

The Effects of CTBN on Mechanical and Viscoelastic Viscosity Properties of Epoxy-Silica Nanocomposites

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Received 30 April 2024, Received in revised form 15 October 2024

Accepted 8 November 2024, Available online 30 January 2025

ABSTRACT

Epoxy resin demonstrates remarkable adhesion, mechanical properties, and heat resistance, however, its inherent brittleness warrants attention. Therefore, hybrid composite was prepared using epoxy resin as the polymer matrix, with carboxyl-terminated butadiene nitrile liquid rubber (CTBN), and nanosilica as the reinforcement materials to increase the mechanical properties. The loading for CTBN and nanosilica are set to (5 wt.%, 10 wt.%, 15 wt.% and 20 wt.%); and (1 wt.%, 2 wt.%, 3 wt.% and 4 wt.%); respectively. The epoxy composites are toughened by adding various loadings of CTBN. Then, fracture toughness and viscoelastic viscosity properties of the composites are measured. At 15 wt.% of CTBN loading, nanosilica are added at different loadings to examine the improvement of composites. Then, fracture toughness (K_{IC}), the glass transition temperature (T_g), loss modulus (E'') and storage modulus (E') were all measured. Incorporating CTBN into epoxy matrix improves fracture toughness up to 79.4%, with optimum loading of 15 wt.%. Nanosilica content also significantly impacts fracture toughness, with a maximum enhancement of 107.7% at 3 wt.% loading. The glass transition temperature increases with CTBN content, reaching 17.01% improvement at 15 wt.% loading and 18.32% improvement at 20 wt.% loading. Nanosilica is also found to increase glass transition temperature, reaching 74.49°C, at 3 wt.% loading and 83.33°C, at 4 wt.%. The loss modulus increases as CTBN and nanosilica loading increases. At a loading of 20 wt.% CTBN, it reaches a maximum value of up to 164.7%. Adding further 4 wt.% nanosilica to 20 wt.% CTBN, resulted in an increase in loss modulus up to 1600%. The storage modulus also increases as CTBN and nanosilica loading increases to 20 wt.% and 4wt.%, respectively and it reached 1662% from neat epoxy. In conclusion, a combination of 15 wt.% CTBN and nanosilica have increased the fracture toughness and viscoelastic viscosity properties of epoxy composites.

Keywords: Fracture toughness; glass transition temperature; CTBN; nanosilica; hybrid

INTRODUCTION

Epoxy resins have been used extensively across a variety of industries, from the matrix in high-performance composite materials to everyday sealing agents and adhesives appliances. They are being extensively utilized in diverse industries, including automotive, aerospace, and construction, for the purpose of adhering different materials together. The temperature range spanning from 50 to 70°C proves particularly fitting for numerous bonding applications, wherein a moderate level of heat resistance is sought.

Unfortunately, the resulted epoxy often causes problems due to brittleness. As such, fillers such as carboxyl-terminated butadiene acrylonitrile copolymer (CTBN) are incorporated to tackle these hurdles, as reported by Gonzalez et al. (2007). The microstructure which is created is made up of an elastomeric phase that is sparsely or completely dispersed in the epoxy matrix. These particles significantly increase the original toughness while barely influencing on its thermal and other mechanical properties. Among the most significant enhancement in fracture toughness was observed using 10 wt.% CTBN, where the K_{IC} increases 52%, 64.5%, and

90.8% for Araldite F-piperidine, Aradur 2954-DDS, and Aradur 2954-Araldite F epoxy mixtures, respectively (Zhang et al. 2016). The values of fracture energy, G_{IC} were reported to increase significantly as well. Besides CTBN, nanosilica are often added and has been demonstrated to enhance the toughness properties of the composites. The toughness of composites containing silica nanoparticles were reported to increase 50%, with the addition of only 10 wt.% silica nanoparticles (Sprenger 2020).

