The Effect of Surface Modification of Silica Nanoparticles on the Morphological and Mechanical Properties of Bismaleimide/Diamine Matrices

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ABSTRACT: Silica and surface-modified silica nanoparticles were successfully incorporated into bismaleimide/diamine (BMI/DDM) matrices using a combinatory procedure that involved pretreatment of filler, mechanical mixing, ageing in BMI melt, and melt mixing. Fillers with different sizes and surface modification (of expoxide and BMI groups) showed to some extent the catalytic effect of the cure reaction on the matrix, without any negative effects. Nonmodified nanoparticles were found to interact with the BMI/DDM matrix through hydrogen bonding, whereas the surface-modified nanoparticles exhibited strong adherence to the polymer matrix through covalent bonding. Morphological analysis revealed that surface-modified nanoparticles were homogenously distributed within the polymer matrix, whereas the pure silica filler formed large aggregates due to strong filler–filler interactions. Nanocomposites reinforced with surface-modified silica nanoparticles showed significant improvements over pure silica, and improvements were also noted in the thermo mechanical properties and thermal stability of the neat BMI/DDM, such as the storage tensile modulus and glass transition temperature. A reduction in the coefficient of thermal expansion was also noted. © 2014 Wiley Periodicals, Inc. Adv Polym Technol 2015, 34, 21492; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21492

KEY WORDS: Bismaleimide/Diamine, Nanoparticle, Polymers, Surface Chemistry, Silica

Introduction

Polymer nanocomposites are a two-phase system comprising a polymer matrix incorporating reinforced fillers.[1,2] Recent studies have demonstrated that nanosized fillers with a high surface area can enhance the physical and mechanical properties of the resulting composites.[3,4] The potential of silica nanoparticles as fillers in advanced polymer matrix composites can be evaluated based on a number of criteria: (i) dispersion of the fillers within a polymer matrix, (ii) the effects of fillers on curing profiles, (iii) filler–matrix interactions, and (iv) the effects of fillers on the final properties of the nanocomposite. In many cases, appropriate surface modifications have been reported to enhance the dispersion of silica nanoparticles within a polymer matrix and to provide a covalent interaction between fillers and matrix.[4–7] However, the performance of different nanocomposite system is difficult to compare and the same filler may produce different effects on different matrices.[8] For example, the presence of silica nanoparticles has been reported to have both catalyzed[6] and inhibited[9,10] the cure reactions of the polymer matrix, and in some cases left it unaffected.[11] Similarly, the incorporation of silica nanoparticles has been shown to enhance,[3–7]

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degrade,[12] or result in nonmonotonous variation[8] in the thermal mechanical properties of silica–polymer nanocomposites. This notwithstanding, ideal nanosize fillers should, in principle, be able to homogenously disperse within a polymer matrix without inhibiting polymerization reactions. Such ideal fillers should exhibit strong interaction with the matrix and, ultimately, be able to enhance the thermal mechanical properties of the neat polymer.

Most contemporary work has focused on the use of epoxy resins[13,14] as a matrix in silica–polymer nanocomposites. 1,1′-(Methylenedi-4,1-phenelene) bismaleimide (BMI, Geel, Belgium) is widely used as matrix resins in high-performance composites[13] for high-temperature applications, such as those in the aerospace[15,16] and electronics[17,18] industries. Extensive studies on silica–BMI nanocomposites (SBNs) have not yet been reported, but the combination of silica nanoparticles and BMI is expected to produce an advanced hybrid material with excellent thermal mechanical properties, which could become an alternative to the widely used silica–epoxy composites.

In our recent paper, an optimized preparation of BMI/4,4′-diaminodiphenylmethane (DDM, Buchs, Switzerland) copolymer matrices was introduced. Different effective parameters, such as the effect of the BMI/DDM ratio and the amount of dicumyl peroxide (DCM) (as a curing accelerator) on the curing profiles, postcuring profiles, and also pot life, were studied using different techniques, which included ourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Thermomechanical Analysis (TMA), Dynamic Mechanical Analysis (DMA) and Thermogravimetric Analysis (TGA).[19] In the present work, the incorporation of silica and modified silica nanoparticles into the BMI/DDM matrix was carried out by an initial pretreatment of silica surface in the presence of BMI monomer and appropriate mixing, aging, and melt-mixing processes. In addition, the potential of the filler nanoparticles to enhance the morphological, thermal, and mechanical properties of the neat matrix was investigated.

Experimental

Three types of silica nanoparticles were selected as fillers: (i) pure (nonmodified), (ii) modified with epoxide groups 3-glycidyloxypropyltrimethoxysilane (GPTS, Buchs, Switzerland) (Si-GPTS), and (iii) modified with 3-amino propyltrimethoxysilane (APTES, Buchs, Switzerland)/ maleimide groups (Si-APTS-BMI). The concentration of the fillers varied from 2.5 to 10.0 wt%, and the curing conditions were fixed for the neat BMI/DDM matrix.[19] The silica,[20] modified silica,[21] and BMI/DDM (ratio of 2:1) polymer matrices[19] were synthesized and developed in our laboratory (please refer to the Supporting Information).

TYPICAL PROCEDURE FOR PREPARATION OF SBNs

The BMI–silica admixture was added into 50 mL of dichloromethane (DCM). The suspension was subjected to ultrasonic radiation for 30 min, followed by reflux at 70°C for another 2 h. Then, DCM was discarded from the suspension through slow evaporation at room temperature and dried at 80°C for 2 h. This was followed by agitation of the silica nanoparticles for 20–30 min in the BMI melt. DDM was added to the mixture and stirred for 10–15 min at 150°C. The sample was then heated to remove air bubbles, mixed with Dicumyl peroxide (DCP, Buchs, Switzerland) at 150°C, molded, and then cured.

