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High speed 4D printing of shape memory polymers with nanosilica

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KEYWORDS

Additive manufacturing; 3D printing; 4D printing; shape memory polymer; nanocomposites

ABSTRACT

This work presents a novel development to accelerate the printing speed of photopolymerization-based process by improving resin curability with nanosilica fillers. The nanosilica particles are revealed as “superior catalysts” that altered the light scattering characteristics of the resin. By taking advantage of the large number of compact nucleation sites on their surfaces, the nanosilica facilitated remarkably fast curing rates by greatly reducing the curing time for each layer of printing from 4 s to 0.7 s. The addition of nanosilica into shape memory polymers (SMPs) resins has also invoked new development of SMP composites as reinforced 4D printing materials. The particle-polymer interaction was carefully tuned to control the plasticizing effect of nanosilica domains in the polymer chains. The printed composites exhibited improvement in mechanical properties by an order of magnitude and greater elongation of 85.2% as compared to their neat SMPs. The multifunctional crosslink nature of the nanosilica also maintained the shape recovery ratio within a high range of 87 – 90%. This work achieves fresh mechanistic insights in the critical role and influences of nanosilica in developing high speed 3D printing technology and opens up newly-developed high-performance material.

1 INTRODUCTION

Additive manufacturing (AM), also known as 3D printing, has started to evolve into a next-generation manufacturing technology because of its promising capabilities and liberty in fabrication of complex structures and geometries in a cost-efficient way [1-3]. However, most 3D printing technologies operate at under 10 mm/hour, and have a maximum deposition rate of under 50 cm³/hr [4]. There is a concern that these machines do not provide good return on investment (ROI) because of the fabrication speed. The speed-limiting process for photopolymerization printing systems is resin curing. Most commercially available machines print at speeds between 1.3 mm/hr (Polyjet) and 30 mm/hr (digital light processing (DLP)), where a macroscopic object several centimetres in height can take hours to construct. As compared to traditional manufacturing, current 3D printing technologies suffer from slow printing speed and when printing is accelerated, part quality tends to be compromised. Multi-material inkjet parts, also known as 4D printing parts, printed by Polyjet technology have demonstrated spontaneous and precisely controlled shape recovery abilities [5]. Nevertheless, the high strength polymers often exhibit low elongation at break [6]. The active motion of these 4D printed parts were restrained to only 30% of the linear stretch [7] and thermo-mechanical durability was identified as one of the limitations [8]. This drawback has largely restricted the applications of 4D printing to perform as engineering materials.

Several innovations on speeding up 3D printing process relied on continuous printing technologies which eliminate the time-wasting platform–lifting–reposition process [9], but the printing time can essentially be further reduced by acquiring higher polymerization speed. Here, we demonstrate a novel development to accelerate the printing speed of photopolymerization-based process by improving resin curability with nanosilica fillers. 3D printing of nanocomposites is becoming an increasingly explored commercial opportunity for functional enhancements to assist more industrial uptake. Meanwhile, the addition of fillers is still challenging for photopolymerization-based 3D printing technologies such as stereolithography (SLA) or digital light projection (DLP) processes due to the incurrence of high viscosity and serious light shielding/scattering [10-12]. Enhancing the dispersion of the nanofillers is undoubtedly the most fundamental issue for developing any composites, but it is also essential to consider the nature of the fillers especially in photopolymer resins that cure under ultra-violet (UV) exposure. The genesis involves a selection of filler material and preparation of well-dispersed nanofiller in photopolymer resin with good flowability and curing characteristics.

