

Comparison of the Experimental Mechanical Properties and DMA Measurement of Nanoclay Hybrid Composites[§]

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Abstract

This study explores the effects of nanoclay addition on mechanical response of Glass/Carbon/Glass fiber (G/C/G) reinforced epoxy matrix composite laminates under tensile and flexural loadings. Organomodified nanoclay containing Glass/Carbon/Glass hybrid composite laminate was evaluated for dynamic mechanical properties as well as mechanical strength, stiffness and ductility. Three different weight fractions of nanoclay containing fiber reinforced hybrid composites were manufactured. The amount of nanoclay additions were 0 wt %, 0.75 wt % and 1.25 wt % with respect to epoxy resin and hardener. A nanoclay containing epoxy – Glass/Carbon/Glass hybrid composite laminate were manufactured by using a hydraulic hot press. Then, tensile, flexural tests and dynamic mechanical analysis (DMA) was implemented to ASTM standard specimens which were cut from the plates by using abrasive water jet cutter. Uniaxial tensile and three-point bending tests have been carried out to obtain some mechanical characteristics such Young's modulus, tensile strength, break strain, flexural strength and modulus of the hybrid composites. DMA measurements also performed to compare nanoclay effect. The results of this study demonstrated that the mechanical behavior was positively affected by nanoclay addition into epoxy resin. The tensile strength and flexural strength significantly increased compared to the non-nanoclay hybrid composite (pure). However glass transition temperature (T_g) of hybrid composites decreased with increasing amount of nanoclay.

Keywords: Dynamic mechanical analysis, hybrid composites, mechanical properties, nanoclay.

1. INTRODUCTION

In recent years, using nanoclay particles as filler within the epoxy matrix have been widely used in many applications since addition of nano particles as filler enhances properties of composites such as mechanical, thermal, impact and physical.

Several researchers have investigated the mechanical properties of composites with nanoparticles [1 - 5]. The properties of composites may alter and may strongly rely on the quality and composition of the nano particles. Xu and Hoa investigated interlaminar fracture toughness of carbon fiber reinforced epoxy/clay nanocomposites. It was obtained that Mode I interlaminar fracture toughness of unidirectional carbon fiber reinforced composite was also increased by 53% and 85% with 2 and 4phr nanoclay respectively. Also, they showed that a small amount of nanoclay (2phr) contributed to the augmentation of flexural strength, but adding more clay was not improve the flexural properties more [6]. Zhou and colleagues performed dynamic mechanical analysis, thermogravimetric analysis and flexural tests on unfilled, 1, 2, 3, and 4 wt% clay filled SC-15 epoxy to identify the effect of clay weight fraction on thermal and mechanical properties of the epoxy matrix. The flexural results displayed that 2.0 wt% clay filled epoxy demonstrated the highest improvement in flexural strength. DMA studies also revealed that 2.0 wt% systems exhibit the highest storage modulus and T_g as compared to neat and other weight fraction [7]. Azeez and colleagues have reported that epoxy clay nanocomposites have the greatest potential for applications. They showed that the well dispersion of the clay particles in the polymer matrix yields enhanced tensile modulus, storage modulus and tensile strength even with a small amount of nanoclay ($\leq 5\%$). Also, they explained that the main reason for this improved property in nanocomposites is the large interfacial interaction between the matrix and layered silicate [8]. Dynamic mechanical and fracture toughness properties of the CF/PPc/organoclay composite were experimentally investigated by Gabr and friends. It was focused the effect of organoclay on the interfacial adhesion between plain woven carbon fiber (CF) and compatibilized polypropylene. They obtained weight of organoclay content plays a major role to improve initiation and propagation interlaminar fracture toughness in mode I [9]. Bhattacharya has reviewed nanoparticle filled polymer nanocomposites and their potential application. It is stated

