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Mild processing and characterization of silica epoxy hybrid nanocomposite

Chenggang Chen*, Alexander B. Morgan

University of Dayton Research Institute, 300 College Park, Dayton, OH 45469-0163, USA

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ABSTRACT

Previous research has shown that the inclusion of the spherical silica (SiO_2) nanoparticles into epoxy resin can achieve simultaneous improvement of fracture toughness and modulus. However, the glass transition temperature of the nanocomposite was significantly decreased when loading the nanosilica was higher than 5 wt.%. This perhaps was caused by utilization of the ultrasonication probe in the processing of these materials. In this paper, milder processing procedures were applied to make spherical silica epoxy nanocomposites while investigating if the homogeneous dispersion and morphology of the individual silica nanoparticle dispersed in the epoxy matrix could still be achieved. The results show that even at high loading of the silica nanoparticle, such as 30 wt.% silica, the perfect morphology of the nanocomposite could still be achieved with these milder processing conditions which indicates that ultrasonication is not needed. With the use of milder processing conditions, the glass transition temperature of the nanocomposite of 5 wt.% silica loading did not change, and the drop in the T_g was minimal for silica loading up to 15%, but some effects of self-polymerization of the epoxy were noted on T_g up to 30 wt.% loading of silica. Thermal analysis and flammability testing of the resulting materials suggest that nanosilica has only an inert filler effect (dilution of fuel) on flammability reduction and char yield increase, not a synergistic decrease in heat release as is often observed for clays and carbon nanotubes/nanofibers. So the mild and easy processing procedure only achieved uniform nanoscale morphology with excellent dispersion in the final nanocomposite, but also the effect on the change in the T_g can be minimized as nanosilica loading was increased.

1. Introduction

Epoxy resins have found extensive use in many industrial applications including coatings, adhesives, insulating materials in electrical and electronic applications, and advanced composites. With the large increase in commercially available nanophase materials, the use of these nanoparticles in polymer composites has been drawing great attention as they impart significant improvement in the properties of those polymer materials [1–4]. The incorporation of low-cost silica (SiO_2) nanoparticles into epoxy resin can significantly improve the mechanical properties [1,4–9], anticorrosion and wear resistance [10,11] and tailoring of electronic packaging properties [12,13]. Our previous research showed that the inclusion of the spherical silica nanoparticle into the epoxy resin can achieve simultaneous improvement of the fracture toughness and modulus, while there is no change in the strength and glass transition temperature (T_g) at low loading of the silica [1]. However, the T_g of the nanocomposite was significantly decreased when loading the nanosilica was higher than 5% [1]. As reported in our previous paper [1], the glass transition temperatures of the pure diglycidyl ether of bisphenol F with curing agent W (Epon 862/W epoxy) and epoxies containing 1.25, 5.0, 10.0, 15.0, and 20.0 wt.% silica nanocomposites were 154, 155, 153, 140, 121 and 102 °C, respectively. The significant reduction in the T_g of the nanocomposite at high loading we now believe is related to the utilization of the ultrasonication probe in the processing, which generally results in very high temperatures in the vicinity of the probe [14]. The local high temperature perhaps results in some homopolymerization of the epoxy (or thermal decomposition of the epoxy monomer), especially at high loading of the silica, which could act as a catalyst for the self-polymerization. The partial homopolymerization will affect the following Epon 862/amine stoichiometry, which will in turn affect the crosslinking density and therefore shift the T_g. The purpose of the utilization of the previously used intense ultrasonication probe in the processing was to achieve the best homogeneous dispersion of the silica nanoparticle in the epoxy matrix, so that simultaneous improvement of the modulus and toughness could be achieved. In fact, the nanosilica in used in the previous work (MEK-ST) is originally dispersed in methyl ethyl ketone as individual silica nanoparticles rather than as the aggregation of

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* Corresponding author. Tel.: +1 937 255 9066; fax: +1 937 258 8075.
E-mail address: chenggang.chen@wpafb.af.mil (C. Chen).

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those particles. While the manufacturer has not revealed the exact treatment for these silica nanoparticles, the characterization from thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and solid state nuclear magnetic resonance (^{29}Si NMR and ^{13}C NMR) indicated that the surface organic layer embodied ~3 wt.% of the dried nanosilica [1]. The surface consists of trimethylsilyl groups, short chain alkoxysilanes (possibly Si–OCH_3 and Si–OCH_2CH_3), and a small amount of hydroxyl (–OH) groups. So the surface has been modified to increase hydrophobicity over the native SiO_2 surface, yet the surface retains some hydrophilic and potentially reactive surface hydroxyl groups [1]. The dynamic light scattering (DLS) studies showed that most of the silica nanoparticles were individually dispersed in the methyl ethyl ketone without aggregation [1]. So perhaps it is not necessary to use the very intense ultrasonication probe to break the aggregated silica nanoparticles and achieve homogeneous dispersion of the silica nanoparticles in the epoxy matrix. Therefore, in this research a milder processing procedure was applied in the fabrication of the dispersion of the silica (MEK-ST again) in epoxy (diglycidyl ether of bisphenol F with curing agent W) to see whether the desired morphology of homogeneous dispersion of the silica nanoparticle in epoxy matrix and a small decrease in T_g could simultaneously be achieved at high loading of the silica nanoparticles. As a final study of these materials, micro-combustion calorimetry (MCC) testing of the silica/Epon 862/W nanocomposites was conducted to see if the uniform dispersion of silica would reduce material flammability like that seen in many polymer nanocomposites [15,16], or if the effects would not be as pronounced due to the aspect ratio of the nanoparticles [17,18].

2. Experimental

2.1. Materials

Epon 862 (diglycidyl ether of bisphenol F) and Epi-Cure curing agent W were purchased from Miller-Stephenson Chemical Company, Inc. The silica nanoparticle used is MEK-ST suspension, which was obtained from Nissan Chemicals. MEK-ST suspension has an average particle diameter of about 12 nm as a 30% weight dispersion in methyl ethyl ketone, according to the manufacturer.

2.2. Processing

2.2.1. High-shearing

In this processing procedure, the desired amount of Epon 862 and a corresponding amount of MEK-ST suspension with acetone were mixed using high-shear mixing in a sonication bath for 2 h. After mixing, acetone and methyl ethyl ketone were evaporated at ~65 °C in a vacuum oven. The corresponding stoichiometric curing agent W (Epon 862:curing agent W, 100:26.3, wt.) was added to the resultant mixture and mixed using a stir-bar at ~65 °C for 20 min. The mixture was degassed in a vacuum oven and cured in a silicone mold using the following curing cycle for Epon 862 with curing agent W: heat the mixture in an oven to 121 °C over 30 min, hold at 121 °C for 2 h, then heat to 177 °C over 30 min and hold for another 2 h at 177 °C, and finally cool to room temperature.

