Optimising Nanoparticle Dispersion Time for Enhanced Thermomechanical Properties in DGEBA-Based Shape Memory Polymer Composites

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Abstract: Shape-memory polymers (SMPs) are smart materials that can change shape upon an external stimulus. This phenomenon is called the shape memory effect (SME), which is caused by entropy change due to rapid molecular motion in the polymer segments. Due to the inherently weak thermomechanical properties, use of SMPs is limited in many engineering applications. Therefore, SMPs are often reinforced with fibres and nanoparticles (NPs). NPs offered greater flexibility due to their superior physical, chemical, electrical, mechanical, and thermal properties. However, the homogeneous distribution of NPs is crucial for composition's stability and enhancement of the base material's properties. Among the different techniques used for dispersing NPs, ultrasonic irradiation has shown excellent emulsifying and crushing performance. The sonication process is essential for mitigating agglomerates; however, prolonged sonication time probably increases epoxy temperature, micro-bubbles, cavitation, breaking apart molecules and finally degrading the epoxy resin performances. This paper provides critical insight of nanoparticle dispersion into diglycidyl ether of bisphenol A epoxies (DGEBA). DGEBA epoxy resin was added to TiO_2 NPs and sonicated for 60 min with 5 min intervals while the temperature of epoxy was maintained below 60^oC by using a water cooling throughout the sonication process. The process parameters such as amplitude, mode, epoxy volume and the weight percentage of NPs were kept constant. After each sonication step, Fourier-transform infrared spectroscopy (FTIR) was performed using Thermo Scientific™ and analysed through OMNIC™ Professional quantitation software. In accordance with FTIR results, until 30 min of the sonication, DGEBA resin was not degraded. In order to confirm the performances and the reinforcing effect of NPs, thermo-mechanical and shape memory properties were compared with the neat specimen. The outcomes of this research have suggested quick guidance to find optimum NP dispersion time for DGEBA resins, which has been hardly studied before.

Keywords: Shape memory polymer, sonication, nanoparticles, DGEB, mechanical properties.

INTRODUCTION

Shape memory polymers (SMPs) immensely attracted scientists interest compared to shape memory alloys and ceramics. The SMPs have superior processability, low cost, and low-density, which are prominent in different engineering disciplines such as biomedical, space exploration, soft robotics, consumer electronics, and the textile industry [1,2]. Further, SMPs enhance versatility by responding to stimuli such as thermal, mechanical, electric, light, magnetic, solvent, moisture, pH, and mostly triggered thermally either directly or indirectly [3-5]. However, weak mechanical properties considerably limit SMPs in loadbearing applications; hence they are strengthened with fibres and additives known as shape memory polymer composites (SMPCs).

Additives to composite improve the mechanical strength, recoverable stress, and functional properties such as thermal conductivity, electrical conductivity and light emission. Nanoparticles (NPs) refer to at least one, and usually, two dimensions down to nanoscale (<100 nm) [6]. NPs have a higher surface area to volume ratio than microparticles; therefore, NPs improve shape memory and mechanical properties over microparticles without sacrificing SME [7]. Carbon nanotubes (CNT), Multi-walled carbon nanotubes (MWCNT), Carbon black, Carbon dot, Graphene, Titanium dioxide (TiO_2), Silicon carbide (SiC), and Iron (II, III) oxide (Fe_3O_4) NPs were mostly investigated by the SMP researchers [3, 8, 9].

Uniformly distributed NPs control shape memory polymer nanocomposites' (SMPNC) functional effectiveness, stability, and mechanical properties. These properties are influenced by processing methods, interfacial adhesion, the extent of interphase, weight percentage, surface treatments, the aspect ratio, compatibility with host polymer and size and the shape of NPs [10, 11]. To ensure homogeneity, high-speed stirring, high shear mixing or melting, solution processing, in-situ polymerisation processing, coagulation spinning and electrospinning dispersion techniques were commonly being used [12]. However, each method has advantages and disadvantages; thus,

