°C, thanks to the heat transfer enhancement effect of EG in the SEBS matrix. He et al. (2021) prepared a novel phase change composite (PCC) by adding a mixture of the paraffin@SiO₂ microcapsules and a

Shih et al., International Journal of Applied Science and Engineering, 21(4), 2024018

boron nitride (BN)/poly (ethylene glycol) (PEG) into the polyurethane matrix. The study revealed that the synergistic effect of microcapsules and BN created an effective thermal conductive pathway in the PEG-based polyurethane framework, resulting in an increased thermal conductivity of 32.9% to 0.675 W/m·K. Although the preparation of modified microencapsulation layers for PCMs enhances conductivity and functionality, the incorporation of such modified microencapsulation layers for making SMPs is still rare.

It is well-known that conductive fillers such as CNTs, graphene nanoplatelets (GNPs), or reduced graphene oxide (RGO) in a polymer matrix can provide increased strain set and shape fixity, along with unique characteristics like infrared absorption and electronic conductivity, making them suitable for remote actuation shape memory polymer composites (SMPCs). However, the increased filler contents often impact polymer crystallite distribution, affect the strain-dependence of polymer properties, and reduce the stored energy density for shape recovery and shape memory capability. In this study, nanographite-modified microencapsulated PCMs (GPCMs) were introduced into conductive SMP composites composed of CNTs and a polyurethane matrix. The microencapsulation process involved preparing paraffin wax particles as the core material, followed by the microencapsulation process using a composite with nanographite filler dispersed in a synthesized copolymer made from methyl methacrylate (MMA) and triethoxyvinylsilane (TEVS) acting as the shell layer. Importantly, the characterization methods used to measure the dynamic mechanical properties, thermal conductivity, and electronic conductivity will be subsequently described for the resulting polymer composites to evaluate their shape memory properties. Our goal is to enhance the shape memory performance by using

GPCMs. Additionally, CNTs with high aspect ratios and the exceptional electrical and thermal conductivities can improve the mechanical strength of SMPs and enable the design of SMPs with multiple actuation capabilities triggered by thermal, light, and electrical stimuli.

2. MATERIALS AND METHODS

2.1 Materials

Paraffin was used as phase change material, obtained from from Taiwan Wax Co., Ltd. Triethoxyvinylsilane (TEVS), methyl methacrylate (MMA), benzoyl peroxide (BPO) and ethylene glycol dimethacrylate (EGDMA) was purchased from Acros Organics. All these chemicals were of reagent grade, and were used without further purification. Polyvinyl alcohol (PVA) was purchased from Taiwan Chang Chun Group as a stabilizer. The water-based polyurethane (PU) was purchased from Nanpao Resins Chemical Co., Ltd. Nanographite particles (NGP) supplied by Conjutek Co. and carbon nanotube (CNT) supplied by Scientech Co. were used as modifier to increase the thermal conductivity of the PCM microcapsule.

2.2 Preparation of Acidified Nanographite Particles (a-NGP)

Take 30 g of nanographite and 600 mL of nitric acid in a 1000 mL round-bottom flask. Stir to evenly disperse the nanographite in the acid solution. Reflux the mixture at 120°C for 2 h. After cooling, immerse the mixture in 5000 mL of distilled water. Remove the upper clear liquid after the sedimentation and add fresh distilled water. Repeat the soaking process until the pH value reaches 6–7. Then, proceed to dry and crush it to obtain acidified nanographite (a-NGP).



Fig. 1. Schematic route for (1) the polymerization process of MMA-TEVS copolymer, (2) preparation of paraffin wax particle (3) preparation of mPCM and GPCM microcapsules

Shih et al., International Journal of Applied Science and Engineering, 21(4), 2024018

2.3 Syntheses of Microcapsules (GPCM)

As shown in Fig. 1, GPCM microcapsules were prepared according to our previously reported method (Shih et al., 2021). First, a mixture of monomers MMA (45.00 g), TEVS (11.75 g), and BPO (0.0450 g) were performed at 80 °C for 60 mins to obtain prepolymer (MMA-TEVS copolymer). Second, an aqueous solution of 1.5wt% PVA was prepared by dissolving 22.50 g of PVA into 1477.5 mL of deionized water before adding 60.00 g of paraffin. The temperature was then raised to above the melting point of the paraffin (> 40° C) to initiate liquefaction. The mixture was placed in a homogenizer and mixed thoroughly at 5000 rpm for 5 min. Subsequently, the as-prepolymer was added to this homogenized mixture and homogenized at 8000 rpm for another 5 min. Then, 4.000 g of EDGMA, 34.68 g of a-NGP and 0.4500 g of BPO were added to the mixture and reacted in an oil bath at 80°C for 24 h under stirring. The final mixture was then placed in an ice bath, centrifuged, filtered and dried before obtaining the GPCM microcapsules. In addition, a reference microcapsule without a-NGP was noted as mPCM.