2.2.2. Stir-bar mixing

In the stir-bar mixing process, the epoxy resin and the corresponding amount of MEK-ST suspension were mixed using a stir-bar at room temperature for 2 h. The solvent was evaporated at ~65 °C in a vacuum oven. The silica/Epon 862 mixture was then mixed with a stoichiometric amount of curing agent by a stir-bar at ~50 °C for 5 min. The mixture was degassed and cured using the same curing cycle as above.

2.3. Characterization

Samples for transmission electron microscopy (TEM) analysis were microtomed with a Leica EM UC6 Ultramicrotome (with FC6 attachment) with sections placed onto carbon-coated Cu grids (200 mesh). TEM was performed using a Hitachi H-7600 transmission electron microscope with accelerating voltages of 100 kV. Dynamic mechanical analysis (DMA) was run on a TA Instruments Q800 at steady frequency (1 Hz) at 2 °C/min from room temperature to 200 °C with geometry on a single cantilever. Thermogravimetric analysis (TGA) was carried out with a TA Instruments Q5000 IR under nitrogen and air at a heating rate of 10 °C/min from room temperature to 900 °C. All TGA data were collected in triplicate, and the data shown are an average of the triplicate experiments. Differential scanning calorimetry (DSC) was performed using a TA Instruments differential scanning calorimeter (Q1000) ramped at 2 °C/min from room temperature to 300 °C under nitrogen. MCC tests (MCC-1, Govmark) were run under nitrogen at a heating rate of 1 °C/s from 250 to 750 °C using method A of ASTM D7309 (pyrolysis under nitrogen). Each sample was run in triplicate to evaluate reproducibility of the flammability measurements.

3. Results and discussion

3.1. Nanoparticle dispersion and morphology

Based on the processing intensity, stir-bar mixing is the mildest, high-shear mixing in the presence of the solvent is next, and ultrasonication is the most intense. This could be clearly concluded in our previous work [19,20] covering the research of epoxy nanocomposite with pristine (nonfunctionalized) silica. When the pristine silica nanoparticle was used, the morphology of pristine silica/Epon 862/W nanocomposite after different processing procedures were as follows [19,20]: the stir-bar mixing procedure resulted in inhomogeneous dispersion of the aggregated silica nanoparticles with the size of the aggregation several hundred nanometers. In addition, the mixture of the pristine silica with Epon 862 through the slow-shear mixing was not stable and the silica aggregation was precipitated overnight. The high-shear mixing procedure gave inhomogeneous but relatively smaller aggregation of the silica nanoparticles from 50 nm to about 500 nm. The mixture of the pristine spherical silica particle with Epon 862 produced via these routes was found to be stable for several days. Ultrasonication processing, however, gave a morphology of homogeneous dispersion of the uniform (~100 nm) aggregated silica nanoparticles. The mixture of Epon 862 with the pristine spherical nanoparticles after ultrasonication was very stable, and no pristine spherical silica was precipitated even after one month. So the ultrasonication procedure can help to achieve the maximum dispersion.

Our previous research [1] used the ultrasonication procedure and organically-treated silica nanoparticles which, when received, were suspended in methyl ethyl ketone. Through ultrasonication, the morphology of homogeneous dispersion of the individual silica nanoparticle in the epoxy matrix was achieved with no aggregation observed [1]. However, the T_g of the nanocomposite produced via this technique was significantly decreased when the loading the nanosilica was more than 5 wt.%. So perhaps for the originally well dispersed silica suspension, we can just use a relatively milder processing procedure to see whether the good dispersion of the silica nanoparticle can still be achieved. First, the high-shear mixing was applied for the silica nanoparticle methyl ethyl ketone suspension with Epon 862 in the presence of acetone. After the evaporation of the solvent, curing agent W was added and the mixture was cured. TEM images of the 5 wt.% silica/Epon 862/W nanocomposite after the high-shear mixing procedure were taken and are shown in Fig. 1.

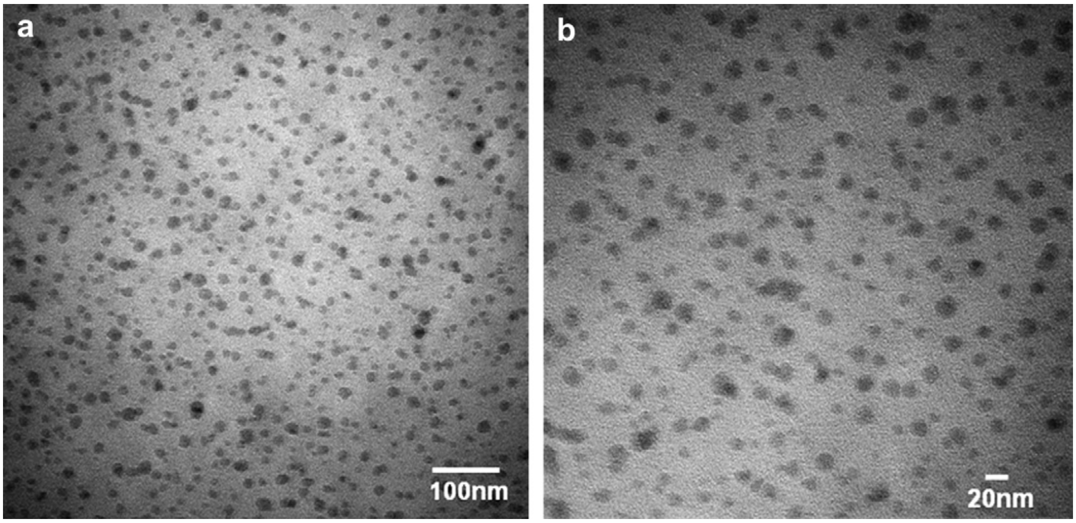

Fig. 1. TEM images (different magnification) of 5 wt.% silica/Epon 862/curing agent W nanocomposite through high-shear mixing.

