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The use of nanosilica in epoxy resins

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The Use of Nanosilica in Epoxy Resins

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THE USE OF NANOSILICA IN EPOXY RESINS

BY

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CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science in Polymer Science and Engineering.

04/24/08

Date

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Abstract

An investigation of the use of nanosilica in diglycidyl ether of bisphenol A (DGEBA), diglycidyl ether of bisphenol F (DGEBF) and cycloaliphatic epoxy resins is conducted. Commercial nano-SiO_2 dispersed epoxy products were used as fillers at incremental wt% concentrations. The mechanical and thermal properties, including coefficient of thermal expansion (CTE), modulus, thermal stability, fracture toughness, and moisture absorption, were determined by TMA, DMA, TGA, Ecosphere moisture. All epoxy resins have shown an improvement in CTE due to the much lower CTE of the fillers. The moduli of all epoxy systems were also increased by addition of nanosilica due to the large boundary surface created by nanosilica. In general, the theoretical predictions for CTE and modulus agreed well with measured values. Except for the cycloaliphatic system, the addition of nanosilica resulted in a reduction of the glass transition temperature (T_g). Interestingly, the fracture toughness, thermal stability and moisture absorption are also found to be improved with addition of nanosilica particles.

Introduction

Epoxy resins are widely used in many industries including coatings, electrical, automotive, aerospace, and civil, as well as the chemical industry. Due to their low density along with their good adhesive and mechanical properties, epoxy resins have become a promising material for high performance applications in the transportation industry, usually in the form of composite materials. Inorganic fillers in epoxy resins have been extensively studied as an approach to improve thermal and mechanical properties of epoxy resins. Improvements in properties such as stiffness and strength of the polymer matrix have been found with incorporation of traditional fillers with dimensions usually on the order of a micron [1-4]. However, there are some drawbacks in using such fillers, for example, a reduction in strain to failure, reduction in impact strength, and sometimes in fracture toughness [2-4].

Recent literature reports have recognized the distinct size effect between microscale inorganic particle and nanoscale inorganic particle on epoxy resin behaviors [1-4]. These reports indicate that nanoparticles can improve the stiffness of polymers more dramatically than micro-fillers. Bagheri and Pearson also found that the use of smaller rubber particles resulted in material with better toughness [5]. Kinloch and coworkers have shown that the addition of nano-SiO_2 particles to a typical rubber-toughened adhesive, based upon a two part epoxy formulation, may increase the glass transition temperature and single-lap shear strength [2]. However, the benefit in using nanoparticles in polymers is still not well understood and warrants additional studies. Ultimately, the basic question is how the polymer properties change with incorporation of nanometer scale particles.

It is well known that the shape of the fillers, the size of the fillers and amount of fillers applied to the composites strongly affect the composite properties. The increase of specific surface area and contents of fillers enhance the mechanical and impact properties of composite. When the size of fillers becomes smaller and the loading of fillers become higher, the viscosity of composite resin will be too high to process. The interfacial strength will be a more important factor due to their increased surface area of fillers. Therefore, the nanocomposite effects can only be effective if the nanoparticles are well dispersed in the surrounding polymer matrix. A considerable improvement of the mechanical and thermal properties of polymer nanocomposite has been shown at very low filler volume content [2]. Many researchers have found difficulty of dispersing those particles into the polymer matrix at nanoscale level with conventional processes, e.g. mechanical mixing, melt compounding, solution bending, high shear mixing and in situ polymerization. The extremely high surface energy of the small particles leads to agglomeration during mixing, consequently resulting in property degradation [6].

Surface chemistry has been studied for understanding the effect of nanoparticle on the polymer matrix, particle-matrix adhesion. Zhang et al utilized physical and chemical approaches to modify the surface of nanoparticles to attain a good dispersion of inorganic fillers [7]. The surface modification by grafting of organosilane coupling agents on nanosilica surface had been considered and is currently being investigated. Other methods have also been tested to prepare epoxy/nanosilica composites. Recently, the sol-gel process for incorporating nanosilica particles into an epoxy resin has proved to be effective to overcome the formation of agglomerates in nanocomposites[8] which is difficult to achieve by mechanical mixing. By this process, the silica nanoparticles with narrow particle size distributions and free of agglomerates are prepared from aqueous sodium silicate using ion exchange techniques. It is shown that the colloidal silica or silica sols produced by this chemical method have shown dramatically improved material properties. In this thesis, the nano-SiO_2 particles are prepared by sol-gel process and well dispersed in epoxy resins.

In addition to particle size, the mechanical properties of polymers are also strongly influenced by other various environmental factors, such as moisture. Moisture absorbed into the polymer can lead to unwanted expansion and reliability failure behaviors in the polymer, such as stress cracking and delamination [9-10]. Such moisture and temperature induced failure has long been recognized as an important issue for package reliability but there is often a lack of reliable material data.

Models are important to predict and fit the experimental data. For CTE, those models include Rule of Mixture (ROM) and the Kerner model. The Rule of Mixtures (ROM) has been widely used to predict the effective coefficient of thermal expansion

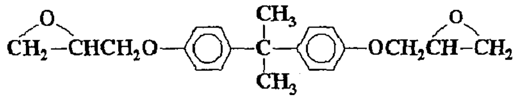
(CTE) for composites [11]. However, the ROM expressions do not consider the interphase interaction between the filler and polymer matrix. The Kerner model, on the other hand, estimates the CTE of the composite base on the bulk modulus of the filler and matrix. The measured CTE of composite is found to have a good agreement with experimental results studied by Shin and Lee [12]. For the mechanical properties, those models include the rule of mixture, self consistent, Hashin-Shtrikman's bounds Mori-Tanaka, and Halpin-Tsai. The Halpin-Tsai model has been found to give a good prediction for carbon nanotube, nanoclay as well as nanosphere silica in nanoscale at low volume content of fillers. However, as the filler contents increases, the predicted modulus is found to be underestimated compared to the experimental results. In this study, the Kerner and Halpin-Tsai models were evaluated for the CTE and stiffness of particulate composites, respectively.

In this thesis, epoxy resins including diglycidyl ether of bisphenol A (DGEBA), diglycidyl ether of bisphenol F (DGEBF) and cycloaliphatic epoxy with various amounts of nanosilica were studied. The investigation aims to evaluate each epoxy resin system for the coefficient and thermal expansion (CTE), modulus, thermal stability, fracture toughness, and moisture absorption. The results are also compared to the Kerner and Halpin-Tsai models for the CTE and stiffness of particulate composites. The results of these studies will assist in the fundamental understanding of fillers in epoxy resins at the nanoscale, and therefore, recommendations are provided for improvements of mechanical and thermal properties.

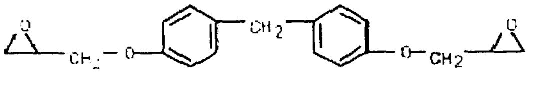
Experimental

Materials

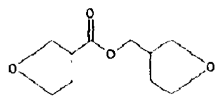
The epoxy resins used in this study were standard diglycidyl ether of bisphenol A (DGEBA, Dow Chemical Company), standard diglycidyl ether of bisphenol F (DGEBF, Dow Chemical Company), and cycloaliphatic epoxy (Dow Chemical Company). The surface modified nano-SiO_2 particles (Hans Chemie, Geesthacht, Germany), were obtained at a 40 wt% concentration in the corresponding epoxy resins. The nano-SiO_2 material was surface modified by a sol-gel process to prevent agglomeration and maintain a narrow particle size distribution range with an average particle size of about 20 nm. Aminoethyl piperazine (AEP, Air Products and Chemicals) and 2-ethyl-4-methyl-imidazole (2,4 EMI) were used as the curing agent for DGEBA and DGEBF, respectively, while an anhydride curing agent from was used for the cyloaliphatic epoxy resin. The chemical structure of each epoxy resins are presented as follows:



DGEBA



DGEBF



Cycloaliphatic

The formulations for DGEBA were carried out by mixing 25 g of epoxy resins with between 0-35 wt% nano-SiO_2 concentrations, labeled accordingly in the figures below. 5.75 g of AEP curing agent were added into the mixtures and then agitated under vacuum for 5 minutes. Finally, the samples were placed on a silicone mold and thermally cured at 125 °C for 2 hours. The same procedures were followed for DGEBF but cured with EMI at 60 °C for 4 hrs, followed by 150 °C treatment for 2 hrs in ambient air. Cycloaliphatic epoxies were prepared with nano-SiO_2 concentrations between 0-20 wt% and cured with anhydride curing agent at 125 °C for 3 hrs, followed by 200 °C treatment for 1 hr.