Dispersion has always been an issue regarding enhancing the mechanical properties of composites. Nanoparticles tend to agglomerate with each other due to Van der Waals attraction, which causes the homogeneous dispersion becomes difficult to achieve. As such, employing more than one fillers become an alternative to address this problem. Therefore, it is interesting to study the effects of employing various fillers that have been proven to enhance toughness properties. As reported by Zhang et al. (2016), significant improvement in both K_{IC} dan G_{IC} was observed for Araldite F-piperidine, Aradur 2954-DDS, and Aradur 2954-Araldite F epoxy mixtures by adding CTBN rubber, nano-silica, and halloysite. Fracture toughness has reported to increase by 207.26% at room temperature and 243.02% at 90 K by employing 10 parts of polyurethane and 0.1 parts of graphene oxide into 100 parts of epoxy (Guo et al. 2024). A study by (Raghavendra et al. 2024) also indicates the synergistic effects obtained by employing dual filler, where banana fibre and nano MgO are added to epoxy. The value of K_{IC} improves tremendously from 201.7 MPa.m^{1/2} to 318.22 MPa.m^{1/2}.

This research aims to investigate the synergistic effects of employing both silica nanoparticles and CTBN into DGEBA type of epoxy. First, CTBN will be added to determine the optimum wt.% that yields the highest value of fracture toughness. Next, silica nanoparticles will also be added to the mixture containing DGEBA and the optimum CTBN content obtained.

METHODOLOGY

In this experiment, Bisphenol A diglycidyl ether (DGEBA) resin and amine hardener is used. Resin is added to hardener at a mixing ratio of 2:1 (wt.%), as specified by local manufacturer. Table 1 below shows the properties of epoxy and hardener. The liquid carboxyl-terminated butadiene acrylonitrile (CTBN), with CAS number 68891-46-3 consists of 22-26% acrylonitrile and 4.5-5.5% carboxyl. Nanosilica was purchased from Elite-Indus, China, with particle size of 30 ±5 nm.

TABLE 1. Epoxy and Hardener Properties

Properties	Epoxy	Hardener
Viscosity, Pa.s (25°C)	8.0 + 2.0	0.03 + 0.02
Molar mass, g	189-200	96
Color	White	Dark brown
Mixing ratio	2	1
Glass transition temperature, T_g (°C)	40 – 60	
Density (g/cm ³)	1.16	1.15

First various loadings of CTBN (5 wt.%, 10 wt.%, 15 wt.% and 20 wt.%) were added into epoxy and stirred for 10 minutes at a rate of 500 rpm. Next, hardener was added to the mixture and further stirred for another 10 minutes. After left curing for 24 hours at room temperature, the samples underwent various test to determine the optimum CTBN that gives the highest values of mechanical properties. The next stage of experiment consists of adding silica nanoparticles into epoxy, together with CTBN that yields the highest mechanical properties, which is determined from the previous set of experiments. The amount of silica nanoparticles added was set at 1 wt. %, 2 wt. %, 3 wt. % and 4 wt. %. Similar mixing procedure was performed where the epoxy containing silica and CTBN was first stirred for 10 minutes at a rate of 500 rpm, before adding hardener and stirred again at the same stirring conditions.

Both tensile test fracture toughness (K_{IC}) were conducted by using INSTRON 5569A Universal Testing Machine. Tensile test and fracture test are conducted in accordance to ASTM D638 and ASTM5045, respectively. Viscoelastic properties was assessed by using Dynamic Mechanical Thermal Analyser (DMTA), under single cantilever mode [Perkin Elmer DMA 800], with heating range and heating rate set at 35°C – 150°C and 5 °C/min; respectively.

