PERFORMANCE OF RARE EARTH ORGANIC COMPLEXES BASED LIGHT ACTIVATED SHAPE MEMORY POLYMER COMPOSITES

Madhubhashitha Herath[1], Jayantha Epaarachchi[2], Mainul Islam[3], Liang Fang[4], Fenghua Zhang[5] and Jinsong Leng[6]

[1] Centre for Future Materials, University of Southern Queensland, Toowoomba, Australia, Madhubhashitha.Herath@usq.edu.au, www.usq.edu.au
[2] School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, Australia, Jayantha.Epaarachchi@usq.edu.au, www.usq.edu.au
[3] School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, Australia, Mainul.Islam@usq.edu.au, www.usq.edu.au
[4] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Materials Science and Engineering, Nanjing Tech University, Nanjing, China, Lfang@njtech.edu.cn, www.en.njtech.edu.cn
[5] Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin, China, fhzhang_hit@163.com, www.en.hit.edu.cn
[6] Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin, China, lengjs@hit.edu.cn, www.en.hit.edu.cn

Keywords: Shape memory polymer composite, Light activation, Thermomechanical behaviour, Structural performance, Photothermal effect

ABSTRACT

The shape memory polymers (SMPs) have the ability to retain a temporary shape and recover its original shape once exposed to a particular external stimulus. Compared to other stimulation methods, light activated shape memory polymers have a significant potential in developing breakthrough technologies in biomedical, aerospace and space engineering industry since the shape memory effect can be remotely controlled by a light beam. Introduction of photothermal fillers into thermally activated SMPs is one of the convenient and commercially available approaches to prepare light activated shape memory polymer composites (LASMPCs). The cost-efficient filler system based on rare earth organic complexes of $Nd(TTA)_3Phen$ and $Yb(TTA)_3Phen$ demonstrate selective photothermal effect by absorbing near infrared (NIR) radiation. However, due to inadequate structural properties, LASPMCs are incapable to use in a wide range of large-scale engineering applications. In this study, the effects of rare earth organic complexes and glass fibre reinforcements on mechanical properties and shape memory behaviour have been investigated. Inclusion of photothermal fillers has shown a negative effect on the mechanical properties of the LASMPCs. However, the glass fibre reinforcement has increased the mechanical properties except the compression strength as anticipated. In addition, it has been observed that the glass fibre reinforced LASMPCs with $Nd(TTA)_3Phen$ and $Yb(TTA)_3Phen$ have demonstrated photothermal effect due to 808 nm and 980 nm NIR irradiation as anticipated. Interestingly, the combination of photothermal fillers and glass fibre reinforcements have shown the LASMPCs potential to apply in large-scale engineering applications.

1 INTRODUCTION

The shape memory polymers (SMPs) have an interesting capability of keeping a temporary shape and then recovering the original shape once subjected to a particular external stimulus [1]. Advantageously, light stimulated shape memory polymer composites have the capability of remote activation as light can travel a long distance even without a medium. In addition, localized activation can be performed as light can be focused on a certain area [1, 2]. Researchers have introduced photothermal fillers into thermally activated SMPs in order to prepare LASMPCs [2]. Under irradiation, the fillers absorb the light energy and transfer it into heat, which indirectly increases the temperature of the composite. Due to the photothermal heating, the shape recovery occurs when the temperature reaches the glass transition temperature (Tg) [1, 2]. Photothermal fillers such as gold nanoparticles, carbon nanotubes, carbon black, carbon fibres and rare earth organic complexes responsive to different light wavelengths, including UV light, visible light, and infrared light, have been explored to produce LASMPCs [2-7]. Among all such fillers, rare earth organics complexes of Nd(TTA)$_3$Phen and Yb(TTA)$_3$Phen have demonstrated selective photothermal effect to NIR light of 980 and 808 nm, respectively [2, 8]. Rare earths are a special group of elements in the periodic table. In addition to SMP activation, the rare earth organic complexes have the technical versatility for various applications such as energy harvesting, ultraviolet light detection, temperature sensing, laser and light emitting diodes [9, 10]. The incorporation of rare earth ions or their complexes into polymer matrix has been carried out for a few decades [11]. The development of photothermal fillers, selectively responsive to a certain wavelength of light has attracted the interest in order to facilitate successive multi shape changes of polymers, which can be used in smart actuators or structures [2].