Materials Characterization

1. Coefficient of thermal expansion

The coefficients of thermal expansion (CTE) of cured materials were determined by thermal mechanical analysis (TMA, TA Instruments TMA-2940). The specimen samples were sized to dimensions of 3 mm x 3 mm x 3 mm. The experiments were conducted at 1 °C/min from 25-200 °C. The CTEs of glassy and rubbery state were taken from the slope of thermal expansion-temperature curves at below the glass transition temperature (Tg) and above Tg, respectively.

Tensile modulus

The dynamic mechanical analysis (Advanced Rheometric Expansion System (ARES)) was utilized to measure the mechanical properties of the modified DGEBA system. The storage shear modulus, loss shear modulus and tan δ were determined at a constant frequency of 1 Hz, raising the temperature from 25 to 175 °C at a constant heating rate of 5 °C/min. For the DGEBF and cycloaliphatic systems, the storage Young's modulus, *E*, was investigated in a 3-Point Bending mode using a TA Instruments DMA2980 Dynamic Mechanical Analyzer (DMA). The specimens, with sample dimensions of 1.3 cm x 5.4 cm x 0.3 cm, were performed at a constant frequency of 1 Hz at a temperature range from 30 to 200 °C at heating rate of 5 °C/min.

2. Thermal stability

The thermal stabilities of the cured samples were carried out by thermogravimetric analysis (TGA, TA Instrument TGA2950). The specimens, typically with an approximate weight of 30 mg, were placed in an alumina dish and measured from 25-600 °C at 10 °C/min. The decomposition temperature, T_d, is considered at 10% weight loss, and the char residue is compared at 600 °C. Weight loss against temperature was determined under nitrogen flowrates of 56 sccm.

3. Fracture toughness

The plane strain fracture toughness (K_{IC}) was measured using pre-cracked, single edge notched (SEN) specimens in three-point bending (3PB) geometry (Instron model 5567), in accordance to the ASTM D5045 standard. A pre-crack was made by lightly tapping a fresh razor blade between adjoining plates, with sample dimension of 75.6 mm x 12.7 mm x 6.36 mm, yielding a very sharp natural crack. The tests were performed at a rate of 1 mm/min and conducted at least three times for each composition.

4. Moisture uptake

The cured materials were subjected to temperature/humidity aging at 85 ^oC and 85% relative humidity using an ECOSPHERE humidity chamber. The water absorption was determined by measuring the increased weight due to moisture uptake. The average measurements with standard deviations were reported from three specimens with dimension of 1.3cm x 2 cm x 0.3 cm for each composition.

Modeling CTE and E

1. Kerner's model for CTE.

For spherical particles dispersed in a matrix, the Kerner model [13] derives the following equation for the coefficient of volume expansion of a composite:

$$\alpha = \alpha_1\phi_1 + \alpha_2\phi_2 - (\alpha_1 - \alpha_2)\phi_1\phi_2 \frac{\frac{1}{K_1} - \frac{1}{K_2}}{\frac{\phi_1}{K_2} + \frac{\phi_2}{K_1} + \frac{3G}{4}} \tag{1}$$

where volume coefficients of thermal expansion of the composite, polymer, and filler are α, α_1, and α_2, respectively. The bulk moduli of the components are K_1 and K_2, and G is the shear modulus. It is noted that the relationship between K and G is given by the following standard expression:

$$K = \frac{E}{3\left(3 - \frac{E}{G}\right)} \tag{2}$$

where E is the Young's modulus.

2. Halpin-Tsai model.

The Halpin-Tsai model [14] is used for predicting the stiffness of particulate composites. The property of a composite material is expressed in terms of the properties of the matrix and reinforcing phases together with their proportions and geometry. The Halpin-Tsai is expressed by the following equation for modulus of composites:

$$\frac{E_c}{E_m} = \frac{1 + \zeta\eta\phi}{1 - \eta\phi} \tag{3}$$

where E_c and E_m are the moduli for composite material and polymer matrix, respectively. ϕ is the filler sphere volume fraction, and η is expressed by:

$$\eta = \frac{\left(\frac{E_s}{E_m}\right) - 1}{\left(\frac{E_s}{E_m}\right) + \zeta} \tag{4}$$

where E_s is the modulus of filler and shape factor (ς) = 2a (where aspect ratio (a) = 1 for a spherical particle).

Results

Coefficient of Thermal Expansion

The coefficients of thermal expansion (CTE) of the modified epoxies from the TMA were calculated from the slopes from the critical Tg values to ±50 °C. CTE for below and above Tg of nanosilica filled DGEBA, DGEBF, and cycloaliphatic epoxies are shown in Table 1. In general, the CTE clearly decreases with increasing wt% of nanosilica for all filled systems. The decrease in CTE at higher filler fractions is due to a correspondingly lower CTE of the "plain" fillers compared to the epoxy. Comparing the CTE with the type of epoxy, DGEBA versus DGEBF versus cycloaliphatic, the CTE for the DGEBF system was revealed to be lower than other nanosilica filled system at below and above Tg at the same weight % filler content, or glassy and rubbery states. It is likely that the lower DGEBF CTE values arises from the higher packing density in the system and is, therefore, one desirable characteristic of DGEBF in industrial applications.

TMA also provided the glass transition temperature of modified epoxies, presented in Table 1 for the corresponding wt% nanosilica concentrations. The Tg values are observed to decrease with the addition of nanosilica for the DGEBA and DGEBF systems. In particular, the nano-silica filled DGEBF system appears to be have a greater impact on the Tg change from ~ 152 to ~131 °C for 0 to 30 wt%, respectively, as compared to the nano-silica filled DGEBA, which only decreased 116 to ~111 °C in the same corresponding wt% range. Regardless, the decrease in Tg values of nanocomposites is due to plasticizing effect of silica particles in the epoxy matrix, which is particularly useful for polymer processing where fillers are added to lower the Tg. However, for epoxy systems, a higher Tg is desired for thermal stability. In addition, the decreasing Tg values may be caused by the increase of free volume of epoxy resins with the addition of nanosilica particles. The Tg values of the cycloaliphatic system, on the other hand, are improved with nanosilica as shown in Table 1. The Tg was increased from 140 to 156 °C for 0 to 20 wt%, respectively. By comparison of the molecular structure of these three epoxy systems, the DGEBA and DGEBF have very stiff backbone of aromatic rings in the structure while the cycloaliphatic system contains flexible chains in the structure. Therefore, with addition of silica, the effectiveness of the increase in free volume is more prominent with the non-cycloaliphatic systems. Chain mobility of such epoxies is much less than that of cycloaliphatic which only has alkane rings in the structure. The plasticizing effect does not have a significant impact on the cycloaliphatic system due to these chemical properties.

Figures 1, 2, and 3 show the correlation between the measured CTE datapoints and predicted CTE by Kerner model for the glassy and rubbery states. Interestingly, at the glassy state, the estimated values for CTE correlate well over the full range of nanosilica concentration for the DGEBA and DGEBF epoxies, however, the model slightly over predicts the CTE at higher nanosilica content of the cycloaliphatic epoxy. At the rubbery state, the predicted values of CTE for DGEBF and cycloaliphatic systems correlate well with the experimental data, however, the model under predicts and deviates below the measured values.

