



Degradation of nano-ZnO particles filled styrene-based and epoxy-based SMPs under UVA exposure



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ABSTRACT

Styrene-based and epoxy-based SMPs (SSMPs and EPSMPs) filled with different contents of nano-ZnO particles were fabricated, their decolouration, UVR absorbabilities, surface hardness, dynamic mechanical properties and shape memory effects under UVA degradation test were then investigated. Experimental results showed that all samples subjected to the UVA degradation were yellowish with different degree. By adding 2 wt.% of nano-ZnO particles, all SMPs achieved full UVR blockage. 2 and 4 wt.% nano-ZnO/SSMP and 5 and 7 wt.% nano-ZnO/EPSPMP could maintain their surface hardness at moderate level after the UVA degradation. Storage modulus of 4 wt.% nano-ZnO/SSMP and EPSPMP before and after UVA degradation obtained satisfactory results compared with their pure forms. It was proven that shape recovery ratio was not affected by nano-ZnO particles inside SMPs. Treated EPSPMPs could obtain 100% shape recovery. However, UVA degradation was proven to have effects on the shape memory effect in SSMPs. UVA-degraded SSMPs had better recovery than non-UVA-degraded SSMPs, this could be explained by the degraded surface which was changed to be hardened. 4 wt.% of nano-ZnO particles filled into SSMP and EPSPMP could maintain a similar full recovery time before and after UVA degradation and could significantly reduce the recovery reaction time.

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1. Introduction

Traditionally, shape memory alloy (SMA), which is a kind of metal alloys, has been recognised the only material that possesses the shape memory effect (SME) based on its twinned and de-twinned phase transformation characteristics. Until recently, smart memory polymer (SMP), like Polyurethane-based (PU-based) polymers [26], styrene-based (S-based) polymers [27] and epoxy-based (EP-based) polymers [10] have been discovered to also possess the SME. PU-based SMP, which is physically cross-linked, has been proven to increase residual stress and decreased shape recovery rate, which cannot provide an effective function for the SME when compared with that of chemically cross-linked structures [26,27]. Therefore, to popularise the SMP for SME applications, chemically cross-linked S-based and EP-based SMPs are investigated in this study.

SMPs have been broadly investigated by integrating them with different fillers to become a new class of composites that are

thermo- [10,25,27], photo- [18], electrical- [12,29], magnetic- [3] and chemo- [14] sensitive. These composites have many advantages over traditional SMAs, for examples, they have high tailorability and functionality by changing their compositions or adding different fillers to alter their shape recovery temperature, stiffness and bio-degradability. Low density, low cost, high shape recovery strain (can be achieved up to 400%), reliable recovery behaviour and convenient fabrication technique (compared with SMA which requires over 100 °C and high pressure) make it to become more attractive in recent years. Because of these advantages, SMP composites are widely applicable in aerospace [1,11], textiles [30], automobiles [2] and biomedicine [3,9] areas.

In some applications, SMPs are utilised at different harsh environments, which may affect or even degrade their mechanical properties and lower their service lifetime. UV (100–400 nm) degradation is always a critical problem for polymer-based materials including SMPs, especially when they are used as primary structures that are exposed to sunlight. Around 95% UVA (315–400 nm), out of 9% UVR from the sun, entered onto the Earth surface has the highest average intensity of 1.37 mW/cm² and the highest penetration ability into human bodies and

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polymers [4,24]. UVA usually attacks human bodies [7] and polymers [16,27] under ageing (a long period of time) in physical and chemical ways. The degradation of polymers results in yellowing on materials' surface and alternation in their mechanical properties. Xu et al. [27] have discovered that the exposed surfaces of SMPs were discoloured under UVR in the air. Their compressive strength and ductility were also severely decreased as compared with their tensile strength. Generally speaking, UV degradation in polymers is a combination of physical movements and chemical reactions between chains of polymer molecules. UV degradation requires oxygen to proceed and produces water molecules and several types of free radicals, so it is also said to be photo-oxidation. UVR also induces thermal degradation, which speeds up the damage in polymers. The damage is commonly seen as depolymerization [17].

Kumar et al. [8] have discussed that nano-scaled inorganic particles would be a new trend for polymer-based materials to improve their UV resistibility. ZnO and TiO₂ are semiconductors, metal oxides and inorganic UVR absorbers, this kind of substances has intrinsic ability of UVR absorption. TiO₂ has been extensively investigated for its UVR absorbability. In fact, ZnO particle has relatively wider band gap energy of 3.37 eV at room temperature so as it has a broader range of UVR absorption of 290–400 nm (a full UVA and UVB absorption) than TiO₂. TiO₂ has band gap energy of 3.02 eV at room temperature and has a UVR absorption within the range of 290–350 nm. The refractive index of ZnO in visible light is 1.9 while TiO₂ is 2.6 so as ZnO possesses better light transmissibility [5,15,20,22]. In general, nano-sized (less than or equal to 100 nm) ZnO particles have relatively high UVR absorbability and transparency. In addition, ZnO is inexpensive, relatively abundant and chemically stable making it suitable for many applications, such as an ingredient of cosmetics and clothing [20,23]. Some researchers have integrated ZnO particles into different polymer materials for UVR protection [13,19,22]. Lowry et al. [13] have studied the UVR permeability in nano-ZnO filled coating and discovered a low dose of 7 wt.% of ZnO layer was sufficient to block UVA and UVB and outperformed 4 wt.% of ZnO in terms of UVR protection. In this study, different weight percentages of nano-ZnO particles were introduced into S-based and E-based SMPs. Their influences in terms of UV degradation, decolourisation, UVR absorbability and surface hardness were investigated.