LABELING OF NANOCOMPOSITE

The SBNs were labeled using the template BMI/DDM-S*XY*-*Z*. The base term BMI/DDM-S is fixed, whereas the *X* refers to the type of surface modification (G for silica modified with epoxide and B for silica modified with maleimide groups; note: no designation is given for pure silica), *Y* refers to the filler (silica nanoparticles) size, and *Z* refers to the filler concentration. As an example, if the nanocomposite was prepared using 7-nm silica particles modified with maleimide groups, at a concentration of 5 wt%, it is referred as BD-SB7-5.

CHARACTERIZATION TECHNIQUES

The FTIR spectra (using KBr) were recorded using a PerkinElmer 2000 FTIR spectrometer. Field Emission Scanning Electron Microscope (SEM) images were taken using a LeoSupra 50 VP Field Emission SEM system at 15 kV accelerating voltage. The fracture surface of the nanocomposite was used for this task, as the samples were prepared by dipping them into liquid nitrogen for ~15 min and then broken to produce the fracture surfaces. DSC analysis was conducted using a Pyris 1 DSC instrument (PerkinElmer) with a heating rate of 10°C min^{-1} under N_2 flow in the range of –50 to 400°C. The curing profiles of the nanocomposites were obtained by the mixing of BMI and DDM in a ratio of 2:1 in the presence of 0.1 wt% DCP and an appropriate amount of silica at 150°C for 10–15 min. The DMA was carried out on a PerkinElmer DMA 7e at a heating rate of 5°C min^{-1}. A TMA was performed for measuring the thermal expansion behavior and glass transition temperature (T_g) of the nanocomposite by TMA Q400 at a heating rate of 5°C min^{-1}.

Results and Discussion

The work described here focused on the evaluation of silica nanoparticles (with or without surface modification) as fillers in the preparation of an SBN. The effects of silica nanoparticles on the curing profile of a BMI/DDM (BD) polymer matrix, with ratio of 2:1, were studied using DSC, and filler–matrix interactions and morphological examinations were investigated using FTIR and SEM techniques, respectively. Finally, the thermal mechanical properties of the hybrid materials were determined using DMA, TMA, and TGA. This study was focused mainly on evaluating the potential of 7-nm silica particles (S7, SG7, and SB7) as fillers in SBN. The 7-nm particles, as reported in a previous paper,[20] possess many attractive properties, such as a high surface area and high silanol concentration, and showed the highest loading by functional groups after the surface modifications.[21] In addition, modified silica with sizes of 20 and 130 nm (SG20 and SG130) was also used as filler to study the effect of particle

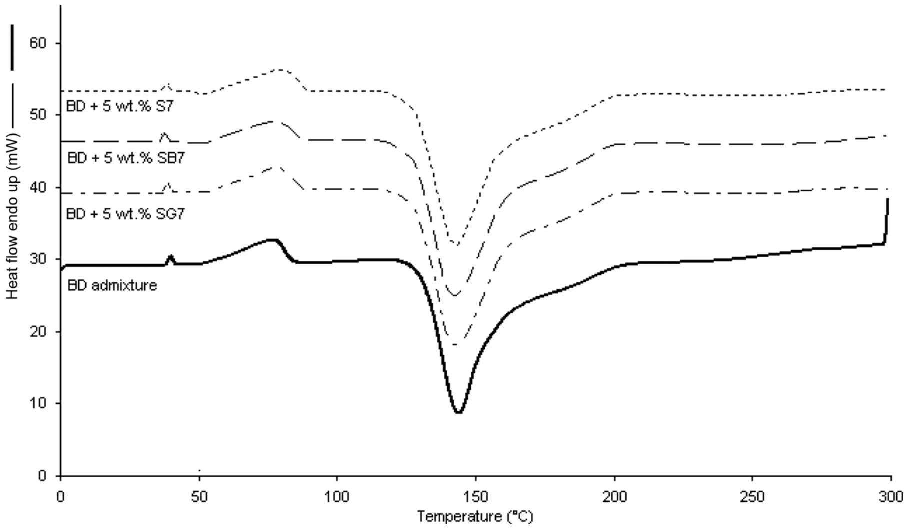

FIGURE 1. DSC thermo grams of BMI/DDM–SiO_2 admixtures containing various surface-modified 7-nm silica particles at 5.0 wt% filler content with 0.1 % DCP.

size on the properties of SBN. The terms SG and SB are defined as 3-glycidyloxypropyltrimethoxysilane and maleimide/amine-grafted silica nanoparticles, respectively, while the numerical values indicate the particle size. SG and SB have been fully characterized by FTOR, Solid-state Cross-Polarization Magic Angle Spinning Carbon-13 and Silica-29 Nuclear Magnetic Resonance (^{13}C and ^{26}Si CP/MAS NMR), Elemental (Carbon, Hydrogen & Nitrogen) analysis CHN, TGA–FTIR, and DSC.[21] The loading of modifiers was estimated by the amount of carbon, which was found to be 12.9 and 7.15 mmol g^{-1} for SG and SB, respectively.[21] Details of the mechanism of surface modification (via condensation reaction and nucleophilic addition reaction) of the silica can be found in our published paper.[21] The preparation of BD (BMI:DDM in a ratio of 2:1) matrices was introduced in our recent paper,[19] and the effect of different factors such as curing time and postcuring, processing time (pot-life), BMI/DDM ratio, and concentration of accelerator (DCP) on thermal mechanical properties (DMA and TMA) and thermal stabilities (TGA) was studied. The mechanism of the reaction between BMI and DDM was also investigated by FTIR. It is useful to highlight that the upper limit of the filler concentration was fixed at 10.0 wt% because, above this level, the viscosity of the BMI/DDM matrix increased dramatically, resulting in processing problems.