The TEM images clearly showed that the individual silica nanoparticles are homogeneously and continuously dispersed in the whole epoxy matrix. Each individual silica nanoparticles with sizes ranging from 12 nm to 20 nm are very well dispersed in the epoxy resin, and there is no aggregation of the silica nanoparticles. Therefore high-shear mixing procedures (intensity less than that of ultrasonication) can achieve the perfect morphology and uniform dispersion of the organically-treated nanoparticle silica. The next step is using an even milder and easier processing procedure of low-shear mixing (stir-bar mixing) without using additional solvent. The silica nanoparticle suspension was mixed with Epon 862 using stir-bar mixing, and the solvent was evaporated after the completion of mixing. Then the mixture was cured with curing agent W. TEM images of the 5 wt.% silica/Epon 862/W nanocomposite after the low-shear mixing procedure were taken and are shown in Fig. 2. The TEM images clearly show that the silica nanoparticles are homogeneously dispersed in the epoxy matrix. The size of the individual silica nanoparticles ranged from 12 nm to 20 nm, just as seen with high-shear mixing. There were a few aggregations of the silica nanoparticles observed by TEM such as double or triple particle agglomerates. Therefore, the low-shear mixing procedure can achieve the almost perfect morphology and nanoscale dispersion.

Our next study was to investigate the effect of the high loading of the silica nanoparticles on the morphology when utilizing these lower intensity mixing techniques. The 15 wt.% Silica/Epon 862/W nanocomposite was made through the low-shear mixing procedure (stir-bar), and its TEM images are shown in Fig. 3. The ~15 nm silica nanoparticles are homogeneously and continuously dispersed in the whole matrix. There is almost no aggregation of the silica nanoparticles. In addition, 20 wt.% silica loading was also tried using the low-shear mixing procedure. The TEM images of the 20 wt.% silica/Epon 862/W nanocomposite after the low-shear mixing procedure were taken and are shown in Fig. 4. Again, it can be clearly seen that that the silica nanoparticles are homogeneously and continuously dispersed in the whole matrix. Amazingly, there is almost no aggregation of the silica nanoparticles. So the low-shear mixing procedure can also achieve perfect morphology even at high silica loading of 20 wt.%.

Silica loading higher than 20 wt.% may be preferred for some nanocomposite applications where a hard surface is needed to resist

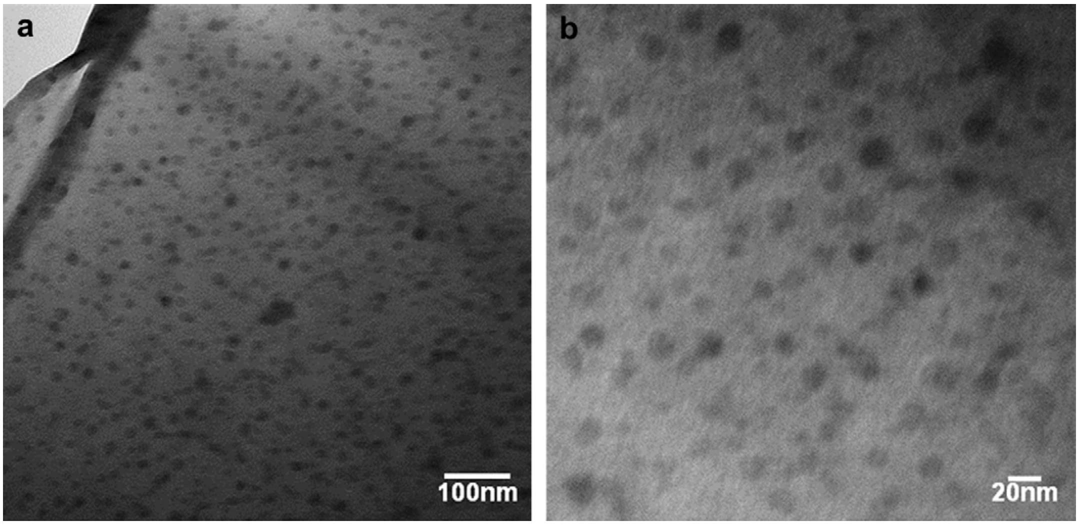

Fig. 2. TEM images of 5 wt.% silica/Epon 862/W nanocomposite through low-shear mixing.

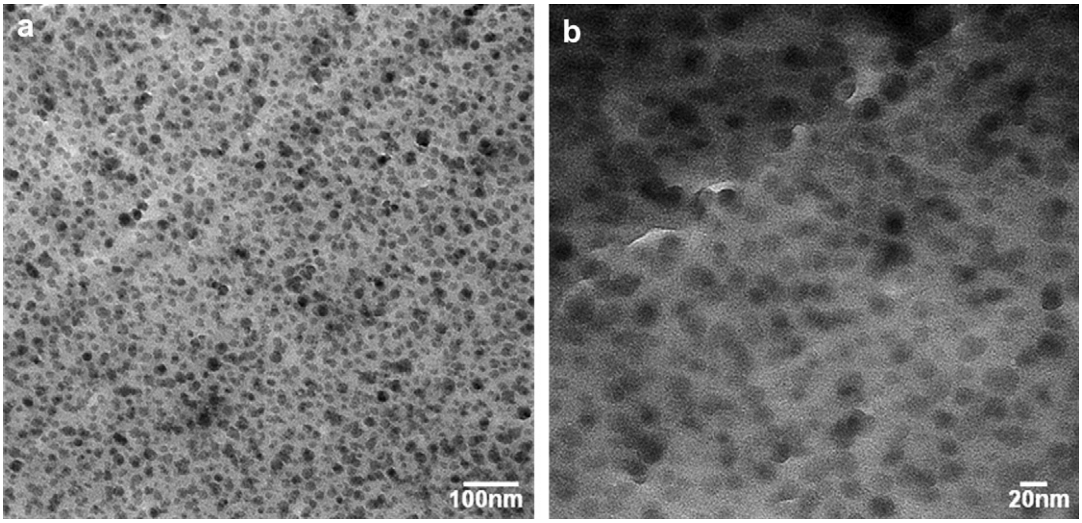

Fig. 3. TEM images of 15 wt.% silica/Epon 862/W nanocomposite through low-shear mixing.

abrasion or erosion conditions. So in this research, even higher loading of the silica nanoparticles (30 wt.%) was tried. Making the 30 wt.% silica/Epon 862/W nanocomposite was smooth and successful. The TEM images of the 30 wt.% silica/Epon 862/W nanocomposite after the low-shear mixing procedure are shown in Fig. 5. Perfect morphology of individual silica nanoparticles homogeneously and continuously dispersed in the whole epoxy matrix was achieved. It appears from the TEM images that the silica nanoparticles are even denser than the epoxy polymer matrix, which may suggest that the resulting inorganic/organic structure appeared as a hybrid stitching net.