2. Experimental setup

2.1. Raw materials

Styrene-based SMP (SSMP) and Epoxy-based SMP (EPSMP) were thermoset plastics in the analytical grade and used without further purification. Both SMP matrices were fabricated in Harbin Institute of Technology (HIT) [10,28]. The glass transition temperatures (T_g) of neat SSMP and neat EPSMP were claimed to be 85 °C and 100 °C respectively. Nano-ZnO particles with a diameter of approximate 100 nm and white in colour, were purchased commercially.

2.2. Specimen preparations

Precursor solutions of SSMP and EPSMP were mixed with 2, 4, 5 and 7 wt.% of nano-ZnO particles. The resins were firstly mechanically stirred for 20 min and then sonicated for another 10 min. Afterwards, they were degassed until bubble-free mixtures were obtained. The resulting mixtures were poured into a two-plate glass mould with a thickness of 3 mm. Thermal curing of ZnO/SSMPs was performed at 75 °C for 36 h while that of ZnO/EPSMPs was at 80 °C for 3 h, followed by 100 °C for 3 h and 150 °C for 5 h. All samples were cooled down at room temperature

and then machined into a square shape with the dimension of 30 mm × 30 mm × 3 mm for investigations. For the comparison purpose, neat SSMP and neat EPSMP samples were also prepared.

2.3. Accelerated UVA ageing

The effects of nano-ZnO particles in SSMPs and EPSMPs under UVA degradation were investigated. Two groups of samples and their pure forms were exposed under UVA with 250 mm apart from the source for 12 h inside an UVA chamber. The intensity of UVA from the lamp (100 mW/cm²) was approximately 11 times higher than that of terrestrial UVA (9.1105 mW/cm² in average) [4]. Generally, UVR is alerted from 10 am to 4 pm (6 h) in every day [24]. For a 12-h exposure under the UVA lamp, it could simulate the effect similar to 22-day exposure under the sunlight. In addition, the samples were experienced at a temperature (80 °C) 3 times higher than that on the Earth's surface at sea level (25 °C), this further accelerated the effect of UVA degradation. The exposed temperature (80 °C) was slightly lower than the T_{gs} of neat SSMP (85 °C) and neat EPSMP (100 °C).

2.4. UVR absorption test

The UVR absorbabilities of ZnO/SMPs before and after UVA degradation were tested and compared. UV-vis Spectrophotometer (Dynamica DB-20, 190–1100 nm) was used to test the absorbabilities of UVA (315–400 nm), UVB (280–315 nm) and UVC (190–280 nm) of all samples. Absorbance displays along the Y-axis with maximum absorbance index of 5 while UVR displays along the X-axis with wavelength ranging from 190 nm to 400 nm. For the comparison purpose, UVR absorption tests on neat SSMP and neat EPSMP were also conducted.

2.5. Yellowing of neat SMPs and ZnO/SMPs by UVA degradation

Different degrees and rates of yellowing of neat SMPs and ZnO/SMPs before and after UVA degradation were observed and compared.

2.6. Surface hardness test

The surface hardness of ZnO/SMPs were measured before and after the UVA degradation by using Microhardness Tester (Future-Tech) with test load of 100 gf and dwell time of 15 s. For the comparison purpose, the surface hardness tests on neat SSMP and neat EPSMP samples were also conducted.

2.7. Dynamic mechanical analysis (DMA)

DMA testing is commonly used to determine the dynamic molecular motion changes of SMP. DMA (Perkin Elmer Diamond DMA Lab System) was used to conduct the tensile test mode with the different setting parameters as shown in Table 1 for non-UVA-degraded and UVA-degraded SSMP and EPSMP samples with and without 4 wt.% nano-ZnO particles.

Table 1
Setting parameters of DMA test for neat SMP and 4 wt.% ZnO/SMP samples.

	Neat SSMP and 4 wt.% ZnO/SSMPs	Neat EPSMP and 4 wt.% ZnO/EPSMPs
Sample size		30 × 5 × 2 mm ³
Temperature range	25–130 °C	–30 to 150 °C
Testing rate	2 °C min ^{–1}	5 °C min ^{–1}
Testing frequency	0.2 Hz	1 Hz

2.8. Shape memory effects (SMEs)

SMEs including the shape recovery ratio, full recovery time and recovery reaction time of SMP were determined by a series of steps. Different set parameters of the SME test for SSMP and EPSMP samples with and without nano-ZnO particles are shown in Table 2. Dimethicone was used to be the isothermal medium for heat treatment on SMPs because it has high transparency and high chemical stability. SMPs were heated to a temperature of their $T_{gs} + 20\text{ }^{\circ}\text{C}$ in an oven for 20 min. Then the softened SMPs were immediately bent into U-shape around an aluminium plate with 2 mm radius arc at a bending rate of 10°s^{-1} . U-shape SMPs were fixed on the plate and the whole pieces were put into cooling chamber at $0\text{ }^{\circ}\text{C}$ for 20mins. Deformed SMPs were immersed into Dimethicone bath at $T_{gs} + 20\text{ }^{\circ}\text{C}$ to investigate their shape recovery behaviour which the processes were recorded by video. The shape recovery ratio is the ratio of shape recovery angle to 180° . Full recovery time and recovery reaction time were evaluated from the video to distinguish the differences in SME of non-UVA-degraded and UVA-degraded SSMP and EPSMP with and without nano-ZnO particles.