2.4 Preparation of PU Composites

The obtained PU composites were prepared according to the formulation in Table 1 through mixing the additives into the aqueous polyurethane (PU). Then, the mixture of the PU dispersion, CNT, and GPCM were magnetically stirred for 1 h at room temperature, followed by ultrasonication for 2 h at room temperature. After that, the PU composite films prepared by casting the mixed PU dispersion onto a Teflon disk under ambient conditions and were allowed to dry at 50°C for about 24 h. The formulation (wt%) of the PU nanocomposite is shown as Table 1.

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Code	PU (%)	CNT (phr)	GPCM (phr)
PU	100		
5CPU	100	5	
2.5G5CPU	100	5	2.5
5G5CPU	100	5	5
7.5G5CPU	100	5	7.5
10G5CPU	100	5	10

2.5 Characterization

The morphology of GPCM was observed by TEM (JEM-2100, JEOL, Ltd., Tokyo, Japan). The sizes of GPCM were measured by particle size analyzer (Fritsch Analysis 22). Differential scanning calorimetry (DSC) were used to analyse the phase change behaviour of paraffin and GPCM under a N₂ atmosphere operated at a heating rate of 10 °C/min (TA Instruments, TA-Q20). A Hitachi scanning electron microscope (SEM; model S-3000 N) was used to evaluate the fractured surface of the PU and its composites. The acceleration voltage was 3 kV, and the sample surfaces were sputter coated with gold. The storage and loss moduli of PU and its composites were determined by a dynamic mechanical analyzer (DMA; TA Instruments, Q800) in a force-controlled mode, with a heating rate of 2°C/min. The amplitude and frequency of dynamic oscillatory loading were set at 20 μ m and 1 Hz, respectively. The thermal conductivity of the materials was measured using TCD (Hot Disk, TPS-500). Before placing them into the detector, the samples were compressed into dimensions of 5 cm (L) × 5 cm (W) × 0.5 cm (H). The operating power and time used for the measurement were 50 mV and 40 s, respectively. The surface resistance of the materials was measured using an Ultra Megohm meter (HIOKI, SM-8220). Prior to the measurement, the samples were compressed and molded to dimensions of 0.4 cm (L) × 0.7 cm (W) × 0.07 cm (H).

In this study, the shape memory properties analysis of the PU composites was performed with the fold-deploy experiments (Wang et al., 2018), through a digital camera (Electrophysics Micro-Viewer 7290A) equipment. The fold-deploy experiments was carried out as follows: The PU composites were heated to 60°C above its T_m for 5 min and then bended into "L" shape. The folded angle of 90° was recorded as θ_{max} . Subsequently, the "L" deformed shape composite was kept at 0°C for 10 min, while the angle of the deformed sample after this process was recorded as θ_{fixed} . Then, the "L" shape sample was heated from 0 to 60°C to recover its original shape, and the angle was recorded as $\theta_{recovery}$. The shape fixity ratio (R_f) and shape recovery ratio (R_r) could be calculated based on the following Equations (1) and (2)

$$R_{\rm f} = \theta_{\rm fixed} / \theta_{\rm max} \times 100\% \tag{1}$$

 $R_r = (\theta_{max} - \theta_{recovery}) / \theta_{max} \times 100\%$ (2)

