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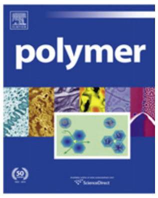

Solvent-Free One-Pot Synthesis of high performance silica/epoxy nanocomposites

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ABSTRACT

High performance silanized silica/epoxy nanocomposites were prepared through mixing epoxy, tetraethyl orthosilicate (TEOS), (3-aminopropyl)trimethoxysilane (APTMS) and ammonia solution at 50 °C. This all-in-one "Solvent-Free One-Pot Synthesis" results in nanocomposites with uniform dispersion of oval shaped silica nanoparticles and strong adhesion between silica and epoxy matrix. The influence of the synthesis conditions, such as molar ratio of NH_3:TEOS, aging time, curing process and silica content on the thermal mechanical properties of nanocomposites were studied. The silanized silica/epoxy nanocomposite prepared in this study exhibits better thermal mechanical property in comparison with neat epoxy, non-functionalized silica/epoxy and commercialized silica/epoxy systems. The prepared nanocomposite with 3 wt% silanized silica exhibits 20%, 17% and 6% improvements on flexural, tensile and storage modulus over those of neat epoxy, respectively.

1. Introduction

Silica/epoxy nanocomposites exhibit improved thermal and mechanical properties over neat epoxy system and have been used as high strength material for aerospace, automobile, electronic and sporting equipment industries [1,2]. However, the homogeneity of dispersed silica nanoparticles in matrix and their adhesion with epoxy resin are two main challenges in preparation of high performance silica/epoxy nanocomposite. Therefore, many approaches have been devised to overcome these issues by improving the blending process and surface functionalization of silica nanoparticles [3–7].

Solution blending process of fumed or sol–gel silica/epoxy in the presence of solvent has been widely applied for the preparation of silica/epoxy nanocomposite due to better dispersion of silica in epoxy resin than that from melt blending process [1,2,8–10]. However, the aggregation of its primary particles is still occurred [11,12]. Further surface functionalization of silica or the modification of epoxy resin by amine-terminated coupling agents are required to improve the dispersion of silica nanoparticles and their adhesion with matrix [13]. As solvent is involved in the process, there is a need for subsequent removing, recycling and disposing of the solvent, which poses environmental, health, safety and cost issues. To obtain nanocomposite with good mechanical and thermal properties, large amount of silica is also required, normally 5–30% by weight of total composite composition [1,2,8]. High percentage of silica significantly increases the viscosity of compositions and renders it difficult to be applied to the designed molds before curing. Moreover, the preparation of silica/epoxy nanocomposite by the solution blending process involves complicated manufacturing process, including synthesis of silica nanoparticles, surface functionalization of silica, high pressure and temperature mixing with epoxy compositions, and solvent evaporation [13]. This limits the silica nanocomposite to only high tech applications, such as the aerospace, automotive and electronics due to its high processing cost. Therefore, there is a need to develop an effective, convenient and low cost process to prepare high performance silica/epoxy nanocomposite that exhibits uniform dispersion of silica with great silica-epoxy adhesion, to target a wide range of applications.

In situ sol–gel process in the presence of solvent has been developed to simplify the preparation process of silica/epoxy nanocomposite by combining the silica nanoparticle synthesis with its dispersion in epoxy matrix [14–16]. However, because of the non surface modification of silica, the problems of silica aggregation and poor adhesion between silica and epoxy cannot be solved by this method, resulting in poor thermal mechanical properties of prepared composite. The use of solvent and high percentage of silica content

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(up to 15 wt% of total composite composition) also causes the same problems as mentioned in the solution blending process.

In the present work, a “Solvent-Free One-Pot Synthesis” process was developed to prepare oval shaped silica/epoxy nanocomposites. The silica formation, surface functionalization and dispersion in epoxy compositions are combined into one step at 25–50 °C with mechanical stirring, where high silica dispersion and strong silica-epoxy adhesion are simultaneously achieved. As solvent was not involved in this method, high shear rate was applied for the mixing of viscous mixture, which benefits to the formation of oval shaped silica (aspect ratio >1) and is also friendly to the environment. The influence of synthesis conditions such as NH_3:TEOS molar ratio, aging time, curing process, silica content on the thermal mechanical properties of nanocomposites were studied and the results were compared with those of neat epoxy system, non-functionalized silica/epoxy and commercial available silica/epoxy.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA, D.E.R.™ 332) was supplied by Dow Chemicals. Diethyltoluenediamine (Ethacure 100-LC) was obtained from Albemarle. Tetraethyl orthosilicate (TEOS, ≥ 99%) and (3-aminopropyl)trimethoxysilane (APTMS, 97%) were purchased from Sigma–Aldrich. Ammonia solution (25 wt%) was supplied by Merck. The commercial available silica/epoxy (Nanopox F400) was supplied by Nanoresins AG.

2.2. Preparation of silanized silica/epoxy nanocomposite

A mixture of epoxy, Ethacure 100-LC, TEOS and APTMS was stirred vigorously at 50 °C. The weight ratio of epoxy: Ethacure 100-LC was fixed at 3.8:1. The amount of TEOS and APTMS was varied to obtain 1–4 wt% silica in total composite composition and 2–15 wt% APTMS to silica amount. An ammonia solution with NH_3:TEOS molar ratio varied from 2:1, 2.3:1 to 2.7:1 was injected into the above solution and aged at various aging time (30, 60 and 120 min). The mixture was degassed under vacuum at 75 °C and poured into a mold coated with releasing agent. The sample was then cured in an air purged oven at 130 °C for 1 h and 160 °C for 2 h. The final curing temperature was varied from 230, 250–270 °C with the curing time of 4 h. For the study on influence of post-curing process to the properties of nanocomposite, the cured samples with final curing temperature of 270 °C were post-cured at 250 and 270 °C for 3 h, respectively.