However, due to SMP's relatively low mechanical properties, the use of LASMPCs in a wider range of engineering applications is limited. As such, LASMPCs need to be reinforced for use in engineering applications [1, 12]. Unfortunately, selectively triggered LASMPCs with increased mechanical properties have not introduced in order to develop large-scale engineering applications such as deployable or reconfigurable structures. Also, the shape memory behaviour and mechanical properties of such LASMPCs need to be accurately quantified, for developing engineering applications such as deployable satellites, space habitats and rovers [13, 14]. In this study, different combinations of LASMPCs with Nd(TTA)$_3$Phen, Yb(TTA)$_3$Phen and glass fibre reinforcements have been prepared. Subsequently, the mechanical properties, shape memory behaviour and photothermal effect of those samples were tested and the effects of rare earth organic complexes and glass fibres have been investigated.

2 MATERIALS AND METHODS

The shape memory epoxy resin used in this research has been supplied by the Harbin Institute of Technology (HIT), China. The detailed chemical composition of the SMP matrix is proprietary to Center for Composite Materials and Structures of HIT. The roving plain (400 g/m^2) glass fibre was supplied by Changzhou Jlon Composite Co., Ltd, China. Sigma Aldrich, Australia has supplied $NdCl_3.6H_2O$, $YbCl_3.6H_2O$, TTA and Phen.

2.1 Preparation of test specimens

The rare earth organic complexes of Nd(TTA)$_3$Phen and Yb(TTA)$_3$Phen have been prepared by following the co-precipitation method described by Fang et al. [2]. First, the 1 mmol of $NdCl_3.6H_2O$ or $YbCl_3.6H_2O$, 3 mmol TTA and 1 mmol Phen were dissolved in ethanol, respectively. Then the ethanol solution of TTA was first added to a beaker and it was stirred at 60 °C. Successively, the ethanol solution of $NdCl_3.6H_2O$ or $YbCl_3.6H_2O$ and the ethanol solution of Phen were added into the ethanol solution of TTA. The mixture was stirred for 15 mins at 60 °C. Subsequently, drops of 1 mol/L sodium hydroxide ethanol solution was added into the mixture until the pH value reaches 6-7. Afterward, the mixture was reacted in a 60 °C water bath for 6 hrs. Once the reaction is finished, the mixture was centrifuged at a

Sample ID	Composition of the fillers		
	Glass fibre (Layers)	Nd(TTA)$_3$Phen (%)	Yb(TTA)$_3$Phen (%)
A	0	0	0
B	0	1	0
C	4	1	0
D	0	0	1
E	4	0	1

Table 1: Composition of the fillers and respective sample ID.

speed of 3000 rpm for 3 hrs to obtain the precipitation. Then the precipitation was dried in a vacuum oven at 50 °C for 12 hrs. Finally, the complexes were powdered by using a ball mill.

Five different test samples were prepared including pristine SMP, LASMPCs only with photothermal fillers and LASMPCs with both photothermal fillers and glass fibre reinforcements. Table 1 illustrates the composition of the five samples. The photothermal filler particles were added into SMP resin and the solution has been stirred for 15 mins at 30 °C followed by ultrasound sonication for 10 mins at 30 °C under 80 W ultrasound power. The pristine SMP epoxy or the SMP epoxy mixed with photothermal fillers were poured into a mould, which is prepared using two glass sheets. The inner surfaces of the two glass sheets were coved with a peel fly for easy removal of the samples. In addition, four layers of glass fibres were inserted only for the samples with reinforcement. Subsequently, those moulds were kept in the oven for 9 hours at 80 °C, 100 °C and 150 °C respectively with equal time spacing, where the curing has taken place. Successively, five different sheets of 300 x 300 x 2.5 mm were prepared. The sample sheets were cut into standard test specimens for tensile test (250 x 15 x 2.5 mm), compression test (140 x 12.8 x 2.5 mm), impact test (100 x 12 x 2.5mm) and DMA test (60 x 8 x 2.5 mm) by using a diamond saw.

2.2 Experimental methods

The light absorbance capabilities of the photothermal fillers were measured by using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. MTS 100 kN, Insight Electromechanical Testing Systems has been used for the tensile and compression testing. SCHMIDT Shore Durometer HPSC has been used to determine the hardness of the polymer material. The impact testing has been performed by using an Instron Dynatup Drop Weight Impact Testing Instrument (8200). TA Instruments Dynamic Mechanical Analyzer (DMA Q800) with a double cantilever clamp has been used to investigate the thermomechanical and shape memory behaviour of the pristine SMP and LASMPCs. The sample C and E (glass fibre reinforced LASMPCs) were exposed to three different power densities of NIR radiation of 808 nm and 980 nm respectively, and the respective photothermal behaviour has been investigated by using a FLIR A65 thermal imaging camera.