3. RESULTS AND DISCUSSION

3.1 Characterizations of Microencapsulated Phase Change Materials

The microencapsulated phase change materials (mPCMs) and the additionally acidified nanographite (a-NGP) modified microencapsulated phase change materials (GPCMs) were prepared according to our previous report (Fig. 1) (Shih et al., 2021). In a three-step preparation process, nanographite was dispersed in a MMA-TEVS aqueous copolymer in an dispersion for the microencapsulation process of paraffin wax particles suspended with PVA. As a result, GPCMs with a core-shell structure were achieved, with paraffin acting as the core and a conductive shell layer containing a-NGP. In Fig. 2(a), the aggregated structure of a-NGP particles was observed due to the large surface area-induced Van der Waals forces between nanographite. The neat mPCM (without a-NGP) depicted in Fig. 2(b) exhibits a spherical appearance and a transparent outer layer, confirming that the PCM was completely encapsulated to prevent leakage during the phase change state. A similar spherical appearance is observed in the microcapsule containing a-NGP (GPCM) as shown in Fig. 2(c). However, it lacks a clear transparent outer layer compared to the mPCM in Fig. 2(b). Multiple dark-colored spots on an outer layer indicate that a-NGP was successfully embedded in the shell of the microcapsules. Consequently,





Fig. 2. TEM analysis of (a) a-NGP (b) mPCM (c) GPCM

this can enhance the thermal and electrical conductivities of the microcapsules.



Moreover, a comparison between Fig. 2(b) and Fig. 2(c) reveals that the diameter of the mPCM is larger than that of the GPCM. This may be attributed to the heterogeneous nucleation effect of the nanoscale a-NGP, which minimized the size of the dispersed phase. Fig. 3 shows the particle size analysis of GPCMs. The analysis indicates that the microcapsules prepared using the suspension polymerization method for the thermally conductive phase

change material have a diameter of approximately 2 μ m. Table 2 displays the calculated diameters of the GPCMs. The values for Q1 (10%), Q2 (50%), and Q3 (90%) are 1.56 $\pm 0.06 \,\mu$ m, 1.92 $\pm 0.02 \,\mu$ m, and 2.32 $\pm 0.03 \,\mu$ m, respectively. The average diameter is reported as 1.93 $\pm 0.31 \,\mu$ m. The relatively smaller diameter of the GPCM could enhance its dispersibility in the matrix.

Distribution (%)	Diameter (µm)
Q1 (10%)	1.56 ± 0.06
Q2 (50%)	1.92 ± 0.02
Q3 (90%)	2.32 ± 0.03
Total	1.93 ± 0.31

Fig. 4 shows the DSC thermograms of paraffin wax and GPCM. From the graph, the main peak temperatures of melting and crystallization for GPCM (49.37 and 41.55°C, respectively) closely match those of paraffin wax (48.36 and 43.52°C, respectively). The enthalpy of fusion (ΔH_m) for paraffin wax and GPCM were recorded at 79.17 and 133.90 J/g, respectively. The encapsulation efficiency, defined as the content of paraffin wax, calculated by comparing the latent heat of paraffin wax and GPCM using Equation (3), was found to be up to 59.13%.

Encapsulation efficiency(%) = $\frac{\Delta Hm(GPCM)}{\Delta Hm(paraffin wax)} \times 100$ (3)

Shih et al., International Journal of Applied Science and Engineering, 21(4), 2024018



Fig. 4. DSC thermograms of paraffin wax and GPCM

3.2 DMA Analysis of PU and Its Composites

Fig. 5 and Table 3 present the storage modulus (E') and loss modulus (E") graphs, along with the results of DMA analysis for PU and its composites, respectively. From the Fig. 5(a), two distinct phase transitions can be observed in the materials. The first transition occurs at -50°C, which is the glass transition temperature of the polyurethane (PU). When the temperature exceeds -50°C, the molecular chains of the material begin to move, transitioning the material from its glassy state to a flexible rubbery state, resulting in a decrease in storage modulus. The second transition occurs at 50°C, which is the melting temperature of the soft segments of the PU. When the temperature goes above 50°C, the soft segments of the PU melt, making the material even more flexible and leading to a further decrease in storage modulus. However, the hard segments of the PU molecular chains continue to support the overall structure of the material, preventing it from completely melting.

At room temperature (25°C), similar E' values were observed for PU and its composites in the glassy state. However, around 65°C, it can be observed that the storage modulus of PU decreases significantly and falls below that of all the composite materials. The higher E' of composites compared to pure PU at 65°C suggests that the presence of CNT and GPCM can improve the stiffness of composites and maintain their shape more stable (Liu et al., 2015). Table 3 reveals that at a temperature of 85°C, the storage modulus of PU is only 1.73 MPa, while the highest storage modulus of 6.08 MPa is observed in the composite containing 7.5 phr of GPCM (7.5G5CPU). From Fig. 5(b) and Table 3, it can be observed that the maximum loss modulus of PU is 203.2 MPa. When CNT is added, the loss modulus decreases to 139.5 MPa. This decrease is attributed to CNT's higher aspect ratio, which enhances the material's strength but reduces its toughness. However, with the addition of GPCM, a significant increase in the loss modulus is observed,

reaching a maximum of 197.1 MPa with a 10 phr addition (10G5CPU). This is because the particulate GPCM has effectively increased the material's toughness, resulting in the enhancement of the loss modulus. Based on the above results, it can be concluded that the addition of GPCM improves the storage modulus of the composite material, indicating that composites containing GPCM may possess better shape recovery capabilities (Wu et al., 2020a).