EFFECT OF FILLERS ON THE CURING PROFILES OF SBN: DSC STUDIES

The curing behaviors of SBN with and without pure and surface-modified silica fillers were characterized by DSC. Figure 1 shows a typical DSC thermogram depicting the curing profiles of BMI/DDM–SiO_2 admixtures containing 5.0 wt% of pure and surface-modified 7-nm silica particles. All the admixtures contained 0.1% DCP content as a promoter. In general, the curing behavior of nanocomposites was found to be similar to that of the BMI/DDM, as indicated by similarity between DSC curves.[19]

Table I shows the typical DSC data of onset temperature, peak temperature, and the enthalpy values of the exothermic reaction of BMI/DDM–SiO_2–DCP admixtures prepared at different filler sizes, filler concentrations, and surface functional groups. From the results presented in Table I (entries 1 and 2), it can be seen that the T_{onset} and T_{peak} of the formulations containing silica fillers were slightly reduced compared with the neat BD.

TABLE I

DSC Data of the Exothermic Reaction of SBN Containing Various Types of Silica Nanoparticles at 5.0 and 10.0 wt%

			Exothermic Peak		
Entry	Sample	Filler Content (wt%)	T_{onset} (°C)	T_{peak} (°C)	ΔH (J/g)
1	BD (BMI/DDM)	–	144.2	162.8	–162.3
2	BD-S7-5	5.0	142.2	161.8	–168.1
3	BD-SB7-5	5.0	140.0	160.3	–178.5
4	BD-SG7-5	5.0	138.2	159.2	–201.6
5	BD-S7-10	10.0	140.9	161.6	–183.2
6	BD-SG7-10	10.0	136.0	157.2	–218.1
7	BD-SG20-10	10.0	142.4	159.7	–198.5
8	BD-SG130-10	10.0	142.8	160.6	–205.8

The presence of functional groups on the surface of silica plays an important role in reducing the reaction temperature of the BMI/DDM–SiO_2–DCP formulations. The lowest T_{onset} and T_{peak} was obtained for modified fillers, SG7 and SB7 (Table I, entries 3 and 4), in comparison with nonmodified fillers (Table I, entry 2) at the same filler size and loading amount. This phenomenon could be explained in terms of the different reactivity of the functional groups grafted onto the filler (silica) surface. The epoxide groups grafted on the silica surface (SG7) were found to be more reactive than the maleimide groups grafted on the silica surface (SB7) in the reaction between the functional groups and DDM. This might be due to more efficient interactions between the epoxide groups of the filler with the functional groups of the polymer, as compared to the presence of the maleimide group, because a higher loading amount of GPTS existed on the filler surface than BMI.[21] The lower loading of BMI was associated with steric hindrance between the

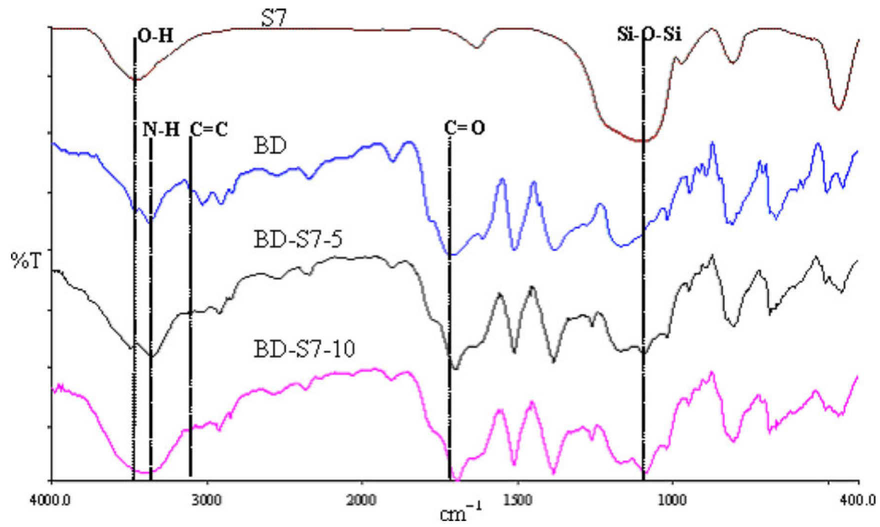

FIGURE 2. Normalized FTIR spectra of S7, cured BD matrix, and cured SBN containing 5.0 and 10.0 wt% of SG7.

amino-propyl group of APTS and BMI monomer during the filler surface modification.[21] Similarly, the epoxide groups of SG7 are able to react with DDM from the BMI/DDM–SiO_2–DCP admixture at a much lower temperature than the maleimide groups of SB7. The T_{onset} and T_{peak} were shown to decrease further at higher filler concentrations (10.0 wt%) due to an increase in amounts of surface functional groups (grafted on the silica surface) in the BMI/DDM–SiO_2–DCP formulations (Table I, entries 2 and 5).

The T_{onset} and T_{peak} of the exothermic reaction were also affected by the filler size, such that they both decreased with decreasing silica size (Table I, entries 6–8). This phenomenon could also be related to the amount of reactive functional groups present on the silica surface. The loading or amount of organofunctional groups (epoxide and maleimide groups) increased with a decrease in particle size from 130 to 7 nm. Because higher concentrations of functional groups/reactants can lead to rapid/faster reactions,[22] it is reasonable to infer that the decrease in T_{onset} and T_{peak}, in the order of BD-SG130-10 < BD-SG20-10 < BD-SG7-10, is a result of increasing the amount of grafted epoxide on the silica surface.[21] Overall, these results demonstrate high consistency with previous findings reported by Kang et al.[5]