RESULTS AND DISCUSSIONS

Figure 1 below shows the results of epoxy containing CTBN. The Young's modulus of DGEBA epoxy increases with increasing CTBN content. This is because CTBN is a rubbery polymer, which means that it has a high molecular weight and can undergo large deformations without breaking. When CTBN is added to DGEBA epoxy, it forms a network of cross-linked chains (Srivastava et al. 2018). This network of cross-linked chains makes the material more stiff and less susceptible to deformation. The Young's modulus of neat DGEBA epoxy is 5.7 E+05 Pa. When 5 wt.% CTBN is added, the Young's modulus

increases to $7.2 \text{ E}+05 \text{ Pa}$. The Young's modulus of neat DGEBA epoxy increases by 24.1% when 5 wt.% CTBN is added and continues to increase with increasing CTBN content, up to $1.3 \text{ E}+06 \text{ Pa}$, which is 132.5% increment. However, the value decreases to $1.2 \text{ E}+06 \text{ Pa}$ at 20 wt.% CTBN. This is likely because the high concentration of CTBN in the epoxy resin disrupts the network of cross-linked chains, which reduces the stiffness of the material. Based on this, epoxy with 15 wt.% CTBN was selected for the studying the synergistic effects with silica nanoparticles.

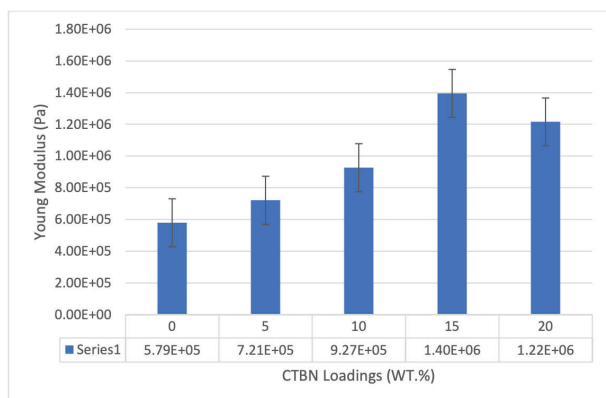


FIGURE 1. Young's Modulus of CTBN loadings

Figure 2 shows the Young's Modulus of epoxy mixture containing 15 wt.% CTBN, with silica nanoparticles, added at various loadings. The introduction of 1 wt.% nanosilica results in a significant enhancement of the Young's modulus, which reaches a value of $1.5 \text{ E}+06 \text{ Pa}$. The Young's modulus exhibits a 10.2% increase upon the addition of 1 wt.% nanosilica. The Young's modulus demonstrates a progressive increase as the nanosilica content is elevated, reaching a maximum enhancement of 107.7% when the nanosilica concentration reaches 3 wt.%. Nevertheless, the Young's modulus experiences a reduction of 52.7% when the nanosilica content reaches 4 wt.%.