The difference of the morphology of the nanocomposite between our previous work [19,20] and this present work is due to the different silica used. The silica used before [19,20] is the pristine silica nanoparticle (no organic treatment – silica is organophobic), while in this present work and the work in Ref. [1], the silica nanoparticle has an organic treatment (silica is organophilic) [1]. There is a lot of silanol group in the surface of the pristine silica nanoparticle, which can form strong hydrogen bonding between the nanoparticles. These nanoparticles are easily aggregated together, and those same hydrogen bonds make dispersal and breakup of the aggregates difficult in polymeric media. So the more intense the processing procedure, the better dispersion can be achieved. However, even the most intense processing can only achieve the homogeneous dispersion of the aggregated nanoparticles and not a full breakup of the original particles into their primary components (individual pristine silica nanoparticles) [19,20]. By comparison, the silica nanoparticle in the present study was covered or at least partially covered by organic groups, although there are likely some silanol groups still present on the surface [1]. This treatment and lower concentration of silanol groups means that the interaction between the silica nanoparticles is significantly reduced. The silica nanoparticle is individually dispersed in the methyl ethyl ketone in the starting material with no additional shear needed [1]. Therefore, since the material is already dispersed to begin with, the milder processing procedure (both high-shear and low-shear) used in this research can still achieve the same perfect nanoscale morphology as that in Ref. [1] without the need for intense ultrasonication probe. In effect, due to the organic treatment on the silica, nanocomposite synthesis becomes an easy solvent mediated solution mixing experiment since the epoxy and the nanosilica are both effectively "in solution" and mix freely.

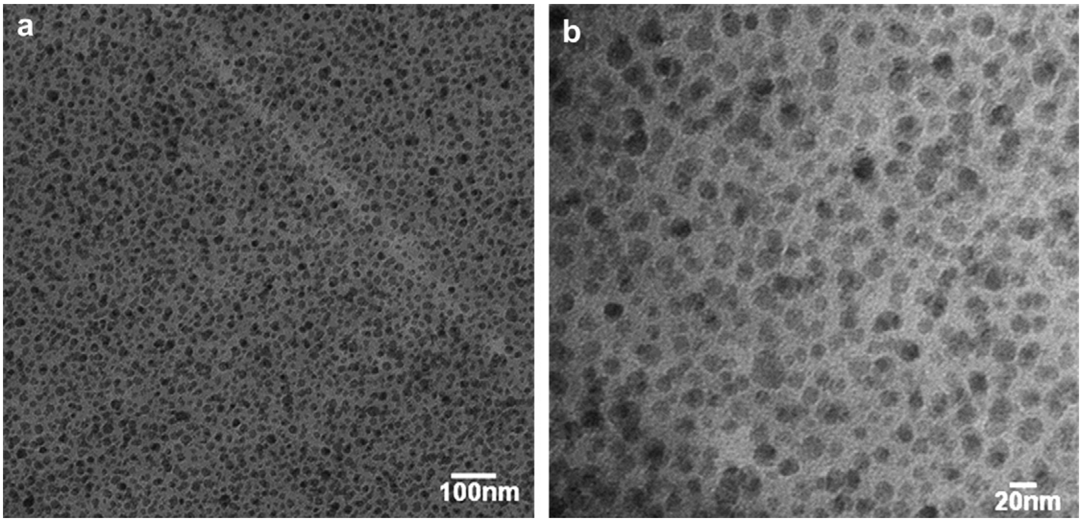

Fig. 4. TEM images of 20 wt.% silica/Epon 862/W nanocomposite through low-shear mixing.

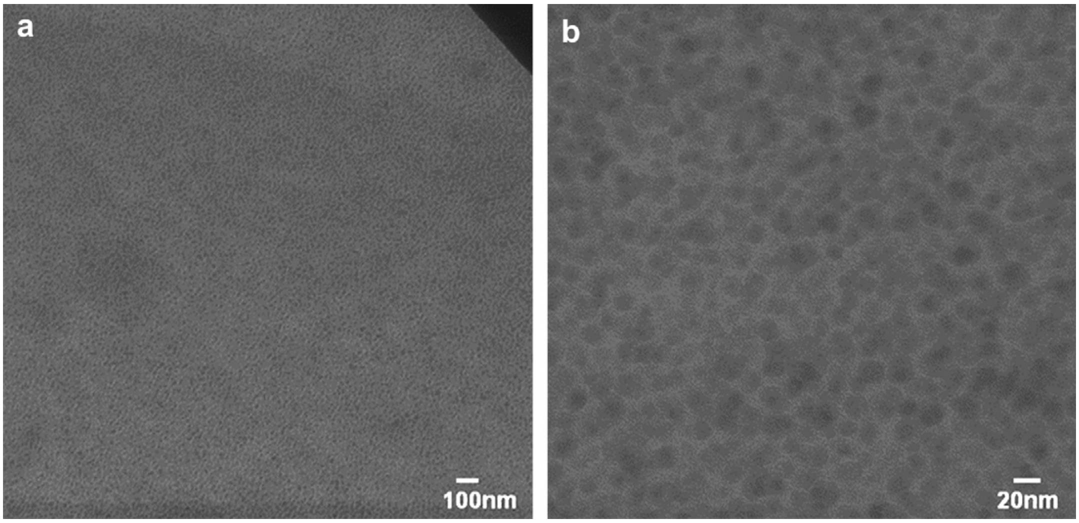

Fig. 5. TEM images of 30 wt.% silica/Epon 862/W nanocomposite through low-shear mixing.

3.2. Mechanical and thermal (T_g) properties

Now that it has been determined that the low-shear mixing procedure can achieve homogeneous dispersion of the silica nanoparticles in epoxy even at high loading, it is important to check whether mild processing can minimize the effect on the T_g of the nanocomposite. DMA was carried out for these nanocomposite samples. The glass transition temperatures of the nanocomposites with different silica loadings were determined based on the maximum tan δ curve, the maximum of the loss modulus (G''), and the transition of the storage modulus curve (G'). The summary of the glass transition temperatures of the silica/Epon 862/W nanocomposites through low-shear mixing is shown in Fig. 6. There is minimal change in the glass transition temperature of the nanocomposite for the silica loading up to 15 wt.%. Based on the maximum tan δ curve, the comparison of the glass transition temperatures of the nanocomposites through low-shear mixing with those through ultrasonication is shown in Fig. 7. The T_g for pure resin is 155 °C, which is well consistent with that (154 °C) in our previous paper [1]. The T_g of 5 wt.% silica/Epon 862/W nanocomposite is 158 °C, which is close to 153 °C for the 5 wt.% silica/Epon 862/W nanocomposite after ultrasonication [1]. Both are close to that of the control epoxy resin, indicating the processing procedure has little effect on the crosslinking density of the polymer when the loading of the silica is less than 5%. Amazingly, the T_g of 15 wt.% silica/Epon 862/W nanocomposite is 150 °C, which is a very small decrease compared with that of pure resin (155 °C) (the reduction of T_g (ΔT_g): 5 °C). Compared with the T_g (121 °C, ΔT_g: 33 °C) of 15 wt.% silica/Epon 862/W nanocomposite after ultrasonication procedure [1], the decrease in the T_g for the nanocomposite produced through the low-shear mixing procedure is minimal. The T_g of 20 wt.% silica/Epon 862/W nanocomposite through low-shear mixing is 142 °C, which is only 13 °C lower than that of pure resin. Compared with the T_g (102 °C, ΔT_g: 52 °C) of 20 wt.% silica/Epon 862/W nanocomposite after ultrasonication procedure [1], the decrease (13 °C) in the T_g for the 20 wt.% silica/Epon 862/W nanocomposite produced through the low-shear mixing procedure is very small. Via low-shear mixing, even the highest silica loading of 30 wt.% results in a T_g of 128 °C, only a reduction of T_g by 27 °C, which is almost half of the reduction of T_g for 20 wt.% silica/Epon 862/W nanocomposite (low silica loading, 30% versus 20%) produced via the ultrasonication procedure. So the milder processing procedure not only helps achieve uniform dispersion of the nanoparticles, but it really helps to limit the reduction in the glass transition temperature for the nanocomposite, thus ensuring that these nanocomposites will still have high use temperatures in structural applications.