Tensile Modulus

DMA measures the response of a given material to an oscillatory deformation as a function of temperature. Three parameters provided by the DMA results are the storage modulus (E'), the loss modulus (E"), and tanδ (E"/E') which are useful for determining the occurrence molecular mobility transition, such as the glass transition temperature (T_g). Figures 4, 5, and 6 show the modulus as a function of temperature results for nanocomposites of DGEBA, DGEBF and Cycloaliphatic epoxies, respectively. Two features are observed. Firstly, the enhancement of the storage moduli for all the filled systems at various nanosilica contents can be clearly observed in the investigated temperature range when compared to the neat epoxy resin as depicted in Fig. 4-6 which is consistent with the literature [2]. This enhancement indicates that the nanosilica has a strong effect on the elastic properties of epoxy resins. With a much higher modulus on the filler surface than the bulk polymer and large surface area exposed to the polymer, the significant increases in the modulus with very low filler content were found undoubtedly. It can be thought that the polymer chain mobility is restricted by nanofiller which contributes to an improved tensile modulus[15]. Secondly, the tanδ does not stay consistent or even slightly enhance with increasing wt% from literature reports, but in fact, promotes the damping of the tanδ intensity with increasing wt%[7]. For the DGEBA, the tanδ are clearly improved with addition of nanosilica content which can also be explained by restricted chain mobility in epoxy system with presence of nanosilica. This phenomenon can be attributed to the coefficient of thermal expansion between the matrix and the particles. The CTE of the bulk silica is much lower than the CTE of the epoxy resin, resulting in a residual compressive stress between the two phases, resulting in the increase in the modulus of epoxy resins.

This difference in behavior is emphasized when comparisons are made to the theoretical model for the Young's moduli. Figure 7 depicts the fit of the Halpin-Tsai model to the experimental datapoints for the Youngs modulus versus volume fraction of fillers. Only the Halpin-Tsai model for the cycloaliphatic epoxy system appears to correlate well to the measured results, whereas, the model under predicts the experimental values in the DGEBA and DGEBF system, particularly when fillers are added. In addition, it appears that the non-cycloaliphatic systems appear to be increasing non-linearly whereas the cycloaliphatic system increases linearly. Overall, it can be seen that increasing the wt% of fillers can improve the thermal expansion and also increase the Young modulus of all epoxy systems.

Fracture toughness

Fracture toughness is a measure for the ability of a material to resist the growth of pre-existing cracks or flaws. It is assumed that the high stress concentration in front of the razor notch within the neat resin is changed into a more uniform stress distribution due to the fine distribution of the nanoparticles, thus enhancing the toughness of the system. The improvement of the fracture toughness of DGEBF and cycloaliphatic epoxies due to the nanosilica was investigated, shown in Figure 8. The increase in fracture toughness with nanosilica fillers of these two systems indicates crack growth resistance of neat epoxy. It is clear that nanosilica/DGEBF with 20 wt% and nanosilica/cycloaliphatic with 15 wt% give the highest improvement in fracture toughness of nanocomposites. Beyond these nanosilica concentrations, the fracture toughness appears to remain constant or decrease slightly. The reasons for this behavior at higher concentrations will be discussed in greater detail below.

Thermal stability

The thermal stability of epoxy resins is studied by thermogravimethric analysis (TGA). The weight loss is due to the formation of volatile products after degradation at high temperature is monitored as a function of temperature. Figures 9 and 10 show the plot of % weight loss as a function of temperature for the nanosilica filled DGEBF and cycloaliphatic epoxy resins, respectively. Also, Table 2 summarizes the temperature of the onset weight loss or decomposition temperature at 10% weight loss (T_d) and char residuals at 600 ^{o}C of DGEBF and cycloaliphatic epoxy, respectively. The T_d of DGEBF with incorporation of nanosilica is found to be higher than the neat resin, indicating a higher decomposition temperature with fillers, and improves with concentration. The T_d of cycloaliphatic epoxy, on the other hand, increases with fillers up to 10 wt%, then decreases slightly above 15 wt% of nanosilica. The second feature of the TGA is the char residuals at 600 °C. It is seen that the char residuals of both epoxy resins at 600 °C increases with increasing the amount of nanosilica used in epoxy resins. This demonstrates that the thermal stability of the epoxy resins improved with the addition of nanosilica and the magnitude of improvement increased by increasing the amount of loading. Furthermore, the char yield has been correlated to the level of flame retardance [22].

Moisture Absorption

The moisture absorption behavior of the nanosilica epoxies (starting from a dry sample and normalized by equal sample sizes) is measured as the weight gain% as a function of time. The plots for 0-35 wt% nanosilica filled DGEBA and 0-20 wt% nanosilica filled cycloaliphatic epoxy are depicted in Figures 11 and 12, respectively. It is shown that for both systems, the rate of absorption increases with time, however, the nanosilica filled DGEBF increases linearly while the cycloaliphatic epoxy increases non-linearly. Furthermore, the moisture absorption is unaffected by the different concentrations of the nanosilica filled DGEBF whereas the moisture uptake is strongly affected by the filler wt% of the cycloaliphatic epoxy.

Discussion

Evaluation of models for CTE

Several models have been presented in the literature to model the CTE of composite systems. The Rule of Mixtures (ROM) has been widely used to predict the effective coefficient of thermal expansion (CTE) for composites [11]. However, the ROM expressions do not consider the interphase interaction between the filler and polymer matrix. Wong et al reported that the CTE prediction from the ROM model is much higher than experimental results [15]. Vo et al proposed the CTE model of polymeric composites by considering the effect of an interphase zone surrounding the filler particles in a polymer matrix [17]. The CTE model has found to resolve several conflicts regarding the effect of filler concentration, filler size, and filler-polymer interaction. However, the model prediction can be effective for only their specific filler-polymer system in micro-scale study and for very low filler concentration. Another frequently used model was proposed by Kerner and coworkers [13]. The Kerner model estimates the CTE of the composite based on the bulk modulus of the filler and matrix. The measured CTE of composite is found to be in agreement with experimental results studied by Shin and Lee [12]. This model is currently being examined by researchers for thermal and mechanical properties of polymer composites with nanoscale reinforcement [12-13]. However, the most commonly used models for CTE prediction is the Kerner model.

In the current study, the Kerner model was applied and found to predict well for only selected epoxy systems. For example, the model predicts the CTE for

DGEBF well at glassy and rubbery states but over predict at high filler content. This trend confirms the previous literature reporting that the agglomerations occur at high filler concentration and is not compensated by the model. In addition, the model over predicts the CTE for the cycloaliphatic system at rubbery state while under predicting the CTE for DGEBA at glassy state. The results suggest that the temperature range affects the model resulting in the deviations particularly at higher temperature. It is concluded that the Kerner model is limited in CTE predictions due to the nano-size of the reinforcement.

Evaluation of the Halpin-Tsai model

Predicting the mechanical properties of nanocomposites is also a challenge. There are many theoretical models proposed to predict the properties of polymer with incorporation of fillers, as reviewed by Shin and Lee [12]. Those models include the rule of mixture, self consistent, Hashin-Shtrikman's bounds and Mori-Tanaka. These models were initially evaluated by studies in elastic moduli of epoxy molding compound (EMC) with silica particles where the matrix and the particles were assumed to be linear-elastic, isotropic, and perfectly bonded. From these conclusions, the rule of mixture was usually found to give poor estimations in nanocomposite system [18]. The self consistent and Hasin-shtrikman's bounds were found to only be applicable at the specific system where the particles were well distributed in polymer matrix [12]. Tandon and Weng [19] reported that Mori-Tanaka model worked best only for particles with high aspect ratio and particles which were perfectly aligned in the composites. At high aspect ratio, the reinforcing effect can be negligible, however, in nanocomposite systems a reinforcing effect exists and cannot be neglected. Therefore, these models will not be considered for nanocomposite systems. Currently, the most widely used model is the Halpin-Tsai model by Halpin [14]. This model takes into consideration the modulus of the composite as a function of filler contents, specifically, the modulus of filler, E_f, the modulus of epoxy matrix, E_m, as well as the aspect ratio by the incorporation of a shape factor. The Halpin-Tsai model has been found to give a good prediction for carbon nanotubes, nanoclay and nanosphere silica in nanoscale at low volume content of fillers. However, as the filler contents increases, the predicted modulus has been found to be underestimated the experimental results. Additionally, this model ignores any agglomeration and particle-particle interactions.