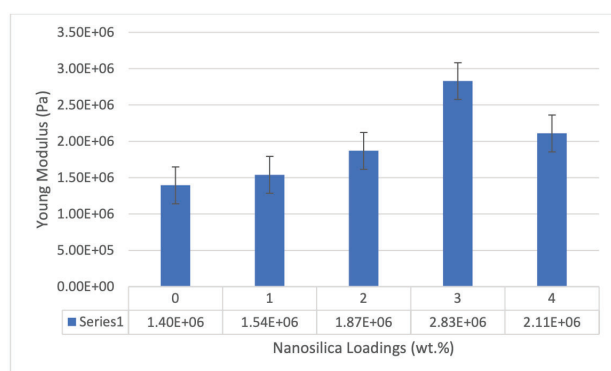


FIGURE 2. Young's Modulus of Nanosilica loading

Figure 3 show that the fracture toughness of DGEBA epoxy increases with increasing CTBN content. Since CTBN is a rubber-toughening agent, it can absorb energy and prevent cracks from propagating. The fracture toughness of neat DGEBA epoxy is 65.8 MPa.. When 5 wt.% CTBN is added, the fracture toughness increases to 103.9 MPa, which is about 59.2% increase. The fracture toughness continues to increase with increasing CTBN content, up to 79.4% at 15 wt.% CTBN. Adding more loading to 20 wt.% causes fracture toughness decreases to 41.5% at 20 wt.% CTBN. Similar work was performed by (Zhang et al. 2016) using adding CTBN on different set of DGEBA. The authors recorded an increase in the values of K_{IC} from $0.93 \text{ MPa.m}^{1/2}$ (neat epoxy) to $1.35 \text{ MPa.m}^{1/2}$ (5 wt.% CTBN). The highest value is recorded to be $1.61 \text{ MPa.m}^{1/2}$ after adding 10 wt.% CTBN. Their SEM images for epoxy containing 10 wt.% CTBN showed that the fracture surfaces become rough, which indicates an increase of crack surfaces and larger formation at the crack tip, as a results. As a result, the molecular chains between cross-links of the epoxy are extended and increase the composite's ductility (Puglia & Kenny, 2017).

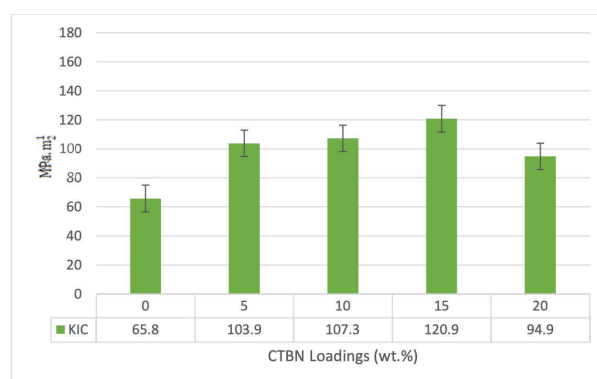


FIGURE 3. Fracture Toughness for various CTBN loadings

Based on the results, the optimum composites with CTBN loading is 15 wt.%, as it yields the highest value of fracture toughness. As such, 15 wt.% of CTBN are added to nanosilica loading to investigate the improvement of fracture toughness in hybrid epoxy/CTBN/nanosilica. Figure 4 shows the fracture toughness of neat DGEBA epoxy is 120.9 MPa.. When 1 wt.% nanosilica is added, the fracture toughness increases to 124.2 MPa.. When 2 wt.% nanosilica is added, the fracture toughness increases to 137.5 MPa.. The fracture toughness of epoxy with 15wt% CTBN epoxy increases by 3.1% when 1 wt.% nanosilica is added. The fracture toughness continues to increase with increasing nanosilica content, up to 37.9% at 3 wt.% nanosilica. However, the fracture toughness decreases to 28.1% at 4 wt.% nanosilica. Therefore, the

highest value of fracture toughness is added with 3 wt.% of nanosilica which increase to 164.3 MPa. Figure 4 demonstrates the synergistic effects by employing both CTBN and nanosilica. Similar results are obtained by Zhang et al. 2016, where K_{IC} increases up to 128.4% for epoxy containing 10 wt.% CTBN and 10 wt.% nanosilica. The ductility of the epoxy increases by adding CTBN liquid rubber. Adding nanosilica further increase the surface roughness, which contributes to the synergistic toughening effects of CTBN rubber and nanosilica (Zhang et al. 2016).