Silanized silica nanoparticles for XPS analysis was prepared by extracting the particles from uncured silanized silica/epoxy (2 wt% silica, NH_3:TEOS molar ratio of 2.3:1 and aging time of 60 min) using acetone. The silica particles were collected from suspension by centrifugation and dried in a vacuum oven at 50 °C for overnight.

To study the APTMS-epoxy linkage, epoxy resin was mixed with APTMS at molar ratio of 1:1. The mixture was degassed and cured at 130 °C for 1 h, 160 °C for 2 h and 270 °C for 4 h.

2.3. Preparation of comparative samples

The neat epoxy sample was prepared by mixing an epoxy resin with Ethacure 100-LC at weight ratio of 3.8:1. A commercial available silica/epoxy sample (Nanopox F400, 2 wt% silica) was formed by mixing epoxy, Ethacure 100-LC and Nanopox F400 at weight ratio of 3.6:1:0.24. The non-functionalized silica/epoxy (2 wt% silica) was prepared following the process shown in 2.2 without adding APTMS (NH_3:TEOS molar ratio of 2.3:1 and aging time of 60 min). These mixtures were degassed under vacuum at 75 °C before transferred into a mold and cured following the same curing process as that for silanized silica/epoxy nanocomposite with final curing temperature of 270 °C.

2.4. Material characterization

2.4.1. Morphology and chemical composition

The morphology, size and dispersion of silica were investigated using transmission electron microscope (TEM) that was conducted in high resolution mode using a JEOL 2100F instrument and operated at 200 kV. The samples were cut using a Leica Ultracut UCT ultramicrotome and placed on 200 mesh copper grids. The chemical compositions of nanocomposites were analyzed using an energy dispersive X-ray spectroscopy in a transmission electron microscope (EDX-equipped TEM). The chemical state of elements in nanocomposite was determined by X-ray photoelectron spectroscopy (XPS) that was conducted using a VG Escalab 220i instrument with monochromatic Al radiation and spot size of 700 μm. The infrared spectrum was obtained using an attenuated total reflectance (ATR) mode of the FT-IR2000 (Perkin Elmer) Fourier transform infrared (FR-IR) spectrometer.

2.4.2. Viscosity of uncured silica/epoxy compositions

The viscosity of the uncured neat epoxy and silica/epoxy compositions were measured using the Rheostress 600 (Thermo-Haake) at 25 °C.

2.4.3. Thermal mechanical properties

Single-cantilever mode of the dynamic mechanical analyzer (DMA Q800, TA Instruments) was used to measure the dynamic modulus (E′) and glass transition temperature (T_g) of materials by heating the samples from 25 to 250 °C with a ramping rate of 3 °C/min, frequency of 1 Hz and oscillation amplitude of 20 μm. Thermogravimetric analysis (TGA) was performed with a TA instrument Q500 thermogravimetric analyzer. The degradation temperature (T_d) of materials was measured under nitrogen atmosphere by heating the samples to 800 °C at a ramping rate of 5 °C/min. The temperature at the middle of thermal transition of composites was defined as the degradation temperature (T_d).

2.4.4. Mechanical properties

The flexural strength and modulus of nanocomposites were determined by 3-point bending test according to the ASTM Standard D 790-96, with specimens of 55 mm × 13 mm × 2.2 mm. The tests were conducted with crosshead speed of 1 mm/min, at a span length of 40 mm. The tensile tests were carried out according to the ASTM Standard D 638-03 using an Instron 5569 testing machine at tensile speed of 1 mm/min. The specimens were cut into dog-bone shape with dimension of 55 mm × 3 mm × 2.2 mm.

3. Results and discussion

3.1. Morphology and chemical compositions

Nanocomposites with homogeneous dispersion of silica nanoparticles in epoxy matrix were obtained as shown in TEM micrograph (Fig. 1a) by using the “Solvent-Free One-Pot Synthesis”. In contrast to conventional silica nanocomposite in which the silica nanoparticles normally exhibit spherical shape, our in situ preparation method yield oval shaped silica, possible due to a high shear rate of viscous mixture under vigorous stirring. This unique of high aspect ratio silica nanoparticles could provide added benefit to the mechanical properties of the resulting nanocomposite system [3].