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that homogeneous dispersion of the nanofiller in the polymeric matrix and strong interaction between the filler and the polymer is absolutely necessary for good reinforcement. It is also pointed out that at higher nanofiller content, composite properties decrease indicating difficulties in dispersing the fillers [10]. Studies obtained from literature were understood that with a small amount of nanoclay dispersed in an epoxy resin a substantial improvement in the mechanical properties. However, mechanical improvement and the thermal characterization of composites must still be investigated in depth to provide understanding of the microstructure system. The main focus of this study was to evaluate the influence of the nanoclay particles as filler on the static and dynamic mechanic properties of hybrid composites that manufactured with hand lay-up method. Organomodified nanoclay was dispersed into epoxy resin with using ultrasonic cavitation techniques. Epoxy resin with or without nanoclay was poured and distributed on glass and carbon fabrics to produce prepreg sheets. Glass and carbon prepreg sheets added up and pressed to obtain hybrid plates. Tensile, flexural and dynamic mechanic analyses were implemented to Glass/Carbon/Glass fiber reinforced epoxy matrix hybrid composites to identify the characteristics of the specimens.

2. MATERIALS AND METHODS

2.1 Manufacturing of the Epoxy– Nanoclay Matrix and Hybrid Plates

The studied matrix included epoxy resin, hardener and nanoclay. Nanoclay was one of the most widely used nano filler materials. EsanNANO 1-140 montmorillonite nanoclay was used as filler, which had 40 Å enhanced gaps between layers for homogenous dispersion, supplied from Esan, Eczacıbaşı, İstanbul, Turkey. The areal weights of the twill weave carbon and plain weave E-glass fibers mats were 245 g/m² and 200 g/m², respectively. Both fibers and epoxy resin system was supplied from Fibermak, İzmir, Turkey.

The epoxy resin and the nanoclay were first thoroughly mixed by using ultrasonic mixer for different volume fractions of nanoclay. The nanoclays were dispersed in the epoxy resin at 0, 0.75, and 1.25wt% with respect to epoxy resin (Fig. 1a). The weight fraction of nanoclay was selected depending on the literature studies [11, 12]. The desired weight percent nanoclays added into the epoxy resin and then the mixing was performed by using Hielscher UP400S ultrasonic device (UP400S 400 watts, frequency 24 kHz, amplitude adjustable 20 - 100 %) with circulated cold water system. At least half an hour sonication energy was applied to epoxy nanoclay mixture for complete distribution (Fig. 1b). Then, a layer of epoxy-nanoclay mixture was carefully applied using hand roller to the carbon and E-glass fibers. The productions of laminates were performed after 10 days. Dried fabrics became resin pre-impregnated (prepreg) sheets. Five layers E-glass prepreg sheets were placed bottom and upper part of the Teflon film while five layers carbon prepreg sheets were placed between E-glass prepreg sheets (Fig. 1c).

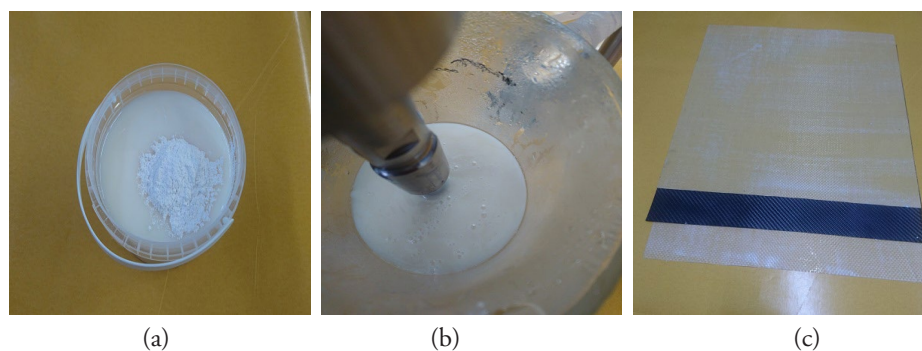


Figure 1. Production stages of plates, (a) adding nanoclay into epoxy, (b) dispersing nanoclay and (c) hybrid plate stacking sequence

The nanoclay reinforced epoxy – Glass/Carbon/Glass fiber composite laminates were fabricated using a hydraulic hot press. Teflon film placed in hydraulic hot press and 10 bar pressure applied. Temperature of the press increased from room temperature to 125°C. A plate was waited at 125°C for 1 hour as optimized in earlier work [13] and then cool down to room temperature and finally gets the part out from the press. A nanoclay reinforced epoxy–Glass/Carbon/Glass fiber hybrid composite laminates were manufactured in dimensions 400 mm square by thickness 2.5 mm. Tensile, three point bending and DMA test specimens were cut from the plates by using abrasive water jet cutter.