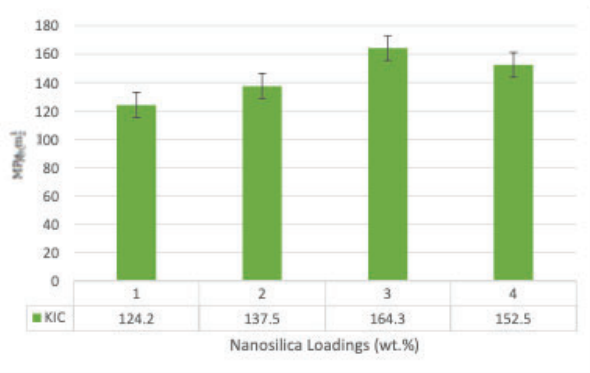


FIGURE 4. Fracture Toughness for various nanosilica loadings

As shown in Figure 5 below, the loss modulus of DGEBA epoxy increases with increasing CTBN content. This is because CTBN is a rubbery polymer, which means that it has a high molecular weight and can undergo large deformations without breaking. When CTBN is added to DGEBA epoxy, it forms a network of cross-linked chains. This network of cross-linked chains makes the material more flexible and able to absorb more energy (Zhang et al. 2016). The loss modulus of neat DGEBA epoxy at 40°C is 1.91E+08 Pa. When 5 wt.% CTBN is added, the loss modulus increases to 2.90E+08 Pa, which is an 52.4% increment. The value increases further to up to 139% at 15 wt.% CTBN. The highest increment is recorded at CTBN content of 20 wt.%, where the loss modulus increases to 164.7%. At 85°C, which is the temperature above T_g , the loss modulus of DGEBA epoxy decreases as temperature increases. This is because the rubbery polymer becomes soft and flexible at higher temperatures, which reduces the loss modulus of the material. The loss modulus of neat DGEBA epoxy at 85°C is 8.76E+06 Pa. When 5 wt.% CTBN is added, the loss modulus decreases to 1.64E+07 Pa. When 10 wt.% CTBN is added, the loss modulus decreases to 7.69E+07 Pa. When 15 wt.% CTBN is added, the loss modulus decreases to 8.06E+07 Pa. However, when 20 wt.% CTBN is added, the loss modulus increases to 1.11E+06 Pa.

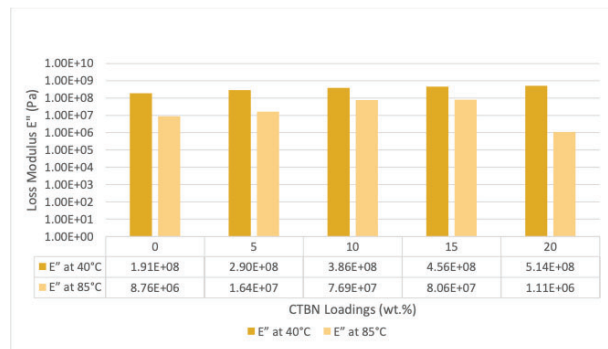


FIGURE 5. Loss Modulus at 40°C and 85°C of various CTBN loadings

Figure 6 shows that the loss modulus of composites increases with increasing nanosilica content at both 40°C and 85°C. This is because nanosilica is a filler material that has a high surface area and can interact with the epoxy resin, which results in a more cross-linked network. The loss modulus of neat DGEBA epoxy at 40°C is 4.56E+08 Pa. The loss modulus is seen to increase as nanosilica loading increases. The highest value of loss modulus recorded is 7.64E+09 Pa, at 4 wt.% nanosilica loading. Similar observation was also observed by (Gao et al. 2022) where particle nanosilica enhanced the value of loss modulus. The value increase from 2640 MPa to 2830 MPa as a result of adding 10 wt.% particle nanosilica in their DGEBA system.

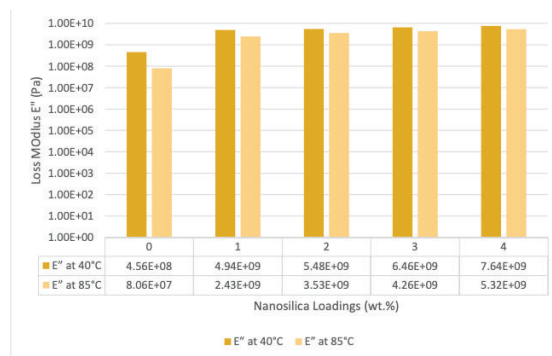


FIGURE 6. Loss Modulus at 40°C and 85°C of various Nanosilica loadings

Figure 7 below shows that the storage modulus of composite increase as the CTBN content increases, both at 40°C and 85°C. The reason for this is that CTBN exhibits elastomeric properties, rendering it more pliable and possessing a lower modulus compared to epoxy resin. The storage modulus of the pure DGEBA epoxy material at a temperature of 40°C is measured to be 5.78E+07 Pa. The incorporation of 5 wt.% of CTBN results in an increase of the storage modulus to a value of 1.00E+08 Pa. Upon the addition of 10 wt.% of CTBN, the storage modulus