3 RESULTS AND DISCUSSION

A thermoset shape memory polymer epoxy and 0/90 woven roving plain glass fibre have been used as the polymer matrix and reinforcement material respectively. Compared to thermoplastics, thermosets are cost effective, have a high level of dimensional stability and thing to thick wall manufacturing capabilities. Due to inherent weak mechanical properties, pristine SMPs have limitations in structural engineering applications. Interestingly, fibre reinforced SMPCs are widely being used as a structural material because of their increased mechanical properties and recovery stresses [1]. Moreover, the 0/90 woven fibre reinforcement will assist to maintain the dimensional stability of the prepared SMPCs. Compared to glass fibres, carbon based fibres or particles demonstrate light absorbance capabilities [1, 6, 7, 13]. Therefore, the carbon fibre and carbon nanotube reinforcements can affect the selective triggering performance of LASMPCs with photothermal fillers. Figure 01 (a) and (b) show the two type of photothermal fillers used to prepare the LASMPCs and their UV-Vis-NIR transmittance spectroscopy respectively. Equitation 1 gives the relation between the absorbance (A) and transmittance (T).

$$A = 2 - log_{10}T \tag{1}$$

Accordingly, both types of photothermal fillers demonstrate an absorbance of ~1 in the UV range. In addition, $Nd(TTA)_3Phen$ demonstrates several absorbance peaks at the visible range of 529 nm (A=0.13), 582 nm (A=0.21) and 683 nm(A=0.05). In the NIR range, $Nd(TTA)_3Phen$ demonstrates absorbance peaks at 747 nm (A=0.15), 799 nm (A=0.13), 876 nm (A=0.07) and 1136 nm (A=0.04). Also, $Yb(TTA)_3Phen$ has shown NIR absorbance around 970 nm (A=0.10) and at 1134 nm (A=0.04). Accordingly, $Nd(TTA)_3Phen$ has demonstrated selective absorbance peaks at both visible and NIR range, where $Yb(TTA)_3Phen$ has shown selective absorbance peaks only at NIR range. However, at UV

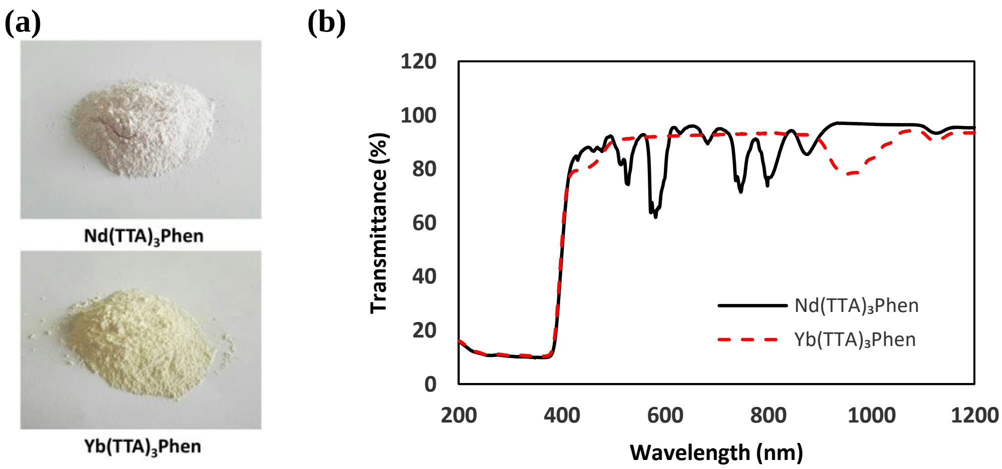

Figure 1: Photothermal fillers and their UV-Vis-NIR transmittance spectroscopy.

range both fillers have demonstrated higher absorbance compared to the selective wavelengths at visible and NIR ranges. Therefore, inclusion of Nd(TTA)$_3$Phen and Yb(TTA)$_3$Phen into SMP matrix will enable photothermal heating due to UV light absorbance or selective wavelength photothermal heating due to visible and NIR light absorbance. However, NIR light beam is relatively safer for human bodies and naked eyes unlike the UV radiation [2].