3. Results and discussions

3.1. UVR absorbability of nano-ZnO particle

ZnO particle is an inorganic UVR absorber, which enables to absorb UVR in the range of 290–400 nm (a whole range of UVA and UVB). A ZnO atom absorbs UVR and deteriorates the energy physically. The reaction is dependent on the ability of a ZnO atom having its band gap energy ($\sim 3.22\text{ eV}$ for a ZnO atom with particle size of 100 nm) to create an electron–hole ($e^{-}\text{--}h^{+}$) pair. A schematic diagram is shown in Fig. 1, electrons present in the valence band (+ve) are excited by UVR having an energy greater than the band gap of a ZnO atom and jump to the conduction band (–ve). These electronic transitions occur between the two bands as long as the ZnO atom exposed to UVR. It was suggested that the electrons are fluctuated in an excitonic system between the internal field [5,6] and it is believed that the energies of electrons decay with travelled distance and time and become exhausted.

The intensity energy of UVR can be calculated by Eqs. (1) and (2):

$$E = hf \quad (1)$$

where E is the intensity energy of light, h is Planck's constant $= 6.626 \times 10^{-34}\text{ J s}$ and f is the frequency of the light vibration and

$$\lambda = \frac{v}{f} \quad (2)$$

where λ is the wavelength of light, v is the speed of the light $= 3 \times 10^8\text{ m/s}$ and f is the frequency of the light vibration.

In this experiment, only UVA (318–400 nm) degradation was considered. The intensity energy of light is $6.251 \times 10^{-19}\text{ J}$ at wavelength of 318 nm while the intensity energy of light is $4.903 \times 10^{-19}\text{ J}$ at wavelength of 400 nm. The smaller the

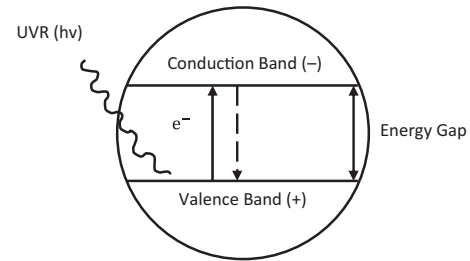


Fig. 1. A schematic diagram shows the UVR absorption of band gap inside a ZnO atom.

wavelength of light, the higher of its energy. The band gap energy of a ZnO atom with particle size of 100 nm is about 3.22 eV which is equal to $1.602 \times 10^{-19}\text{ J}$. The intensity energy of UVA is 3 times more than the band gap energy of a 100 nm ZnO atom which it is large enough to excite electrons from the valence band of a ZnO atom and they iterate between the band gap until their energies are exhausted.

3.2. UVR absorption tests of neat SMPs and ZnO/SMPs

Before the UVA degradation test, the neat SSMP had full UVB and UVC absorptions and most part of UVA but not for UVA from 387.5 nm to 400 nm (Fig. 2) while the neat EPSMP had a full UVC and most part of UVB absorptions but not for UVB from 311.5 nm to 315 nm and the whole range of UVA (Fig. 3). After the accelerated UVA ageing, the neat SSMP had a full UVR absorption (Fig. 2) while the neat EPSMP had a full UVC and less part of UVB absorptions but not for UVB from 295.5 nm to 315 nm and the whole range of UVA (Fig. 3).

The UVR absorbability of the neat SSMP was strengthened while that of the neat EPSMP was weakened after the test. These phenomena were resulted from the difference of UV degradation mechanisms of styrene and epoxy and will be explained in the following session. Additionally, both SSMP and EPSMP with 2, 4, 5 and 7 wt.% of nano-ZnO particles could achieve a full UVR absorption (Fig. 4). 2 wt.% of nano-ZnO particles inside SSMP and EPSMP were enough to achieve a full UVR absorbability.

3.3. UV degradation mechanisms in polymer materials (styrene and epoxy)

Polymer absorbs UVR chemically and it degrades as a result of energy accumulation. Even a low energy of UVR is applied to the polymer for over a long period of time, the cumulative degradation effect is significant. There are two ways of UVR absorption on polymers, one way is that the UVR excites the electrons in the bonds between polymer chains. Another way is the UV produces thermal energy to cause thermal degradation on polymers. The degree and the rate of UV degradation on polymers depends on the intensity and thermal energy of UVR absorbed by polymers. To further explain, the amount of UVR energy required to degrade a polymer is determined by the molecular structures of polymers, such as amorphous or crystalline, and the bonding characteristics, such as secondary bonds (Van der Waals bonds and hydrogen bonds) or crosslinks or covalent bonds, between polymer chains.

Styrene is an amorphous thermoplastic and epoxy is a thermoset plastic. Theoretically, if the energy of UVR is large enough, it is able to break firstly the secondary bonds between the polymer chains and then the covalent bonds of the primary polymer chains because the secondary bond is much weaker than the covalent bond. Generally, amorphous thermoplastic has no crosslinks between polymer chains and low density, so it is more susceptible

Table 2
Setting parameters of SME tests for neat SMP and all ZnO/SMP samples.