Fig. 5. DMA analysis of PU and its composites (a) storage modulus (b) loss modulus

Shih et al., International Journal of Applied Science and Engineering, 2	21(4),	2024018
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composites			
Code	Storage modulus at 85°C (MPa)	Maximum value of Loss modulus (MPa)	
PU	1.73	203.2	
5CPU	2.19	139.5	
2.5G5CPU	2.37	176.8	
5G5CPU	3.23	165.0	
7.5G5CPU	6.08	177.0	
10G5CPU	3.44	197.1	

Table 3. Results of DMA analysis for PU and its

3.3 Morphology Analysis of PU and Its Composites

The morphology of PU and its composites was observed by SEM in order to evaluate the dependency of the additives (Fig. 6). From Fig. 6(a), it can be observed that the crosssection of the PU substrate exhibits more wrinkles, which can be attributed to the softer nature of the PU. In the case of the PU matrix loaded with 5 phr of CNTs (Fig. 6 (b)), it is evident that the CNTs enhance the overall rigidity of the material, consequently reducing the wrinkles on the crosssection of the composite material. However, agglomeration of the CNTs is observed. Figs. 6 (c) to (f) showcase composite materials featuring 5 phr of CNTs and varying amounts of GPCM (2.5, 5, 7.5, and 10 phr), respectively. The SEM images demonstrate that the surface smoothness increases with the addition of GPCM, underscoring the role of GPCM in improving the material's rigidity. Moreover, a notable reduction in the agglomeration of CNTs is observed. These results can be attributed to the hybrid shell on the microcapsule surfaces, consisting of a-NGP and MMA-TEVS copolymer, which facilitates polar bonding interactions between the microcapsule and PU (Li et al., 2022). The latter, featuring silane groups, provides anchor points for CNTs and improves the compatibility in the fabrication of CNT/PU composites. This enhanced compatibility significantly reduces agglomeration. As a result, the reinforcement and better dispersion of GPCM within the PU matrix lead to improved mechanical properties.

However, when the GPCM content was 10 phr (10G5CPU), it was evident that the composite material showed a rough and layered fracture surface (Fig. 6 (f)). This may be attributed to the excessively high content of GPCM, resulting in poor dispersion and phase separation.



Fig. 6. SEM analysis of (a) PU (b) 5CPU (c) 2.5G5CPU (d) 5G5CPU (e) 7.5G5CPU (f) 10G5CPU

Shih et al., International Journal of Applied Science and Engineering, 21(4), 2024018

3.4 Thermal Conductivity and Electrical Resistivity of PU and GPCM/CNT/PU Composites

Table 4 shows the thermal conductivity analysis data of PU and its composites. It can be observed that the thermal conductivity increases with the addition of CNT and GPCM. This is because both CNT and GPCM have excellent thermal conductivity properties. When only CNT is added (5CPU), the thermal conductivity is 0.5393 W/m·K, which is 3.43% higher than that of PU at 0.5208 W/m·K. With the addition of 10 phr GPCM (10G5CPU), the thermal conductivity increases to 0.5975 W/m·K, a 12.84% improvement. These results demonstrate that adding spherical GPCM to composite materials containing CNT may increase the contact area through different-shaped thermal conductive materials, leading to a further enhancement of the composite material's thermal conductivity.