In regards to the low-shear mixing, some explanation is needed for explaining the nonlinear T_g reduction trends seen in this paper,

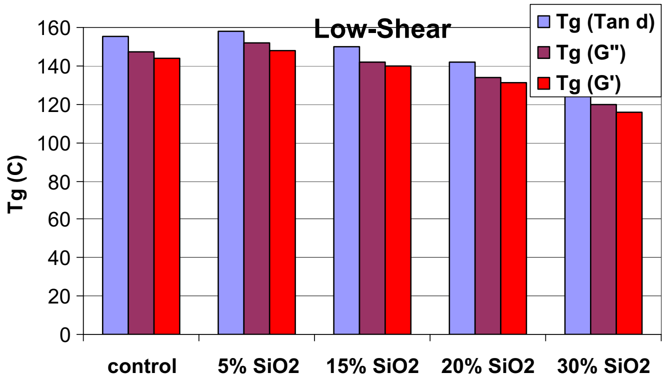

Fig. 6. The glass transition temperatures of the nanocomposite with different silica loading (weight) through the low-shear mixing based on tan δ curve (max), loss modulus max, and transition of the storage modulus of the dynamic mechanical analysis.

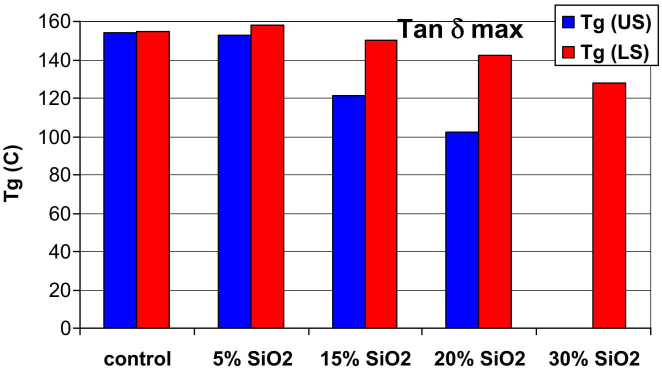

Fig. 7. The comparison of the glass transition temperature of the nanocomposite of the different silica loadings (weight) through the low-shear mixing and those with ultrasonication procedure based on tan δ curve (max) of the dynamic mechanical analysis.

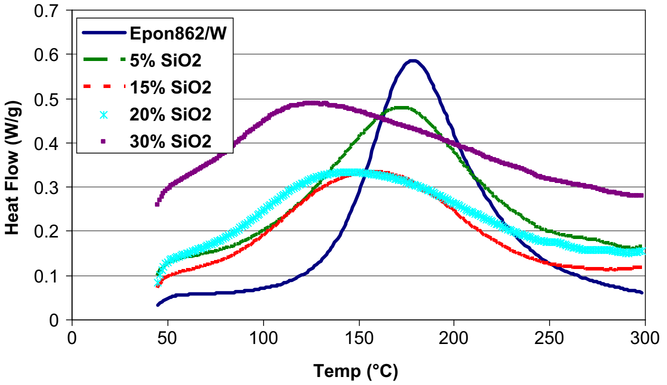

Fig. 8. DSC curves of the pure Epon 862/W, 5 wt.% silica/Epon 862/W mixture, 15 wt.% silica/Epon 862/W mixture, 20 wt.% silica/Epon 862/W mixture, and 30 wt.% silica/Epon 862/W mixture (all through low-shear mixing).

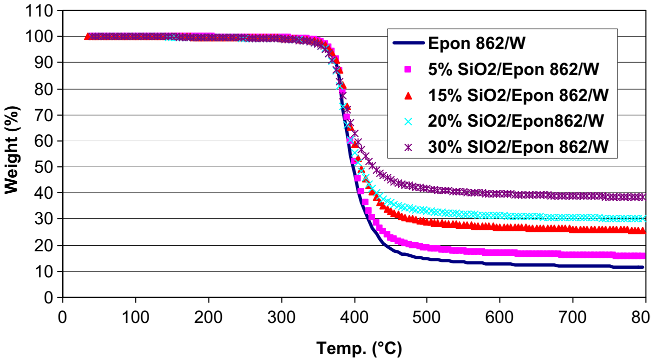

Fig. 10. TGA data of the pure Epon 862/W, 5 wt.% silica/Epon 862/W nanocomposite, 15 wt.% silica/Epon 862/W nanocomposite, 20 wt.% silica/Epon 862/W nanocomposite, and 30 wt.% silica/Epon 862/W nanocomposite (all through low-shear mixing).