Here, we further explored on our successfully developed tBA-co-DEGDA 4D-printable shape memory polymer (SMP) [8, 13] by incorporating nanosilica (SiO₂) particles for DLP printing. SiO₂ particles have very high specific surface area and are widely used in polymer industry and surface coating. However, to the extent of our knowledge, there is still no available SiO₂-SMP resins for photopolymerization-based printing technologies. One possible reason is the poor dispersion of most nanosilica particles in photopolymers. Owing to the poor compatibility between the organic polymer matrix and inorganic fillers, inhomogeneous composites may result due to aggregation of the nanosilica particles [14]. Nanosilica particles are attractive fillers that have chemical interaction with the SMP chains, allowing the SiO₂-SMPs to exhibit excellent mechanical strength, high strain and good shape memory properties. A systematic parameter study is carried out in which the particle-polymer interaction is carefully tuned, opening the door for a mechanistic

understanding of related phenomena. This would have significant practical value since it is plausible to adopt this approach to synthesize fast curing polymers to increase printing speed for both 3D and 4D printing processes.

2 EXPERIMENTAL SECTION

2.1 Materials preparation

The present work is a continuation of our earlier studies [8] using Di(ethylene glycol) diacrylate (DEGDA, Sigma Aldrich) crosslinking agent, *tert*-Butyl acrylate (tBA, Sigma Aldrich) monomer and Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO, Sigma Aldrich) UV photoinitiator. All chemicals were used without any further purification. To enhance the interface interaction between the nanosilica particles and SMP resins, nanosilica suspensions in acrylate monomer was employed to covalently bind the nanofillers with the acrylate based photopolymer. Versatile dispersion of colloidal silica in acrylate monomers (NANOCRYL A 223) was purchased from Evonik Industries. The silica phase consists of surface-modified, synthetic SiO₂ spheres of 20 nm size with a high SiO₂ content of 50 wt%. As for the content of nanosilica particles in the SMP resin, the amounts are indicated according to the weight percentage of 1, 2.5, 5, 10 and 15 with respect to tBA, DEGDA and photoinitiators. Nanosilica suspensions was mixed thoroughly into the photopolymer resin by magnetic stirring for 30 mins and followed by using a planetary centrifugal vacuum mixer (Thinky Mixer, USA) for another 15 minutes. Ultrasonication (S&M Vibracell 500W 20kHz Ultrasonic Processor) at 40% amplitude was applied for 30 minutes with 5 seconds pulse interval to further disperse the nanosilica particles in the photopolymer. The prepared SiO₂-SMP photopolymer was transferred into the vat of a bottom-up DLP printer (ASIGA PICO2, USA) with a fixed wavelength of 405 nm and intensity of 20 mW/cm². Printing was carried out by exposing UV light through a DLP projection to cure an entire cross-sectional area at a time with layer thickness of 50 µm. The process was repeated until the part is completed.

2.2 Curing depth test

To get insights into the effects of nanosilica particles on the photo-polymerization process, the curing depth studies of the SMP resins with and without nanosilica particles were carried out. The studies were done to optimize both the resin compositions and printing parameters. A 0.5 mL amount of prepared resins was pipetted onto the quartz slide and placed above the projector lens where the projector has a light intensity of 20 mW/cm². Rows of square array (5 x 5 mm) were projected for a specific time ranging from 0.5 to 50 seconds (Figure 1). The exposed square array formed thin square layers on the quartz slide, while the remaining uncured resin was washed away with *Iso*-propanol (IPA). The curing depths thus correspond to the thickness of the thin square layers and were measured using a stylus profilometer (Taylor Hobson Talysurf Series 2, UK). By plotting the curing depths of each composition against the exposure time, we can analyse the curing characteristics of the nanosilica on the resins.

Figure 1. Curing depth test illustrating cured resin array from 0.5 to 10 s.

2.3 Characterizations

2.3.1 Fourier transform infrared spectroscopy (FTIR). The chemical interaction of the nanosilica with the SMP is analysed using FTIR Analysis (Thermo Scientific™ Nicolet™ iSTM10 FT-IR) which is accomplished through the Attenuated Total Reflectance (ATR) mode. By interpreting the infrared absorption spectrum, chemical bonds can be identified. FTIR is also used to examine the difference in the network structure during synthesis of an SMP. The ATR-FTIR spectra were taken over 4000 to 500 cm^{-1} range at a resolution of 4 cm^{-1} .

