Thermally Exfoliated Graphene Oxide (TEGO) Reinforced Fast-Cure Epoxy Resin: Cure Behavior and Flexural Properties

Sinem Elmas [1,2,3], **Hatice S. Sas** [*1,2,3]

[1] Integrated Manufacturing Technologies Research and Application Center. Sabanci University. Orhanli-Tuzla. 34956 ISTANBUL, TURKEY

[2] Faculty of Engineering and Natural Sciences. Sabanci University. Orhanli-Tuzla. 34956. ISTANBUL, TURKEY

[3] Composite Technologies Center of Excellence. Sabanci University-Kordsa. Istanbul Technology Development Zone. Pendik. 34906 ISTANBUL, TURKEY

Abstract: Fast-cure epoxy resin systems allow being manufacturing of composite parts in minutes. However, the brittle nature of the polymer limits its usage due to crack initiation and growth. Nanofillers are widely used to enhance the epoxy resin's mechanical performance. However, final mechanical properties are typically governed by the process parameters, including curing temperature and time; therefore, the curing behavior of nano-integrated composites should also be characterized. Thermally exfoliated graphene oxide (TEGO) has an outstanding effect on the mechanical properties of the polymer matrix, even at low loading amounts. This study introduced TEGO into the fast cure epoxy resin system, and the cure kinetics was characterized using dynamic differential scanning calorimetry (DSC). TEGO modification increased curing time, but the system still maintains fast cure properties. Dynamic mechanical analysis (DMA) illustrated the glass transition temperature (T_g) of TEGO-fast cure epoxy resin nanocomposite increased by 10°C. Moreover, flexural tests revealed that flexural stress was increased by 12.85% with even a low percentage of TEGO addition. Scanning electron microscopy was used for fracture surface analysis of the samples, and toughening mechanisms were addressed.

Termal Genleştirme Yöntemiyle Üretilen Grafen Oksit (TEGO) ile Güçlendirilmiş Hızlı Kürlenen Epoksi Reçine: Kür Davranışı ve Eğilme Özellikleri

Öz: Hızlı kürlenen epoksi reçine sistemleri, kısa süre içinde kompozit üretimini sağlamaktadır. Ancak, epoksi polimerin kırılgan yapısı nedeniyle çatlak başlangıcı ve büyümesi kullanım alanını kısıtlamaktadır. Nano boyuttaki katkılar epoksi reçinenin mekanik performansını artırmak için yaygın olarak kullanılmaktadır. Ürünün nihai mekanik özellikleri tipik olarak, kürleme sıcaklığı ve süresi gibi proses parametreleri tarafından yönetilmektedir, bu nedenle, nano-takviyeli kompozitlerin kür davranışı karakterize edilmelidir. Termal genleştirme yöntemiyle üretilen grafen oksit (TEGO), polimer matrisine düşük yüzdelerde eklenmesi durumunda bile polimer matrisinin mekanik özellikleri üzerinde önemli bir etkiye sahiptir. Bu çalışmada, TEGO hızlı kürlenen epoksi reçine sistemine dahil edilmiş ve nanokompozitlerin kür kinetiği dinamik diferansiyel tarama kalorimetrisi (DSC) ile analiz edilmiştir. TEGO modifikasyonu kürlenme süresini arttırmış olmasına rağmen system hala hızlı kürlenme özelliklerini korumaktadır. Dinamik mekanik analizi (DMA) sonucunda, TEGO içeren epoksi nanokompozitin camsı geçiş sıcaklığının (T_g) 10°C arttığı bulunmuştur. Ayrıca, eğilme testi sonuçları eğilme stresinin de %12,85 oranında arttığını ortaya koymuştur. Kırılma yüzeyleri, taramalı elektron mikroskobu ile analiz edilmiştir ve sertleşme mekanizmaları ele alınmıştır.

*Corresponding Author, email: hatice.sas@sabanciuniv.edu

1. Introduction

Epoxy resin systems are the most salient thermosetting polymer materials due to outstanding properties such as high mechanical properties, and thermal stability, excellent resistance against heat and many chemicals [1]–[3]. Epoxy polymers are extensively used in polymer composite materials as primary matrix. In aviation and automotive industry, they are used in the way that advanced composites, adhesive, and surface dressing. However, the epoxy resins cure cycle requires many hours. Exothermic heat release limited to ramp rates to ease the overheating risk. From an economic point of view, such long cure cycles also increase manufacturing costs [1].

Due to environmental regulations, the automotive industry is motivated to adopt lightweight structural composite parts. However, faster cure cycles are demanded in the automotive industry to achieve mass production and reduce the overall manufacturing time [4], [5]. To overcome in shortcomings, fast cure epoxies are developed, allowing for manufacturing the composite parts in minutes [6]. Fast-cure epoxy resin curing reaction is highly exothermic compared to conventional epoxy systems. This may lead to significant temperature gradients over the thickness and temperature overshoot which could result in the degradation and breakdown of the epoxy polymer [1], [6], [7].

Nanocomposites can be defined as polymer matrix that contain homogeneously dispersed nanofillers. Nanofillers are improved the polymer's properties [8]. Although the many advanced properties of epoxy resin, high crosslinking density gives it a brittle nature. The brittle nature of the polymer leads to crack initiation and growth and restricts its usage in some areas [9]. To improve the epoxy resin properties, nanofillers are used widely. One of the main ideas behind the integration of nanofillers into the polymer is to enhance the properties of the final composite material by improving the matrix material properties [10]. The filler's structure and concentration are essential for achieving optimum properties. Also, the capability of the Van der Waals interactions or covalent bond formation of the filler with the epoxy matrix is an important factor. Nanoparticles positively affect epoxy's thermal and mechanical properties because of their superior specific surface area and small size. In the fast-cure epoxy resin systems, nanoparticles also integrated to matrix for reduce the temperature exotherm [6]. Graphene has a two-dimensional structure composed of carbon atoms layers arranged as a honeycomb network. The hexagonal lattice of the carbon atoms leads to a high surface area. Despite graphene's light and thin structure, it is extremely durable and electrically and thermally conductive [11]. Graphene and derivatives are used widely as reinforcement material in polymer matrix due to, even at very low percentages, having a significant influence on the polymer's mechanical performance [11], [12]. However, the dispersion of graphene-based nano reinforcements into epoxy resin depends on the surface chemistry of graphene and its surface functional groups. Thermally exfoliated graphene oxide (TEGO) is obtained by removing most functional groups from the graphene oxide by thermal treatment. The hydrophilic feature of the graphene oxide altered by removal of oxygen groups, increases the exfoliation ratio, which makes it easier to control surface chemistry and enhances interactions between TEGO and the polymer matrix, hence improving the mechanical properties [12], [13].