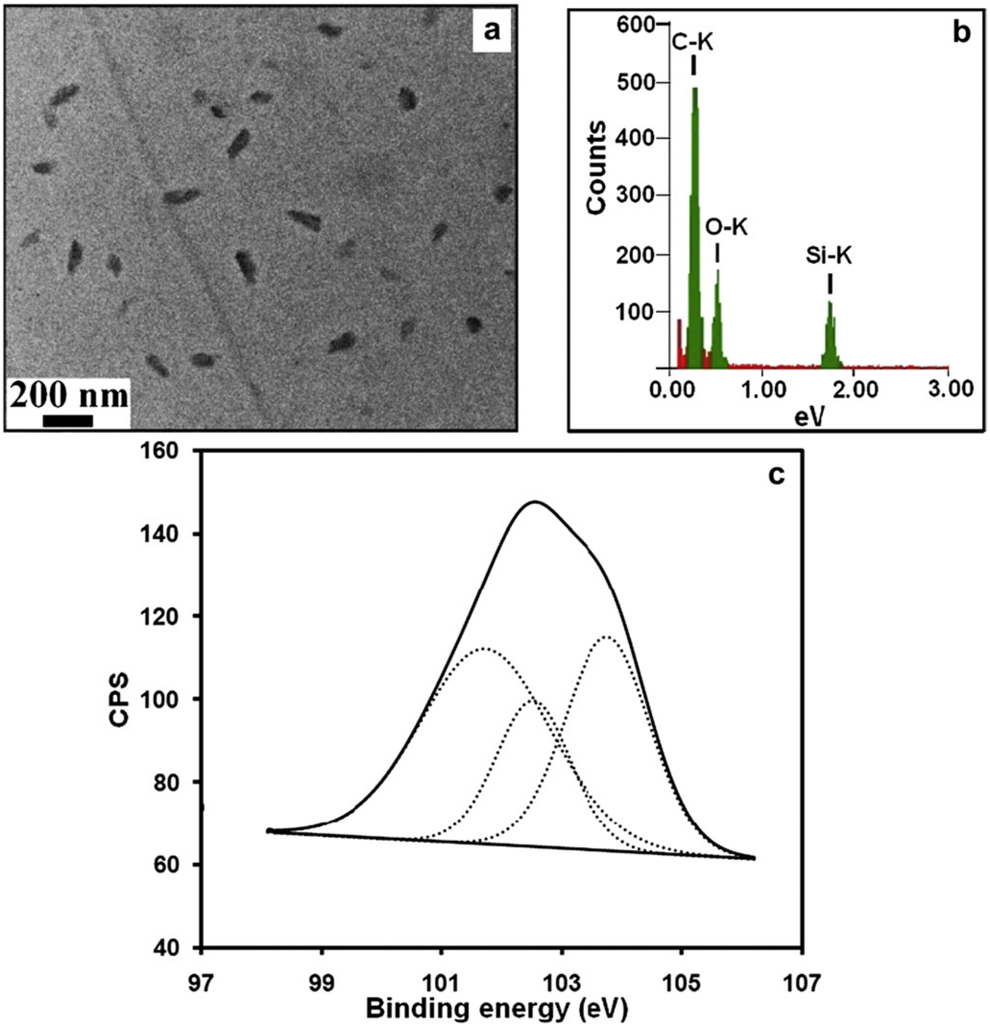


Fig. 1. Homogeneous dispersion of oval shaped silica nanoparticles in epoxy matrix prepared using the "Solvent-Free One-Pot Synthesis" method (a), the chemical composition of silanized silica/epoxy nanocomposite detected by EDX-equipped TEM (b) and the Si2 p curve fit of 2 wt% silanized silica/epoxy (c).

To confirm the chemical structure of these oval shaped particles, a cured sample of 2 wt% silanized silica/epoxy nanocomposite was analyzed by using an energy dispersive X-ray spectroscopy in a transmission electron microscope (EDX-equipped TEM) and X-ray photoelectron spectroscopy (XPS). The Si, C and O peaks were observed from EDX analysis as shown in Fig. 1b. A broad peak of Si2 p corresponding to three Si species was observed from XPS (Fig. 1c). The part at highest binding energy of 103.8 eV represents the silanol groups (Si—OH) on silica surfaces. The Si—O—Si structure of silica particles and Si—alkylamine of functionalized APTMS was found at 102.5 and 101.7 eV respectively.

3.2. Filler-matrix adhesion

In order to elucidate the role of APTMS in formation of nanocomposites and understand how APTMS promotes the interaction between silica particles and epoxy matrix, three model systems, i.e. APTMS-cured epoxy, silanized silica nanoparticles, and silanized silica/epoxy nanocomposite, were prepared and investigated.

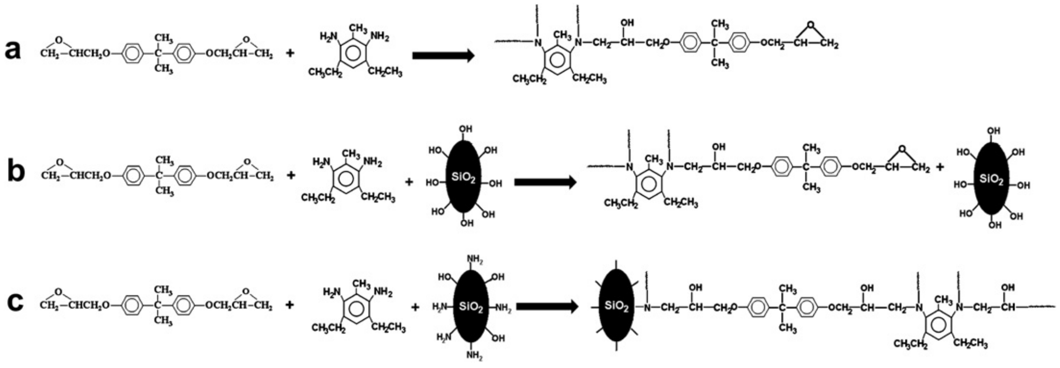
3.2.1. Epoxy-APTMS interaction

In cured epoxy, the amine groups of hardener (Etacure 100-LC) are reacted with epoxy to form a polymer network (reaction a, Scheme 1). To confirm the ability of APTMS to react with epoxy matrix without the condensation to silica particles, the model study using APTMS as a hardener was examined.

As shown in the FT-IR spectra of uncured and cured epoxy/APTMS samples (Fig. 2), the N—H stretching and N—H bending peaks at 3400 and 1560 cm^{-1} represent the amine group of APTMS. Due to the breakage of epoxide groups to form bonds with amine group of APTMS during the curing process, the CH_2 bending peak intensity (1450 cm^{-1}) of a cured sample was decreased compared with an uncured material. At the same time, C—N peak of APTMS at 1090 cm^{-1} was shifted to lower frequency (1050 cm^{-1}) because of the cross-linking reaction.

Two Si and N species were shown from the XPS results of cured epoxy/APTMS sample (Fig. 3a and Fig. 4a). Unlike using the Etacure 100-LC as hardener which obtained single N species (Fig. 4b), the formation of these multi-species may occur through a different cross-linking mechanism that leads to a non-homogeneous polymer network.

Under observation using TEM (image was not shown here), the silica nanoparticles was not found in this sample. Thus, APTMS is unlikely condensed to silica particles but mainly formed bonds with epoxy through C—N linkage. This is understandable since the chance of amine groups in APTMS to react with large amount of epoxy is much higher than that to react with small amount of $H_2N—(CH_2)_3—Si—(OMe)_3$ to form silica.