	Neat SSMP and all ZnO/SSMPs	Neat EPSMP and all ZnO/EPSMPs
Sample size		$30 \times 5 \times 2\text{ mm}^3$
Pre-heating temperature	$105\text{ }^{\circ}\text{C}$ ($T_g + 20\text{ }^{\circ}\text{C}$)	$120\text{ }^{\circ}\text{C}$ ($T_g + 20\text{ }^{\circ}\text{C}$)
Cooling temperature	$0\text{ }^{\circ}\text{C}$	$0\text{ }^{\circ}\text{C}$
Reheating temperature	$105\text{ }^{\circ}\text{C}$ ($T_g + 20\text{ }^{\circ}\text{C}$)	$120\text{ }^{\circ}\text{C}$ ($T_g + 20\text{ }^{\circ}\text{C}$)

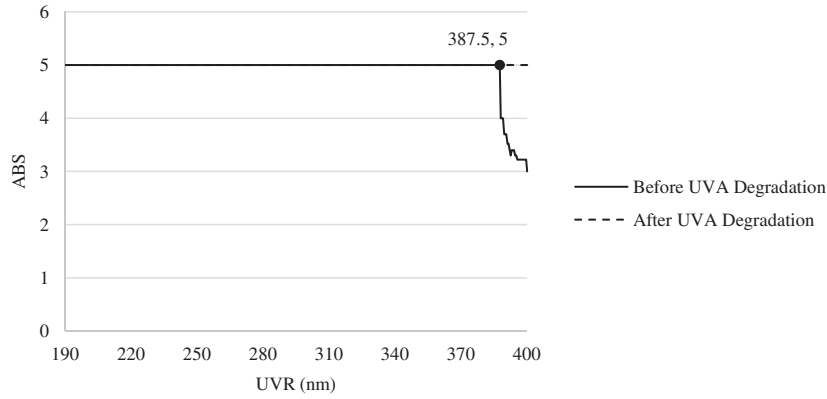


Fig. 2. The UV absorbability of neat SSMP before and after UVA degradation.

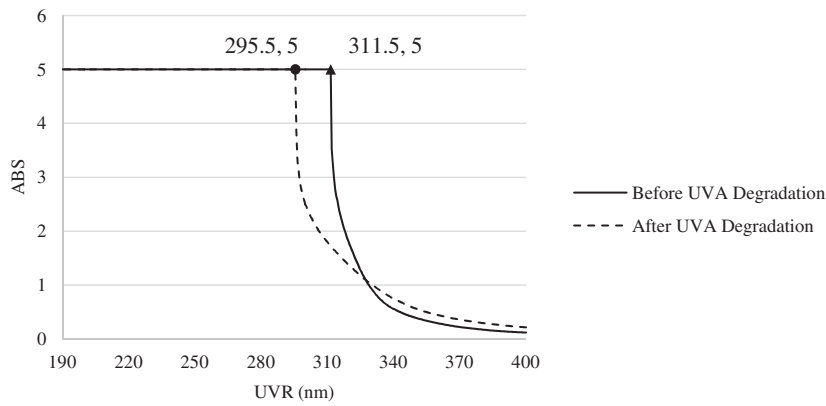


Fig. 3. The UV absorbability of neat EPSMP before and after UVA degradation.

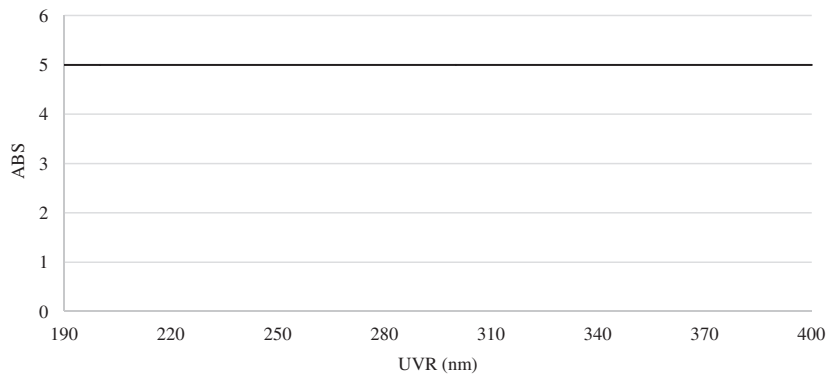


Fig. 4. The UV absorbabilities of 2, 4, 5, 7 wt.% ZnO/SSMPs and 2, 4, 5, 7 wt.% ZnO/EPSMPs before and after UVA degradation.

to UVR. It has been proven that it forms crosslinks and releases a gas under UV degradation with a temperature a little below its T_g . As a result, the degraded amorphous thermoplastic becomes a thermoset plastic. On the contrary, thermoset plastic has crosslinks between polymer chains and high density, therefore, more energy is needed to break the bonds, so it is more resistant to UVR.

The intensity energy of UVA lies between 4.903×10^{-19} J and 6.251×10^{-19} J. The rate of degradation on polymers varies with the thermal energy they are exposed to, it can be calculated by Arrhenius Equation in Eq. (3),

$$\text{Rate} = Ae^{-E/RT} \quad (3)$$

where A is the collision factor, E is the energy required to make the reaction occur, R is the gas constant and T is the temperature in Kelvin the polymer is exposed [21].