From the surface resistance analysis results in Table 4, it is found that PU's surface resistance decreases from $2.302 \times$ 10^9 to $1.034 \times 10^3 \Omega$ /sq after adding CNTs. Moreover, as the content of GPCM increases, the surface resistance of the composite materials shows a decreasing trend. At a content of 10 phr, the surface resistance decreases to 2.452×10^2 Ω /sq. This enhancement is likely due to the spherical nature of GPCM and the cylindrical shape of CNTs. The combination of 3D and 1D structures can significantly improve the formation of a conductive network. Previous literatures (Rajasekar et al., 2021; Koca et al., 2023) indicates that establishing conductive networks with adjacent filler materials is crucial for achieving electrical conductivity. The transition from insulating to conducting electrical properties occurs only upon forming an electrically conductive network at a specified percolation threshold concentration. Moreover, in scenarios with uniformly distributed fillers and a higher aspect ratio, conduction through direct contact is more dominant than through tunneling mechanisms. With hybrid fillers comprising GPCM and CNTs, the chance of creating new conductive paths increases when 1D particles are strategically placed between two GPCM clusters, thereby enhancing electrical conductivity.

Table 4. Thermal conductivity and surface resistance ofPU and its composites

Cada	Thermal conductivity	Surface resistance
Code	$(W/m \cdot K)$	(Ω/sq)
PU	0.5208 ± 0.0038	$(2.3025 \pm 0.0879) \times 10^9$
5CPU	0.5393 ± 0.0015	$(1.0345 \pm 0.0125) \times 10^3$
2.5G5CPU	0.5690 ± 0.0060	$(7.9182 \pm 0.0345) \times 10^2$
5G5CPU	0.5854 ± 0.0034	$(6.2573 \pm 0.0234) \times 10^2$
7.5G5CPU	0.5888 ± 0.0030	$(4.8363 \pm 0.0242) \times 10^2$
10G5CPU	0.5975 ± 0.0048	$(2.4521 \pm 0.0241) \times 10^2$

3.5 Shape Memory Test

3.5.1 Shape memory performance analysis

Table 5 presents the shape memory performance of the

materials, and it can be observed that the shape fixity increases with the addition of CNT and GPCM. After deformation at temperatures above the melting transitions, PU and its composites exhibited good shape fixities of over 95% due to the similar values of storage modulus in the glassy state obtained in DMA analysis. The highest shape fixity is achieved when the GPCM content is 7.5 phr. This increase in shape fixity may be attributed to the addition of CNT or GPCM, which enhances the overall hardness of the material, providing support during fixation. Nevertheless, there are significant differences in shape recovery speed, ranging from 1.00 \pm 0.18 degrees/min for neat PU to 2.40 \pm $0.14 - 3.85 \pm 0.14$ degrees/min for composites. This is attributed to the higher storage modulus in the rubbery state, which often provides larger shape recovery forces (Xiao et al., 2015). As a result, the shape recovery properties increased with the incorporation of CNT. Moreover, the presence of GPCM in CNT/PU further improved the performance, corresponding to the reinforcement effect of GPCM on the storage modulus values for the GPCM/CNT/PU composite. It is found that the composite exhibits the highest shape recovery speed when the GPCM content is 7.5 phr. This is because at high temperature, the composite with 7.5 phr of GPCM exhibits the highest storage modulus, as confirmed by the results obtained from DMA. From the analysis of the recovery rate of the composite materials, it can be observed that the shape recovery ratio of PU is 90.56%. However, after adding CNT (5CPU), the shape recovery ratio of the composite increases to 96.48%. This is because the addition of thermal conductive materials allows for more uniform temperature distribution. As the content of GPCM increases, the shape recovery ratio also shows an upward trend. This is because the GPCM has high thermal conductivity and a capacity for thermal storage. When dispersed in the composite material, it promotes efficient heat transfer and minimizes heat loss, resulting in an enhanced recovery speed of the composite material.

In fact, DSC analysis was performed to investigate the thermal phase transitions of PU, 5CPU, 7.5GCPU (GPCM/PU nanocomposites prepared without CNT), and 7.5G5CPU (Fig. S1). When fillers are introduced into a PU matrix, PU composites can exhibit a melting point (T_m) around 46.6 to 48.4°C. However, the use of CNT as a filler in the PU matrix reduced the melting enthalpy from 17.7 J/g of neat PU to 16.8 J/g of the 5CPU composite. This is because the existence of CNT filler reduced the volume fraction of crystallizable PU in the unit volume, thereby decreasing the enthalpy value. Nevertheless, the increased melting enthalpy values of 21.7 and 19.7 J/g were observed for the 7.5GCPU and 7.5G5CPU samples. The increased melting enthalpy is related to the repeatable enthalpy storage properties of the GPCM, which utilizes paraffin wax as core material for efficient energy storage and release (Jamekhorshid et al., 2014). As a result, phase change materials embedded in composites, such as 7.5GCPU or 7.5G5CPU, with higher latent heat of fusion (enthalpy) properties, provide more switchable enthalpy for polymer

Shih et al., International Journal of Applied Science and Engineering, 21(4), 2024018

composites. This enables the repeatable phase transition process necessary for triggering the shape memory properties.