In the current study, the Halpin-Tsai model was evaluated and found that the predicted and experimental data are in a good agreement for only the nanosilica filled cycloaliphatic system. If the Halpin-Tsai model is to be utilized for predicting the mechanical properties of nanocomposites, the model would have to be modified for other considerations. For instance, Van Es [20] suggested that the aspect ratio (a) used in the equations 3 and 4 for spherical particles is too high and has recommended to use $\varsigma = (2/3)a$ instead. Also, Johnsen and coworkers proposed the modified Halpin-Tsai model by considering the effect of imperfect bonding between the filler and polymer matrix. However, these modified models are still limited to agglomeration at high filler contents and the validity of these models has not yet been proven.

Fracture toughness

The fracture toughness of both DGEBF and cycloaliphatic systems are seen to be enhanced by addition of nanosilica particles as shown in Fig. 8. However, at high filler content fracture toughness appears to either remains constant or slightly decrease. Zhang et al [21] suggested that the improved fracture toughness is due to the decrease in interparticle distance of particles. They suggested that at nanoparticles are close together with increasing the filler content to be able to create three dimensional structures with strong coated with polymer chains. This structure results in very unique morphology of fracture surface leading to the energy-dissipating toughening mechanism. According to this notation, by increasing the nanoparticle filler content, the interparticle distance should be reduced and result in the dramatically improved fracture toughness. However, the current study shows that at high weight fraction of silica particles the toughening effect approaches constant or even slightly decreases. It can be thought that, the fracture behavior can be controlled by the presence of these three dimensional structure at low filler content. But once the particle filler content reaches the critical value, the fracture behavior will be dominated by another mechanism.

The toughening mechanism has been studied by many researchers [22-25]. Zhang et al. [22] studied the SEM fractographs of fracture surface of the DGEBA resins with addition of up to 10 vol.% nanosilica. It was reported that the formation of dimples considered being the major toughening mechanism causing energy dissipation on a micrometer scale. A much rougher fracture surface is also found in the presence of nanosilica which indicates increased energy absorption. Another toughening mechanism is the crack-bowing mechanism studied by Kinloch and coworkers [23]. It is assumed that the crack tends to form secondary cracks with the present of rigid particles, resulting in enhancing plastic deformation in epoxy matrix. However, the work was initially done on a micrometer scale. Johnsen et al. [24] recently studied the toughening mechanism on the in nanometer scale. Their results concluded the lack of the crack pinning and observed nanoparticles surrounded by voids surrounding. These observations provided evidence of debonding of nanoparticles, subsequently plastic void growth which is responsible for the increase in fracture toughness of epoxy system. However, it can be assumed that fine distribution of nanoparticles can enhance the toughness of the system by imparting high stress concentration in front of the crack into a more uniform stress distribution. These studies show merit, however, additional studies on the detailed mechanisms of toughening initiated by nanoparticles are needed to resolve by using microscopic study.

Thermal stability

Lee and Ma [26] suggested that the decrease in crosslink density leads to the lower T_d. Therefore, it can be inferred that the decrease in T_d above 15 wt% of nanofilled cycloaliphatic is likely caused by the decrease in crosslink density. This result also confirms the decrease in fracture toughness of cycloaliphatic system at filler contents above 15 wt%. However, this phenomenon does not occur in the DGEBF system. Some investigators have indicated that the increase in stability is due to the improved barrier properties of the composites. The inorganic phase can act as a radical sink to prevent polymer chains from decomposing.

Moisture Absorption

The moisture absorption into the epoxy is strongly controlled by diffusional effects. It can be thought that as the amount of nanosilica fillers increases, the surface area between filler and polymers increases. As the path for the moisture become larger in size, their diffusion through the polymer is slower, resulting in a lower diffusion coefficient. Although the linear profile for the nanosilica filled DGEBF is somewhat suspect, the cycloaliphatic epoxy better depicts the adsorption. In the latter case, initially at the small absorption times, the rate or slope of adsorption is high. As the material becomes saturated, the absorption of the moisture levels off (slope approaches zero) to a final weight gain% at long times. The rationale for the lower weight % of the higher filler content epoxies is because the higher filler content materials (i.e. 20% filler) have larger surface area which allows for less diffusion of the moisture through the epoxies.

Conclusions

The effect of the addition of nanosilica fillers to epoxies were investigated for the stiffness, CTE, thermal stability, toughness, and moisture absorption. The addition of nanosilica fillers reduces the CTE, and increases stiffness, thermal stability, and fracture toughness. The CTE for DGEBA, DGEBF and cycloaliphatic filled nanosilica particles decreases with the addition of wt% content, while correspondingly increasing in the modulus. 3PB experiments also showed increased fracture toughness at higher wt% filler content. The T_d of DGEBF with addition of nanosilica is found to be higher than the neat resin, indicating a higher decomposition temperature with fillers, and improves with concentration. The T_d of cycloaliphatic epoxy, on the other hand, increases with fillers up to 10 wt%, then decreases slightly above 15 wt% of nanosilica. The moisture absorption is unaffected by the different concentrations of the nanosilica filled DGEBF whereas the moisture uptake is strongly affected by the filler wt% of the cycloaliphatic epoxy. For the models used to predict the experimental results, the Kerner model for the CTE predicts the experimental data well, however, the Halpin-Tsai model only predicts the modulus well for selected epoxies due to the increase in agglomeration and particle-particle interactions at nanoscale level.

Future work

The moisture effect, CTE, and modulus of nano-filled DGEBA will be investigated the relationship among these three properties to better understand the role of nanosilica in epoxy system. Furthermore, all samples will be studied for the fracture toughness surface to evaluate the fracture mechanism using scanning electron microscope (SEM). These future investigations will provide new fundamental understanding and insights for nano-filled, and the role of nano-filled epoxies in nanocomposite materials.

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Table 1. Thermal properties of nano-silica filled DGEBA, DGEBF, and cycloaliphatic epoxies.

Epoxy System	wt % nano-SiO_2	CTE(ppm/°C) (below Tg)	CTE(ppm/°C) (above Tg)	Tg (°C)
DGEBA	Unfilled	79.5	222	116.0
	10	77.8	218	116.6
	20	69.0	202	114.5
	30	66.5	201	111.9
	35	60.6	184	110.0
DGEBF	unfilled	65.7	169	151.8
	5	67.3	158	143.6
	10	64.6	147	136.8
	20	61.5	146	131.9
	30	56.3	133	131.3
	35	51.5	117	139.5
Cycloaliphatic	Unfilled	75.5	189	140.1
	1	73.5	188	141.4
	5	66.1	183	147.8
	10	67.9	173	145.4
	15	72.4	172	146.9
	20	55.6	147	156.4

Table 2. TGA analysis of DGEBF and cycloaliphatic epoxy filled nanosilica at various filler contents under N_2 atmosphere from 25 °C to 600 °C with heating rate of 10 °C.

Epoxy System	Wt % nano-SiO_2	T_d (°C)	Char residual (%) at 600 °C
DGEBF	unfilled	440.2	20.9
	5	443.6	19.3
	10	444.2	25.5
	20	445.6	35.2
	30	448.6	48.3
	35	450.0	52.9
Cycloaliphatic	Unfilled	378.1	0.2
	1	380.6	1.3
	5	379.7	4.8
	10	381.3	9.9
	15	380.1	14.8
	20	378.2	19.6

Figure 1. Coefficient of thermal expansion of DGEBA versus volume fraction of nanosilica fillers at (a) Below T_g and (b) Above T_g.