especially for the 20–30 wt.% silica loadings. The reason for the greater reduction in T_g at high loading of nanosilica in contrast to the minimal reduction in the T_g at loadings up to 15 wt.% nanosilica is related to the kinetics of epoxy polymerization in the presence of silica. DSC studies were carried out for the silica/Epon 862/W mixture after the stir-bar procedure. The DSC data of the silica/Epon 862/W mixtures with different silica loading are shown in Fig. 8. The onset temperatures for curing were 135, 98, 81, 73, and 61 °C for 5, 15, 20, and 30 wt.% Silica/Epon 862/W mixtures, respectively. The earlier onset temperature for curing for higher silica loading is related to the concentration of silanol group in the mixture. Although the silica surface was treated with the organic group, it still likely contains some amount of silanol groups. The silanol group can provide a proton to oxazine to make a cation, which will make the oxazine cation (a protonated epoxy ring) more susceptible to nucleophilic attack. The amine will more likely attack the nucleophilic oxazine cation to make the polymerization occur. Therefore, the silanol group has some catalytic effect for the epoxy polymerization [13,21,22], accelerating it and causing initiation of polymerization to occur at lower temperatures. As the silica level is increased, the concentration of silanols obviously increases, but more importantly, the very small particle size of the silica results in a rapid increase in surface area available for reaction as silica loading is increased. Therefore, the higher loading of silica results in the initiation of polymerization at lower temperatures. However, if the silanol groups only cause early epoxy polymerization between Epon 862 and curing agent W to occur, then it should just change the kinetics of polymerization, and there should be no change of the crosslinking density which is reflected in the T_g. When the loading is higher than 15 wt.%, there is a significant reduction in T_g so we propose that the silica not only catalyzes polymerization of the epoxy, it likely also causes epoxy self-polymerization which would result in a lower T_g. The DSC studies were carried out for the silica/Epon 862 without curing agent W, the data for which are shown in Fig. 9. In order to make the comparison easy, the DSC data of the mixtures of the silica/Epon 862 with stiochiometric curing agent W were also included in the figure. The DSC study shows that there is tiny self-polymerization of Epon 862 for the 15 wt.% silica/Epon 862 mixture, and self-polymerization occurs after 180 °C, which is a temperature not seen during the processing of Epon 862/W during its normal process/cure cycle. While there are small amounts of self-polymerization of Epon 862 for the 20 wt.% silica/Epon 862 mixture at low temperature, there are very significant amounts of self-polymerization of Epon 862 noted for the 30 wt.% Silica/Epon 862 mixture. Therefore, since we know that the amount of silanols available on the surface of the nanosilica is low, we can conclude that only above 15 wt.% loading is there enough surface

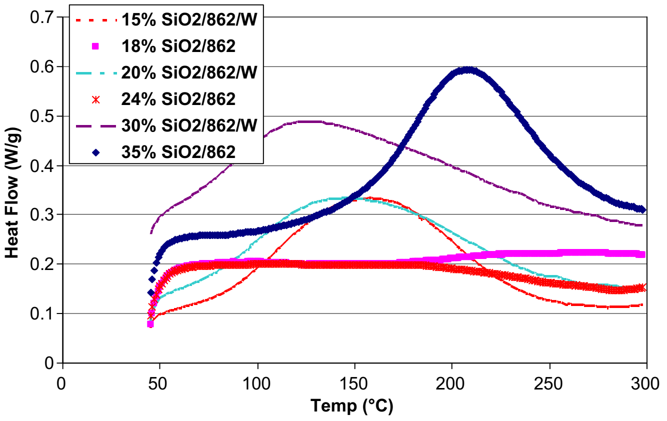

Fig. 9. DSC curves of 15 wt.% silica/Epon 862/W mixture, 18 wt.% silica/Epon 862 mixture, 20 wt.% silica/Epon 862/W mixture, 24 wt.% silica/Epon 862 mixture, and 30 wt.% silica/Epon 862/W mixture, and 35 wt.% silica/Epon 862 mixture (all through low-shear mixing).

Table 1
Summary of TGA data for silica/Epon 862/W nanocomposite samples.

Sample	wt.% char nitrogen	Peak decomp temp (°C)	wt.% char air	Peak decomp temp (°C)
Epon 862/W	9.42	405	1.96	382
	9.86	405	3.45	385
	9.76	403	1.23	384
Averages	9.68	404	2.21	384
Epon 862/W	13.82	404	5.98	389
+5 wt.% silica	13.39	403	6.03	389
	13.55	405	6.54	389
Averages	13.59	404	6.18	389
Epon/862/W	24.11	407	16.26	387
+15 wt.% silica	23.54	405	15.91	387
	23.23	405	16.11	386
Averages	23.63	406	16.09	387
Epon 862/W	28.33	405	20.33	386
+20 wt.% silica	28.92	404	20.54	387
	28.37	407	20.54	390
Averages	28.54	405	20.47	388
Epon 862/W	37.02	406	29.56	392
+30 wt.% silica	37.07	405	29.37	392
	37.13	406	30.51	392
Averages	37.07	406	29.81	392

Table 2
Heat release data for silica/Epon 862/W nanocomposite samples.

Sample	Char yield (wt. %)	HRC peak(s) value (W/g)	Peak decomp temp (°C)	Total HR (kJ/g)	% Total HR reduction	Char notes
Epon 862/W	11.49	397, 355	397	24.2	n/a	Black, shiny foamy char
	11.37	376, 357	396	24.3	n/a	
	11.38	368, 304	392	23.9	n/a	
Averages	11.41		395	24.1	n/a	
Epon 862/W +5 wt.% silica	15.79	358, 374	397	23.3	3.5	Black foamy char on sides of pan
	15.63	378, 343	392	22.9	5.1	
	15.31	358, 354	395	23.5	2.6	
Averages	15.58		395	23.2	3.7	
Epon 862/W +15 wt.% silica	24.92	370, 353, 307	405	20.3	15.9	Black foamy char on sides of pan
	25.22	315, 244, 268	396	20.0	17.1	
	25.46	401, 295, 259	405	20.1	16.7	
Averages	25.20		402	20.1	16.6	
Epon 862/W +20 wt.% silica	29.05	403, 402	411	20.1	16.7	Black foamy char on sides of pan
	28.99	408, 391	411	20.2	16.3	
	29.04	405, 386	403	20.2	16.3	
Averages	29.03		408	20.2	16.4	
Epon 862/W +30 wt.% silica	38.32	362	404	17.5	27.5	Black granules, no flow
	38.65	342	404	17.4	27.9	
	38.26	351	403	17.6	27.1	
Averages	38.41	352	404	17.5	27.5	

area and silanol concentration available to critically promote homopolymerization of the epoxy over polymerization of the epoxy with the amine curing agent. While this clearly indicates that 15 wt.% is probably the practical limit for loading nanosilica into epoxy without degradation of the T_g, the effects of mixing clearly has a far larger effect. The use of low-shear, stir-bar mixing does not affect epoxy polymerization or T_g up to 15 wt.%, while the use of ultrasonication causes large changes and reductions in T_g at all loading levels of nanosilica. Therefore the use of ultrasonication is not only not needed for dispersion of organically-treated nanosilica into epoxy, it is also damaging to the epoxy matrix and perhaps should be avoided. The likely cause for ultrasonication causing such a decrease in T_g is that it causes localized superheating which either decomposes epoxy monomer or provides enough energy to open up the epoxy ring and yield more homopolymerization product versus the polymer product of the Epon 862 with amine (curing agent). Clearly, some additional chemical studies would be needed to elucidate this mechanism, but the data are clear that ultrasonication is not the preferred method.