Scheme 1. Proposed mechanisms for the formation of composite materials.

3.2.2. *APTMS-silica interaction*

Extracted silanized silica nanoparticles from the uncured silica/epoxy sample were analyzed by using XPS to confirm the present of APTMS molecules on silica surfaces. The broad Si2p spectra showed three superimposed Si species at B.E. of 104.3, 102.0 and 100.0 eV, respectively (Fig. 3b). The peak at highest B.E. was identified as a silanol group (Si—OH) on silica surfaces. The Si—O—Si structure of silica particles was shown at 102.0 eV and the Si-alkylamine of APTMS that was functionalized onto the silica surfaces during sol—gel process was shown at 100.0 eV. N atom of these APTMS was confirmed by a single peak of N1s at 399.5 eV and it also demonstrated that the Ethacure 100-LC was completely washed off from the particles before analyzing.

3.2.3. *Epoxy-APTMS-silica interaction*

It was proven by model studies in 3.2.1 and 3.2.2 that the epoxy-APTMS and APTMS-silica linkages can be formed. The formation of strong bond between silica particles and epoxy matrix was studied using a cured silanized silica/epoxy sample with 2 wt% silica content.

Similar to the XPS result of silanized silica nanoparticles, three Si species were detected as shown in Fig. 3c. The Si—OH group on silica surfaces was presented at highest B.E. of 103.8 eV. The Si—O—Si structure of silica was shown at 102.5 eV, while the Si-alkylamine of APTMS-functionalized silica that reacted with epoxy resin through N—C bonds was observed at lowest B.E. of 101.7 eV. Two N1s species were shown in this sample (Fig. 4c), in which a peak at lower B.E. (398.9 eV) represents the N1s of Etacure 100-LC and the one at higher B.E. (400.3 eV) came from APTMS. In Etacure 100-LC, N atoms are connected with a stronger electron donor group (benzene ring) than N atoms of APTMS, therefore, they showed a signal at lower binding energy [17].

The XPS results of non-functionalized silica/epoxy nanocomposite (Figs. 3d and 4d) were compared with silanized silica/epoxy to confirm the role of APTMS in nanocomposite systems. As expected, only two Si species from Si—OH at 103.1 eV and Si—O—Si at 102.1 eV, and one N from C—N linkage between epoxy and Etacure 100-LC at 399.9 eV were observed from the non-functionalized sample.

From these three model studies, it can be concluded that the oval shaped silica nanoparticles were formed by sol—gel process of TEOS, in which APTMS functionalized on silica surfaces also reacts with epoxy matrix to form a strong filler-matrix bonding during curing process at elevate temperature of 130—270 °C (reaction c, Scheme 1).

3.3. *Influences of synthesis conditions on the thermal mechanical properties of silanized silica/epoxy nanocomposites*

3.3.1. *NH_3:TEOS molar ratio*

The influence of ammonia content on the nucleation, growth and dispersion of silica in epoxy matrix was studied by varying the

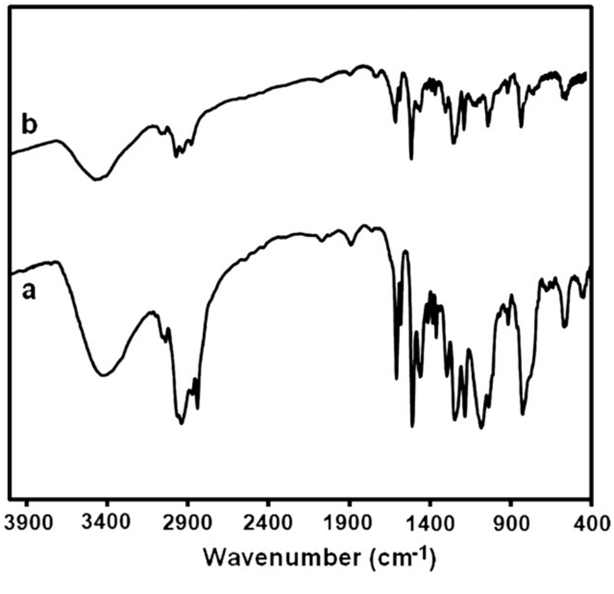


Fig. 2. FT-IR spectra of (a) uncured epoxy/APTMS and (b) cured epoxy/APTMS.

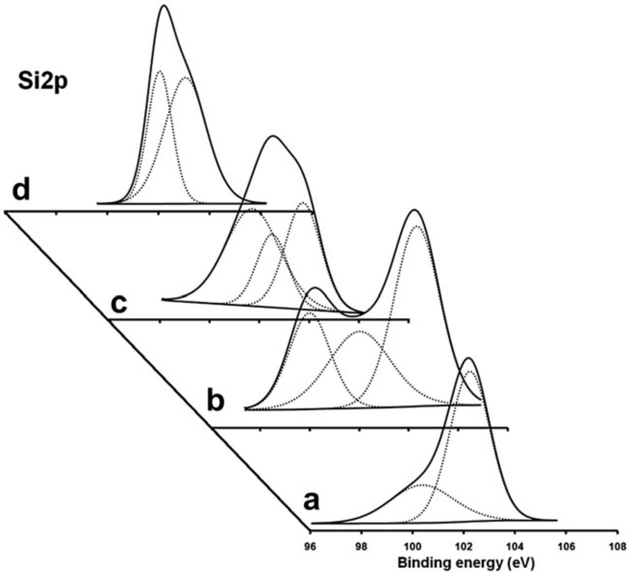


Fig. 3. Si2p curve fit of (a) epoxy/APTMS, (b) silanized silica nanoparticles, (c) 2 wt% silanized silica/epoxy and (d) 2 wt% non-functionalized silica/epoxy.