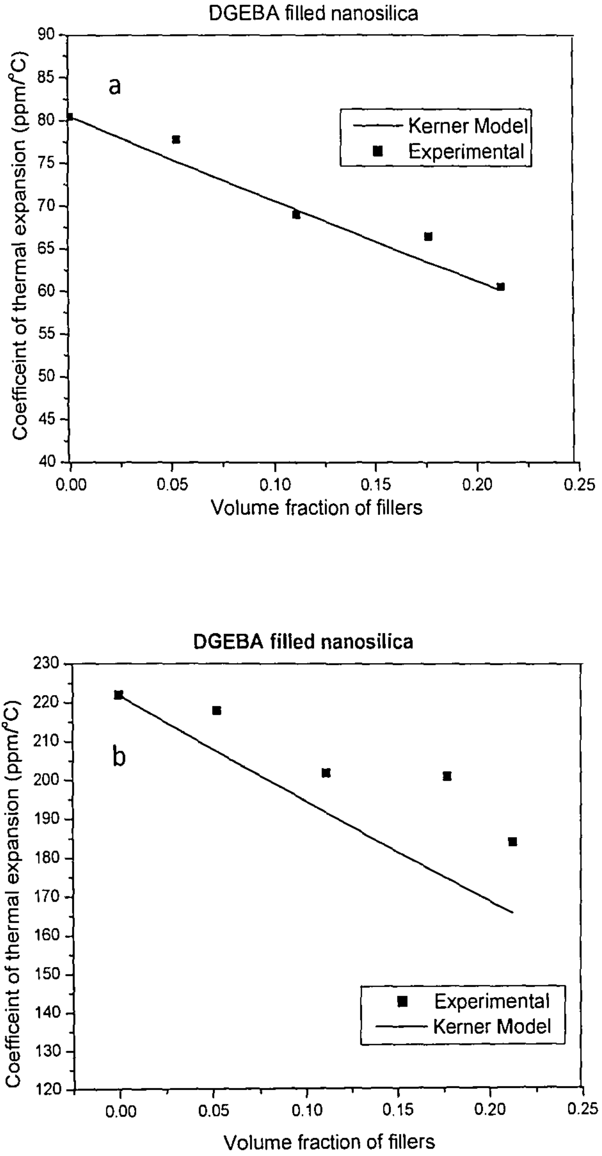


Figure 2. Coefficient of thermal expansion of DGEBF versus volume fraction of nanosilica fillers at (a) Below T_g and (b) Above T_g.

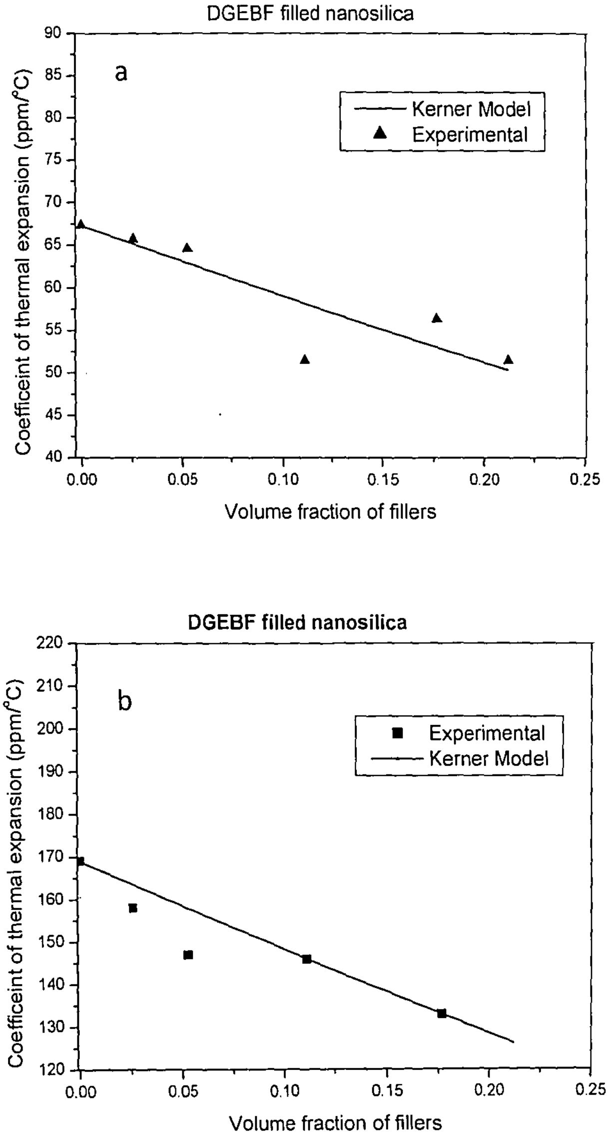


Figure 3. Coefficient of thermal expansion of cycloaliphatic epoxy versus volume fraction of nanosilica fillers at (a) Below T_g and (b) Above T_g.

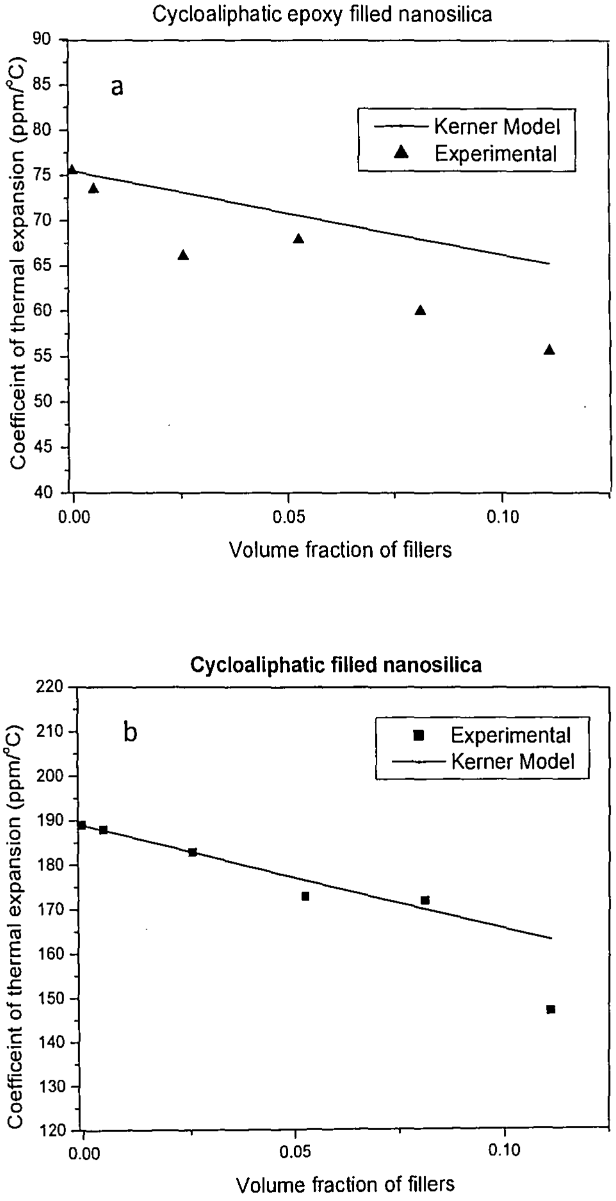


Figure 4. Dynamic mechanical analysis data for DGEBA, showing the storage modulus and tanδ versus temperature at various nanosilica contents.

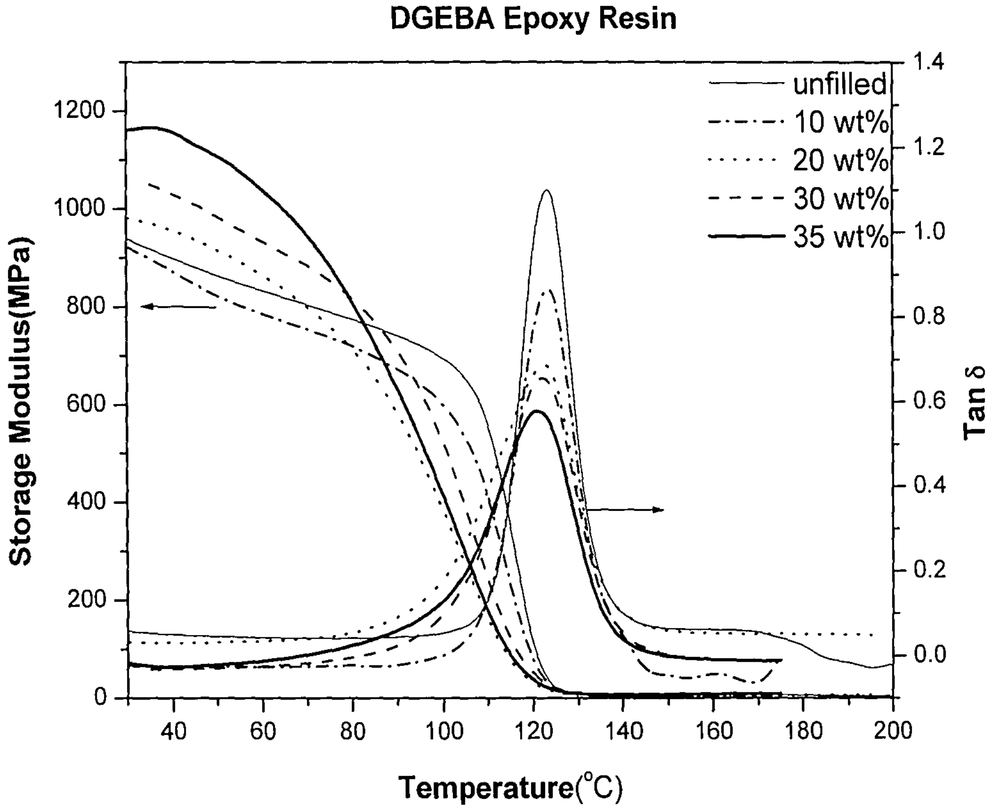


Figure 5. Dynamic mechanical analysis data for DGEBF, showing the storage modulus and tanδ versus temperature at various nanosilica contents.