3.4. Yellowing of neat SMPs and ZnO/SMPs by UVA degradation

Before UVA degradation (Fig. 5), neat SSMP was opaque white and neat EPSMP was transparent white. All ZnO/SSMPs and ZnO/EPSMPs were opaque in nearly the same degree of white because white nano-ZnO particles were added. After accelerated UVA ageing (Fig. 6), all samples were yellowish with different degrees. The neat SSMP and all ZnO/SSMPs were at

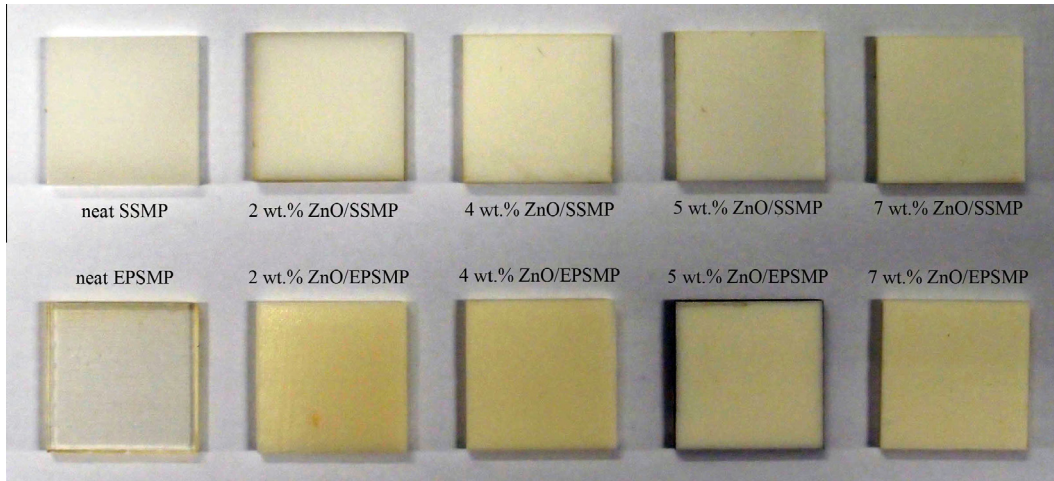


Fig. 5. The neat SSMP, all ZnO/SSMPs, the neat EPSMP and all ZnO/EPSMPs before UVA degradation.

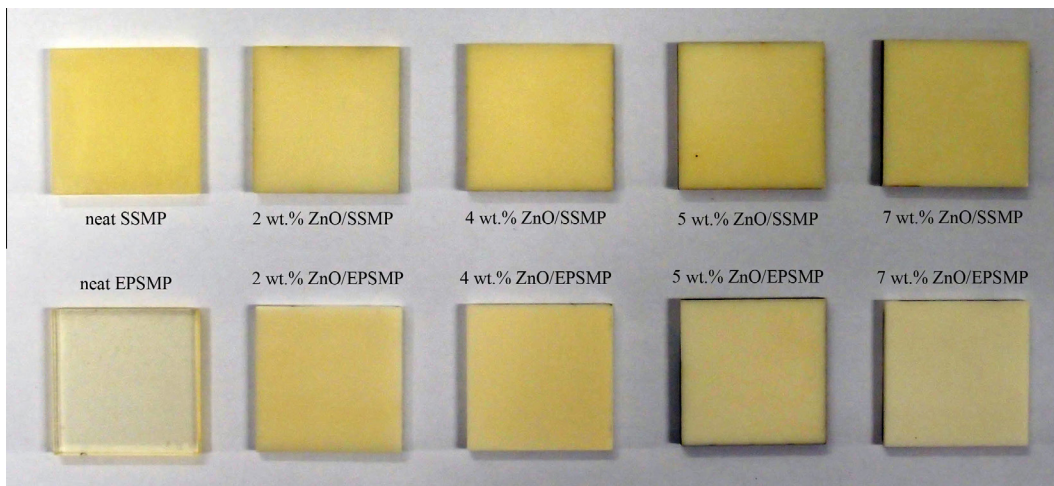


Fig. 6. The neat SSMP, all ZnO/SSMPs, the neat EPSMP and all ZnO/EPSMPs after UVA degradation.

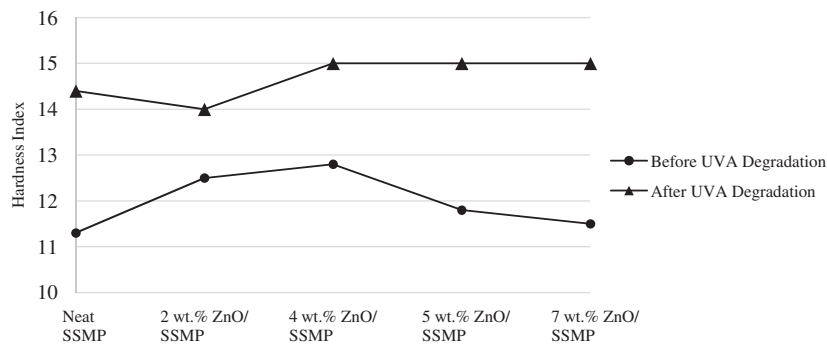


Fig. 7. Hardness of neat SSMP and all ZnO/SSMPs before and after UVA degradation.

nearly the same degree and rate of yellowing and they were much yellower than the neat E-SMP and all ZnO/E-SMPs. The neat EPSMP was transparent in yellow. And it is worth to notice that ESMPs with larger amount of nano-ZnO particles resulted in lower degree and rate of yellowing which this result could not be found in SSMPs.

These phenomena implied that the bonds between polymer chains in SSMP were weaker and more susceptible to UVA than

that in EPSMP. Also, nano-ZnO particles were more compatible in EPSMP than in SSMP in terms of UVR absorptivity.