CHARACTERIZATION OF FILLER–MATRIX INTERACTIONS: FTIR STUDIES

Figure 2 displays the FTIR spectra of the fully cured SBN containing different concentrations of SG7. The main spectral assignments of the cured BD (BMI/DDM) polymer matrix were as follows: harmonic vC=O + NH_2 (3466 cm^{-1}), NH (3373 cm^{-1}), v =C—H maleimide (3100 cm^{-1}), benzene (1516 cm^{-1}), vC=O out of phase (1717 cm^{-1}), and vC—N—C succinimide (1185 cm^{-1}).[23] Three main peaks at 3400, 1110, and 960 cm^{-1} were observed, corresponding to the vO—H stretching, v_{as}Si—O—Si, and δSi—OH vibrations of the silica, respectively.[24]

The spectra of the nanocomposites containing S7 were consistent with the BD spectrum. The disappearance of the maleimide peak at 3100 cm^{-1}, and the presence of a secondary amine peak at 3373 cm^{-1} and a succinimide peak at 1185 cm^{-1}, clearly shows that the S7 fillers did not inhibit the polymerization reaction of the BMI/DDM polymer matrix. Moreover, the maleimide peak completely vanished from the nanocomposite samples compared to the BD. On the other hand, the appearance of peaks at ~3400 and 1100 cm^{-1} shows the successful incorporation of silica nanoparticles into the BMI/DDM matrix. The peaks became broader and more intense at 10.0 wt% due to high concentrations of S7. Interestingly, compared to the BD, the spectra of the nanocomposites showed a significant shift in the carbonyl and hydroxyl peaks toward the lower wave numbers. This shift was found to be more pronounced at higher concentrations of S7 and indicates that the interaction between the S7 and BMI/DDM polymer matrix is due to hydrogen bonding.[25] The silanol groups present on the surface of the silica nanoparticles are able to form hydrogen bonds with the carbonyl groups of the BMI molecules.[26] Similar interactions have been reported in silica–rubber,[27] silica–polyurethane, and silica–poly(butyl methacrylate)[28] nanocomposites.

It is important to highlight that both maleimide and epoxide groups grafted onto the silica surface can react with BMI molecules through a cross-linking reaction and also with DDM through chain extension reactions,[18,29] because both BMI and DDM molecules are present in the BMI/DDM matrix. The proposed reaction mechanisms of SG and SB with DDM are shown in Fig. 3. SG with grafted epoxide groups reacted with DDM via a ring-opening nucleophilic addition reaction. The FTIR spectra of the nanocomposites containing SG7 and SB7 can be found in the Supporting Information. As for the S7, both SG7 and SB7 did not affect the polymerization reaction of BMI/DDM and the presence of silica in the nanocomposites was indicated by the Si—O—Si (1100 cm^{-1}) and —OH (3400 cm^{-1}) peaks. However, unlike S7, no shifts were observed in the hydroxyl and carbonyl peaks of the nanocomposites prepared using SG7 and SB7. Therefore, it can be inferred that the interaction between the surface-modified silica nanoparticles and BMI/DDM polymer matrix is not by hydrogen bonding. However, the formation of covalent bonds between the epoxide or maleimide groups with the BMI/DDM polymer matrix could not be clearly determined from the FTIR analysis due to overlapping peaks.

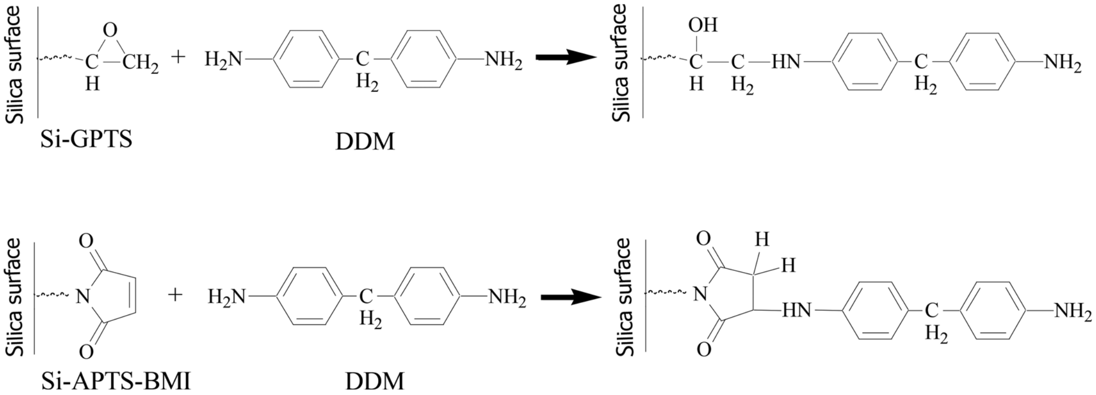

FIGURE 3. Proposed reaction mechanisms of SG and SB with DDM.

MORPHOLOGICAL EXAMINATIONS OF THE CURED SBN

The morphological study provides not only dispersion information, but also an estimate of the interfacial interaction between fillers and matrices. The fractured surface of the nanocomposites was investigated by SEM in terms of filler dispersion and aggregation.

Filler Dispersion

Owing to the existence of the charging effects on the SEM and Energy-dispersive X-ray spectroscopy (EDX) elemental mapping at high magnification, a backscattering mode Quadrant Back Scatter Detector (QBSD) was employed to study the presence and behavior of individual filler particles. Figure 4a reveals that the homogenous phase consists mainly of discrete, very fine silica nanoparticles (highlighted by circles) and a few clusters (highlighted by rectangles) in the nanocomposite containing SG7.

The unmodified silica nanoparticles produced fairly large aggregates (Fig. S3 in the Supporting Information), whereas both SB7 and SG7, having reactive groups on the surface, resulted in suppressed aggregation due to enhanced resin wettability.[5] In addition, the dispersion of fillers was found to be greatly enhanced by surface modification. In other words, the surface treatment of silica nanoparticles was found to play a key role in achieving homogeneous dispersion in the polymer matrix by reducing the surface energy of the nanoparticles.[30] It was also found that the density of the homogenously distributed fillers increased at a high filler concentration (Fig. S4 in the Supporting Information).