From Table 5, it can be observed that when the content of GPCM is 7.5 phr, the shape fixity is the highest at 98.67%, and the recovery speed is also the highest at 3.85 degree/min, with a recovery ratio reaching 99.44%. The data above demonstrate that adding thermal conductive phase change microcapsules to the composite results in a significant improvement in the shape fixity and recovery speed, indicating that the composite has excellent fixation and recovery capabilities, with a significantly increased recovery speed. This is made possible by the thermal storage effect of the GPCM, which enhances the shape fixity and shape recovery of the SMPs. Additionally, the inclusion of conductive GPCM and CNTs with high aspect ratios and exceptional thermal conductivities can improve the rigidity of the matrix and facilitate the thermal activation of SMPs.

Table 5.	Results	of shape	memory	performance	analysis
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Code	Shape fixit (%)	Shape recovery speed (Degree/min)	Shape recovery ratio (%)
PU	97.11	1.00 ± 0.18	90.56
5CPU	97.56	2.40 ± 0.14	96.48
2.5G5CPU	97.78	3.30 ± 0.11	97.04
5G5CPU	98.00	3.55 ± 0.11	97.78
7.5G5CPU	98.67	3.85 ± 0.14	99.44
10G5CPU	95.33	3.80 ± 0.33	96.48

3.5.2 Light-induced shape memory test

The excellent electrical conductivity and radio wave absorption effects of CNT and a-NGP-containing polymer composites indicate that energy can be transferred into the polymer matrices through the light harvesting process or electric current flows, making them widely applicable in stimuli-responsive materials (Pilate et al., 2016; Wang et al., 2016). Therefore, the shape memory performances of the carbon-modified PU composites were studied using two different trigger methods: light trigger and electrical trigger. For further analysis, the GPCM/CNT/PU composite was selected to investigate other shape memory behaviors, as it exhibited the highest storage modulus value and the lowest surface resistivity among all the composites in this study.

The detailed procedures of the light-activated shape memory test were as follows: First, the shape memory testing specimens of $20 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$ were deformed into an "L" shaped structure by heating the samples in hot water at 80°C for a few minutes and then rapidly quenching them in cold water. Next, the composite specimens were heated to near 60°C using a 300 W lamp positioned 200 mm above and maintained at this temperature for 30 min to ensure a uniform temperature distribution.

Fig. 7 shows the results of the light-induced recovery test for the neat PU and the 7.5G5CPU composite under the 300 W lamp. From the graph, it can be observed that the PU shows no significant changes after 1 min of light exposure, and only slight shape recovery can be observed after 2 min. In contrast, the 7.5G5CPU starts to show shape recovery at 1 min and displays obvious changes in shape after 2 min of light exposure. Additionally, after 5 min of light exposure, the composite material exhibits a significantly higher recovery angle compared to the PU. According to the lightactivated shape memory test, it was evident that the 7.5G5CPU composite demonstrated a higher shape recovery speed than that of neat PU. This improvement can be attributed to the synergistic effect of CNT and GPCM, which enhanced the thermal conductivity of the composite. Additionally, the higher storage modulus and enthalpy values also contributed to the higher shape recovery speed. Moreover, light-activated SMPs offer several advantages, including the ability to transmit signals over long distances without a medium, target specific areas precisely, and ensure safety for human tissues. These attributes render SMPs appropriate for a broad spectrum of applications, encompassing biomedical fields as well as space and largescale engineering projects (Herath et al., 2020).

3.5.3 Electro-induced shape memory test

The detailed procedures of the electrical-induced shape memory test were as follows: First, the shape memory testing specimens of $20 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$ were deformed into an "L" shaped structure by heating the samples in hot water at 80°C for a few minutes, followed by rapid quenching in cold water. Then, the electro-induced recovery test was conducted using a 100 V DC regulated power source.