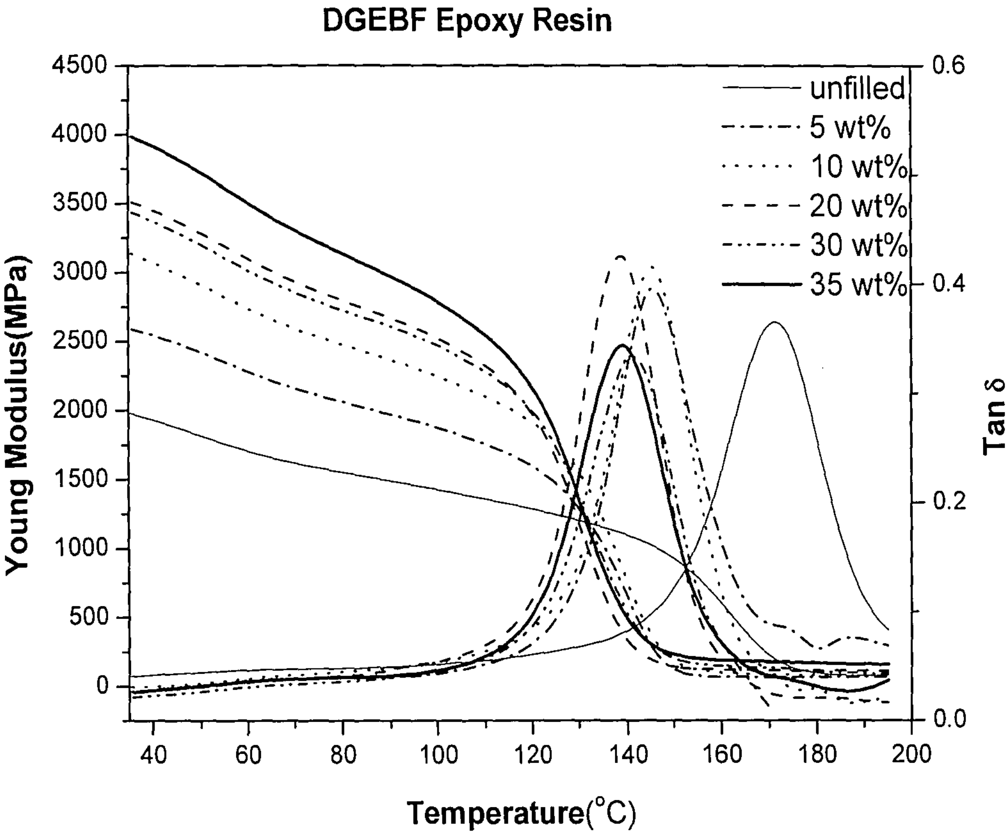


Figure 6. Dynamic mechanical analysis data for cycloaliphatic epoxy, showing the storage modulus and tanδ versus temperature at various nanosilica contents.

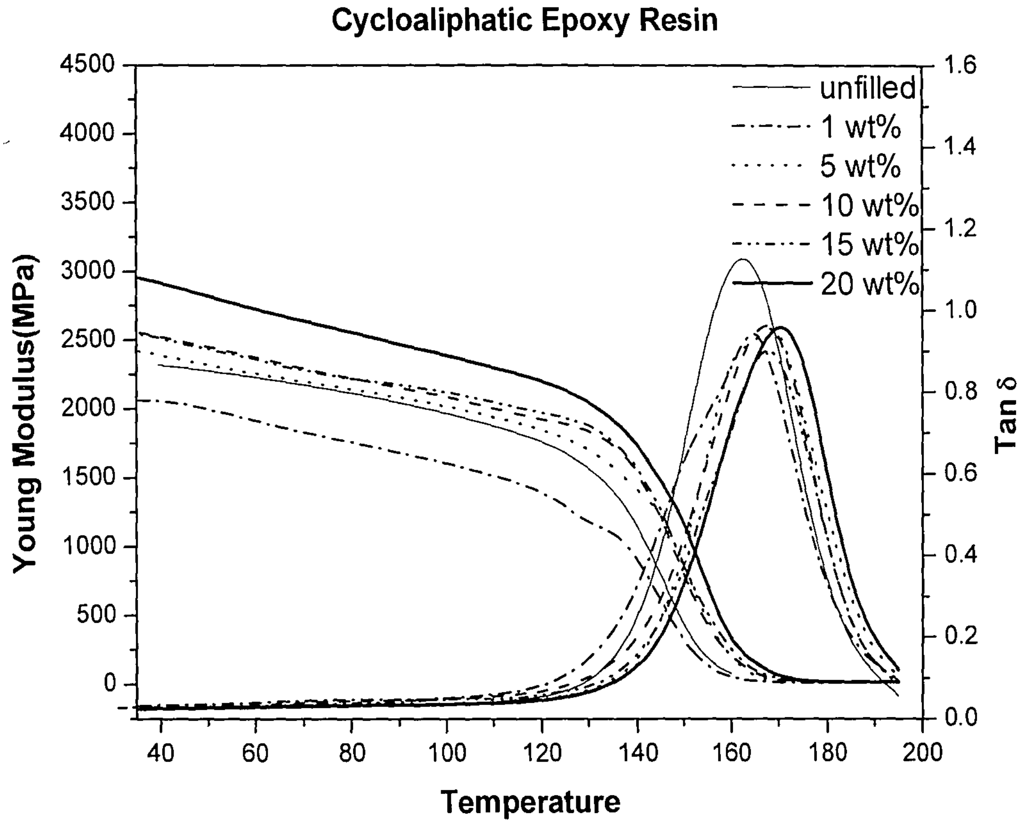


Figure 7. Tensile Modulus versus nanosilica content. Points are experimental data, and solid line is the predicted data from Halpin-Tsai model for (a) DGEBA,(b) DGEBF, and (c) cycloaliphatic epoxy resin.