There are several studies about nano reinforcement integration into the epoxy polymer matrix and its effect on the properties in the literature. Senis et al. [14] have distributed graphene oxide (GO) into a conventional epoxy resin to improve the mechanical performance of the epoxy composite. They measured mechanical performance of composites through an interlaminar shear strength test and found an increase up to 0.63 vol% GO content, and strength decreased above this content due to agglomeration. Monfared Zanjani et al.[12] dispersed TEGO into a conventional epoxy system with three different percentages: 0.0125 wt%, 0.025 wt%, and 0.0 5wt%. They have found a gradual improvement in flexural strength of the nanocomposite up to the 0.025 wt% TEGO content, and finally they observed 85% flexural modulus, and 64% flexural strength improvement by integration of 0.05 wt% TEGO into resin system. Keller et al. [6] have integrated to silica nano reinforcement to reduce the high exothermic reaction of fast cure epoxy resin and studied the curing behavior. They have observed total heat of curing reaction was decreased with 20 wt% of silica nanoparticles addition, which provides a more controllable manufacturing process. In addition, they have found the tensile Young's modulus increased from 3.58 to 4.62 GPa. Nonahal et al. [15] have designed epoxy/amine-functionalized GO nanocomposites by using 0.1 wt% of GO and amine modified GO nanosheets. They have observed a reduction in activation energy of cure reaction after amine-functionalized GO integration into epoxy, indicating a faster cure reaction than neat and GO integrated epoxy. They have supported interfacial adhesion by scanning electron microscopy (SEM) micrographs taken from fracture surface of nanocomposites and stated GO has a poor dispersion compared to functionalized GO.

Process parameters like the temperature of curing and time have influence on the final mechanical performance of the nanocomposites. Therefore, in consequence of the literature review, to the best of our knowledge, the effect of a graphene-based nano additive on cure kinetics and flexural properties of a fast-cure epoxy resin system was

not investigated. The present study aimed to analyze the effect of nano reinforcement on the cure kinetics of the fast-curing epoxy resin system and improvement on the flexural properties of fast-cure epoxy nanocomposites. Although the cure kinetics of conventional epoxy systems have been studied in the literature, fast-curing epoxy systems have their characteristics of cure behavior. In line with these aims, TEGO was chosen as a nano additive and integrated into a fast cure epoxy resin system by 0.05 wt.% as indicated in Monfared Zanjani et al.'s[12] study. The change in cure kinetics with TEGO integration was characterized by dynamic scanning calorimetry (DSC) analysis and modeled through a diffusion-controlled autocatalytic equation. In addition, the gel time measurement was performed to a better understanding the change in rheological behavior of fast-cure epoxy resin. Thermomechanical and flexural properties of the nanocomposite specimens were analyzed through dynamic mechanical analysis (DMA) and three-point bending tests, respectively. To understand failure the fracture surfaces of specimens were analyzed by scanning electron microscopy (SEM).

2. Material and Method

2.1. Materials

Thermally exfoliated graphene oxide (TEGO) Grade-2 with a bulk density of 0.022 $g.ml^{-1}$ and an average of 23 layers was supplied by Nanografen Co., Turkey. The oxygen content is about <4% (provided by the manufacturer). Three-component fast cure epoxy resin system (CM11), epoxy, hardener, and catalyst were supplied by KORDSA, Turkey, and ethyl alcohol (with 99.9% purity) was purchased from ISOLAB.