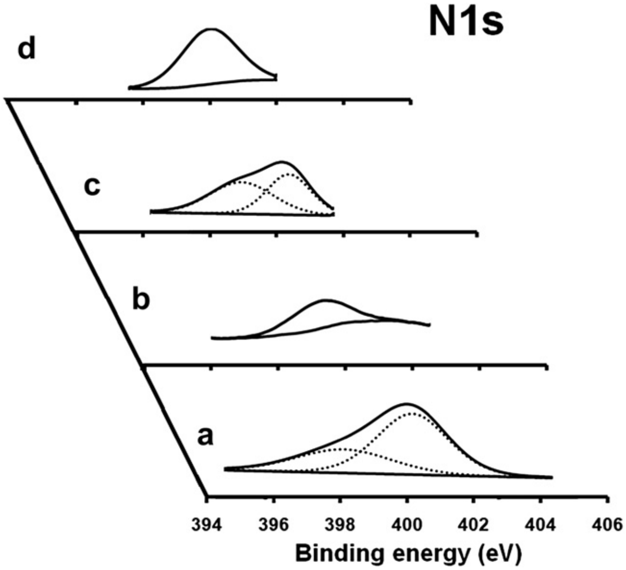


Fig. 4. N1s curve fit of (a) epoxy/APTMS, (b) epoxy/Etacure 100-LC, (c) 2 wt% silanized silica/epoxy and (d) 2 wt% non-functionalized silica/epoxy.

NH_3:TEOS molar ratio from 2:1, 2.3:1 to 2.7:1. The silica content in total composite composition, wt% of APTMS to silica amount, aging time and final curing temperature were fixed at 2 wt%, 10 wt%, 30 min and 230 °C, respectively. A homogeneous dispersion of oval shaped silica in epoxy matrix was observed in all synthesized composites (Fig. 5a–c). The particle size of dispersed silica was increased from 45 nm at molar ratios of 2:1–2.3:1–55 nm at molar ratio of 2.7:1. Similar trend was also observed with silica content. Because NH_3 molecules act as a basic catalyst to promote the hydrolysis and condensation reactions of sol–gel silica, the nucleation and growth of silica particles were accelerated at higher ammonia content. However, the aggregated silica clusters were formed at the highest NH_3:TEOS molar ratio of 2.7:1 (Fig. 5d) because some APTMS molecules were condensed by excess NH_3 and H_2O molecules.

The glass transition temperature (T_g) of nanocomposites prepared at different NH_3:TEOS molar ratios was shown in Fig. 6. A broad peak consisting of two superimposed T_g was found in all composites. The presence of these non-homogeneous nanocomposite networks was due to the incomplete cross-linking reaction and conversion of precursors to silica particles. At large amount of ammonia solution, T_g of composites was shifted to lower temperature because the number of synthesized silica was increased which led to reduction of cross-linking density of epoxy network [3].

The storage, flexural and tensile modulus of materials were enhanced with the molar ratio increasing from 2:1 to 2.3:1 because larger amount of mono-dispersed silica was formed in the epoxy matrix (Table 1). However, the properties became decreased at molar ratio of 2.7:1 due to the aggregation of silica and poor silica-epoxy adhesion. Thus, the NH_3:TEOS molar ratio was fixed as 2.3:1 for further studies.

3.3.2. Aging time

The aging time was varied at 30, 60 and 120 min to optimize a condition for complete silica formation and homogeneous composite network. The molar ratio of NH_3:TEOS, silica content in