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special care must be warranted before selecting a mixing method for NP dispersion. Despite those methods, the authors revealed that the sonication technique is fast responsive and the most prominent way to disperse nanoparticles. The physical Van der Waal forces cause agglomeration. In sonication, NPs must be broken and distributed uniformly within the polymer matrix. Due to the ultrasonic waves, negative and positive pressure cycles act in the liquid. Small cavities filled with vapour form due to the pressure drop below the liquid and vapour pressure. Eventually, cavities grow, and the solution become unstable. Due to the breakdown of cavities, extreme high temperature and pressure zones called hot spots are generated. The hot spots' energy can overdrive physical Van der Waal forces within the NPs and disperse NPs homogeneously without agglomerations. The cavity formation affects several factors such as viscosity, surface tension, and epoxy temperature. On the other hand, a higher temperature in the epoxy resin causes degradation at sonication; thus, special attention is required during the sonication process. In the literature complete sonication specifications were hardly found and therefore this research comprehensively studied and presented the optimum time to disperse TiO_2 NPs in DGEBA epoxy resin. Moreover, the effect of sonication on viscoelastic and thermomechanical properties of SMPNC were examined.

MATERIALS AND METHODS

Materials

Commercially available diglycidyl ether of bisphenol A (DGEBA) organic epoxy, Neopentyl glycol diglycidyl ether (NGDE) aliphatic chain extender and poly(propylene glyol)bis(2-aminopropyl)ether (D-230) di-amine hardener were purchased from Huntsman Australia and Sigma Aldrich Australia. The synthesised mole ratios of DGEBA:NGDE:D-230 are as follows 0.65:0.37:0.20. The TiO_2 NPs were of 99% purity, 20-40 nm diameter with 77.37 m^2/g Brunauer–Emmett–Teller (BET) surface area and ordered from XFNANO China. All materials were used as received.

Methods

DGEBA and NGDE were introduced into 0.4 *wt* % TiO_2 NPs and mixed using an HB502 laboratory mixing device. The solution was degassed in a Labec vacuum oven at 11.15 kPa (~89% vacuum / 111.46 mbar) at room temperature for approximately 15 min to achieve a bubble-free solution. It was then heated to 30°C to reduce viscosity before commencing the sonication process. VS70T sonication horn was attached to the Sonoplues GM2200 ultrasonic generator and sonicated the epoxy with the following settings, frequency 20 kHz±500 Hz, amplitude 100%, pulse mode (5 seconds on and 5 seconds off). During the sonication, the rated ultrasonic power of the instrument was 200 W. At a time, 400 mL was sonicated for 5 min and conducted FTIR analysis; the same steps were repeated until the total time reached 60 min. During the sonication, the epoxy temperature was maintained below 60°C using a water circulation bath. FTIR spectrums were comprehensively analysed through Thermo Scientific™ OMNIC™ Professional software and revealed the optimum time to disperse NPs without epoxy degradation.

After that, a 300×300×2.00 mm^3 SMPNC panel was fabricated using the selected optimum dispersion time. 65°C for 6 hours, followed by 115°C for 1-hour post-curing cycle, has been used. The viscoelastic properties were evaluated with TA instrument Q-800 dynamic mechanical analyser (DMA) under ASTM D7028. The oscillation mode was used in 1 Hz frequency with a temperature ramp of 5°C/min from -20°C to 120°C. The SMPNCs' tensile, compression, flexural, impact properties were evaluated and presented according to the ASTM 638-14, ASTM D6641, ASTM D790, and ASTM D256 at room temperature. Additionally, the shape memory properties were characterised through the fold deploy test method using 100×10 mm^2 specimen at $[dT_g/dT]_{minimum}$ temperature.