3.1 Mechanical properties

Inclusion of rare earth organic complexes based photothermal fillers into SMP matrix has affected the mechanical properties. Table 2 shows the tensile strength, compressive strength, hardness and impact energy absorbance of the five different test specimens. The tensile and compressive strengths have shown a significant reduction due to the incorporation of rare earth organic complexes based photothermal fillers. As anticipated, the glass fibre reinforcements have increased the tensile strength considerably compared to the pristine SMP or LASMPCs with photothermal fillers. However, the glass fibre reinforcements have not benefited to improve the compression properties. Reduced compression properties of the LACMPs were occurred due to the bulking effect. The increasing interest in the design of smart devices and mechanical components has identified buckling and post buckling response as a favorable behavior. Therefore, the enhanced bulking behavior of SMPCs due to the inclusion of rare earth organic complexes based particulate fillers will be advantageous to develop the energy related and motion related smart applications activated by light [15].

Hardness is an important factor, as the resistance to wear due to friction or erosion depends on the hardness of a material. The inclusion of rare earth organic complexes has slightly reduced the hardness of the LASMPCs compared to its parent SMP material. The recent progress of SMP research has been focused to develop LASMPC based space engineering applications. However, one of the challenging

Sample ID	Tensile Strength (MPa)	Compressive Strength (MPa)	Hardness (Shore C)	Impact Energy (J)
A	48	82	95	0.28
B	13	21	93	0.25
C	124	28	94	2.40
D	17	24	93	0.24
E	165	28	94	2.50

Table 2: Mechanical properties of the pristine SMP and LASMPCs.

concern on selecting composite materials for space applications is their robustness at the harsh environment with the presence of micrometeoroids and space debris. Therefore, the LASMPCs with improved impact energy absorbance is an essential requirement. Inclusion of rear earth organic complexes has not shown any significant effect on the impact energy. However, the glass fibre reinforcements have improved the impact energy absorbance.

3.2 Shape memory behavior

Table 2 shows the thermomechanical and shape memory properties obtained from the DMA experiments. A SMP material demonstrates shape memory effect around its Tg. Below Tg a material is at dominant frozen phase and above Tg a material is at dominant active phase. At a certain range around Tg, a material demonstrates combined properties of both phases. Peak of the Tan δ curve obtained from DMA can be defined as Tg. The multi frequency strain mode has been used to determine the Tg. Accordingly, it is revealed that the rare earth organic complexes reduce the Tg compared to pristine SMP.

The stress free strain recovery curves have been obtained under DMA strain rate mode. By considering the stress free strain recovery curves, the shape recovery ratio, shape fixity ratio and shape recovery rate have been calculated. Inclusion of rare earth organic complexes has not demonstrated a significant effect on shape recovery ratio. The glass fibre reinforced LASMPCs have demonstrated a lower shape recovery ratio compared to the LASMPCs without fibre reinforcement. It is revealed that the neat SMP has demonstrated an excellent shape fixity. Inclusion of photothermal fillers and glass fibers has reduced the fixity. The reason being the spring-back effect caused due to incorporated fibres and particles. The neat SMP has shown the highest recovery rate. Inclusion of rare earth organic complexes has reduced the shape recovery rate compared to its parent SMP material.

Sample ID	Glass Transition Temperature (˚C)	Shape recovery ratio (%)	Shape fixity ratio (%)	Shape recovery rate (%/min)
A	98	97.05	99.70	0.12
B	62	97.41	94.27	0.11
C	45	81.21	95.10	0.09
D	69	97.45	98.08	0.10
E	48	85.03	93.73	0.09

Table 3: DMA results of the pristine SMP and LASMPCs.

3.3 Photothermal effect

The photothermal effect is a phenomenon which produces the thermal energy from electromagnetic radiation. Once the electromagnetic radiation is absorbed by a material, free electrons of the material will vibrate at very high frequency, and reach higher energy levels. Part of the vibrational energy is converted into the electromagnetic waves and radiate outwards. The rest is transformed into kinetic energy of electrons and then converted into heat energy through the relaxation process between electrons and lattices [1]. As presented in Figure 1 (b) $Nd(TTA)_3Phen$ and $Yb(TTA)_3Phen$ have demonstrated selective absorbance peaks around 799 nm and 970 nm respectively. Therefore, commonly used NIR laser sources of 808 nm and 980 nm centre wavelengths were used to heat the glass fibre reinforced LASMPCs with $Nd(TTA)_3Phen$ and $Yb(TTA)_3Phen$ respectively. The samples were exposed to a 10 mm diameter circular laser area and the temperature variation was recorded at a 3 x 3 pixels region at the center of the laser exposed area.