2.3.2 Dynamic mechanical thermal analysis. Viscoelastic properties and glass transition temperatures (T_g) of the printed samples were determined using dynamic mechanical analysis (TA Instruments DMA Q800, USA). Samples were printed as rectangular bars (30 x 10 x 1.50 mm) and placed onto the DMA single cantilever clamping fixture under a dynamic frequency of 1 Hz, an amplitude of 15 μm and heated from 25°C to 150°C at a heating rate of 3°C/min. The T_g can be evaluated as a maximum of the loss factor $\tan \delta$.

2.3.3 Electron microscopy. Ultra-thin samples of cured SiO_2 -SMP were characterized by transmission electron microscopy (TEM; JEOL 2010 UHR, Japan) to determine if there are presence of agglomeration. EDAX energy dispersive X-ray spectroscope (EDX) was also performed to determine the chemical compositions.

2.3.4 Tensile mechanical testing. The tensile tests were conducted in accordance with the standard test method for micro-tensile based on ISO 527-1:1996 standards using tensile machine (Instron 5548 Micro Tester, USA) at a strain rate of 1 mm/min. Mechanical properties were analyzed at room temperature as well as at elevated temperatures (temperatures above T_g).

2.3.5 Thermomechanical Analysis. Thermomechanical cycle experiments were performed with dynamic mechanical analysis (TA Instruments DMA Q800, USA) in single cantilever mode to characterize the shape memory behaviour of SiO_2 -SMP printed parts. Prior to deformation, the DMA samples (30 x 10 x 1.50 mm) were heated to above their T_g at a rate of 3°C/min and equilibrated for 5 minutes. In step 1, samples were deformed by applying a moderately increasing static force at a constant rate of 0.1 N/min to a designated strain (ϵ_i). In step 2, the samples were cooled at a rate of 3°C/min to 25°C to fix the deformation. In step 3, the force exerted on the samples was unloaded to a preloaded force of 0.001N at a rate of 0.3 N/min. Upon unloading, part of the strain was instantaneously recovered and the unloading strain (ϵ_u) was recorded. The shape

fixity ratio (R_f) that determines the ability of the SiO₂-SMP to fix the mechanical deformation can be calculated from Equation (1).

$$R_f(\%) = \frac{\varepsilon_u}{\varepsilon_i} \times 100 \quad (1)$$

In the final step, the samples were reheated to above their T_g at a rate of 3°C/min and held isothermal for 10 minutes to recover any residual strain. The final strain (ε_f) was measured and the shape recovery ratio (R_r) that quantifies the ability of the material to memorize its permanent shape and is a measure of how much applied strain is recovered upon reheating can be derived in Equation (2).

$$R_r(\%) = \frac{\varepsilon_i - \varepsilon_f}{\varepsilon_i} \times 100 \quad (2)$$

3 RESULTS AND DISCUSSION

3.1 Enhancement in curing characteristics

In the DLP printing technique, several factors such as light intensity, exposure time, monomer functionality, photoinitiator and photoabsorber concentrations can affect the curing characteristics [15]. The integral effect of all these parameters can be represented by the curing depth, which provides critical information such as the minimum layer thickness and curing time per layer to optimize the printing process. The kinetics of curing depth in photopolymerization system have been studied extensively over the years [16]. In understanding the curing depth dependence on photoinitiator and light absorber concentration, Zissi *et al.* proposed the following equation [17] [Equation (3)].

$$C_d = \frac{1}{\alpha_i c_i + \alpha_a c_a} \ln \left(\frac{t}{t_0} \right) \quad (3)$$

where C_d is the curing depth, α_i is the absorption coefficient of the photoinitiator, c_i is the concentration of photoinitiator, α_a is the absorption coefficient of the photoabsorber, c_a is the concentration of photoabsorber, t is the exposure time and t_0 is the resin threshold time required to start the polymerization. However, due to the absence of photoabsorbers and inclusion of nanosilica particles, the participation of the nanosilica in the photopolymerization process [18] should be considered and thus Equation (3) should be revised into the following Equation 4:

$$C_d = \frac{1}{\alpha_i c_i + \alpha_f c_f} \ln \left(\frac{t}{t_0} \right) \quad (4)$$

where α_f is the absorption coefficient of the nanosilica fillers and c_f is the concentration of nanosilica fillers.