3.5. Surface hardness tests of neat SMPs and ZnO/SMPs

Two kinds of SMPs, SSMP and EPSMP in their pure form and with 2, 4, 5 and 7 wt.% ZnO were tested for the surface hardness before and after the UVA degradation and their results were shown

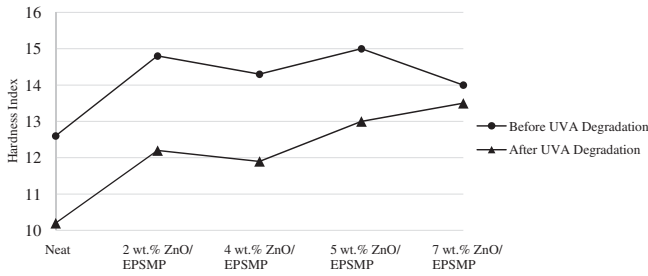


Fig. 8. Hardness of neat EPSMP and all ZnO/EPSMPs before and after UVA degradation.

in Figs. 7 and 8. Before the UVA degradation test, the surface hardness of S-SMPs with 5 and 7 wt.% of nano-ZnO particles had a tendency of decreasing. This might be resulted from the shrinkage of the SSMPs during the curing process that caused the agglomeration of nano-ZnO particles to occur although they were evenly dispersed inside the SSMPs. After accelerated UVA ageing, the surface hardness of all SSMP samples were hardened while that of all EPSMP samples were softened. These implied all SSMP samples behaved more alike amorphous thermoplastics which they formed crosslinks and became a thermoset plastic while all EPSMP samples behaved alike thermoset plastics which their crosslinks were

broken and became more flexible and tough but less strong and stiff after UVA degradation.

It could be concluded that 2 and 4 wt.% of nano-ZnO particles in SSMPs and 5 and 7 wt.% of nano-ZnO particles in EPSMPs could maintain their surface hardness at a moderate level after UVA degradation.

3.6. Dynamic mechanical analysis (DMA)

A good shape memory material depends on a large and sharp drop in the storage modulus around its T_g. From Figs. 9 and 10, the rate of drop of neat SMPs and ZnO/SMPs at their T_g were similar. The most significant deviation appear on UVA-degraded neat SSMP and UVA-degraded 4 wt.% ZnO/EPSMP. Their rate of drop keep similar to other SMP samples but the response in drop is delayed to a higher temperature. The storage modulus is accounted for the hardness of the polymer. The harder the polymer, the larger the storage modulus. It is noted that SSMP would become hardened while EPSMP would become softened of their UVA-degraded surface. From the DMA result, it proved that the storage modulus of UVA-degraded neat SSMP was dominated by the hardened UVA-degraded surface and that of UVA-degraded 4 wt.% ZnO/EPSMP was dominated by the 4 wt.% nano-ZnO particles. The softened UVA-degraded surface of EPSMP was suppressed its effect on storage modulus by the reinforced particles.

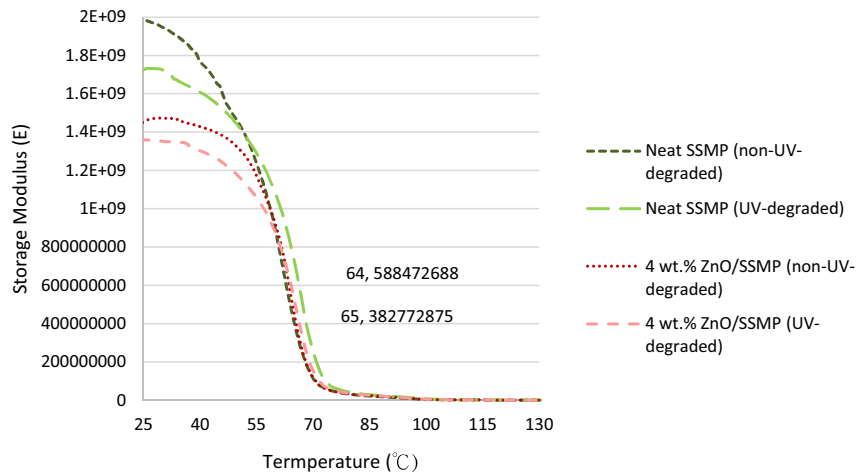


Fig. 9. Storage modulus of neat SSMPs and 4 wt.% SSMPs before and after UVA degradation.

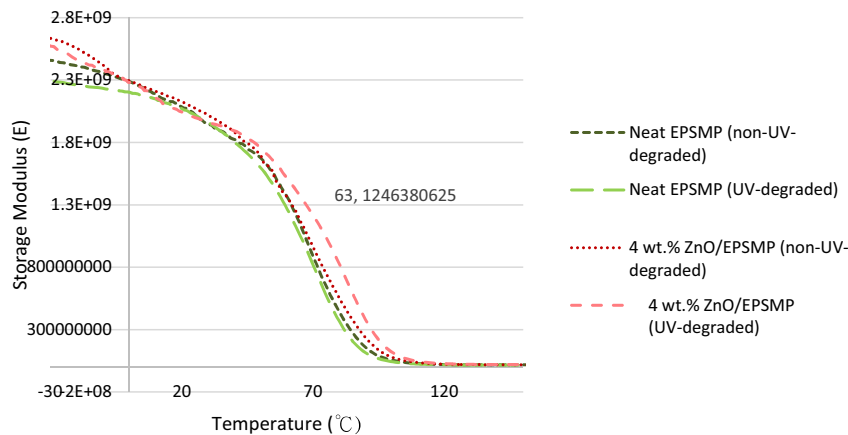


Fig. 10. Storage modulus of neat EPSMPs and 4 wt.% EPSMPs before and after UVA degradation.