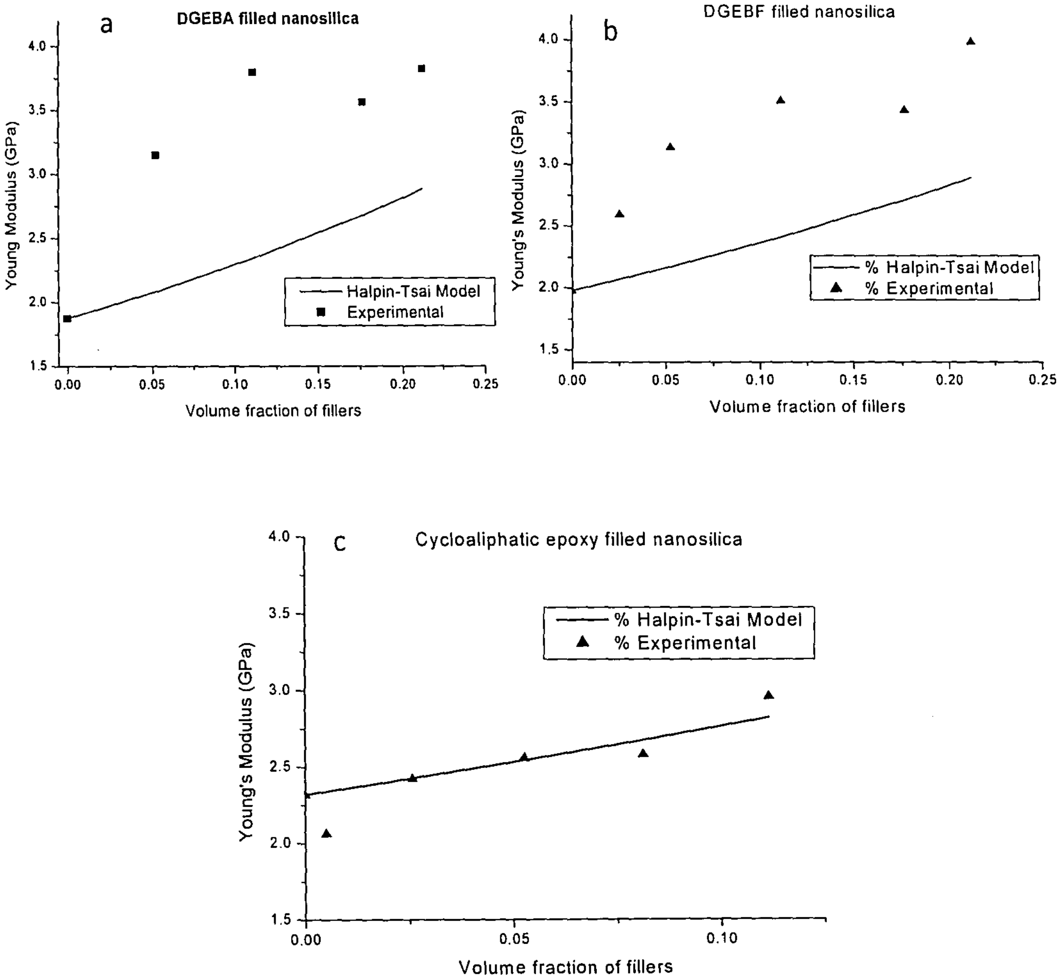


Figure 8. Fracture toughness of DGEBF and cycloaliphatic versus nanosilica contents.

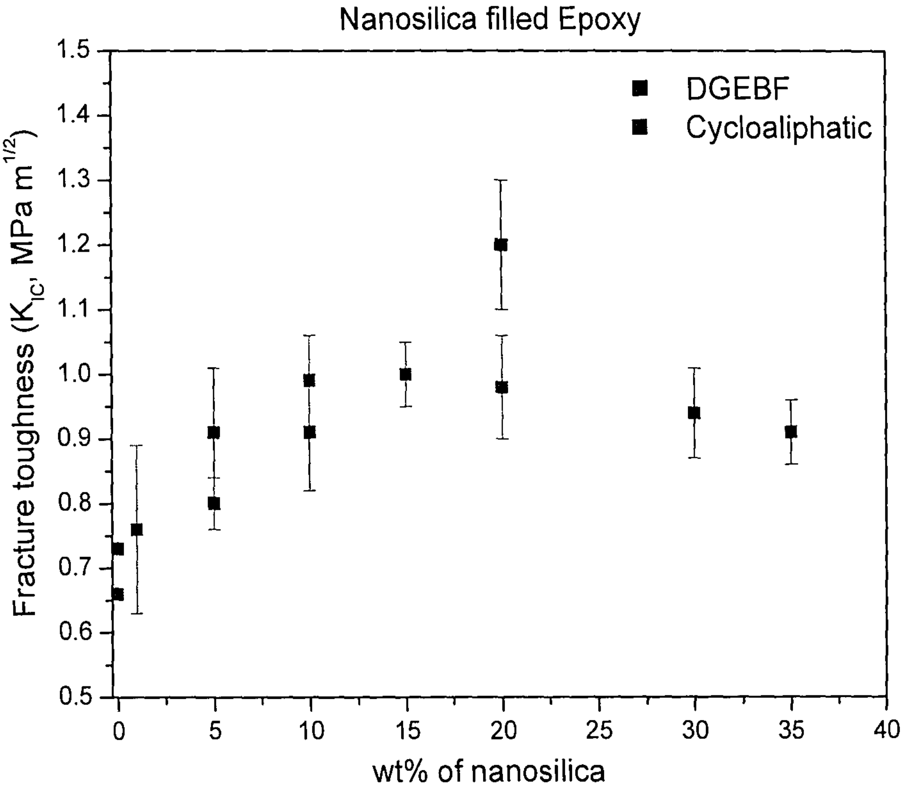


Figure 9. TGA analysis of DGEBF filled nanosilica at various filler contents under N_2 atmosphere from 25 °C to 600 °C with heating rate of 10 °C.

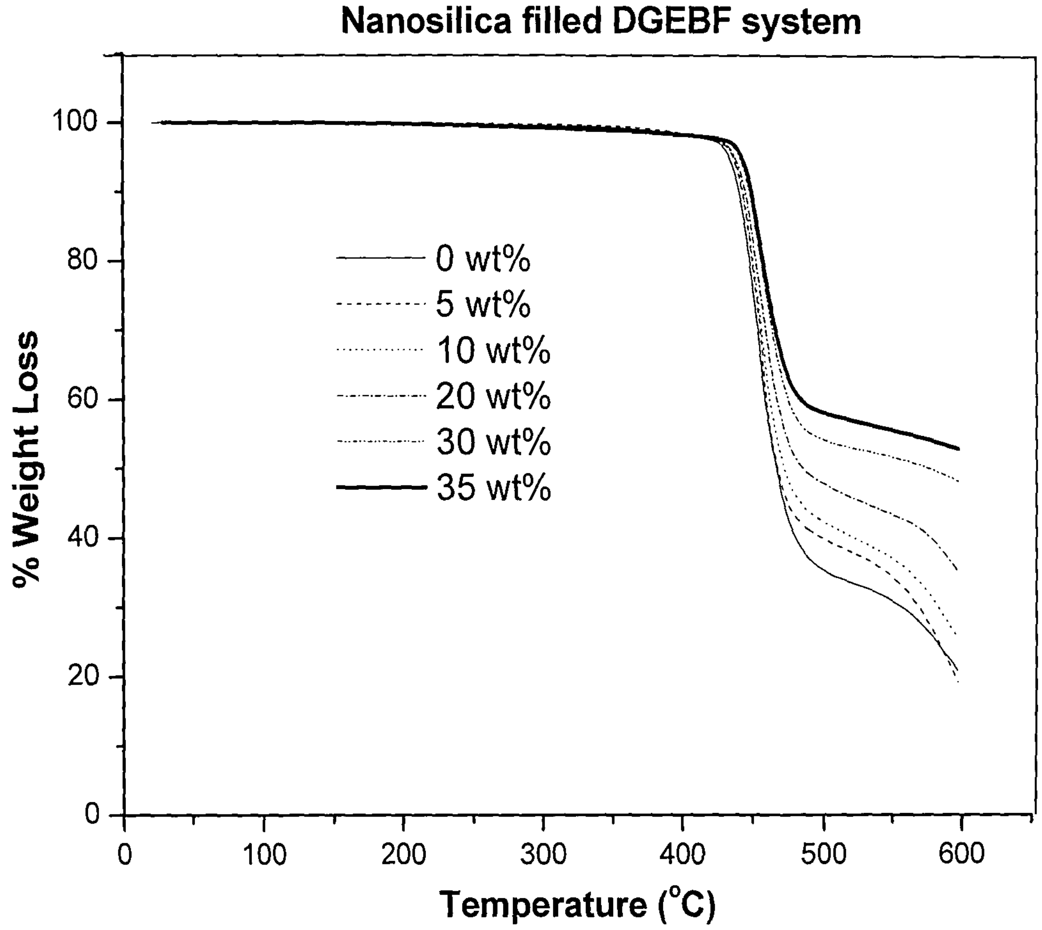


Figure 10. TGA analysis of cycloaliphatic epoxy filled nanosilica at various filler contents under N_2 atmosphere from 25 °C to 600 °C with heating rate of 10 °C.