Figure 2 shows the curing depths of the SMP resins of the same photoinitiator concentration, with and without the addition of nanosilica particles. A logarithmic increase in curing depths with an increase in the exposure time can be observed for all compositions and the experimental data are congruent with the theoretical cure model by Beer Lambert's law [19]. However, the curing profiles of the SiO₂-SMP attain higher curing depths at a faster rate in comparison with the neat SMP. The addition of 1 wt% nanosilica particles improves the curing depth significantly in a very short time by forming a cured layer of 54.2 µm in just 0.7 s, while the neat SMP only achieved

12.5 μm after curing for 4 s. The fast polymerization rate of the SiO_2 -SMP could be attributed to the nanosilica particles acting as heterogeneous nucleation sites [20] for polymerization as shown in Figure 3. It has been known that certain fillers such as natural fibers have nucleation ability and provide a large number of compact nucleation sites on their surfaces [21]. Similarly, the surfaces of the nanosilica particles serve as pre-existing surfaces that allow the polymerization path to initiate, hence reducing the free energy barrier required to create a new surface [22]. The presence of nanosilica with high specific surface area provides remarkably more nucleation sites for polymerization, hence acting as “superior catalysts” which greatly shorten the curing time for the SiO_2 -SMP resin.

Figure 2. Curing depth studies of SMP resin with and without nanosilica particles.

Despite the enhancement in curing characteristics with nanosilica particles, it is observed that the initial curing depths are lower for SMPs with higher nanosilica concentration as shown in the side image of Figure 2. The initial curing depths of 1, 2.5, 5 and 10 wt% nanosilica are 54.2 ± 0.2 , 46.1 ± 0.9 , 31.5 ± 0.4 and 23.66 ± 0.4 μm , in which the experimental results are in alignment with predictions of Equation (4). The nanosilica particles are highly transparent due to their small size and low aspect ratio, hence the nanoparticles are expected to have negligible effect on the resin viscosity, but the addition of nanoparticles changes the refractive index of the mixture. With a high concentration of nanosilica in the mixture, there is a large mismatch in the initial refractive index between the SMP ($n = 1.41$) and nanosilica ($n = 1.5$). The larger the difference in the refractive indices of the polymer matrix and the filler particles, the larger the occurrence of light scattering which causes the light intensity through the resin to attenuate exponentially [23]. Meanwhile, the curing depth of nanocomposites is inversely proportional to the square difference of refractive index between the premix and the nanoparticles [24]. Hence, due to the initial refractive index of the monomer mixture being much lesser than that of the nanosilica, there is a domination of light scattering at the initial stage of curing at 0.7 s. This causes a delay in reaching the maximum light

transmission, hence giving a lower curing depth at initial curing for SMPs with increasing amount of nanosilica particles as illustrated in Figure 3.

Figure 3. Schematic diagram of nanosilica particles acting as nucleation sites for initial polymerization.

On the other hand, increasing the exposure time allows the refractive index of the resin to approximate to that of the nanosilica during polymerization. The refractive indices are known to increase when monomers are cured to form polymers [25]. As the difference between the refractive index of the SMP and nanosilica reduces with increasing exposure time, the effect of light scattering diminishes and is expected to be prevailed by the nucleation effect of the nanosilica to cure further into the resin. To effectively improve the curing characteristics of SMPs, lower concentration of nanosilica should be considered due to their strong nucleation ability dominating over the effect of light scattering, hence forming higher curing depth within an extremely short exposure time.