Due to the introduction of phase change materials embedded in composites such as 7.5GCPU or 7.5G5CPU, larger latent heat of fusion (enthalpy) properties was observed. This provides more switchable enthalpy for polymer composites, enabling the repeatable phase transition process to trigger the shape memory properties. The introduction of rigid filler of CNTs in PU matrices enhanced the mechanical properties, but it sacrificed a certain degree of thermal enthalpy for phase switching. The optimal combination of CNT and GPCM as fillers for PU can enhance tensile properties, achieving the best recovery ratio for the 7.5G5CPU composite in this study.

To verify the internal shape recovery mechanism of electrical activation, we utilized an infrared thermal imager to examine the surface temperature distribution of the 7.5G5CPU sample during the shape recovery process, as shown in Fig. 8. During the electrical-triggered shape memory test, the surface temperature of the deformed sheet was 29.7°C at the beginning of the shape recovery process. As the applied voltage continued to increase, the surface temperature of the deformed sample rose to 54.3°C at 30 sec, which exceeded the T_m (melting temperature) of PU (50°C). Moreover, the temperature of the 7.5G5CPU composite increased to 66.0°C within 150 sec. This observation confirms that GPCM and CNT can create a conductive path, generating heat from the resistance inside



Shih et al., International Journal of Applied Science and Engineering, 21(4), 2024018

Fig. 7. Light-induced shape memory effects of PU (left) and 7.5G5CPU composite (right) irradiated for 0, 1, 2, 3, 4, 5 min

the GPCM/CNT/PU composite under the electric field. Therefore, these energy inputs allow the 7.5G5CPU composite to recover to its original state.

Fig. 9 shows the results of the electro-induced recovery test for both the neat PU and the 7.5G5CPU composite. From the graph, it can be observed that the PU maintains its original 90-degree shape even after 3 min of electrical current application. This is because the PU has a high electrical resistance, preventing the formation of a circuit at 100 V voltage, which consequently hinders temperatureinduced shape recovery. On the other hand, the 7.5G5CPU composite clearly shows shape recovery after just 1 min of applying the 100 V voltage, indicating that the composite material forms a circuit, allowing current to flow, and the electrical resistance generates heat. This process enables the composite material to achieve shape recovery. The electroinduced recovery test demonstrates that the addition of GPCM and CNT allows the composite material to form a circuit under a 100V voltage and undergo shape recovery. Compared to thermo-active SMPs, electro-active SMPs offer the advantage of responding to indirect heating through a relatively low actuating voltage. Consequently, electro-active SMPs have garnered interest due to the extensive control over their properties, positioning them as prime candidates for a broad spectrum of applications such as soft actuators, robotics, and flexible electronics (Hassan





et al., 2024).



Fig. 9. Electro-induced shape recovery process of PU (left) and 7.5G5CPU composite (right)

Shih et al., International Journal of Applied Science and Engineering, 21(4), 2024018

4. CONCLUSION

In this study, a conducting the microencapsulated phase change materials was prepared through a newly incorporation of nanographite layer for the modification of phase change microencapsulated materials. This nanographite based hybrid shell comprising a-NGP and acrylic resin can act not only as compatibilizer between the filler such as CNT and polymer matrix, but also as reinforcements in the thermal conductivity and electrical resistance for CNT/PU composite. The incorporation of GPCM in CNT/PU improved melting enthalpy in DSC analysis, enhanced storage modulus in rubbery state in DMA analysis. It results in a good candidate for shape memory materials with good shape fixity and shape recovery ratios over 95%, and with fast recovery speed. The improved thermal and electrical conductivity enable the wireless remote controllable shape memory polymer materials via light and electrical activation thanks to the synergistic effect of CNT and GPCM. This is due to the thermal storage effect of the GPCM, which can enhance the shape fixity and recovery of the SMPs. Additionally, the inclusion of conductive GPCM and CNTs with high aspect ratios and exceptional electrical and thermal conductivities can improve the rigidity and facilitate light, thermal, or electrical activation of the SMPs. To the best of our knowledge, this is the first microcapsulated PCM-based PU composites with dual activated shape memory properties to express the unique properties of the a-NGP-modified shell microcapsules. This work provides the elaborated design via microencapsulated PCMs for preparing enhanced shape memory performance with multiple actuation capabilities. As a result, these SMPs could be employed in various applications, including biomedical fields, space and largescale engineering projects, soft actuators, robotics, and flexible electronics.

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Shih et al., International Journal of Applied Science and Engineering, 21(4), 2024018

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Fig. S1 curves of nanocomposites based on GMEPCM or CNT in PU matrix.