2.2. Preparation of neat fast cure epoxy and fast cure epoxy / TEGO nanocomposites

The three-component fast cure epoxy resin system that contains epoxy, hardener and the catalyst was used to prepare a neat epoxy composite. Epoxy was put into the oven at 85 °C, and the hardener and the catalyst were put at room temperature one night before as recommended by the manufacturer. The weight percentage of TEGO was determined as 0.05 wt.%, as suggested in Monfared Zanjani et al.'s [12] study. For TEGO modification, firstly, 0.05 wt.% of TEGO was dispersed into 20 ml of ethyl alcohol by using a probe sonicator (Hielscher UP200Ht) at 0.5 cycle and 90 amplitude for 2 hours as shown in experimental scheme (Figure 1). Then, the TEGO+ethanol mixture was combined with hot epoxy liquid and sonicated for another 2 hours with an interval of 2 minutes each 5 minutes of sonication. The mixture was left in oven at the 85 °C and the ethanol is evaporated for one night. The epoxy is mixed with hardener and catalyst by a weight percentage of 78.6:12.7:8.7. A thinky planetary vacuum mixer (PULSAR) was used for the mixing process at 0.02 kPa, 800 rpm for 4 minutes. A hole was made on the thinky mixer box' cover, and degassing was ensured under vacuum. After that small amount of uncured resin was separated and stored at -18 °C for dynamic scanning calorimeter and gel time analysis. The remaining resin was poured into the pre-heated at 140 °C, and the release agent applied Teflon molds. The curing was done in the furnace at 140 °C for 5 minutes. The specimens were cut by a 3-axis computer numerical control (CNC) laser cut machine (POYSAN) in specified dimensions for characterization.
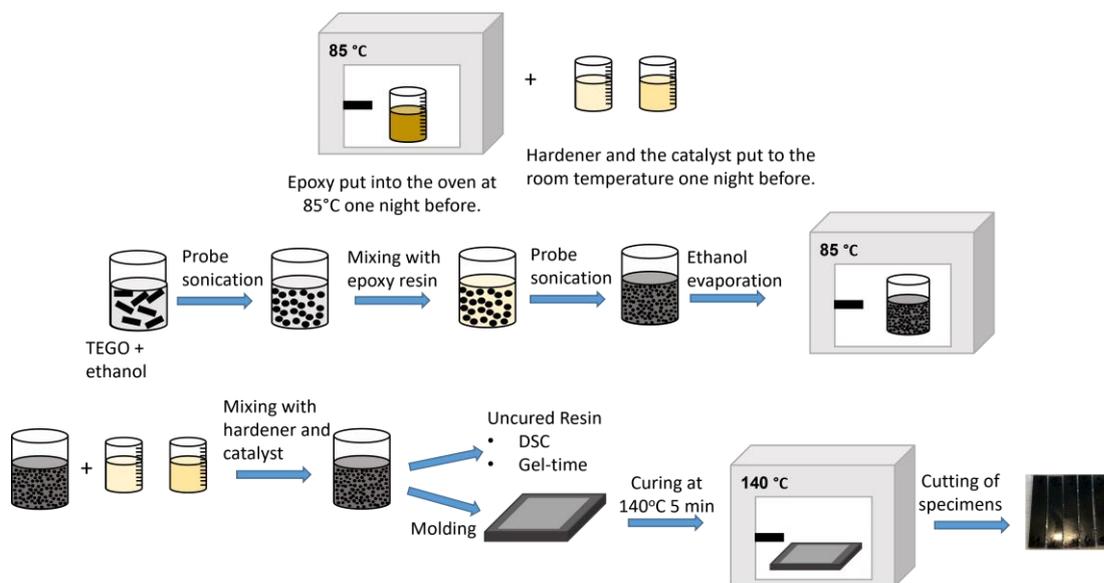
Figure 1. The experimental route of TEGO sheets dispersion into the fast cure epoxy resin by sonication process

2.3. Characterization

Dynamic Scanning Calorimeter (DSC) analyze were performed by utilizing the Mettler Toledo DSC^{+3} instrument under the nitrogen (N_2) environment with an airflow rate of 50 ml/min with approximately a sample mass of approximately 10 mg. Cure reactions of both neat fast cure epoxy, and TEGO-fast cure epoxy were studied by dynamic DSC within a temperature range from 25 to 300 °C at four heating rates of 5, 10, 15, and 20 °C/min. Cure time in different isothermal temperatures was analyzed by Mettler Toledo DSC+3 STARe SW16.30 software.

The degree of cure (α) was calculated according to equation (1); the ratio of the heat of cure reaction, ΔH_t (the area of the under the curve a given temperature T) by total heat of cure reaction (ΔH) [15].

$$\alpha = \frac{\Delta H_t}{\Delta H} \tag{1}$$

Moreover, the fast cure epoxy resin system cure kinetic is analyzed by a fitting study via a MATLAB script through a diffusion-controlled autocatalytic equation [16].

$$\frac{d\alpha}{dt} = K_1 \alpha^{m_1} (1 - \alpha)^{n_1} + \frac{K_2 \alpha^{m_2} (1 - \alpha)^{n_2}}{1 + e^{\left(D(\alpha - (\alpha_{C0} + \alpha_{CT}T))\right)}} \quad \text{with } K_i = A_i e^{-\frac{E_{A_i}}{RT}}, i = 1,2 \tag{2}$$

where $d\alpha/dt$ is the cure rate, D is the diffusion constant, α_{C0} are the critical cure degree at absolute zero, α_{CT} critical resin degree of cure with temperature and m_1, m_2, n_1, n_2 are model parameters; K_1 and K_2 are the Arrhenius temperature dependency, A is the preexponential coefficient, E_A is the activation energy, T is the absolute temperature, R is the universal gas constant.

The fast cure epoxy resin gel time measurement was carried out by Anton Paar MCR 702 TwinDrive rheometer at 120 °C with a 1Hz constant frequency and controlled strain of 0.01%.

Dynamic mechanical analysis (DMA) is performed with two repeats by Mettler Toledo DMA/SDTA861e instrument in single cantilever mode at 1Hz frequency with a heating rate of 3 °C/min within a temperature range from 25 to 300 °C with the specimens in a dimension of 80 mm x10 mm x 4±0.2 mm according to ASTM D7028-07 standard.

The mechanical performance was characterized by a three-point bending test according to ASTM D790-03 standard using Instron Universal Testing Machine (5982) equipped with a static load cell of ±100 kN. The test was done on five specimens with 76.8mm x 12.7mm x 4±0.2 mm dimensions and a 1.7 mm/min crosshead rate. After that, fracture surface of the specimens was analyzed by scanning electron microscopy (SEM). The images were taken using Leo Supra35VP field emission scanning electron microscopy by utilizing the secondary electron mode at electron high tension (EHT) = 3 kV and a working distance of 6 mm after coated with carbon solution to increase conductivity.