3.2 SiO₂-SMP formation

The FTIR spectra in Figure 4 confirms the presence of tBA-co-DEGDA polymer binding with the nanosilica. The C-O stretching vibrations between 1000 and 1075 cm⁻¹ and C=O vibration at 1732 cm⁻¹ are characteristics of the tBA-co-DEGDA polymer. With an addition of 1 wt% nanosilica, the SiO₂-SMP spectra shows a shift and an increase in the peak intensity of the absorbance band towards 1100 cm⁻¹, which is attributed to the stretching vibration Si-O-C group, a signature that validates the successful bonding between the acrylate polymer group and the silanol groups in nanosilica. Further increment in the nanosilica concentration to 5 wt% shows the formation of a new peak at 1080 cm⁻¹, which belongs to the stretching Si-O-Si group. The presence of the Si-O-Si bond indicates that there is excess nanosilica particles which can no longer form crosslinkages with the acrylate polymer group. This also explains why further increment of nanosilica does not improve but aggravate the shape memory properties as discussed in the next section. Meanwhile, further addition of nanosilica leads to a shift in the peaks which causes the Si-O-Si and Si-O-C peaks to overlap and form wider absorbance bands. The chemical interaction between the polymer group and nanosilica indicates that the nanosilica particles not only act as reinforcing fillers, but also participate as multifunctional cross-links.

Figure 4. FTIR spectra of (a) SMP without addition of SiO₂; (b) SMP with addition of SiO₂ in different concentrations.

3.3 Thermal analysis of SiO₂-SMP

The effects of the nanosilica concentrations on the T_g and the modulus in the rubbery state G' of the SiO₂-SMP printed samples were shown in Figure 5. The T_g in Figure 5a can be evaluated as the maximum of the loss factor $\tan \delta$, where we observed that an addition of 1 wt% nanosilica particles into the neat SMP gradually increases the T_g from 53.96 to 56.23°C. This slight increase is attributed to the restrictions of nanosilica particles on the molecular motions of tBA-co-DEGDA chains. However, the incorporation of higher nanosilica concentrations of 2.5 and 5 wt% reflects a shift of the peaks to the left, indicating a drop in the T_g values to 47.59 and 37.77°C respectively. This phenomenon has been reported by various research groups that the decrease in T_g with increasing particle loadings is due to the plasticizing effect of the nanosilica particles in the acrylate domains [26, 27]. The localized chain mobility has been enhanced from the repulsive particle interactions, hence forming regions of free volume to reduce their T_g s. However, at even higher nanosilica content of 10 and 15 wt%, the T_g values rise again to 44.11 and 62.56°C as the motion of polymer chains becomes heavily inhibited by the nanosilica domains [14]. The high T_g indicates a wide transition from its glassy state at room temperature to rubbery state at above T_g , which limits the ability of a SMP since it gives rise to a slower recovery at heating [28].

Figure 5. (a) Loss factor $\tan \delta$ and (b) storage modulus of SiO₂-SMP printed parts as a function of temperature.

The presence of nanosilica particles also increases the crosslinking of the SMP network as validated by the FTIR spectra. This enhances the chain stiffness which leads to a higher modulus in the rubbery state G' as shown in Figure 5b, where the storage modulus that determines the molecular mobility of the network increases from 641.97 MPa (neat SMP) to 2562 MPa (SMP with 1 wt% nanosilica). These observations also provided implications for the increased T_g . At slightly higher amount of nanosilica particles (2.5 and 5 wt%), the plasticizing effect dominates and the formation of more flexible chains gives rise to a simultaneous effect on the network structure where there is a drop in the modulus (to 715.73 and 293.38 MPa respectively) and decrease in T_g . This is however, true only at a low and medium nanosilica amount as further increment in nanosilica concentrations (10 and 15 wt%) increases the modulus in the rubbery state (to 482.96 and 1135.37 MPa) since the network chains become immobilized by interaction with nanosilica domains, hence indicating structural confinement of the chains from the increased crosslinking. Therefore, optimization of the nanosilica content is thus necessary to avoid having very high T_g with a widening of the glass transition.