2.2 Tensile and Flexural Testing

Uniaxial tensile and three point bending tests have been carried out by using a universal test machine (Shimadzu) with a loading speed of 2 mm/min according to ASTM D 3039-14 [14] and 1 mm/min, respectively. In tensile test, at least three specimens were evaluated for each reinforcement weight ratio to provide the quality of the experimental results. Besides, for three point bending test at least five specimens were tested. The rectangular specimens with dimensions 250 x 25 mm² for tensile test and 76.8 x 14 mm² for three point bending test was used. Composite tabs were bonded to the

ends of the tensile test coupons. Span length was set to 64 mm for three point bending tests. The elongation in specimen through load direction was monitored with sensitive camera system in tensile test. The horizontal axes of stress – strain curve was drawn with that data. Both Young’s modulus and flexural modulus were obtained with drawing tangent line to stress - strain curve. Tensile and three point bending tests were shown in Fig. 2.



Figure 2. Test setup of composite specimen, (a) tensile test and (b) three point bending test

2.3 Glass Transition Temperature Testing

The glass transition temperature (T_g) of the hybrid composite materials was measured using a DMA Q800 (TA Instruments) test device. Dynamic Mechanical Analysis (DMA) was done in accordance with the ASTM D4065 – 12 Standard [15]. Composite specimens were heated at rate of 2 °C/min and the temperature increased from 25 °C to 150 °C for composites. Test specimen dimensions had 10 mm in width, 65 mm in length and 2.5 mm in thickness. Tests were done dual cantilever mode with 1 Hz frequency and 15 μ m amplitude. Two specimens were tested for each nanoclay group. The results were evaluated with storage modulus – temperature, loss modulus – temperature and $\tan \delta$ – temperature curves.

3. RESULTS AND DISCUSSIONS

The objective of this study was to improve static and dynamical mechanical properties of epoxy – Glass/Carbon/Glass fiber hybrid composites. Improvements in that could be achieved because of nanoclay additions.

3.1 Mechanical Results

Tensile and three point bending tests were performed in order to define the effects of the nanoclay weight fraction on the tensile and bending strength, modulus and break strain. The tensile and three point bending tests were conducted at room temperature with a camera system to determine Young’s modulus on the elastic part of the test. The tensile and bending test results presented in Table 1 and 2 for each weight fraction, respectively.

Table 1. Tensile test results of hybrid composite plates

Test/ Composite	Tensile strength (MPa)		Young’s modulus (GPa)		Break strain (%)	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Pure	599.85	37.96	52.82	2.63	1.16	0.11
0.75 Clay	625.32	24.48	52.35	1.86	1.20	0.08
1.25 Clay	617.54	8.93	50.96	1.39	1.21	0.05

According to Table 1, 0.75 wt % nanoclay loaded specimen had the highest tensile strength. This could be because of good particle distribution or even exfoliation. The average tensile strength for 0.75 wt % nanoclay loaded specimen showed 4 % greater than the pure material. At higher nanoclay loadings, a reduction in tensile strength was occurred since large aggregates could form in the matrix, but still that value higher than that of pure specimen. The Young’s modulus (E) was decreased for all nanoclay containing specimens. The reduction in modulus negligible for 0.75 wt % nanoclay containing specimen, but approximately 4 % decrease was shown from 1.25 wt % nanoclay loaded specimen. Interaction and bonding between fibers and matrix increased with nanoclay presence. When nanoclay added to matrix, the applied force to composite material was easily transferred to fiber from matrix. So nanoclay containing composite material could withstand more elongation than pure specimen and consequently, break strain of 0.75 and 1.25 wt % nanoclay epoxy hybrid composite specimens showed approximately 4 and 5 % higher than that of pure specimen, respectively.