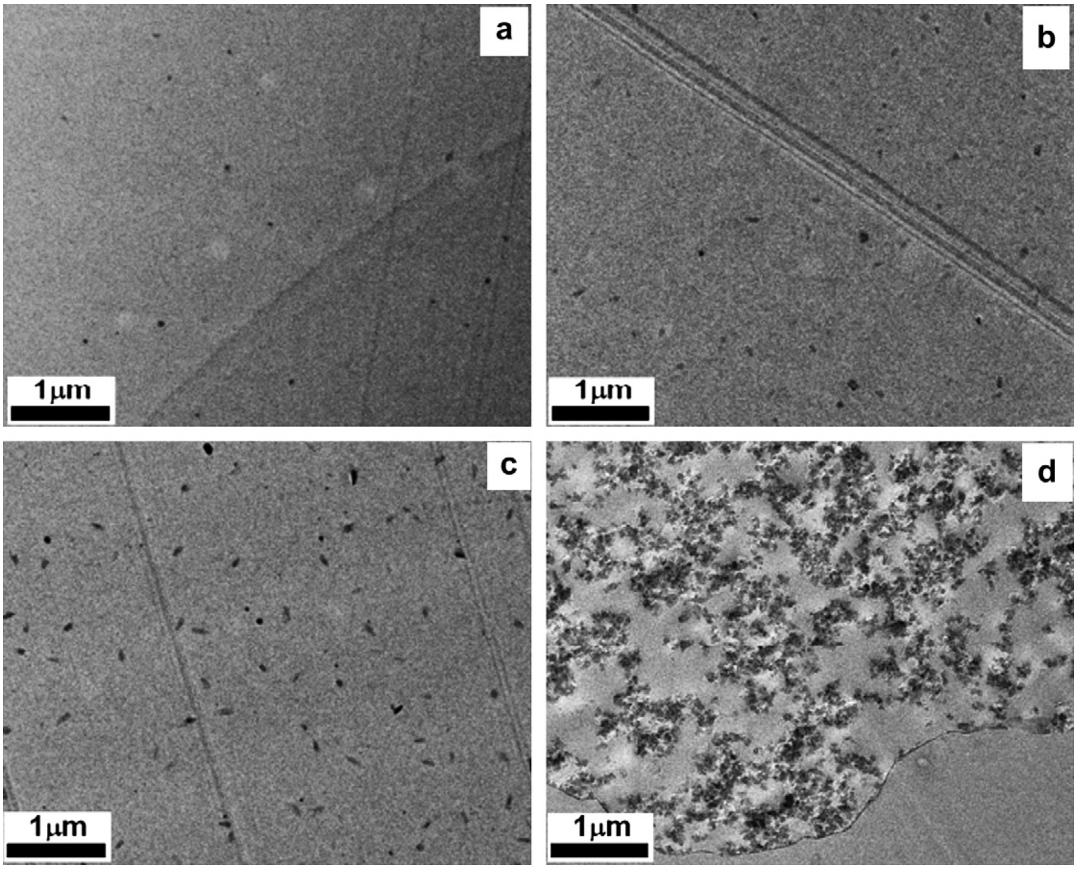


Fig. 5. Effect of NH_3:TEOS molar ratio on the dispersion of silica nanoparticles (a) 2:1, (b) 2.3:1, (c) 2.7:1 and (d) the formation of aggregated silica clusters at high ammonia content (2.7:1).

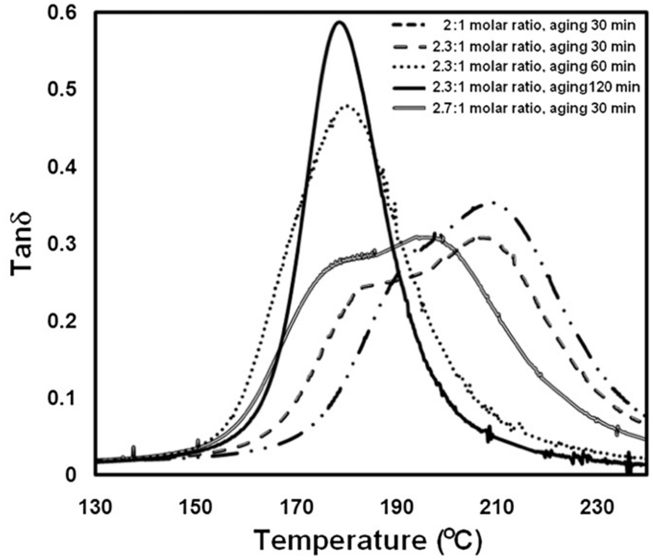


Fig. 6. T_g of composites prepared at different NH_3:TEOS molar ratios (2:1–2.7:1) and aging times (30–120 min).

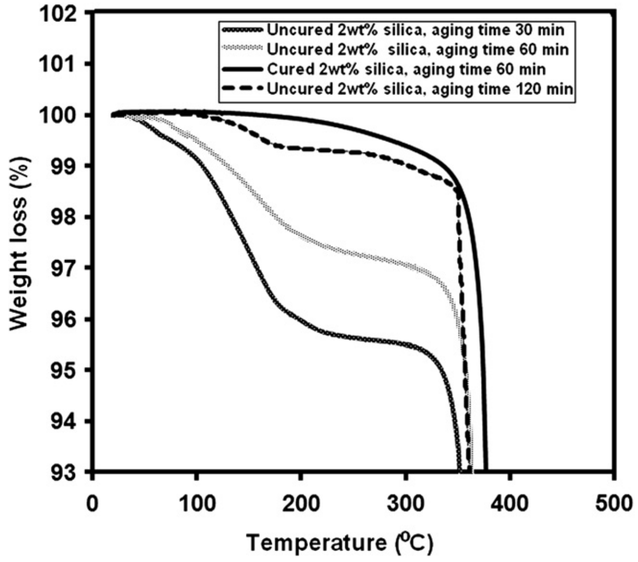


Fig. 7. Weight loss (%) of uncured and cured silica/epoxy nanocomposites prepared at different aging time (30–120 min).

total composite composition, wt% of APTMS to silica amount and final curing temperature were fixed at 2.3:1, 2 wt%, 10 wt% and 230 °C, respectively. From the plot of tanδ vs temperature (Fig. 6), while a broad peak consisting of two superimposed T_g at 183 and 207 °C was obtained at aging time of 30 min, a single T_g indicating a homogeneous composite system was shown at longer aging time (60 and 120 min). Under observation using TEM, silica particles with larger size were also formed at longer aging time (increased from 45 to 75 nm at 30 and 60 min). The flexural and tensile modulus of composite were improved accordingly with increasing aging time from 30 to 60 min and leveled off at 120 min (Table 1). It means that aging time influences the nucleation and growth of silica particles as well as their surface functionalization. Therefore, a homogeneous composite network with high conversion of precursors to silica was formed at optimal aging time of 60 min. Non-significant improvements were obtained from composite aged at longer aging time of 120 min because most of the precursors were completely reacted after aging for 60 min.

To confirm the completed formation of silica, TGA results of uncured silica/epoxy aged for 30, 60 and 120 min were compared with a cured silica/epoxy with aging time of 60 min (Fig. 7). Weight loss corresponded to the evaporation of unreacted TEOS at 133–135 °C was shown in all uncured samples and it is 4.5%, 2.8% and 0.8% with silica/epoxy aged for 30, 60 and 120 min, respectively. In contrast, no transition was observed from cured sample as unreacted TEOS molecules were evaporated during curing process. Although an uncured sample aging at 60 min showed 2% higher weight loss than that at 120 min, their thermal mechanical properties were hardly changed as shown in Table 1.

3.3.3. *Curing process*

The influence of final curing temperature on the thermal mechanical properties of silanized silica/epoxy nanocomposites was studied by varying the temperature from 230, 250–270 °C. The molar ratio of NH_3:TEOS, silica content in total composite composition, wt% of APTMS to silica amount and aging time were fixed at 2.3:1, 2 wt%, 10 wt% and 60 min, respectively. As listed in Table 2, T_g and mechanical properties of the nanocomposites were improved at high curing temperature because of the higher degree of cross-linking among APTMS-functionalized silica, epoxy resin and hardener to form a strong composite network.