Furthermore, the strong filler–matrix interaction was also supported by the lack of particle–matrix debonding (phase separation) observed in the fractographs (Fig. 4b). These experiments also show that the nanocomposites exhibit good miscibility between organic and inorganic phases.[5,11,31] The other types of fillers used in this study (i.e., SB7, SG20, and SG130) were found to demonstrate similar dispersion characteristics as that discussed for SG7.

Analysis of Filler Aggregation

Filler aggregation is a common problem in silica–polymer nanocomposites due to the high surface area and intense particle–particle attractions of nanometer silica.[10] Table II shows the details of the silica aggregates observed in various SBN samples. It can be seen that the size and area occupancy of the aggregates were greatly reduced after surface modification. The largest aggregates were observed for S7 at 10.0 wt% with an average size of 7.5 μm and with the aggregates occupying ~23% of the fracture surface area. These aggregates were formed due to intense filler–filler attractions caused by hydrogen bonding between the silanol groups and also the van der Waals attraction.[5,10,22,32]

The lowest level of filler aggregation was found in the nanocomposites containing SG7. As an example, 5.0 wt% of SG7 resulted in aggregates with an average size of 1.5 μm almost two times smaller than the aggregates observed for S7 at a similar filler content. Moreover, aggregate size was found to increase with increasing filler concentration, consistent with previous studies.[33,34] Nonetheless, all the nanocomposites filled with the surface-modified silica nanoparticles occupied less than 10% of the fracture surface area. Finally, the aggregation level (based on aggregate size at 10.0 wt%) increased in the order of SG7 < SB7 < SG20 < SG130 < S7.

THERMAL MECHANICAL PROPERTIES OF SBN

The incorporation of silica nanoparticles with an enhanced adhesion toward the polymer matrix can have a great influence on the thermal mechanical properties of hybrid materials.[35] Therefore, the SBNs were characterized using DMA and TMA to determine their viscoelastic properties, for example, storage tensile modulus (E') and damping behavior (tan δ), and thermo mechanical properties, for example, T_g and coefficient of expansion (CTE), respectively. The resulting properties were evaluated based on filler concentrations, surface functional groups, and filler size.

Viscoelastic Properties

Figure 5 shows the temperature dependence of the storage modulus and tan δ of SBN. The analysis error of the E' and tan δ measurements was below 12%. It can be seen that the incorporation of silica fillers increased the E' and high temperature reliability of the BMI/DDM thermoset. Figure 5 also clearly indicates that the E' of the nanocomposites containing SG7 increased

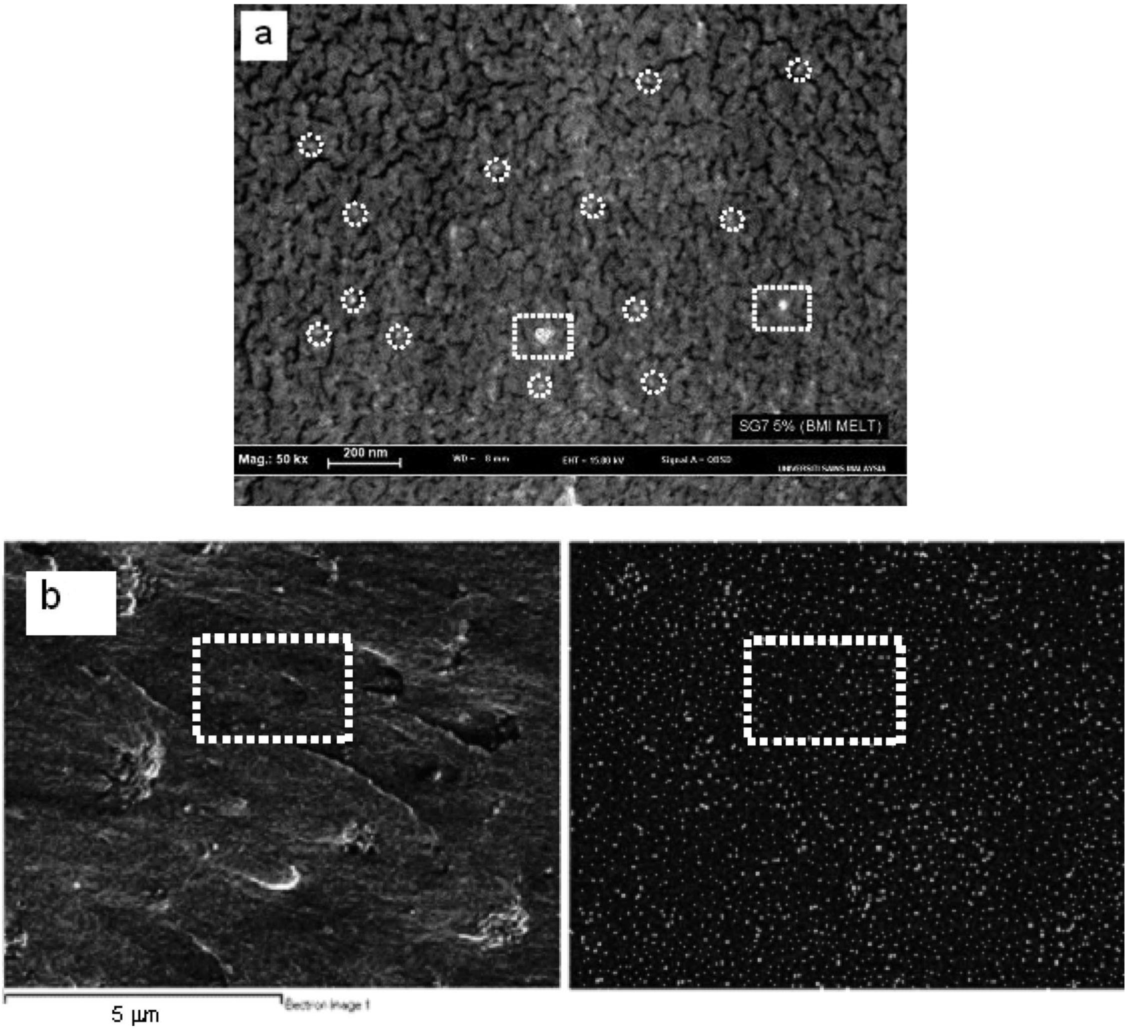

FIGURE 4. (a) High-magnification SEM micrograph (QBSD mode) and (b) SEM image and EDX elemental mapping of SBN containing SG7 at 5.0 wt% filler content.