RESULTS AND DISCUSSION

The infrared (IR) spectrum can be divided into three major regions and mid-IR (400-4000 cm^{-1}) is considered during most of the analysis. The result revealed that the fingerprint region (600-1500 cm^{-1}) did not see transmittance change during 60 min of sonication. Gonzalez *et al*. presented characteristics 772, 831, 915,1036, 1509, 1608, 2965-5873, 3057 and ~3500 cm^{-1} wavenumbers related to DGEBA epoxy, which represent CH_2, C-O-C oxirane, C−O oxirane, C−O−C ether, C−C aromatic, C=C aromatic, C−H aromatic and aliphatic, C−H oxirane and O−H stretching of DGEBA epoxy [13]. These critical wave numbers transmittance (%) hardly changed even after 60 min of sonication, as illustrated in Figure **2**. However, 2000-2500 cm^{-1} region shows an interesting behaviour and a further enlarged view is shown in Figure **1** *section A-A*.
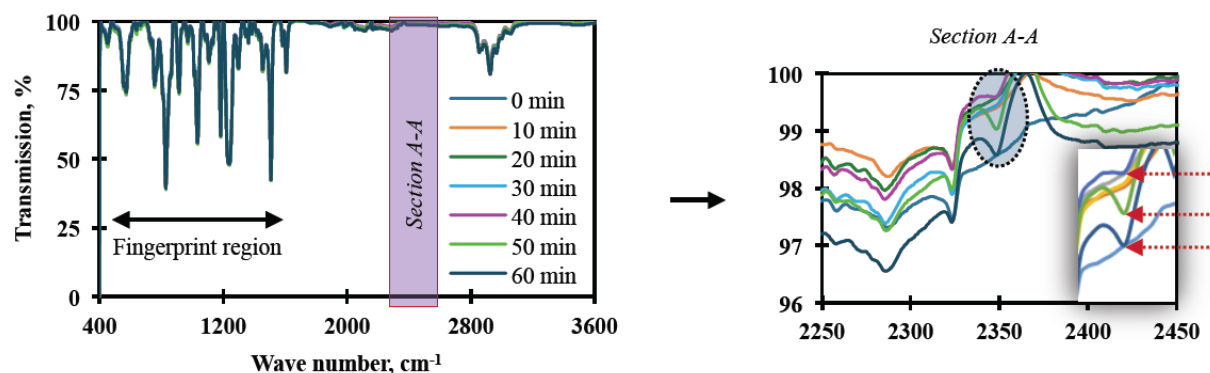
Figure 1: FTIR analysis of DGEBA epoxy with 0.4 *wt* % of TiO$_2$.

At 2350 cm^{-1}, there is a slight drop in transmittance after 40 min of sonication and this could be an initial clue for degradation of the resin due to the ultrasonic dispersion. However, there was no change until sonication time reached 30 min. On the other hand, the delicate SME is driven through net points and switching segments. To date, the effect on SME is not comprehensively studied against the ultrasonic dispersion time; however, it is beyond the scope of this paper. The FTIR spectrum reflects the epoxy resin degradation, and this technique can be used to evaluate optimum dispersion time subjective to other sonication parameters.

Thermomechanical and shape memory properties of neat SMP and SMPNCs are illustrated in Figure **2**.