increase, reaching a value of $3.08\text{E}+08$ Pa. Upon the addition of 15 wt.% of CTBN the storage modulus is measured to be $4.63\text{E}+08$ Pa. The highest value of storage modulus is recorded to be $5.67\text{E}+08$ Pa, at CTBN loading of 20 wt.%.

The storage modulus of neat DGEBA epoxy at a temperature of 85°C is measured to be $2.99\text{E}+06$ Pa. At 5 wt.% CTBN loading, the storage modulus decreases to a value of $2.83\text{E}+07$ Pa. The values decrease further to $5.72\text{E}+07$ Pa, by adding 10 wt.% CTBN. Upon the addition of 15 wt.% of CTBN, the storage modulus reduces further to $7.44\text{E}+07$ Pa. The storage modulus value continue to increases to $8.00\text{E}+07$ Pa, for the incorporation of 20 wt.% of CTBN.

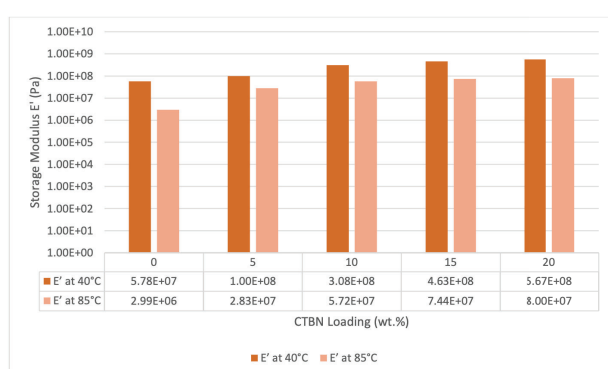


FIGURE 7. Storage Modulus at 40°C and 85°C of various CTBN loadings

The data presented in the Figure 8 shows the trend that the value of storage modulus continues to increase with the addition of nanosilica particle, which further confirm the role of nanosilica in enhancing the storage modulus of DGEBA epoxy. This trends hold true for both 40°C and 85°C temperatures. The rationale behind this phenomenon lies in the utilization of nanosilica as a filler substance, which has the capability to enhance the cross-linking density of the epoxy resin, thereby resulting in an increase in the material's stiffness.

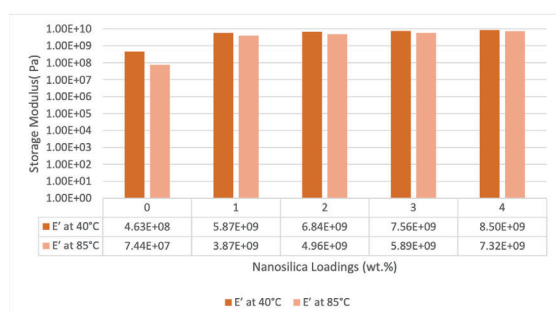


FIGURE 8. Storage Modulus at 40°C and 85°C of various silica nanoparticles loadings

The storage modulus of the pure diglycidyl ether of bisphenol A (DGEBA) epoxy resin at a temperature of 40°C is measured to be $4.63\text{E}+08$ Pa. The addition of 1 wt.% nanosilica results in an increase in the storage modulus to $5.87\text{E}+09$ Pa. The addition of 1 wt.% nanosilica to neat DGEBA epoxy at 40°C results in a significant increase in the storage modulus, specifically by 1,222.22%. The storage modulus exhibits a progressive rise as the nanosilica content is increased, reaching a notable enhancement of 1,662.09% when the nanosilica concentration reaches 3 wt.%. In contrast, the storage modulus exhibits a significant decrease of 876.92% when the weight percentage of nanosilica is increased to 4 wt.%.