TABLE II
Details of the Silica Aggregates Observed in the SEM Fracture Surface of SBN Containing Various Types of Fillers at 5.0 and 10.0 wt% Filler Content

Sample	Average Area Occupancy (%)	Average Aggregate Size (μm)
BD-S7-5	14.7	3.4 ± 3.0
BD-SB7-5	2.4	2.1 ± 1.6
BD-SG7-5	1.8	1.5 ± 1.2
BD-S7-10	22.6	7.5 ± 5.9
BD-SB7-10	9.2	2.3 ± 1.6
BD-SG7-10	8.6	2.1 ± 1.9
BD-SG20-10	7.7	2.7 ± 2.4
BD-SG130-10	6.8	2.9 ± 2.3

linearly with the filler content, again consistent with previous work.[34,36–39] A similar trend has been reported for silica–epoxy and silica–polymethacrylate nanocomposites.[39] The results also indicate that, at any particular 7 nm filler loading, the highest E' was demonstrated by the nanocomposite containing SG7, followed by SB7 and S7. Similar to the 7-nm particles, both SG20 and SG130 showed a linear relationship between E' and filler concentration. Generally, the E' value increased with a decrease in the particle size.

The surface-modified silica nanoparticles (e.g., SG7 and SB7) resulted in higher E' values at any specific filler content compared to the nonmodified silica particles (S7). This was due to the formation of covalent bonds between the fillers and the BMI/DDM polymer matrix, as shown by the FTIR studies. The covalently bonded hybrids exhibited higher E' values since the strong interface between silica nanoparticles and the matrix restricted the shearing or deformation of the polymer chains around the fillers.[40] In addition, this strong interface also enhances the stress transfer from matrix to filler.[5] In comparison, larger fillers (e.g., SG20 and SG130) resulted in a much lower storage modulus than SG7, which could be due to the lower interface area created by the larger fillers. This phenomenon could be directly related to the specific surface area of the silica nanoparticles, which increases with decreasing of the particle size. Therefore, smaller silica nanoparticles provide a much

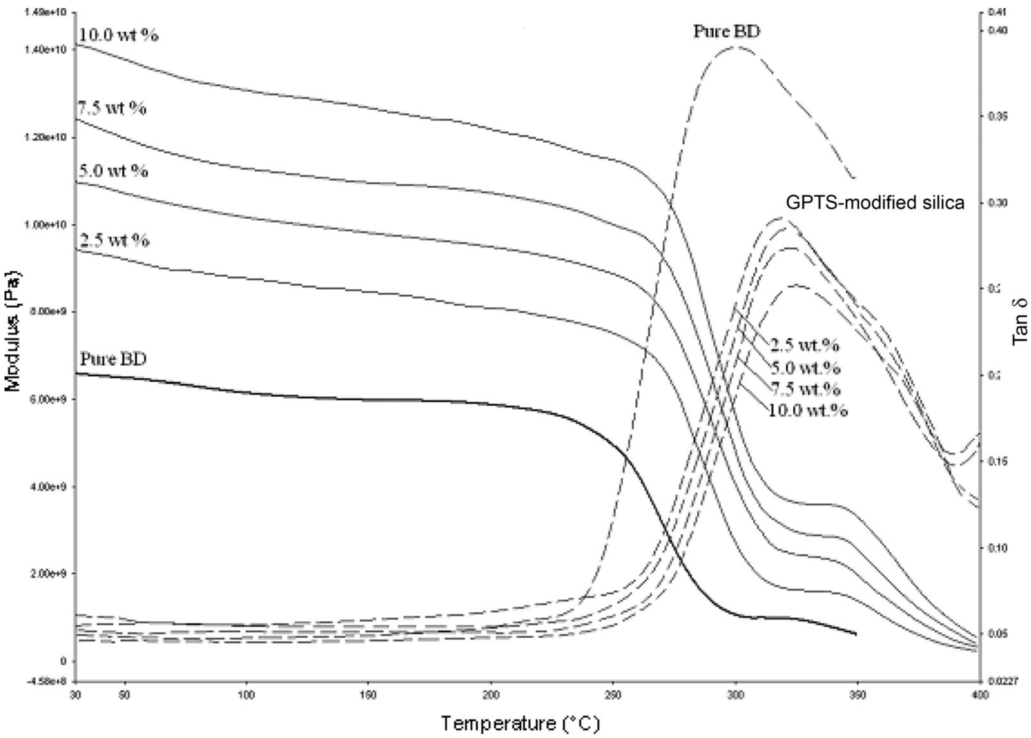

FIGURE 5. Temperature dependence of storage modulus (solid line) and tan δ (dashed line) of silica–bismaleimide nanocomposite containing SG7 at various concentrations.

higher interface by increasing the efficiency of the stress transfer from the matrix to filler compared to the larger particles.[36] Figure 5 also shows that the E' values of the nanocomposites are not constant in the glassy region (below T_g) but decrease slightly with the increase in temperature. More specifically, all the nanocomposites exhibited around 6.1–9.9% decrease in the E' value as the temperature was increased from 30 to 100°C.