3. Results

3.1. Effect of the TEGO on the curing behavior

The final mechanical performance of nano-reinforced epoxy nanocomposites highly depends on the interfacial adhesion between the nanofiller and the epoxy matrix. In order to understand network formation with TEGO modifications, dynamic DSC analysis was performed at four heating rates: 5, 10, 15, 20 °C/min. Heat flow curves as a function of temperature were given in Figure 2, and the main parameters of the curing such as glass transition temperature of uncured state (T_{g0}), onset temperature (T_{onset}), the peak temperature (T_{peak}), the end temperature (T_{end}) and the total heat of reaction (ΔH) were summarized in Table 1.
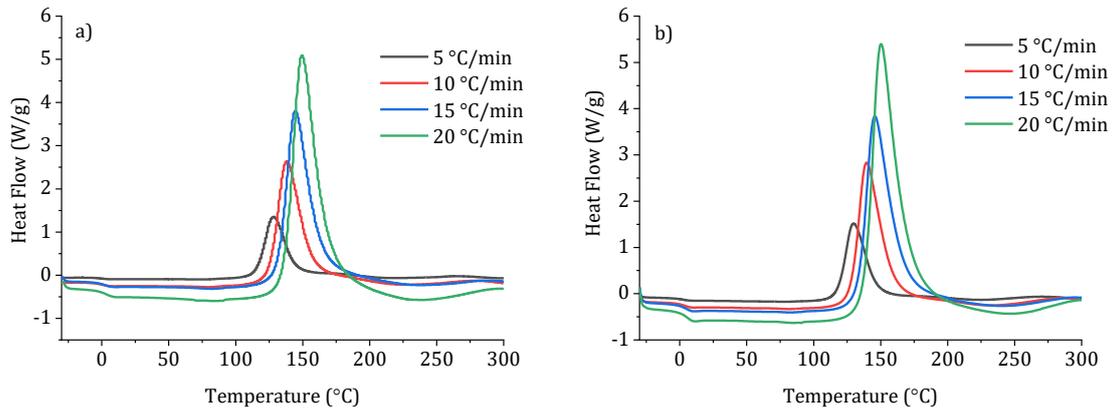
Figure 2. Dynamic DSC thermograms at various heating rates 5, 10, 15, and 20 °C/min as a function of the temperature of a) neat fast cure epoxy, b) TEGO-fast cure epoxy

Table 1. The main curing parameters: glass transition temperature of uncured state (T_{g0}), onset temperature (T_{onset}), the peak temperature (T_{peak}), the end temperature (T_{end}), and the total heat of reaction (ΔH) obtained from dynamic DSC

	Neat fast cure epoxy				TEGO- fast cure epoxy			
Heating rate (°C/min)	5	10	15	20	5	10	15	20
T_{g0} (°C)	0.20	0.46	1.78	3.32	2.51	2.97	3.55	4.84
T_{onset} (°C)	116.07	125.68	132.13	136.74	118.22	127.99	133.65	138.18
T_{peak} (°C)	128.05	137.92	144.44	149.48	129.80	139.60	145.55	150.50
T_{end}(°C)	144.85	157.91	164.80	170.32	147.82	161.12	168.82	172.88
ΔH (J/g)	311.59	347.42	350.29	389.96	380.38	447.76	428.67	461.24

As given in Table 1, the T_{g0}, T_{onset}, T_{peak}, and T_{end} temperatures of TEGO included fast cure epoxy resin shifted to higher temperature values compared to neat fast cure resin. The increase of the T_{g0}, T_{onset}, T_{peak}, and T_{end} temperatures can be ascribed to raising of the viscosity of the system due to TEGO sheets hindering the mobility of the polymeric chains [17]. The peaks of the curing curves did not become wider with TEGO integration, indicating a homogeneous network formation [18]. Also, an increase in the ΔH is observed for the resin system integrated TEGO. The increase in enthalpy can be assigned to the decreased chain mobility of the polymer due to the epoxy resin units bound to TEGO [15], [18]. Obviously, T_{g0}, T_{onset}, T_{peak}, and T_{end} raised to higher temperature values as the heating rate increased in neat fast cure epoxy and TEGO-fast cure epoxy samples. Due to high heating rates, the resin remains shorter at any temperature and the resin reaches the gel point quicker, hence, the T_{g0}, T_{onset}, T_{peak}, and T_{end} temperatures shift higher values and increase in ΔH [19].

The degree of cure (α) of the neat fast cure epoxy and the TEGO-fast cure epoxy resin was evaluated as a function of temperature (Figure 3). The sigmoidal pattern of the curves indicates the autocatalytic signature of the epoxy curing reaction [20]. The degree of cure of the TEGO-fast cure epoxy resin shifts to higher temperatures, which means that curing begins at higher temperatures due to retardation effect of the TEGO [15].
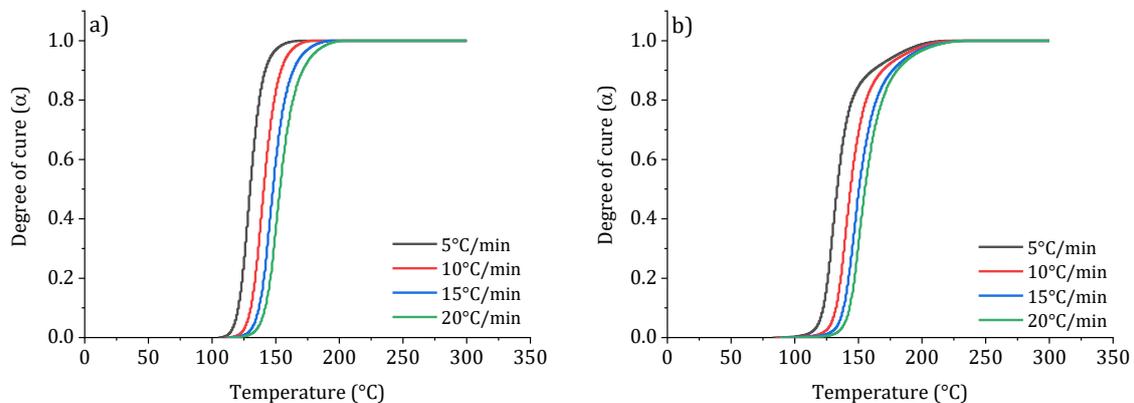
Figure 3. Degree of cure (α) curves at various heating rates 5, 10, 15, and 20 °C/min as a function of the temperature of a) neat fast cure epoxy, b) TEGO-fast cure epoxy