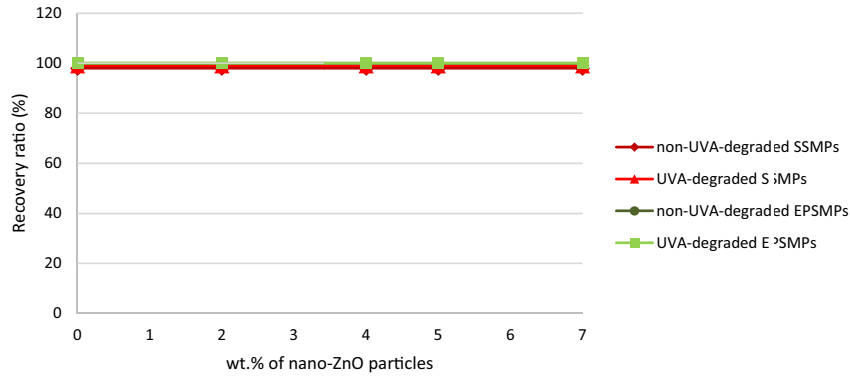


Fig. 11. Shape recovery ratio of different SMPs before and after UVA degradation.

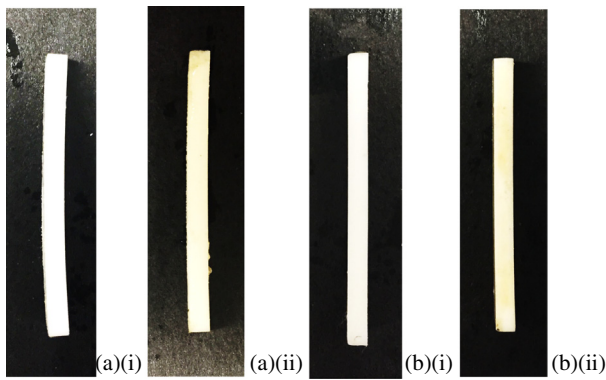


Fig. 12. Shape recovery for non-UVA-degraded (i) and UVA-degraded (ii) 4 wt.% ZnO/SSMP (a) and 4 wt.% ZnO/EPSMP (b).

The deviation of temperature at the same storage modulus for the UVA-degraded neat SSMP was +5.2 °C (5.9%) and for the UVA-degraded 4 wt.% ZnO/EPSMP was +4.3 °C (4.3%) from their non-UVA-degraded samples. It could also be concluded that nano-ZnO particles, at the amount enough for obtaining a full UVR absorption, would not significantly affect the dynamic mechanical property of SMPs but UVA degradation would have more effects on the property.

It is assumed that by implementing appropriate amount of ZnO particles into SMPs for the UVA absorption, the drop of storage modulus could be maintained at the nearest temperature to their non-UVA degraded samples after UVA degradation.

3.7. Shape memory effects (SMEs)

3.7.1. Shape recovery ratio

Fig. 11 shows the shape recovery ratio of all neat SMPs and all ZnO/SMPs. Fig. 12 shows the final shape after recovery for non-UVA degraded and UVA-degraded 4 wt.% ZnO/SSMP and 4 wt.% ZnO/EPSMP. UVA-degraded SSMPs had slightly higher recovery ratio than non-UVA-degraded SMPs. Non-UVA-degraded and UVA-degraded EPSMPs had full recovery ratio. Under the same circumstance, SSMP was more sensitive to UVA degradation. Nano-ZnO particles, at the amount enough for obtaining a full UVR absorption, would not alter the recovery ratio but UVA degradation would have effect on the property. The shape recovery ratio depended mostly on the base shape memory polymer, its cross linking agent content of SSMP or linear monomer content of EPSMP.

3.7.2. Recovery reaction time and full recovery time

Besides counting the full recovery time, reaction time for starting the recovery is also an important factor to be considered. From Figs. 13 and 14, EPSMPs showed having the faster recovery reaction time and full recovery time than SSMPs. This could be explained by the linking network structure of polymer molecular chains of base shape memory matrix. SSMP and EPSMP have two-phases (soft and hard) or a cross-linked structure to exhibit the SME. EPSMP has long linear monomer chain of C–O bonds and two epoxy groups at the chain ends which crosslink points are far more linked together with higher flexible segment mobility.

For non-UVA-degraded and UVA-degraded SSMPs and EPSMPs, the larger the content of nano-ZnO particles, the higher the hardness of SMPs, the faster their recovery reaction time. Hard segment of SMP dominated the recovery reaction time.

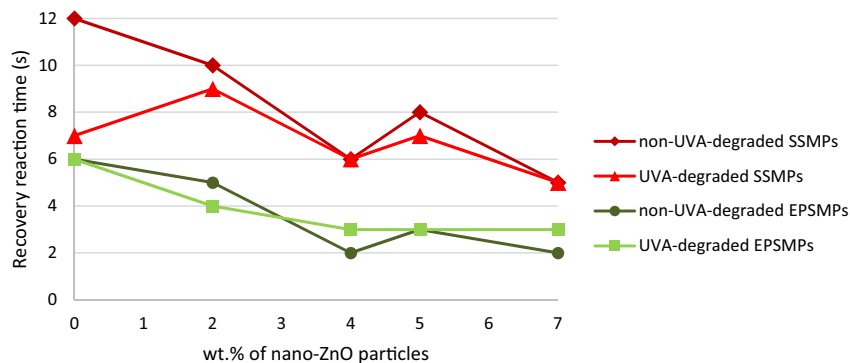


Fig. 13. Recovery reaction time of different SMPs before and after UVA degradation.