3.4 Mechanical properties

The effects of nanosilica particles on the mechanical properties of SiO₂-SMP printed dog-bone samples were examined at below T_g (i.e. at room temperature 25°C) and above T_g to consider the material behaviour at deformation which is closely related to the shape memory properties. Figure 6 shows the comparison of mechanical properties between SMPs with and without nanosilica particles. The overall mechanical properties significantly increased with the addition of nanosilica. The elongations at break and Young's modulus were remarkably improved by the presence of nanosilica, though the improvement in tensile strength was less pronounced.

In Figure 6a, the tensile strength at room temperature decreased as the nanoparticles were introduced into the brittle matrix. However, at elevated temperature, the tensile strength of the SiO₂-SMP in rubbery state were improved 2.4 to 3.6 times the corresponding values of the neat SMPs as the much higher specific surface area of the nanosilica promotes stress transfer from the matrix to nanoparticles [29]. The reinforcement effects of the nanosilica particles on the SiO₂-SMPs also enhances the extensibility of the parts as illustrated in Figure 6c, where elongation at

break for low nanosilica contents (1, 2.5 and 5 wt%) at rubbery state reach 85.2%, 44.7% and 27.7% as compared to the neat SMP that only elongate till a maximum of 18.2%. The incorporation of nanosilica particles brings about higher elongation at break only at low nanosilica content since it is evident that the SiO₂-SMP starts to become brittle when nanosilica concentration are higher considering the corresponding SMPCs with 10 wt% and 15 wt% concentration break at $\approx 10\%$ elongation. Hence, the nanosilica content should be kept low to allow for higher deformability during the shape memory process.

The addition of nanosilica particles consistently increases the stiffness as illustrated in Figure 6b. The Young's modulus of SiO₂-SMPs with increased loading at room temperature were improved from 8 times higher than that of the control sample without nanosilica. At elevated temperature, the Young's modulus only showed improvement when the nanosilica concentration is 2.5 wt% and above. The moduli of the SMP containing nanosilica particles agrees with many models that are used to predict the moduli of such nanocomposites systems [30, 31]. In particular, the Halpin-Tsai model [32] is used to predict the modulus, E , of the SMPC containing nanosilica as a function of the modulus, E_0 , of the SMP without nanosilica addition, and of the modulus of the particles, E_p . The modulus of the SMPC, E , is given by:

$$E = \frac{1 + \zeta \eta V_f}{1 - \eta V_f} E_0 \quad (5)$$

Where ζ is the shape factor, V_f is the volume fraction of particles, and η is given by:

$$\eta = \left(\frac{E_p}{E_0} - 1 \right) / \left(\frac{E_p}{E_0} + \zeta \right) \quad (6)$$

The shape factor $\zeta = 2w/t$ is used, where w/t is the aspect ratio of the particles. Given that the nanosilica particles are spherical which is observed from TEM images discussed in the next section, the aspect ratio is unity, hence $\zeta = 2$. When the nanosilica concentration is very low at 1 wt%, the effect of nanosilica on the Young's modulus of the SiO₂-SMP becomes significantly reduced. Based on the experimental data in Figure 6b, the optimal nanosilica concentration is identified as 2.5 wt% which gives satisfactory enhancement in terms of mechanical properties in the rubbery state.

Figure 6. Comparison of mechanical properties of neat SMP and SiO_2 -SMP printed parts at room temperature and above T_g in terms of (a) tensile strength; (b) Young's modulus; (c) elongation.