To understand the TEGO retardant effect on the curing time, different isothermal temperatures were also analyzed by Mettler Toledo DSC[+3] STARe SW16.30 software. The software is used model free kinetics to calculate the cure degree at desired temperature. Firstly, exothermic reaction is measured with dynamic scanning at various dynamic heating rates. Experimental cure degree is calculated from dynamic DSC results as function of temperature, then model free kinetic program calculates the activation energy and finally, results from preceding steps are used make calculation of degree of cure at any isothermal temperature [21]. The degree of cure curves at the selected temperatures are given in Figure 4 and the required cure time summarized at Table 2 as a function of the cure degree and the isothermal temperature. The time required for curing after TEGO modification was greater for each cure degree, and the cure retardancy effect is more prominent at higher temperatures Table 2. The curing time is increased almost two times at 150 °C but since the curing still takes about 10 minutes in total, the epoxy system maintains its fast-curing feature. At higher temperatures, the curing time shortens, and the interactions between the epoxy and amine groups of the hardener become harder in the presence of TEGO due to chain restrictions. The restrictive effect of TEGO is not dominant as there will be time for crosslinking reaction at relatively low temperatures. Therefore, the cure delay effect is become more dominant at high temperatures [15], [19].
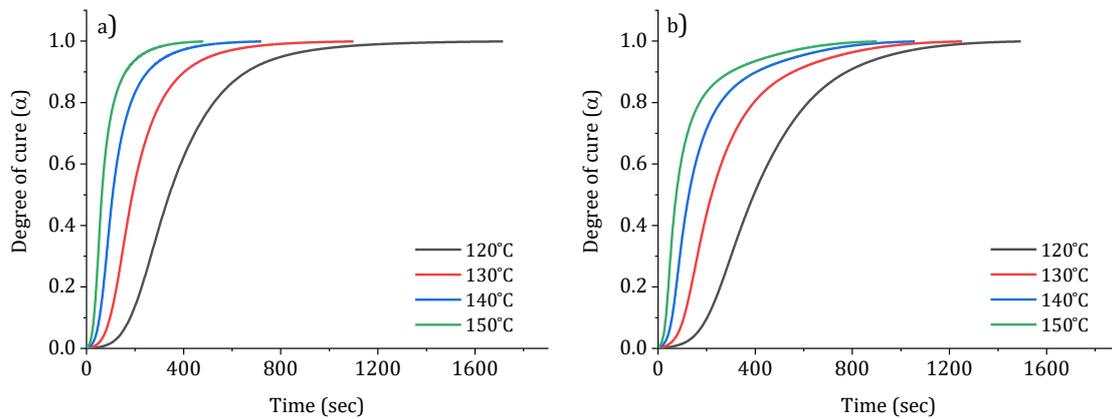
Figure 4. The degree of cure (α) evolution at isothermal temperatures of a) neat fast cure epoxy, b) TEGO-fast cure epoxy

Table 2. The degree of cure time calculated by Mettler Toledo DSC[+3] STARe SW16.30 software at isothermal temperatures

	Neat fast cure epoxy				TEGO - fast cure epoxy			
Temperature (°C)	120	130	140	150	120	130	140	150
Degree of cure (α)	Time (min)				Time (min)			
0.10	3.00	1.61	0.89	0.50	3.36	1.76	0.95	0.53
0.20	3.79	2.06	1.16	0.67	4.26	2.27	1.24	0.70
0.30	4.41	2.42	1.37	0.79	5.00	2.69	1.49	0.85
0.40	5.02	2.77	1.57	0.91	5.75	3.14	1.77	1.02
0.50	5.68	3.15	1.79	1.05	6.57	3.67	2.11	1.24
0.60	6.46	3.61	2.07	1.22	7.53	4.33	2.56	1.55
0.70	7.43	4.22	2.46	1.47	8.72	5.22	3.21	2.02
0.80	8.74	5.10	3.05	1.87	10.30	6.57	4.28	2.85
0.90	10.99	6.71	4.20	2.69	12.95	9.27	6.74	4.98
0.95	13.44	8.50	5.49	3.62	15.57	12.16	9.60	7.67
0.97	15.40	9.89	7.29	4.35	17.33	13.96	11.36	9.34
0.99	20.07	13.01	8.62	5.82	20.60	17.04	14.22	11.97

A fitting study can predict the cure behavior of epoxy resin via a MATLAB script. The dynamic DSC results were fitted simultaneously to the model described by Arikan et al.'s study [16], and one set of model parameters was obtained to fitting. Models fitting quality is presented in Figure 5, and the model parameters of equation (2) are given in Table 3. The degree of cure of neat fast cure epoxy resin and TEGO - fast cure epoxy system was precisely characterized by the kinetic model. The model correctly predicts the experimental degree of cure in dynamic conditions neat, whether or TEGO is added. The fitting accuracy is better in the case of TEGO containing fast cure

epoxy resin with a higher correlation factor (R^2) value of 0.9526 and 0.9942 at the 20°C/min heating rate, neat fast cure epoxy and TEGO-fast cure epoxy, respectively. The slight difference between numerical and experimental values may be due to increased viscosity once the reaction reaches the vitrification threshold [15]. It is observed from the model parameters that the activation energies (E_{A1} and E_{A2}) increased with TEGO modification. Amino groups are attached to the TEGO surface and enhances the dispersion of TEGO into epoxy, increased the viscosity, hence the activation energy of the reaction [22].
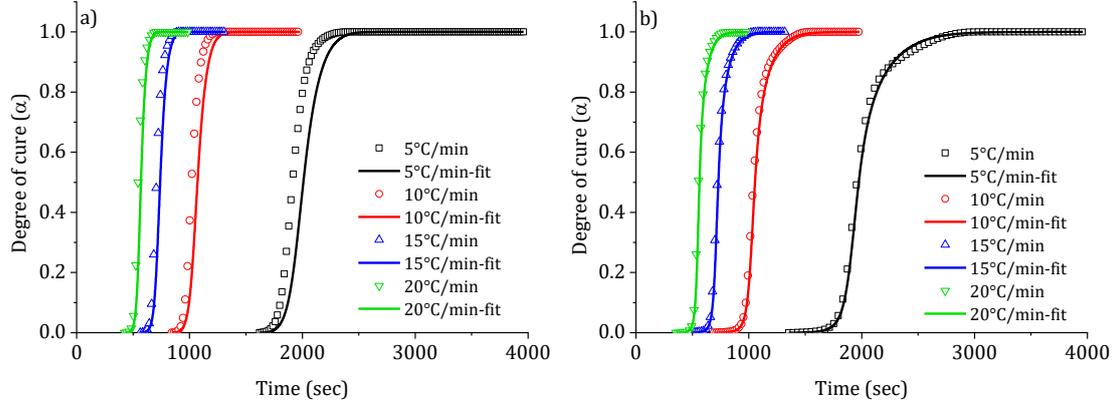
Figure 5. Degree of cure (α) profiles at dynamic heating rates a) neat fast cure epoxy, b) TEGO-fast cure epoxy. The experimental data were compared with the model predictions (continuous lines)