3.3. *Thermogravimetric analysis and micro-combustion calorimetry*

The thermal stability of the epoxy resin after the addition of the silica nanoparticle was also studied through TGA under air and nitrogen. The TGA analysis in air was done to deliberately remove all of the epoxy to determine the actual loading of silica in the sample. The TGA analysis in nitrogen was done to determine if the silica had any effect on thermal stability of the epoxy where anaerobic thermal decomposition mechanisms dominate such as those occurring under the flame front where polymer converts to pyrolyzed fuel in a fire.

The TGA data are shown in Fig. 10 and tabulated in Table 1. Overall the data trends nicely with the amount of silica added to the

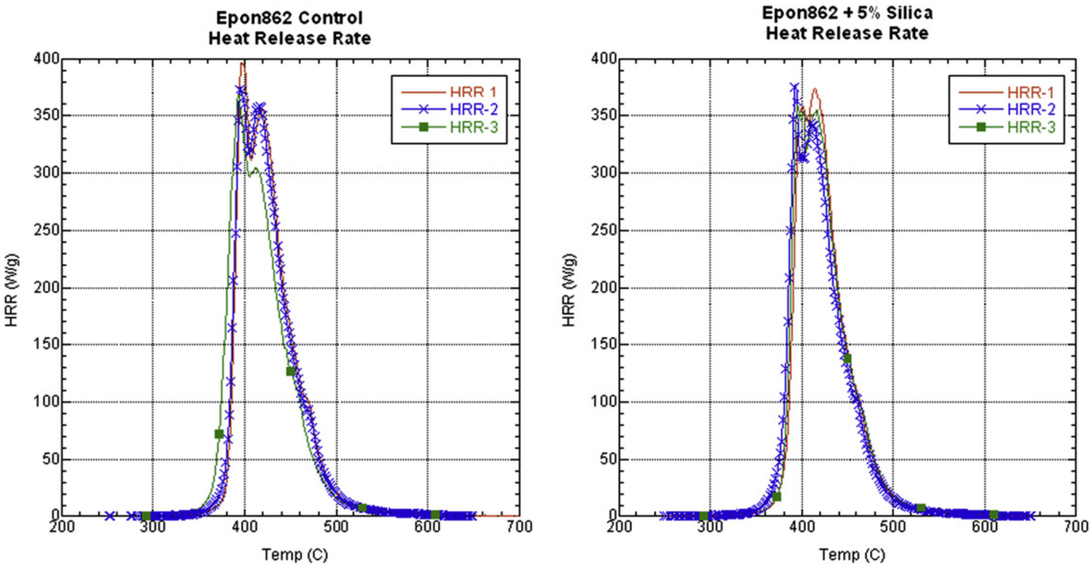

Fig. 11. Heat release rate curves for pure Epon 862/W (left) and 5 wt.% silica/Epon 862/W nanocomposite (right).

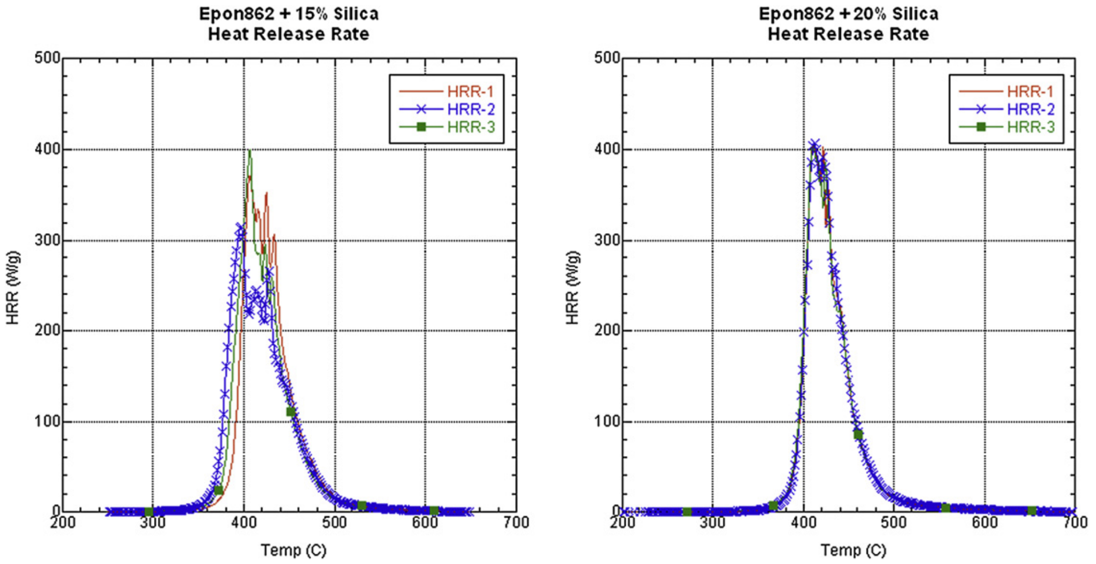

Fig. 12. Heat release rate curves for 15 wt.% silica/Epon 862/W nanocomposite (left) and 20 wt.% silica/Epon 862/W nanocomposite (right).

material. As silica levels are increased, the char yields increase an amount equal to the level of silica added. This is shown clearly in the TGA data collected in air, but the trends can be seen in the nitrogen TGA data as well. What is noteworthy beyond this linear trend is that the silica does not change thermal stability of the epoxy much at all. As silica levels are increased, the peak decomposition temperatures are unchanged compared to the base epoxy, suggesting that the silica has little to no effect on the polymer decomposition chemistry. The lack of effect on polymer decomposition can be seen in the flammability results as well.