Figure 2 (a) and (b) illustrate the temperature increment for 300 seconds due to 3 different power

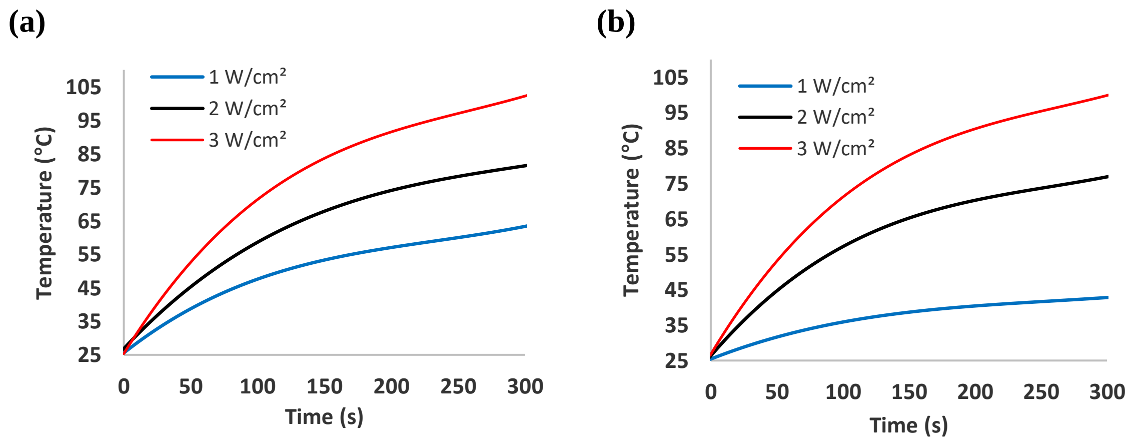

Figure 2: Temperature increment due to photothermal heating (a) Sample C exposed to 808 nm NIR radiation (b) Sample E exposed to 980 nm NIR radiation.

densities (1, 2 and 3 W/cm^2) of 808 nm (irradiated to sample C) and 980 nm (irradiated to sample D) respectively. Both samples have reached above Tg within 300 seconds once exposed to a power density of 2 W/cm^2 or more. The increment of power density reduces the time required to reach Tg. The demonstrated photothermal behavior will assist to perform NIR triggered shape recovery of glass fibre reinforced LASMPCs.

4 CONCLUTIONS

This paper presents the mechanical properties, shape memory behavior and photothermal effect of Nd(TTA)$_3$Phen and Yb(TTA)$_3$Phen based LASMPCs. In addition, the necessity of glass fibre reinforcements for such LASMPCs is revealed. Nd(TTA)$_3$Phen has demonstrated multiple absorbance peaks in the visible and NIR wavelength ranges. Yb(TTA)$_3$Phen has selective absorbance peaks in the NIR wavelength range. The inclusion of photothermal fillers has reduced the tensile and compressive strengths of the LASMPCs. The glass fibre reinforcement has increased the tensile properties and impact energy absorbance as anticipated. Inclusion of rare earth organic complexes based photothermal fillers has reduced the Tg compared to pristine SMP material. However, the photothermal fillers have not shown any significant effect on the shape fixity and recovery ratios. The glass fibre reinforced LASMPCs with Nd(TTA)$_3$Phen and Yb(TTA)$_3$Phen have demonstrated photothermal effect due to 808 nm and 980 nm NIR irradiation. Both samples have reached above Tg within 300 seconds once exposed to a power density of 2 W/cm^2 of the respective wavelength of NIR radiation. The increment of power density reduces the time required to reach Tg. The light stimulation of LASMPCs were not studied in-depth in this study. However, observations have confirmed that the fibre reinforced LASMPs with selective triggering capability have the potential for applying in large-scale engineering applications.

ACKNOWLEDGEMENTS

This work was financially supported by the Asian Office of Aerospace Research and Development (AOARD), Air Force Office of Scientific Research (AFOSR), U.S. Air Force [grant number FA2386-16-1-4043]. The authors are indebted to the Harbin Institute of Technology for providing help and material used in this work.

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