Table 2. Bending test results of hybrid composite plates

Test/ Composite	Flexural strength (MPa)		Flexural modulus (GPa)		Break strain (%)	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Pure	794.28	39.09	29.68	0.81	2.94	0.18
0.75 Clay	825.93	14.43	28.82	1.04	3.21	0.06
1.25 Clay	892.05	26.34	31.25	0.84	3.08	0.11

Flexural strength increased significantly with nanoclay existence according to Table 2. When 0.75 and 1.25 wt % nanoclay was added to epoxy matrix, flexural strength increased approximately 4 and 12 % compared to pure specimen, respectively. However, 3 % decrease was seen in flexural modulus with 0.75 wt % nanoclay containing specimen compared to pure one. But the highest flexural modulus belongs to 1.25 wt % nanoclay loaded specimen. A 5 percent increase in flexural modulus was seen from this specimen compared to that of pure specimen. Besides flexural strength and modulus, percentage of break strain significantly increased with nanoclay addition. The highest increase was shown from 0.75 wt % nanoclay containing hybrid composite specimen. As in tensile test, applied force successfully transferred to fibers so break strain value increased.

3.2 DMA Measurements

In a dynamic mechanical analysis (DMA) of the composite material storage modulus – temperature curve was shown in Fig. 3a. In the beginning, the highest and the lowest storage modulus belongs to 1.25 wt and 0.75 wt % nanoclay containing hybrid laminates, respectively. 1.25 wt % nanoclay addition increased storage modulus approximately 9 % compared to pure specimen. The increase actualized probably the restricted molecular motion. When temperature increased with time, storage modulus decreased for all specimens. Rate of drop was smaller in glassy state, but the rate was increased while approaching to glass transition temperature. Modulus drop was actualized in 1.25 wt % nanoclay containing specimen earlier than others. After glass transition temperature exceeded storage modulus became stable for all specimens. This region was called rubbery plateau. The difference between glassy state and rubbery plateau was the projection of crosslink density. The lowest difference in storage modulus in test means the higher crosslink density. 0.75 wt % nanoclay containing specimen showed the lowest decrease in modulus so crosslinking density was the highest for this specimen.

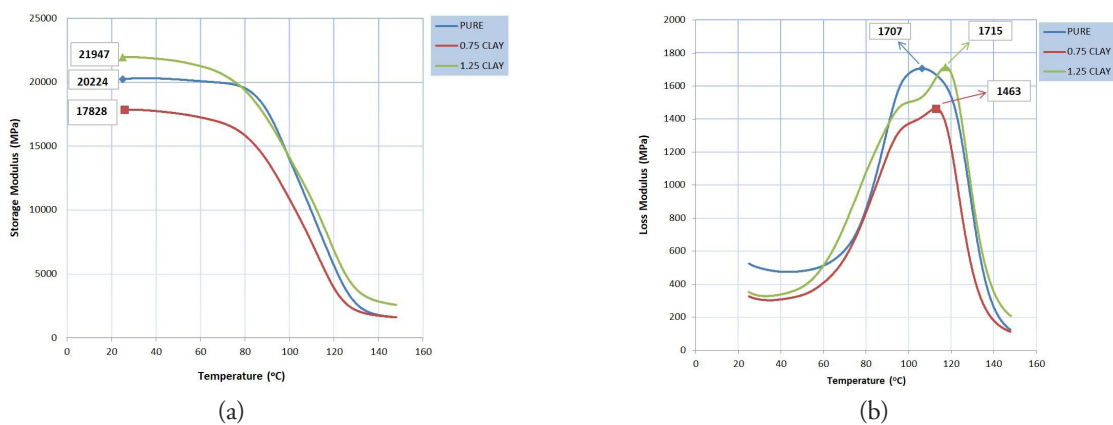


Figure 3. DMA results of hybrid composites, (a) Storage modulus vs temperature and (b) Loss modulus vs temperature

Different nanoclay loaded epoxy - Glass/Carbon/Glass fiber hybrid composites' loss modulus – temperature curve was shown in Fig. 3b. The highest loss modulus belongs to 1.25 wt % nanoclay containing specimen. Pure specimen showed 1707 MPa loss modulus. Addition of 0.75 wt % nanoclay decreased loss modulus 14 % compared to pure specimen. Peak points of loss modulus were shifted to higher temperature with nanoclay addition.