Table 3. Fast cure epoxy resin and TEGO (0.05wt %) / fast cure epoxy systems cure kinetics model parameters

Model Parameters	Neat fast cure epoxy	TEGO - fast cure epoxy
1st reaction Pre-exponential cure rate coefficient (A_1) (1/s)	1.14E+07	3.69E+07
Activation energy of reaction I (E_{A1}) (kJ/mol)	76.0800	90.5300
2nd reaction Pre-exponential cure rate coefficient (A_2) (1/s)	1.37E+07	6.35E+07
Activation energy of reaction II (E_{A2}) (kJ/mol)	71.7400	74.4400
1st exponential constant (m_1)	0.4591	0.0010
2nd exponential constant (m_2)	0.8640	3.2810
3rd exponential constant (n_1)	1.1140	0.8959
4th exponential constant (n_2)	1.7600	1.6979
Diffusion Constant (D)	2.5711	5.4658
Critical α at 0 K (α_{C0})	0.0095	0.0135
Increase in α with temperature (α_{CT}) (1/K)	0.0021	0.0016

To address the retardation effect of TEGO, gel time of the neat and TEGO - fast cure epoxy is measured at 120 °C isothermal temperature. Indeed, the gel time increased from 3.20 to 5.65 min with TEGO integration into the fast cure epoxy resin, as shown in Figure 6. It provides more time in the liquid composite molding manufacturing processes before the matrix reaches the gel point and solidifies, indicating more controllable production [6], [23].
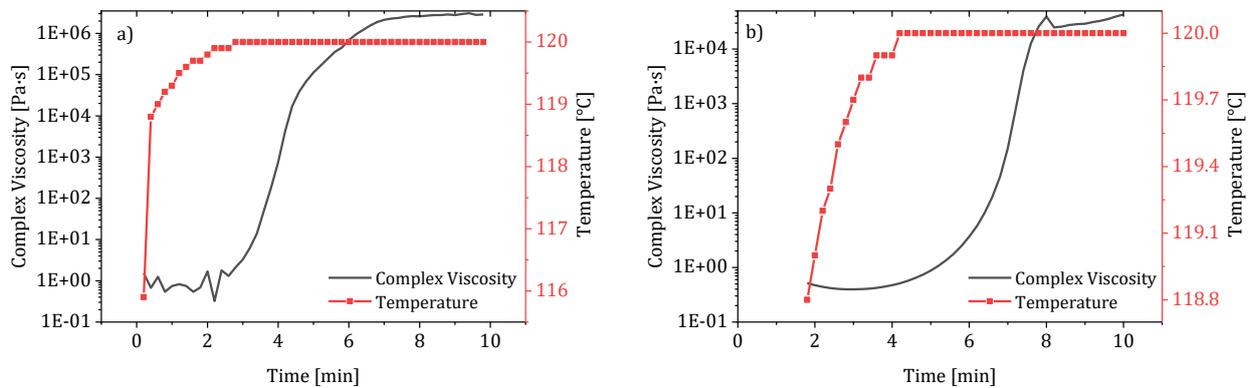
Figure 6. The gel time measurement at 120°C of a) neat fast cure epoxy, b) TEGO-fast cure epoxy.