The influence of post-curing process on the thermal mechanical properties of composite was also studied by post-curing the cured nanocomposite (2 wt% silica, 2.3:1 M ratio of NH_3:TEOS, 10 wt% APTMS, aging time of 60 min and final curing of temperature 270 °C) at 250 and 270 °C for 3 h. The storage modulus and T_g value of nanocomposite before and after post-cured at 250 °C were comparable (210 and 211 °C respectively). However, the T_g was dramatically decreased by 18 °C (from 210 to 192 °C) after post-cured at 270 °C. The lowering of T_g after post-cured at 270 °C may be due to the mobility of cross-linked APTMS molecules after exposed at high temperature for long time. Therefore, the curing process with final curing temperature of 270 °C and without post-curing step was selected for further studies.

Table 1
Influence of NH_3:TEOS molar ratio and aging time on the particle size and thermal mechanical properties of silanized silica/epoxy nanocomposites (silica content in composite of 2 wt%, final curing temperature of 230 °C).

	Sample				
	A	B	C	D	E
NH_3:TEOS (molar ratio)	2:1	2.3:1	2.3:1	2.3:1	2.7:1
Aging time (min)	30	30	60	120	30
Particle size (nm)	45	45	75	75	55
Storage modulus (MPa)	2110	2220	2380	2480	1750
T_g (°C)	192,208	183,207	180	178	176,197
Flexural modulus (GPa)	1.9 ± 0.1	1.9 ± 0.1	2.0 ± 0.2	2.0 ± 0.5	1.9 ± 0.3
Tensile modulus (GPa)	2.5 ± 0.2	2.4 ± 0.2	2.7 ± 0.4	2.6 ± 0.4	2.3 ± 0.3

Table 2
Influence of curing conditions on the thermal mechanical properties of silanized silica/epoxy nanocomposites (silica content in composite of 2 wt%, NH_3:TEOS molar ratio of 2.3:1, aging time of 60 min).

	Sample				
	F	G	H	I	J
Final curing temperature (°C)	230	250	270	270	270
Post-curing temperature (°C)	–	–	–	250	270
Storage modulus (MPa)	2380	2300	2510	2610	2730
T_g (°C)	180	201	210	211	192
Flexural modulus (GPa)	2.0 ± 0.2	2.3 ± 0.1	2.8 ± 0.2	–	–
Tensile modulus (GPa)	2.7 ± 0.4	2.6 ± 0.1	2.6 ± 0.3	–	–

Table 3
Influence of APTMS content on the properties of silanized silica/epoxy nanocomposite (silica content in composite of 2 wt%, NH_3:TEOS molar ratio of 2.3:1, aging time of 60 min, final curing temperature of 270 °C).

	Sample			
	P	Q	R	S
APTMS (wt%)[a]	2	5	10	15
Storage modulus (MPa)	2380	2420	2510	2620
T_g (°C)	197	197	210	203
Flexural modulus (GPa)	2.2 ± 0.2	2.3 ± 0.3	2.8 ± 0.2	2.3 ± 0.4
Tensile modulus (GPa)	2.0 ± 0.2	2.2 ± 0.1	2.6 ± 0.3	2.4 ± 0.0

[a] Percentage by weight of APTMS to the amount of silica.

3.3.4. APTMS content

The content of APTMS functionalized on silica surfaces was varied by changing the wt% of APTMS to silica from 2, 5, 10–15%. The molar ratio of NH_3:TEOS, silica content in total composite composition, aging time and final curing temperature were fixed at 2.3:1, 2 wt%, 60 min and 270 °C, respectively. The storage modulus, flexural modulus, tensile modulus and T_g were enhanced at higher APTMS content as more APTMS molecules were functionalized onto silica surfaces, resulting in strong interfacial interaction between silica and epoxy matrix (Table 3). However, a reduction on mechanical properties were observed when the percentage of APTMS is 15 wt% because an excess APTMS was condensed to form aggregated silica clusters.

3.3.5. Silica loading

The thermal mechanical properties of silanized silica/epoxy nanocomposites prepared at various amounts of silica (1–4 wt% of silica in total composite composition) were studied at the fixed NH_3:TEOS molar ratio of 2.3:1, wt% APTMS to silica amount of 10, aging time of 60 min and final curing temperature of 270 °C. From Table 4 and Fig. 8, the storage modulus of composite was increased with increasing silica loading and the highest value of 2730 MPa was achieved for nanocomposite with 4 wt% of silica concentration. However, the T_g of nanocomposite with 3 and 4 wt% silica was decreased from that of neat epoxy by 25 and 49 °C (Fig. 9) due to retardant of cross-linked reaction of polymer by large amount of silica particles.

In addition, the viscosity of the epoxy system before curing increases significantly when the concentration of silica nanoparticles was increased further, possibly due to strong interaction between silica particle and epoxy. As a result, 2–4 wt% of silica was used in our epoxy system.

3.4. Comparison of 2 wt% silanized silica/epoxy nanocomposite, neat epoxy, 2 wt% non-functionalized silica/epoxy and 2 wt% Nanopox F400/epoxy

The properties of silanized silica/epoxy nanocomposite prepared using the present method (silica content of 2 wt%, NH_3:TEOS molar ratio of 2.3:1, aging time of 60 min and curing temperature of 270 °C) were compared with those of neat epoxy, non-functionalized silica/epoxy and Nanopox F400/epoxy systems (Table 5). Because of the uniform dispersion of silica and strong silica/epoxy adhesion, the high performance silica/epoxy nanocomposites were formed by the present method, which only a few percentage of silica was required to achieve high performance nanocomposites. Unlike those high silica loaded composite prepared using conventional solution blending process, the viscosity of silanized silica/epoxy is in a comparative range with that of neat epoxy system (5000 and 2000 mPa s respectively) but showed enhanced properties. Therefore, high performance nanocomposite prepared using the present method can easily be applied to many types of designed molds because it can easily be fed into the cavities of molds before curing.