In the DMA curves, the magnitude of the tan δ curves decreased with increasing filler content, once again suggesting that the presence of silica nanoparticles had suppressed the mobility of the polymer chains.[35] The decrease in the magnitude of the tan δ and the shift to a higher temperature range was highest for the nanocomposites filled with SG7, followed by SB7 and S7. This finding further proves that the strongest filler–matrix interaction is provided by SG7, followed by SB7 and S7. Moreover, the results also show that the surface-modified silica nanoparticles are homogenously distributed and covalently bonded to the polymer matrix.[5,35,39,41]

Thermo mechanical Properties

TMA studies were conducted to determine the effects of silica nanoparticles on the CTE and T_g of the SBN. These two parameters are important criteria in the evaluation of semiconductor packaging materials.[10,35] Figure 6 illustrates the typical dimensional change versus temperature curve obtained for the nanocomposites reinforced with S7, SB7, and SG7 at 5.0 wt% filler contents. As shown in the figure, all the nanocomposites exhibited distinctive slopes indicating different CTE values. Moreover, a clear change in slope was observed at T_g indicating an increase in CTE above the T_g value. The analysis error of the CTE and T_g measurements determined from the TMA analysis was below 11%.

The incorporation of silica nanoparticles was able to suppress the linear thermal expansion of pure BMI/DDM. Essentially, the CTE of the nanocomposites containing silica nanoparticles (S7, SB7, SG7, SG20, and SG130) decreased with increasing filler content. A similar trend has been reported for silica–epoxy nanocomposites filled with both treated and untreated 100-nm silica particles in the concentration range of 0–40 wt%.[10] Figure 7 shows that the α_1 decreased in the order of BD < S7 < SB7 < SG7. In other words, the CTE is relatively low for the hybrid materials where strong interfaces (covalent bonding) exist.[5,10,35] For example, the α_1 value of the nanocomposite filled with SG7 decreased nearly 25% compared to the neat BMI/DDM thermoset at 5.0 wt% filler content. At similar filler contents, SB7 and S7 resulted in approximately 21 and 6% decrease in the α_1, respectively. The CTE of the hybrid material has been reported to be dependent on the interaction between the phases and also the volume fraction of the reinforcement.[35] Accordingly, in the present study, the strong interfacial system (e.g., SG7) resulted in a more suppressed CTE than the poor interfacial system (S7). The amount of epoxide groups present on the silica surface also decreased with an increase in the particle size leading to limited interfacial (covalent) bonding with the BMI/DDM matrix. Therefore, the CTE of hybrid materials increased in the order of SG7 < SG20 < SG130, as shown in the Supporting Information.

T_g is a complex phenomenon that is influenced by many factors including free volume, molecular mobility, and cross-link density.[42] It is an important parameter that determines the operating temperature range of a polymeric/composite material.[43] Figure 8 shows the T_g of the nanocomposites reinforced with

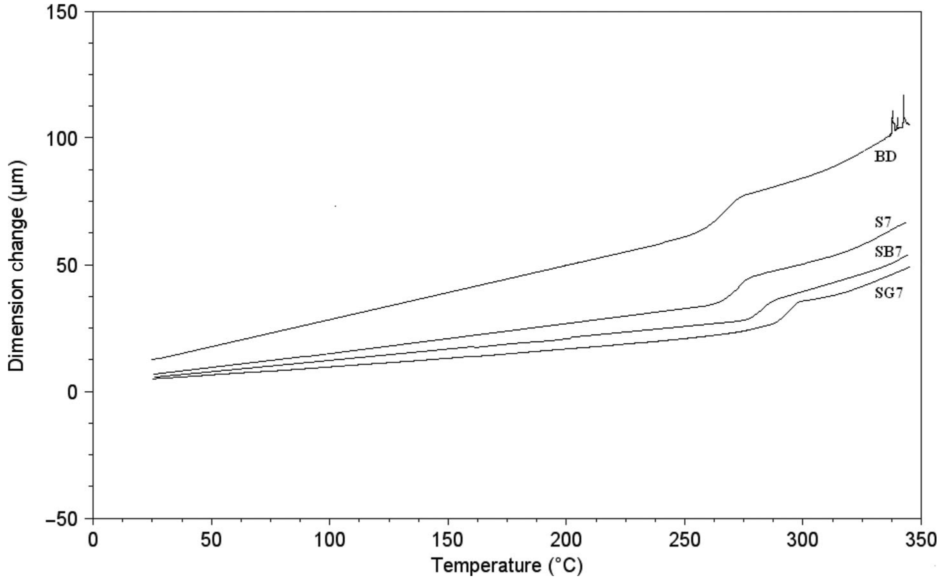

FIGURE 6. Variation of dimensional change with the temperature for pure BMI/DDM (BD) and nanocomposites filled with various surface-modified silica nanoparticles at 5.0 wt% filler content.

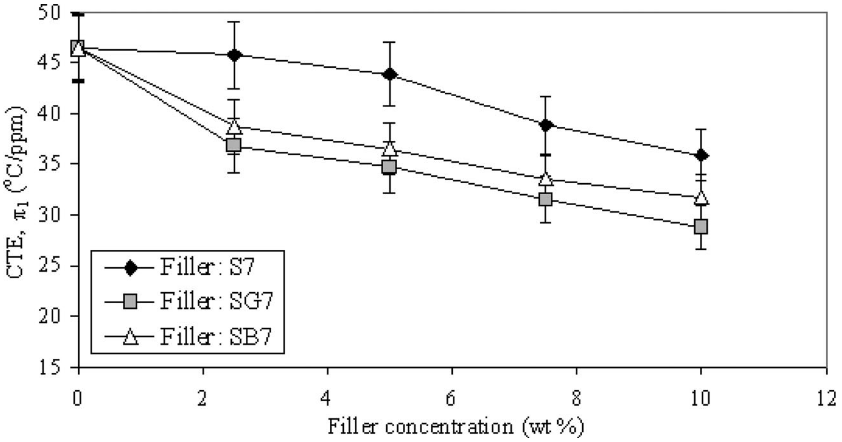

FIGURE 7. Variation of CTE below T_g (α_1) with the filler concentration for various types of 7-nm silica particles modified with epoxide groups.