3.5 Dispersion of nanosilica particles

The significant reinforcement by nanosilica particles may be attributed to its excellent dispersion. TEM images in **Error! Reference source not found.** indicates that the SiO_2 particles are spherical, reasonably uniform in size, and have an average diameter close to the manufacturer's reported mean value of 20 nm. It is well established that the dispersion state of nanoparticles is a crucial factor in determining the final properties of nanocomposites. Possessing high surface energy, the nanosilica particles tend to form agglomerates or clusters in the polymer matrix,

consequently resulting in property degradations. From Figure 7, aggregated nanosilica was not readily apparent in the TEM images, suggesting its excellent dispersion within the SMP. The EDX and map analysis confirmed the existence of the nanosilica particles and revealed that the percentage of nanosilica in the printed SMP was distributed uniformly at 2.58 wt%. Moreover, the optical transparency is also well maintained to enable high curing characteristics of the SiO₂-SMP due to the small reduction of light transmission by the well-dispersed nanosilica particles.

Figure 7. TEM image showing the distribution of nanosilica particles and spectrum of EDX analysis performed on the printed SMP.

3.6 Shape memory properties

To examine the shape memory performance of the SiO₂-SMP, cyclic thermomechanical tests by varying nanosilica concentrations were performed using DMA in the single cantilever mode. The 3D representation of the thermomechanical cycles is shown in Figure 8a. The results in terms of shape fixity ratio (R_f) and shape recovery ratio (R_r) for SMPs with 0, 1, 2.5 and 5 wt% nanosilica concentration under different applied strains of 10, 20 and 30% are presented in Figure 8b and c. SiO₂-SMP with 10 and 15 wt% nanosilica concentration do not exhibit shape memory properties as the addition of nanosilica has formed high crosslinking within the polymer matrix, making it brittle and unable to withstand high deformation for shape recovery. On the other hand, SMPs with 5 wt% nanosilica were fractured at 20%, while 1 wt % nanosilica and the neat SMP were fractured at 30% applied strain, hence results were eliminated from the chart.

Figure 8. a) 3D representation of thermomechanical cyclic tests; (b) Shape fixity ratio (R_f) and (c) shape recovery ratio (R_r) of SiO_2 -SMP under varying applied strains.

With respects to shape deformation under 10% applied strain, Figure 8b shows that all SiO_2 -SMP exhibit higher shape fixity ratio as compared to the SMP without nanosilica, in particular the SMPs with 2.5 wt% and 5 wt% nanosilica having 100% shape fixity after the strain has been unloaded. Even at larger strain loading of 20%, the SiO_2 -SMPs demonstrated higher shape fixity ($\approx 87\%$) than the corresponding shape fixity of the neat SMP ($\approx 69\%$), while the addition of 2.5 wt% nanosilica concentration demonstrates excellent shape fixity of 94.89% under 30% applied strain. The significant improvement in shape fixity is due to the triple effects of the nanosilica particles as reinforcing fillers, multifunctional crosslinkers and stress relaxation retarder [33]. The nanosilica introduced additional crosslinking networks into the polymer chains which hinders the retraction force of the network to recoil upon removal of the loaded strain, hence allowing the SMP to effectively freezes the deformation and gives higher fixity. However, the effect of multifunctional chemical crosslinks does not increase with further addition of nanosilica concentration of 5 wt% and above. The crosslinking density cannot increase further due to a misbalance between the reactive groups of the polymer and the nanoparticles, whereby this phenomenon has also been justified by the FTIR results. The additional nanoparticles only function as reinforcement which augment rigidity and stiffness. Hence, it is established that the influence

of nanosilica particles as multifunctional crosslinkers is evident at low nanosilica content up to 2.5 wt%.

By contrast, the shape fixity is improved at the expense of the shape recovery as illustrated in Figure 8c which shows a slight decrease in shape recovery ratio to 90 – 97% with increasing concentration of nanosilica particles. This is attributed by a reduction in the retraction force stored during fixation to drive the strain recovery upon release of stress in the rubbery state. Nonetheless, the SiO₂-SMPs with 2.5 wt% nanosilica content still exhibit excellent shape memory performance as compared to the neat SMP when subjected to 10 thermo-mechanical cycles at a 20% applied strain as shown in Figure 9.