Flammability data collected from the MCC (Table 2) show that the presence of the nanosilica reduces flammability in a linear manner. Specifically, as more silica is added, the total heat release (total HR) is reduced by a similar amount. So for the 5 wt.% silica/Epon 862/W nanocomposite sample, the total HR is reduced by about 3–5%; for 15 wt.% silica/Epon 862/W nanocomposite sample, the total HR is reduced by 16%; and for the 30 wt.% silica/Epon 862/W nanocomposite sample, the total HR is reduced by 27%. The total HR reduction for 20 wt.% silica/Epon 862/W nanocomposite is the same as that of the 15 wt.% silica/Epon 862/W nanocomposite sample (∼16%), but the char yields are higher for the 20 wt.% silica/Epon 862/W nanocomposite sample. We believe that these measurements are just within the region of error for the MCC technique, which is typically ±10% for oxygen consumption calorimetry methods. The other key measurement of heat release, peak heat release rate (peak HRR) is not greatly reduced much at all until 30 wt.% silica loading, and even then the reduction in peak HRR is not very large. Further, the heat release curve shapes are almost identical between the Epon 862/W control sample (Fig. 11 left) and the other samples tested (Fig. 11 right, and Figs. 12 and 13). So with this similarity in behavior one can make the argument that this particular form of nanosilica only reduces flammability by dilution in that as epoxy is replaced with nonflammable silica, the total HR is reduced but peak HRR is unchanged. These results collected are unusual for a polymer nanocomposite in that the nanoparticles do not synergistically reduce flammability and in this case act strictly as inert fillers. We believe that the lack of synergistic heat release reduction is due to the lack of a network structure formed by the nanoparticles, so there is no net reduction in mass loss rate which in turn would slow down heat release rates [23,24]. Further, even though silicas by themselves have shown reductions in flammability due to hydrogen bonding that slows down mass loss during polymer decomposition [17,25,26], this particular system does not show that behavior. Therefore it appears that the surface chemistry of the nanosilica does not change the mass loss rate (which appears to be the case from the TGA data collected) which in turn does not lower flammability and on top of the lack of a network structure, the nanosilica only acts as an inert filler. Still, the silica does not make flammability worse, so we can argue that the lower total HR is still an improved flammability property when compared to the base resin.

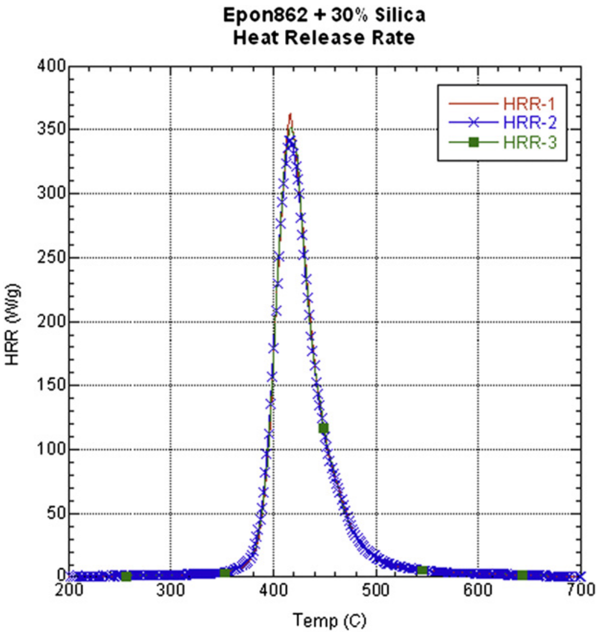

Fig. 13. Heat release rate curves for 30 wt.% silica/Epon 862/W nanocomposite.

4. Conclusions

Milder processing procedures, including the high-shear and low-shear mixing, were applied to make spherical silica epoxy nanocomposite with silica nanoparticle in methyl ethyl ketone suspension as starting material. The use of this solvent blending technique along with very low-shear enabled us to obtain a morphology of the individual silica nanoparticles dispersed in epoxy matrix homogeneously. Further, such dispersions could be continuously achieved for the nanocomposite even at high loading of the silica nanoparticle (up to 30 wt.%).

The T_g of the nanocomposite of 5 wt.% silica loading has no change, as expected, and the drop in the T_g is minimal for the silica loading up to 15% compared to that obtained previously with ultrasonication. The reductions in T_g (ΔT_g) are 13 °C and 52 °C for the 20 wt.% silica/Epon 862/W nanocomposite when using low-shear mixing and ultrasonication, respectively. While there was a large reduction in T_g at 30 wt.% silica loading using this low-shear technique, the drop in T_g was less than that obtained with 20 wt.% silica loading dispersed via the ultrasonication procedure. DSC studies show that there is very small self-polymerization of Epon 862 for the 15 wt.% silica/Epon 862 mixture in the low-shear mixing procedure, and no self-polymerization detected for the 5 wt.% loading level. So, for the silica loading lower than 15 wt.% in the low-shear mixing procedure, there is a very small change in the crosslinking density, and the change in the glass transition temperature is very limited. The small amounts of self-polymerization of Epon 862 in the 20 wt.% silica/Epon 862 mixture begin to increase though, due to proposed changes in the stoichiometry of epoxy caused by silanol groups on the silica now in a critical enough concentration to change polymerization chemistry, and thus the crosslinking density of epoxy resin is reduced to some extent (13 °C of ΔT_g). This trend is increased with more self-polymerization noted for Epon 862 with 30 wt.% Silica/Epon 862, which resulted in an even larger drop in T_g with 27 °C of ΔT_g. Still, as mentioned previously, this reduction at 30 wt.% silica is still less of a reduction in T_g (effective use temperature of the epoxy) when compared to the 20 wt.% material.

The TGA studies showed that there is almost no change in the decomposition temperatures for the nanocomposite, but the char yield for the nanocomposite was increased in a linear manner as more silica was added, the char yield increased. From a flammability perspective the total increase in char was reflected in the lowering of the total HR for these samples, but the nanosilica only reduced the total HR by acting as an inert filler. It did not slow down the mass loss rate, so peak HRR was mostly unchanged, even with up to 30 wt.% silica loading. This is an unusual result for a nanocomposite, but the lack of peak heat release flammability reduction can be explained in light of the fact that no network structure is formed by the nanosilica during thermal decomposition and burning of the polymer and the surface chemistry of the silica did not enable any changes in polymer decomposition and decrease in mass loss rate.

Therefore, the use of a mild and easy processing procedure not only achieves a morphology with excellent dispersion in the hybrid nanocomposite, but also the effect on the change in the T_g can be minimized. Flammability is not made worse and is improved in regards to total HR (fuel load), so the addition of nanosilica improves overall mechanical properties makes the material more fire safe (but not flame retardant) compared to the base epoxy. When looking at this data in relation to the previous study on this material [1] we can see that since mild mixing achieved excellent dispersion of the nanoparticles, we have eliminated the effects of mixing and processing on polymer properties and instead have generated results which are solely due to nanoparticle chemistry and loading levels in the polymer. So while low intensity mixing is a more viable process for researchers and industrial practitioners, it is an important finding here that these particular nanoparticles do not require high-shear/high intensity mixing to break apart their primary particle aggregates. Indeed, by avoiding the high intensity mixing we have ensured that no damage occurred to the polymer during processing allowing the study of just nanoparticle effects on polymer properties that have been reported in this paper.

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