S7, SB7, and SG7 as a function of filler concentration. The result shows that the T_g of the hybrid materials increased significantly up to 5.0 wt% filler content and started to stabilize above this concentration. For the 7-nm silica fillers, the highest T_g value was obtained for the formulation containing SG7, followed by SB7 and S7. At 5.0 wt% filler content, the highest T_g was produced by the nanocomposites filled with SG7, which is 44°C higher than the T_g value of the neat BMI/DDM thermoset (251.6°C). The results also indicated that SB7 and S7 increased the T_g value of the neat BMI/DDM thermoset by 29 and 21°C, respectively.

The T_g of the nanocomposites reinforced with SG20 and SG130 also significantly increased up to 5.0 wt% filler content, with the rate of increment slowing down above this concentration in a similar fashion to the 7-nm silica fillers. The T_g produced by SG20 was higher than that by SG130 (6–14°C higher), whereas the T_g of the latter was slightly higher than that of SG7 (2–7°C higher) at various filler concentrations. Overall, the highest T_g was shown by SG20 at 10.0 wt% (315°C), which is almost 25% higher than that of pure BMI/DDM. The lowest increment in the T_g was provided by S7 at 2.5 wt% (262°C), which is only 4% higher than that of pure BMI/DDM. The trends established using the T_g values determined from TMA were also consistent with the trends provided by the T_g measured from the DMA.

It is generally accepted that the introduction of nanoparticles increases the free volume of a polymer matrix. This increase will yield negative effects on the T_g of the polymer, that is, $T_g \propto 1/$free volume.[43] However, for the 7-nm silica particles, it appears that the increase in the free volume has been compensated for by the strong interfacial bonding between the filler and matrix. Therefore, the T_g of the nanocomposites reinforced with the 7-nm fillers was always higher than that of the neat BMI/DDM thermoset.

The nanocomposites filled with larger silica nanoparticles (SG20 and SG130) resulted in higher T_g values, compared to

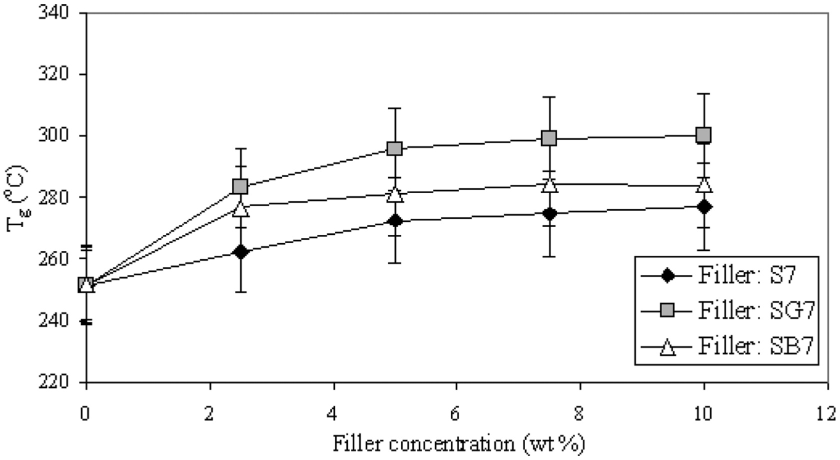

FIGURE 8. Variation of T_g with the filler concentration for various types of 7-nm silica particles modified with epoxide groups.

the SG7 systems (see the Supporting Information). This phenomenon could be due to the larger free volumes created by the SG7 due to its superior surface area compared to the SG20 and SG130. The higher free volume of the SG7 filler is expected to enhance the large-scale segmental motion of the polymer at the filler–matrix interface, leading to lower T_g values compared to the SG20 and SG130. Similarly, based on DSC and DMA studies, Sun et al.[44] reported that the T_g of the micrometer size silica–epoxy composites was higher than that of the nanosize silica composites (~25°C higher) at 20 wt%.

Conclusions

Preparation of SBNs was carried out with different sizes of nonmodified silica and silica with different surface modifiers. The presence of silica nanoparticles did not yield negative effects on the cure reaction of BMI/DDM matrices. In contrast, all the fillers, that is, S7, SB7, SG7, SG20, and SG130, showed some degree of catalytic effects on the cure reactions. The morphological studies, using a high-magnification SEM, showed that the surface modification of fillers could significantly improve the dispersion of the filler into the polymeric matrix and that the homogenous phase consisted mainly of discrete silica particles. The nanocomposites reinforced with surface-modified silica nanoparticles showed significant improvements in thermal mechanical properties, such as E' and T_g, over the neat BMI/DDM. A reduction in CTE due to the homogenous filler distribution and strong filler–matrix interactions was also observed. Additionally, E' was found to increase with decreasing particle size, whereas CTE decreased with decreasing particle size. These findings are attributed to the higher specific surface areas of the smaller silica nanoparticles, as compared to the larger ones. The T_g of the nanocomposites was found to decrease with decreasing particle size due to enhanced free volume at the smaller particle sizes. All the thermal mechanical properties increased with an increase in filler contents. The best thermal mechanical properties were obtained for the nanocomposites containing 10.0 wt% of SG7, namely, E': 14.1 GA (at 30°C), T_g: 300°C (TMA), α_1: 28.8 ppm/°C, and $T_{d\ (onset)}$: 451°C. Overall, the silica nanoparticles prepared in this study showed great potential as fillers in an SBN.

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