The storage modulus of neat DGEBA epoxy at a temperature of 85°C is measured to be $7.44\text{E}+07$ Pa. Upon the addition of 1 wt.% nanosilica, the storage modulus exhibits a notable increase, reaching a value of $3.87\text{E}+09$ Pa. The addition of 2 wt. nanosilica results in an increase in the storage modulus to $4.96\text{E}+09$ pascals. The addition of 3 wt. nanosilica results in an increase in the storage modulus to $5.89\text{E}+09$ pascals. In contrast, the introduction of 4 wt.% nanosilica results in increases of the storage modulus to a value of $7.32\text{E}+09$ Pa.

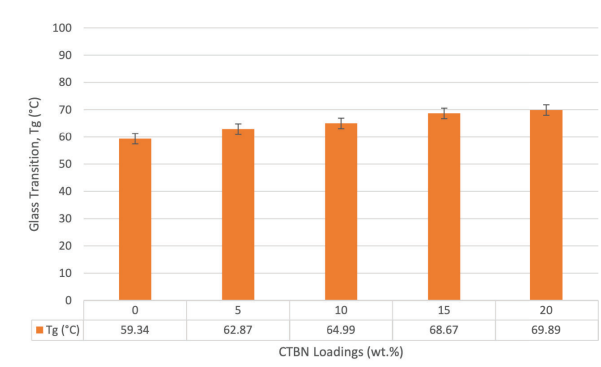


FIGURE 9. Glass Transition Temperature of various CTBN loadings

The data shows at Figure 9 stated that the glass transition temperature of DGEBA epoxy increases with increasing CTBN content. This is because CTBN is a rubbery polymer, which means that it has a high molecular weight and can undergo large deformations without breaking. When CTBN is added to DGEBA epoxy, it forms a network of cross-linked chains. This network of cross-linked chains increases the stiffness of the epoxy resin, which results in an increase in the glass transition temperature. The glass transition temperature of neat DGEBA epoxy is 59.34°C . When 5 wt.% CTBN is added, the glass transition temperature increases to 62.87°C . The glass transition temperature of neat DGEBA epoxy increases by 5.85% when 5 wt.% CTBN is added. When

10 wt.% CTBN is added, the glass transition temperature increases to 64.99°C. When 15 wt.% CTBN is added, the glass transition temperature increases to 68.67°C which is up to 17.01%. Then, the CTBN content is further increased to 20 wt.%, the glass transition temperature decreases to 18.32% which is 69.89°C. Similar trend was also observed by (Neves et al. 2022) where the incorporation of CTBN causes an increase in the value of glass transition temperature. The authors reasoned this due to a wider distribution of local crosslink density than in the neat sample.

The glass transition temperature of a material can be affected by several factors, such as the type of polymer, the molecular weight of the polymer, and the cross-linking density of the polymer. The addition of a rubbery polymer, such as CTBN, can increase the glass transition temperature of a material. This is because the rubbery polymer acts as a plasticizer, which reduces the stiffness of the material. The addition of a cross-linking agent, such as an amine hardener, can also increase the glass transition temperature of a material. This is because the cross-linking agent forms bonds between the polymer chains, which makes the material more rigid.