Table 4
Influence of silica content on the properties of silanized silica/epoxy nanocomposites (NH_3:TEOS molar ratio of 2.3:1, aging time of 60 min, final curing temperature of 270 °C).

	Sample				
	K	L	M	N	O
Silica content (%)	0	1	2	3	4
Storage modulus (MPa)	2512	2550	2510	2670	2730
T_g (°C)	210	200	210	185	161
T_d (°C)	375	370	376	374	360

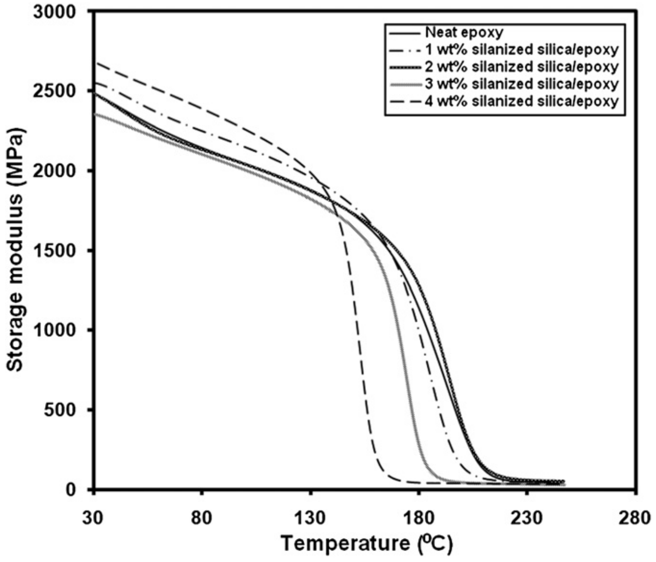


Fig. 8. Plot of storage modulus against temperature of silanized silica/epoxy nanocomposites prepared at different silica contents (1–4 wt% silica).

The T_g of silanized silica/epoxy was comparable with that of neat epoxy and Nanopox F400 silica/epoxy (209–210 °C), while the non-functionalized silica/epoxy showed the lowest value (207 °C) due to

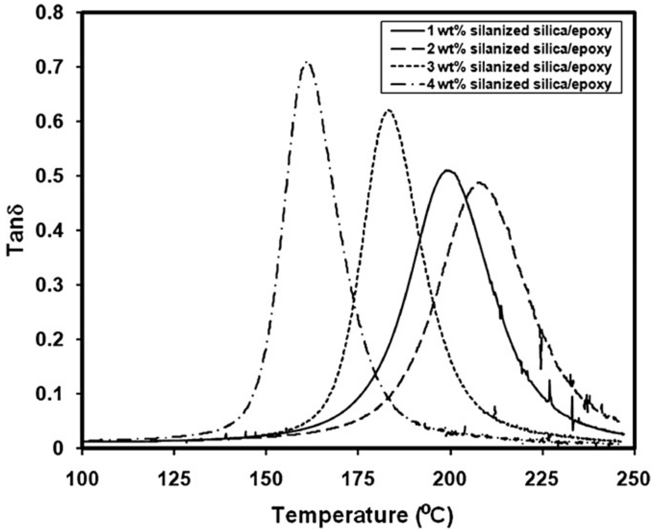


Fig. 9. Plot of tanδ against temperature of silanized silica/epoxy nanocomposites prepared at different silica contents (1–4 wt% silica).

Table 5
Comparison of the properties of silanized silica/epoxy nanocomposite with those of neat epoxy, non-functionalized silica/epoxy, commercialized Nanopox F400/epoxy.

	Sample			
	Neat epoxy	Non-functionalized silica/epoxy	Silanized silica/epoxy	Nanopox F400/epoxy
Viscosity (mPa s)	2000	4600	5000	3000
Storage modulus (MPa)	2512	2330	2510	2370
T_g (°C)	210	207	210	209
T_d (°C)	375	372	376	374
Flexural modulus (GPa)	2.4 ± 0.1	2.5 ± 0.2	2.8 ± 0.2	1.8 ± 0.1
Tensile modulus (GPa)	2.5 ± 0.7	2.7 ± 0.3	2.6 ± 0.3	2.2 ± 0.4

the weak interaction between silica nanoparticles and epoxy matrix. The highest flexural and tensile modulus were also achieved with silanized silica/epoxy nanocomposite, with 20 and 17% improvements over neat epoxy system. At the same time, the highest T_d was achieved from silanized silica/epoxy nanocomposite (376 °C).

4. Conclusions

Oval shaped silica/epoxy nanocomposites with uniform silica dispersion and strong silica-epoxy adhesion were effectively and conveniently synthesized via the “Solvent-Free One-Pot Synthesis” method from TEOS, APTMS, ammonia solution, and epoxy compositions at 50 °C. The size and dispersion of oval shaped silica nanoparticles, and the thermal mechanical properties of nanocomposites were influenced by the synthesis conditions. The amount of NH_3 solution and aging time influence the nucleation and growth of silica nanoparticles as well as their interaction with epoxy matrix. Our study demonstrates that the optimal synthesis condition with the current silica/epoxy systems is NH_3:TEOS molar ratio of 2.3:1, aging time of 60 min and curing temperature of 270 °C. Small amount of silica incorporation in the nanocomposite (1–4 wt% silica in total composite composition) could enhance the property of silica/epoxy composite significantly. The lower T_g at higher silica loading is due to the decrease of the cross-linked density of epoxy network. The high performance silica/epoxy nanocomposites prepared using the present method exhibit better mechanical properties over neat epoxy (20% and 17% improvements on the flexural and tensile modulus) and commercial available silica/epoxy nanocomposite systems (36% improvement on the flexural modulus).

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