The glass transition temperature (T_g) of the laminates were identified by the highest point of $\tan \delta$ was seen. $\tan \delta$ – temperature curve was shown in Fig.4. $\tan \delta$ was obtained by dividing loss modulus with storage modulus. According to figure, pure specimen's T_g value was 127°C. Adding nanoclay into epoxy matrix resulted decrease in glass transition temperature. When 0.75 wt % nanoclay added to matrix, T_g value decreased 4 %. Also 1.25 wt % nanoclay containing specimen's T_g decreased 1 % compared to that of pure specimen. However, $\tan \delta$ values give some information about fiber/matrix interaction. Fiber/matrix interaction and surface properties were increased and molecular motion was decreased with $\tan \delta$ decreased. So adding nanoclay into hybrid composites resulted in decrease in $\tan \delta$. 1.25 wt % nanoclay containing specimen had the lowest $\tan \delta$, hence the surface properties and fiber/matrix interaction improved compared to pure hybrid composite.

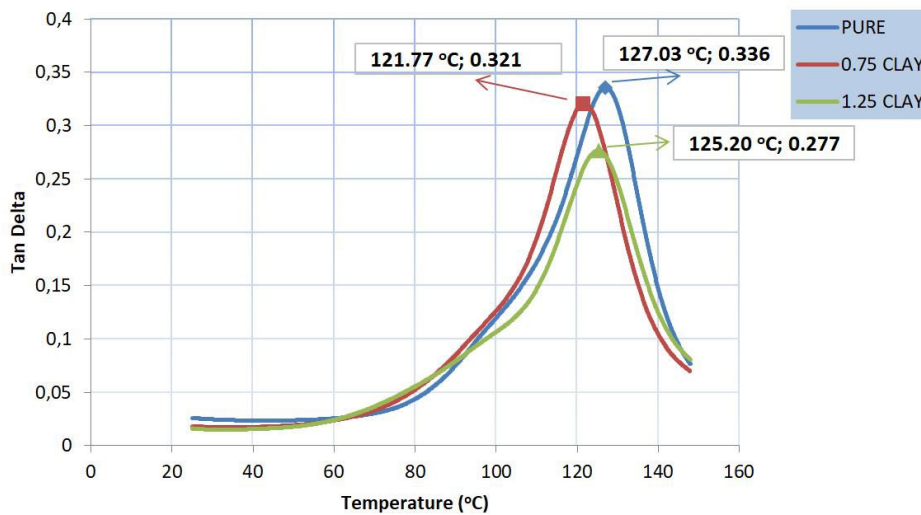


Figure 4. Tan δ vs temperature curve of hybrid composite laminates

4. CONCLUSION

This study showed that mechanical property improvements could be acquired in an epoxy – Glass/Carbon/Glass fiber hybrid composite laminate reinforced with organomodified nanoclays under tensile and flexural loadings. Addition of nanoclay produced a substantial increase in tensile and flexural strengths of hybrid composites. The results showed that the montmorillonite nanoclay reinforced hybrid composite would have a greater strength, break strain and flexural modulus than the pure hybrid composite. However, glass transition temperature (T_g) of nanoclay containing hybrid composites' decreased compared to that of pure composite, according to dynamic mechanical analysis (DMA). The following conclusions can be highlighted from this study.

- (1) The tensile strength of hybrid composites showed a peak at 0.75 wt % nanoclay, whereas the flexural strength increased continuously with nanoclay content.
- (2) The flexural strength and modulus of hybrid composites significantly enhanced by the addition of nanoclay. 12 % and 5 % increases in the flexural strength and modulus were found with 1.25 wt % nanoclay dispersed in the epoxy resin hybrid composite sample.
- (3) Nanoclay loaded hybrid composite specimen showed more elongation than that of pure specimen. It could be shown that nanoclay improved the interaction between matrix and fibers so the applied force transferred from matrix to fibers.
- (4) The glass transition temperature decreased 4 and 1 % compared to pure specimen for 0.75 and 1.25 wt % nanoclay containing hybrid composites, respectively. But, fiber/matrix interaction and surface properties were increased with nanoclay addition.

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