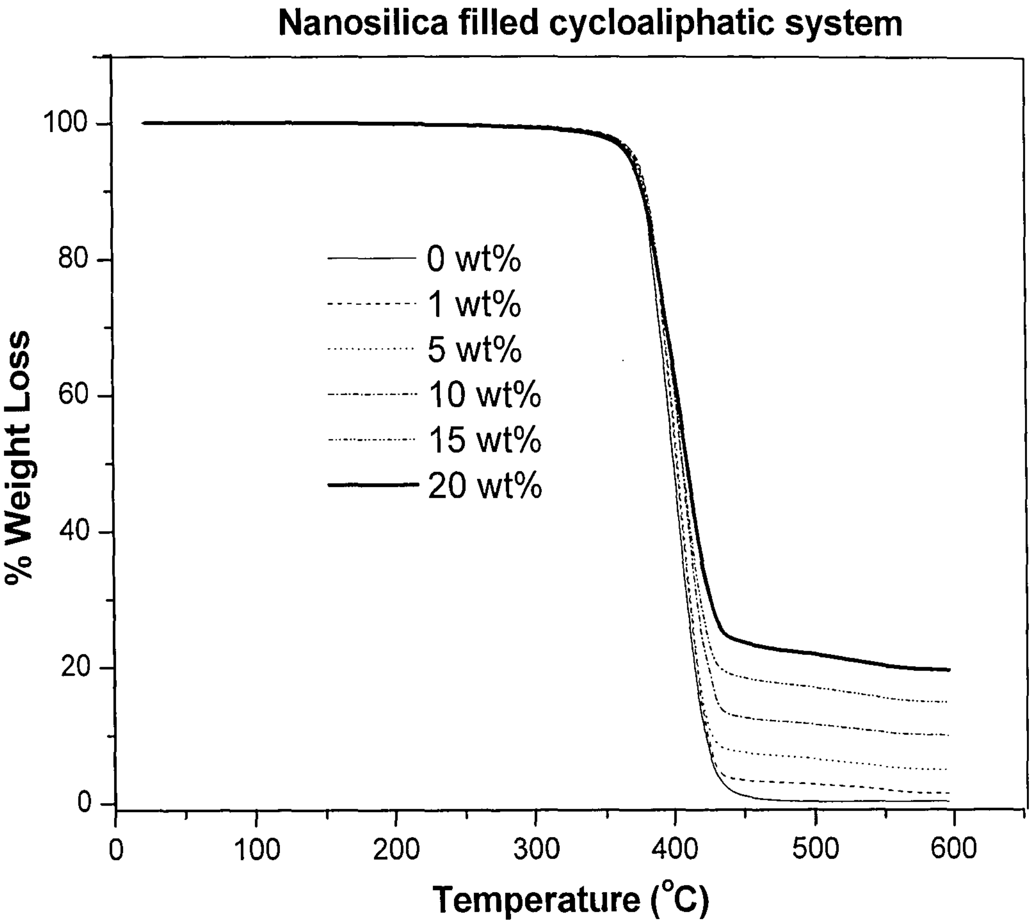


Figure 10. Weight gain% vs. time curve showing the water absorption behavior of the nanosilica filled DGEBA epoxy systems.

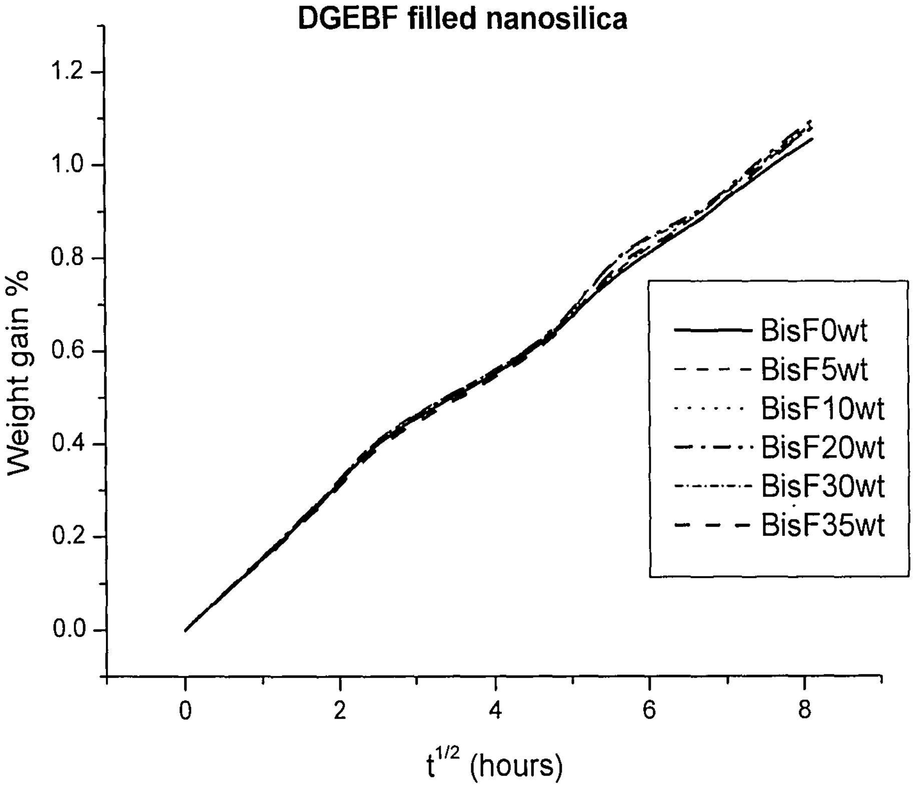
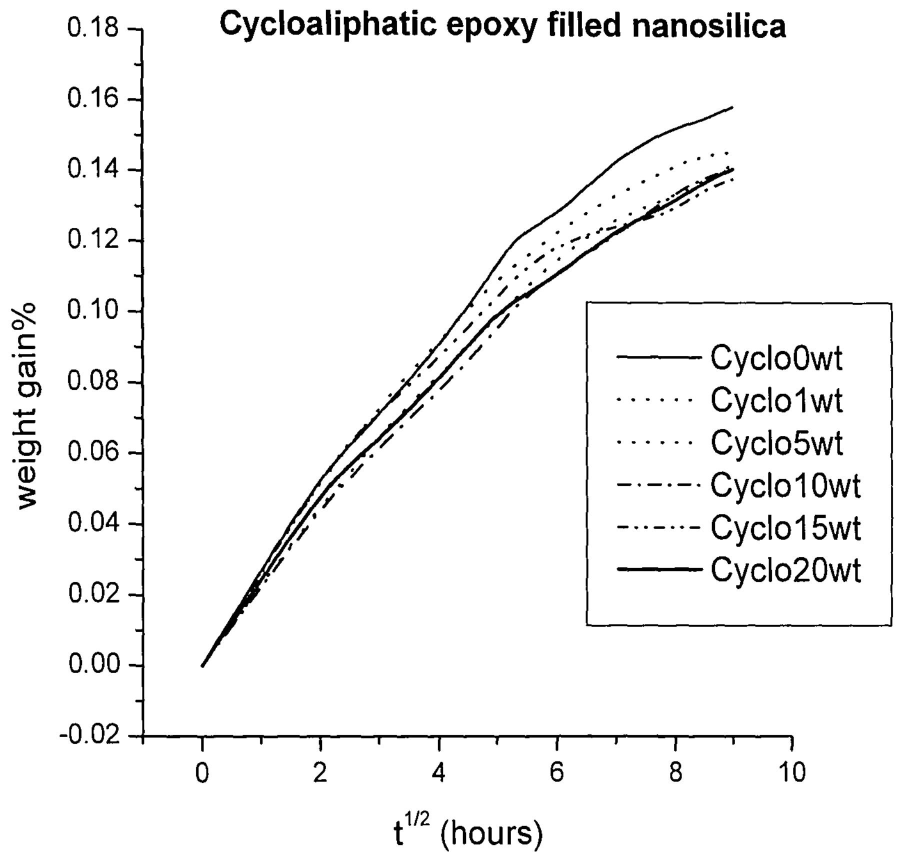


Figure 11. Weight gain% vs. time curve showing the water absorption behavior of the nanosilica filled cycloaliphatic epoxy systems.



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