3.2. Effect of the TEGO on thermomechanical performance

Dynamic mechanical analysis (DMA) was performed for characterize to thermo-mechanical properties of neat fast cure epoxy and TEGO-fast cure epoxy resin nanocomposites. The analysis describes the interactions between the fast-cure epoxy resin polymer chains and TEGO. Storage modulus (E'), loss modulus (E''), and tan delta (tan δ) graphs are presented in Figure 7. The storage modulus of the TEGO-fast cure epoxy nanocomposite is 1135.83 MPa at room temperature, which is slightly higher compared to the neat fast cure epoxy nanocomposite. The addition of TEGO sheets into fast-cure epoxy resin enhances the E' over the entire temperature range. The higher E' in the glass transition area is showed that the TEGO layers have strong covalent interaction with the epoxy matrix and formed covalent bonds that eventuated in an important stress transfer at the interface, that promotes to the increase of the E'. The maximum E'' value of the nanocomposite decreased relatively, from 71.64 MPa to 69.31 MPa. This suggests that TEGO nanoparticles decrease the additional internal friction with the polymer chains since the loss modulus is associated with the polymer chains' energy dissipation [18]. Tan δ is known as the ratio of the E'' to the E', and the glass transition temperature (T_g) corresponds to temperature at maximum tan δ value. As shown in Figure 8.c, the T_g of the TEGO-fast cure epoxy nanocomposite is 10°C higher than neat fast cure epoxy. The increase in T_g can be explained as excellent TEGO dispersion into the fast cure epoxy matrix, and due to the high surface area and the morphology of graphene nature might slightly increase the T_g value [24], [25].
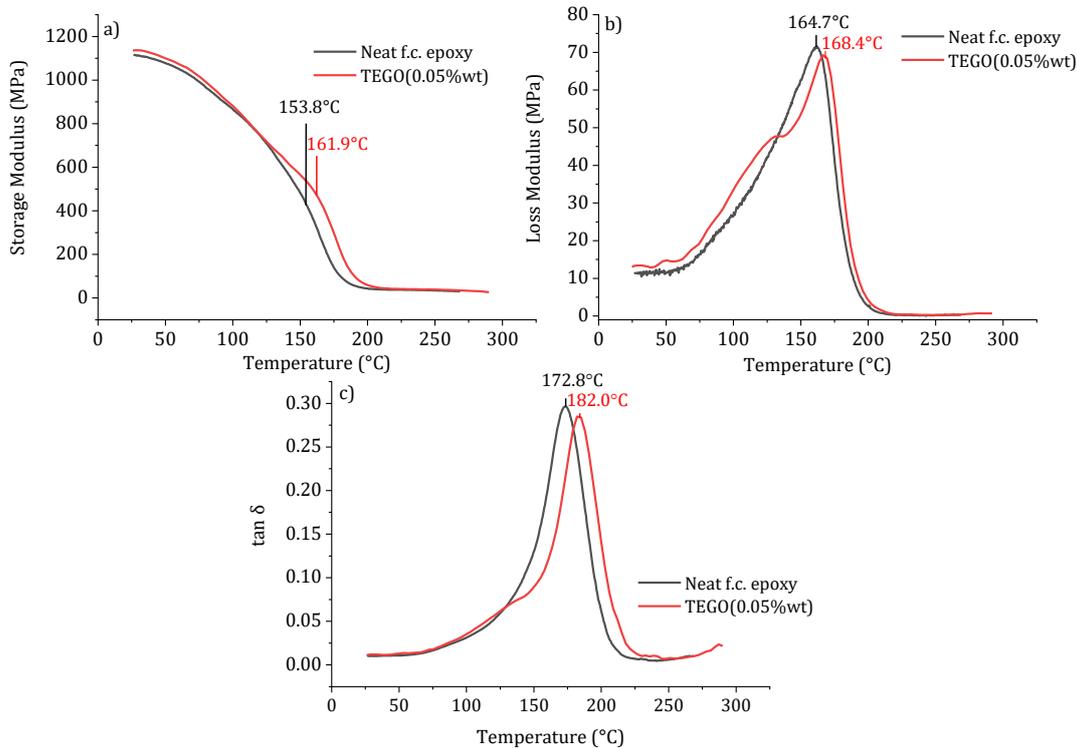
Figure 7. DMA thermograms of neat fast cure epoxy and TEGO-fast cure epoxy nanocomposites for a) storage modulus (E'), b) loss modulus (E''), and c) tan (δ).

3.3. Effect of the TEGO on flexural properties

Figure 8.a shows the flexural stress-strain curves of the neat fast cure epoxy and TEGO - fast cure epoxy nanocomposites, and Figure 8. b-d shows changes in flexural stress, strain, and modulus with TEGO integration. It is found that the flexural stress is increased by 12.85% with TEGO modification. The TEGO–fast cure epoxy nanocomposite required more strain before failure as the strain at breaks is increased by 34.21% [26]. Overall, an enhancement in flexural properties is found out with the TEGO modification to fast cure epoxy resin. Even such a low loading amount, TEGO has a significant influence on the flexural properties of fast cure epoxy resin due to good adhesion into the matrix and specific large surface area [14]. The graphene existence in the matrix is improved to matrix stress transfer hence the flexural properties. The modification of TEGO into the resin improves the fracture path hence the strength of the nanocomposites. The nano reinforcement provides more resistance to damage of the epoxy nanocomposites due to their small size and high specific surface area [11]. Neat fast cure epoxy nanocomposite is more brittle and resistance to crack growth is weak [10]. Homogeneously dispersed TEGO nanofiller can improved the interfacial properties due to matrix compatible functional groups and provide an efficient stress distribution. Also, rough surfaces ease the energy dissipation during failure, that shows the