Figure 9. Comparison of shape memory cycles in terms of shape fixity (R_f) and shape recovery (R_r) of SMPs with 0 wt% and 2.5 wt% nanosilica content under 20% applied strain.

The presence of nanosilica has proven to give better shape fixity of 87.61% at the initial cycle to that of the SMP without nanosilica which only achieve 68.87% fixity ratio. The fixity improves after several cycles due to relaxation of the entangled amorphous polymer network and enables the SiO₂-SMP to obtain 100% fixity after the 7th cycle, while the neat SMP loses its shape memory properties after the 5th cycle. On the other hand, the shape recovery properties of the SiO₂-SMP (91%) may be lower than that of the neat SMP ($\approx 95.7\%$), but the multifunctional crosslink nature of the nanosilica maintained the shape recovery ratio within a high range of 87 – 90% over 9 thermomechanical cycles. Moreover, the incorporation of nanosilica into the SMP network has significantly doubled the shape memory life cycle of the SiO₂-SMP as compared to the neat SMP.

Figure 10 demonstrates the projection stereolithography fabrication of 2 complex features using the developed SMPCs. The entire fabrication process of a flower (76 mm in height) was completed in 27 mins, which means its printing speed is about 2.8 mm/ min ≈ 168 mm/ hr. The fabrication speed is improved 5.6 times faster than a conventional DLP that fabricates at 30 mm/hr. Figure 11

illustrates the shape recovery process of a SMPC thermally simulated under a hot air gun. The recovery process took a total of 12 s for a complete recovery.

Figure 10 a-b) Printing process of SMPCs on DLP; c-d) Fabrication of complex structures.

Figure 11. Shape recovery process of SMPCs under hot air stimulation.

4 CONCLUSIONS

In this work, we explored on the development of a new SMPC incorporated with nanosilica particles for DLP 3D printing process and evaluated the roles of the nanosilica in influencing the printing process and its SMP properties. Curing depth studies showed that nanosilica particles serve as nucleation sites that promote remarkably fast polymerization rates. The curing time of each layer was greatly reduced to 0.7 s, which effectively shorten the total printing time and overcome the issue of long polymerization with traditional moulding methods. Besides possessing enhanced nucleation activities, the nanosilica particles were also discovered to function as crosslinking agents. The chemical interaction between the nanosilica and the polymer network showed that the nanosilica not only reinforces the polymer matrix, but also forms multifunctional crosslinks that improve the mechanical and shape memory properties of the SiO_2 -SMPs. Tensile tests revealed its high mechanical properties with 2.4 to 3.6 times higher in tensile strength, while elongation at break in rubbery state reaches 85.2% as compared to the 18.2% elongation for neat SMP. Young's modulus of SiO_2 -SMPs with increased loading at room temperature were improved by an order of magnitude higher than that of the control sample without nanosilica. The significant reinforcement in properties is highly attributed to the excellent dispersion of the nanosilica as seen from the minimal aggregation in the microscopy images. To further elucidate the

thermomechanical properties of the SiO₂-SMPs, multiple thermomechanical cycle tests were performed. The SiO₂-SMPs exhibited outstanding shape memory performance with 100% shape fixity, 90 – 97% shape recovery and more importantly, the shape memory life cycle was doubled as compared to the neat SMPs. Because of the high curing characteristics, excellent dispersion, improved mechanical and shape memory properties, this approach appears promising for use in the manufacturing of advanced reinforced composites. The incorporation of nanosilica particles into SMPs for 4D printing serves to provide better understandings on the effects of nanosilica particles in both the development and fabrication of SiO₂-SMP resin for photopolymerization based processes. These breakthroughs in quality and speed will accelerate the widespread adoption of 3D printing, delivering advantages in build speed and control over part and material properties.

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