The experimental data in Figure 10 indicates a positive correlation between the concentration of nanosilica and the glass transition temperature of DGEBA epoxy with CTBN. The reason for this phenomenon is attributed to the utilization of nanosilica as a filler substance, characterized by its substantial surface area and ability to engage with the epoxy resin. Consequently, this interaction leads to the formation of a more interconnected network structure. The glass transition temperature (T_g) of 15wt.% of CTBN is measured to be 68.67°C. The incorporation of 1 wt.% nanosilica into the material results in a notable elevation of the glass transition temperature, which reaches a value of 72.45°C. The addition of 1 wt.% nanosilica to neat DGEBA epoxy results in a 5.16% increase in the glass transition temperature. The observed trend indicates that the glass transition temperature exhibits a positive correlation with the concentration of nanosilica. Specifically, the glass transition temperature progressively rises as the nanosilica content is augmented, reaching a maximum value of 74.49°C at a weight percentage of 3%. Incorporation of 4 wt.% nanosilica into the system results in a notable elevation of the glass transition temperature, which reaches 83.33°C. An increase in the value of glass transition temperature is also reported by (Neves et al. 2022) in the case of adding rigid fillers into liquid rubber/epoxy system. The rubber structure and the fillers seemed to have a synergistic effects on the viscoelastic properties of the epoxy (Neves et al. 2022).

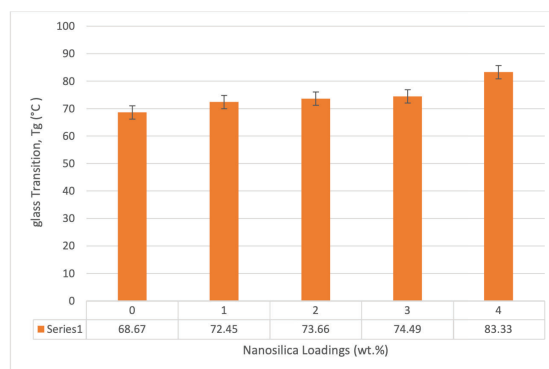


FIGURE 10. Glass Transition Temperature of various Nanosilica loadings

The introduction of a filler, irrespective of its size and quantity, consistently results in an increase in the modulus of a cross-linked epoxy resin. This finding is corroborated by Stephan Sprenger's research, which indicates that silica nanoparticles have no discernible effect on the glass transition temperature (T_g) at low addition levels, below 10 wt.%. However, at higher addition levels, a slight reduction of 2-5°C can be observed (Białkowska et al. 2023).

CONCLUSIONS

The present investigation centred on the utilisation of incorporating modifiers to improve the mechanical characteristics of hybrid nano silica epoxy composites. The project involved the execution of a series of tests to determine various material properties. Specifically, fracture test was performed to ascertain the fracture toughness, and a dynamic mechanical thermal analysis test was carried out to determine the glass transition temperature (T_g), storage modulus (E'), and loss modulus (E''). Based on the results obtained from these tests, the project can be concluded.

1. The incorporation of CTBN into the epoxy matrix leads to notable enhancements in fracture toughness. The optimum CTBN loading improves fracture toughness up to 79.4% at 15 wt.% CTBN. Adding 3 wt.% nanosilica into the previous blend (epoxy + 15 wt.% CTBN), further increases the fracture toughness, reaching a maximum enhancement of 107.7%.
2. The T_g values of DGEBA increases as much as 18.32%, by adding 20 wt.% CTBN. Further adding 4 wt.% nanosilica leads to an increase in to 83.33°C.
3. The addition of 20 wt.% CTBN causes the value of loss modulus to increase 164.7%, compared to the neat epoxy matrix. Substantial improvement up to

1600% relative to neat epoxy is observed by adding 4 wt.% nanosilica into the mixture.

4. At 20 wt.% CTBN loading, the value storage modulus achieves $1.67E+08$ Pa, which is 61.4% increment. Further adding 4 wt.% nanosilica leads to substantial increase of up to 1662% when compared to the neat epoxy matrix.

ACKNOWLEDGEMENT

The authors would like to thank the Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, Kuala Lumpur, Malaysia

DECLARATION OF COMPETING INTEREST

None.

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