According to the DMA results, 0.4 *wt* % of TiO$_2$ improved the storage modulus of SMPNC by 36%. However, SMPNC T$_g$ was dropped by 8%, with reference to the neat SMP. The molecular bonds were weakening due to NPs could be a reason for the drop-in T$_g$. Compared to the neat SMP, the tensile strength and strain at failure improved 23% and 19% in SMPNC. It was observed that neat SMP and SMPNCs were plastically deformed before failing under the "LGM" mode and the stress/strain relationship can be fitted to a second-order polynomial function. A significant difference could not be identified in compression properties between neat SMP and SMPNC. However, the flexural strength was improved by 11% in SMPNCs, but both the specimens were not broken during the experiment due to the low stiffness.
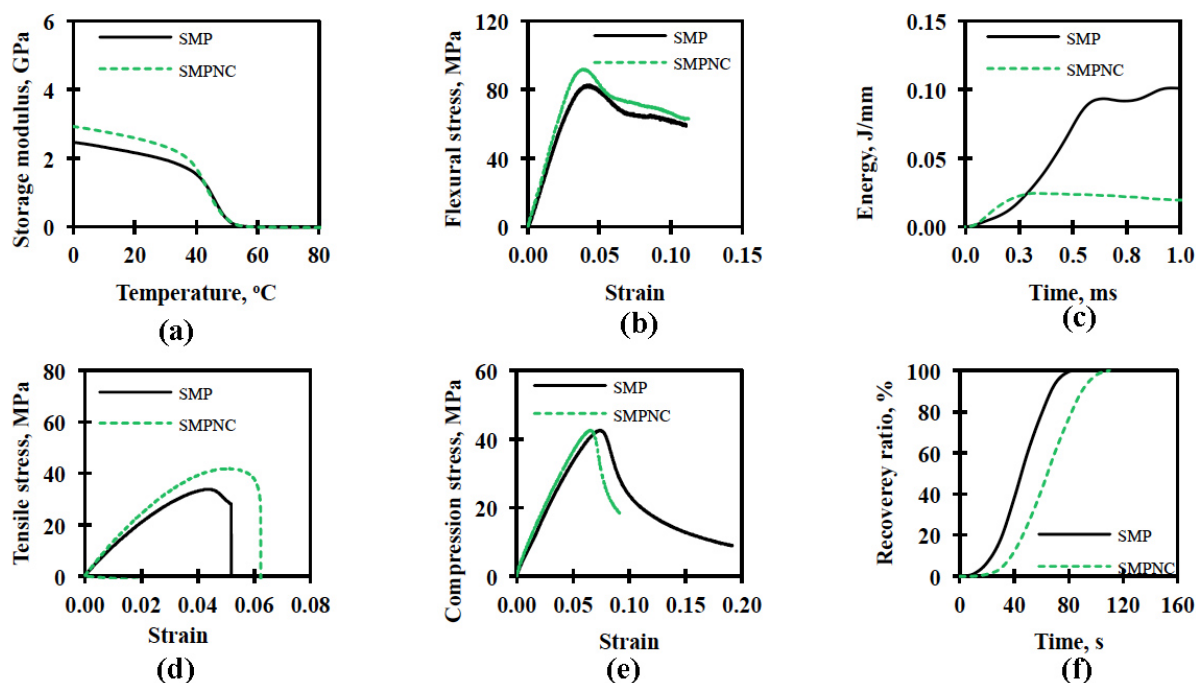

Figure 2: (**a**) DMA, (**b**) Tensile, (**c**) Flexural, (**d**) Compression, (**e**) Impact, and (**f**) Shape memory properties, of neat SMP *vs* SMPNC.

A significant difference was seen in the impact properties of SMPNCs. According to the results, the impact properties of SMPNCs were dropped by 90%. This should be addressed during the designing stage of SMPNC based applications. The neat SMP and SMPNCs were fully recovered at $[dT_g/dT]_{minimum}$ temperature. However, SMP specimen shows a fast response compared to the SMPNC. Except for initial and final recovery, the rest of the region recovered linearly; this could be an exciting property to develop SMPNC based applications.

CONCLUSIONS

NP dispersion is a challenging process, and the number of studies is still limited to conclude completely. From the literature, it was clear that different process parameters, such as amplitude, mode, duration, horn type, volume, viscosity, NP type, size, and weight percentage, affect the quality of SMPNC. In this study, except sonication time, other parameters were kept constant. According to the FTIR analysis, the authors conclude that 30 min of short dispersion avoids DGEBA matrix degradation, making it a suitable process parameter for maintaining the structural integrity and thermomechanical properties of the composite. This method is more convenient since researchers can understand optimum dispersion time without processing solid specimens.

Additionally, thermomechanical and shape memory properties of SMP and SMPNC were compared using proposed (200 W, 20 kHz, pulse mode (5s On, 5s OFF)) dispersion parameters. The DMA results showed a 36% improvement in storage modulus for SMPNCs containing 0.4 *wt* % TiO_2 compared to neat SMP, highlighting the reinforcing effect of the NPs. The tensile strength and strain at failure were improved by 23% and 19%, respectively, while the flexural strength increased by 11%. The impact strength, however, dropped significantly by 90%, which should be considered during the design phase of SMPNC-based applications. Finally, the authors conclude that these revisions are important to select appropriate sonicating parameters without scarifying properties of SMPNC.

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