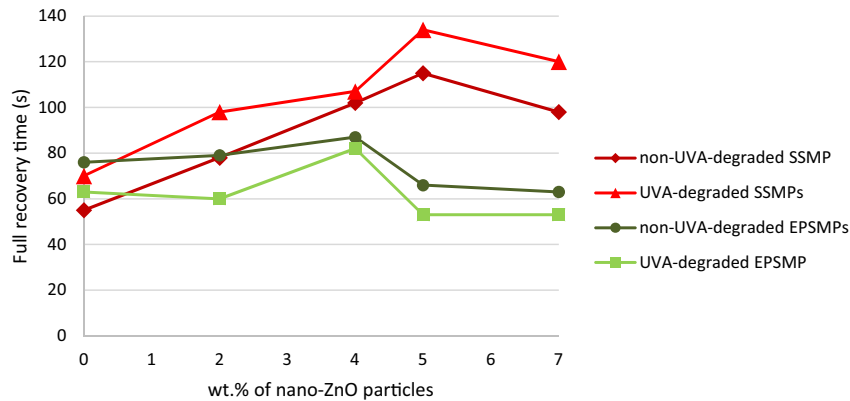


Fig. 14. Full recovery time of different SMPs before and after UVA degradation.

For non-UVA-degraded and UVA-degraded EPSMPs, the larger the content of nano-ZnO particles, the faster their full recovery time but it was contrary to that of SSMPs and at 7 wt.% of nano-ZnO particles, SSMP showed a reduced full recovery time. Although implementing nano-ZnO particles would increase the hardness of SMPs, it did not show significant changes as the same as the results in recovery reaction time. The soft segment of SMP dominated the full recovery reaction time.

It is more preferable for the SMP having the less variation of recovery reaction time before and after UVA degradation. In general, 4 wt.% ZnO/SSMP and 5 wt.% ZnO/EPSMP had less variation and time for recovery reaction and full recovery before and after UVA degradation. And the hardened and softened UVA-degraded surface of SSMPs and EPSMPs respectively agreed with the conclusion stated: the hard segment of SMP dominated the recovery reaction time and the soft segment of SMP dominated the full recovery reaction time.

4. Conclusions

Different weight percentages of nano-ZnO particles were introduced into styrene-based (SSMP) and epoxy-based (EPSMP) shape memory polymers respectively. Their decolouration, UVR absorbabilities, surface hardness, dynamic mechanical properties and shape memory effects under UVA degradation test were then investigated. They were under accelerated UVA ageing at intensity 11 times higher and a temperature 3 times higher than that of the ambient environment. It is equivalent to a situation that the samples were exposed to 22 days under the Sunlight in terms of UVA intensity. The purpose of adding nano-ZnO particles into a polymer was to absorb UVR between 290 and 400 nm (whole range of UVA and UVB) to protect the polymer from full UV degradation.

The UVR absorption tests showed that 2 wt.% of nano-ZnO particles was enough to absorb the whole range of UVR (190–400 nm) for SSMP and EPSMP samples. Besides nano-ZnO particles, shape memory matrix which is in polymer base would also absorb part of the UVR and this showed in the yellowish of all neat SMP and ZnO/SMP samples after UVA degradation test.

All SSMP samples had nearly the same degree of yellowing, but they were much yellower than EPSMP samples. EPSMP samples with large amount of nano-ZnO particles could achieve lower degree and rate of yellowing. This implied that nano-ZnO particles could effectively resist the UVA degradation for EPSMP samples as compared with SSMP samples.

Apart from examining the functionality of nano-ZnO particles in SMPs, it is worth to mention that neat SSMP and neat EPSMP had different behaviours under UVA degradation. Surface hardness tests showed that the neat SSMP was harder while neat EPSMP

was relatively softer after UVA degradation. This could be explained that SSMP had more like amorphous thermoplastic in which crosslinks were formed between the polymer chains inside it and became thermoset plastic after the degradation test. EPSMP was like a typical thermoset plastic in which the crosslinks between the polymer chains inside EPSMP were broken by the incident UVA energy and become more flexible and tough but less strong and stiff after UVA degradation.

From the surface hardness test, 2 and 4 wt.% ZnO/SSMPs and 5 and 7 wt.% ZnO/EPSMPs could maintain their surface hardness at a moderate level after UVA degradation.

For the shape memory behaviour, 4 wt.% ZnO/SSMP and 5 wt.% ZnO/EPSMP would be the good candidate to achieve fast recovery reaction time and full recovery time while minimising the effects of UVA degradation on the shape memory effects of SMPs.

Nano-ZnO particles at the tested weight percentages had no significant variation to the dynamic mechanical properties and recovery ratio of SSMP and EPSMP, but UVR had considerable effects to that of SMPs. It is believed that by controlling the content of nano-ZnO particles and the linking network structure of polymer molecular chains inside SMP, its UVR absorbability, surface hardness, dynamic mechanical properties and shape memory effects could be enhanced in an acceptable performance to against the UV degradation.

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