strengthening effect of TEGO nanofiller and enhance the flexural properties of nanocomposite [12], [26], [27]. For a better understanding of the failure mechanism, the specimens' fracture surface was examined by SEM (Figure 9). It is clearly shown that from Figure 9.a, the fracture surface of the neat fast cure epoxy nanocomposite is smooth as a brittle characteristic of epoxy resin systems. The cracks propagated in straight line and moved without diversion on the fracture surface [28]. On the contrary, the TEGO-fast cure epoxy nanocomposite fracture surface is rougher compared to the neat fast-cure epoxy nanocomposite, as seen in Figure 9.b, and no apparent crack was observed on the surface. The uniform roughness and the micro voids that marked in the Figure 9.b is indicated the homogeneous dispersion of TEGO nano reinforcement into the epoxy matrix. The rough fracture surface is related to creating additional surfaces during fracture due to nanoparticle reinforcement. The TEGO sheets lead to effective load distribution and act as an obstacle to preventing crack growth [12], [15], [29].
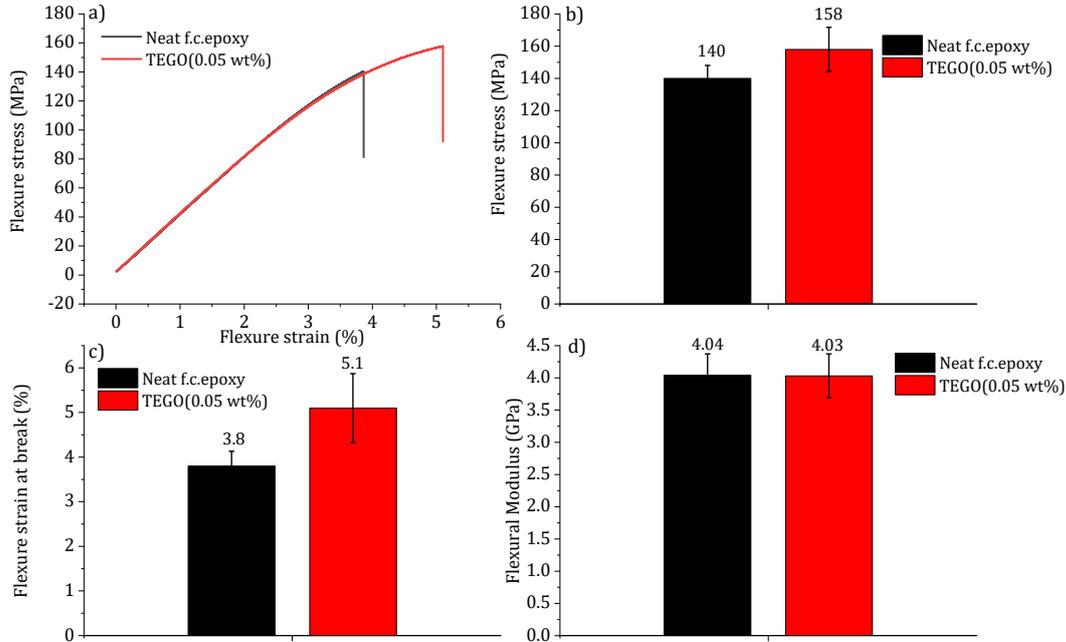
Figure 8. Flexural test results for neat fast cure epoxy and TEGO-fast cure epoxy nanocomposites, a) representative stress-strain curves, and b-d) bar charts for stress, strain, and modulus, respectively
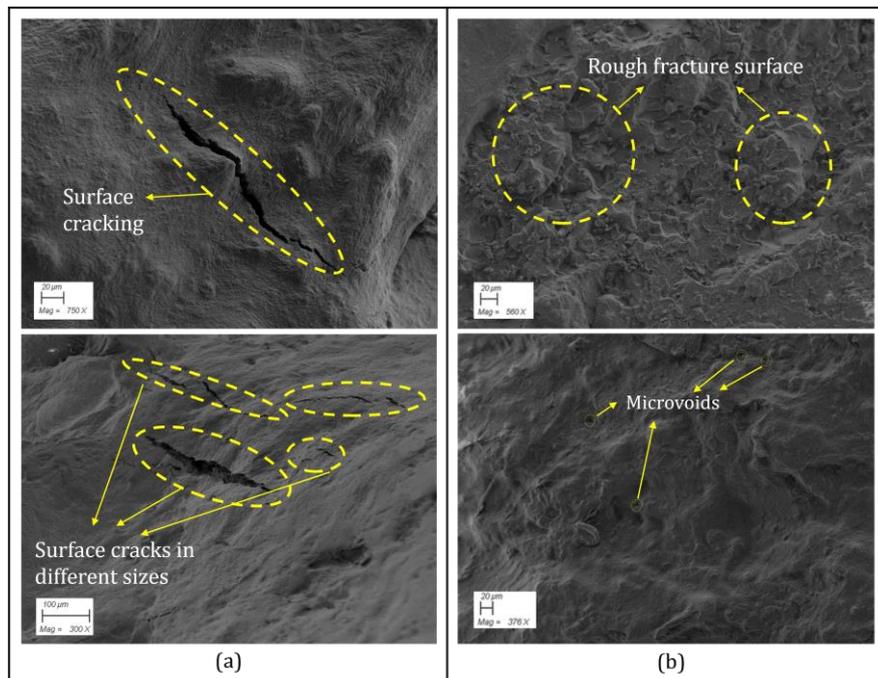
Figure 9. SEM images of three-point bending samples fracture surface at different magnifications of a) neat fast cure epoxy nanocomposite and b) TEGO- fast cure epoxy nanocomposite

4. Discussion and Conclusion

In this study effect of the thermally exfoliated graphene oxide (TEGO) modification to the fast-cure epoxy resin system on the cure kinetics and flexural properties are investigated. 0.05 wt.% TEGO was distributed homogeneously into the fast cure epoxy resin system by sonication method. The DSC results revealed that the addition of TEGO hinders the curing of fast-cure epoxy. Curing time was increased as TEGO existence restricted the mobility of polymer chains. The restriction effect is more significant at higher temperatures as the time is less for crosslinking. The cure kinetics of the fast-cure epoxy resin is also characterized by a fitting study via a MATLAB script with a diffusion-controlled autocatalytic equation. The script predicts the experimental degree of cure with higher accuracy in the case of TEGO- fast cure epoxy resin with a correlation factor (R^2) value of 0.9942. The results of the DMA analysis show that the thermomechanical properties improved as the T_g increased about 10 °C. The flexural strength and strain of TEGO-fast cure epoxy nanocomposites are improved by about 12.85% and 34.21%, respectively. Contrary to epoxy's brittle smooth surface structure, a rougher fracture surface was observed in the SEM images after TEGO modification. Also, the crack growth is prevented as the TEGO sheets act as an obstacle. The large surface area and good adhesion properties of the TEGO greatly influence the mechanical properties even at low percentages. In future studies, the effect of TEGO modified fast cure epoxy resin on the fiber-reinforced composite production process, and the effect on the final product quality.

Acknowledgment

References

[1]   D. Incerti, D. Carolan, and A. Fergusson, "Fast vs tough; The effect of faster cure cycles on the fracture properties of toughened epoxies," *Int. SAMPE Tech. Conf.*, vol. 2019-May, no. May, 2019, doi: 10.33599/nasampe/s.19.1491.

[2]   D. A. Lakho, D. Yao, K. Cho, M. Ishaq, and Y. Wang, "Study of the Curing Kinetics toward Development of Fast-Curing Epoxy Resins," *Polym. - Plast. Technol. Eng.*, vol. 56, no. 2, pp. 161–170, 2017, doi: 10.1080/03602559.2016.1185623.

[3]   P. Murias, Ł. Byczyński, H. Maciejewski, and H. Galina, "A quantitative approach to dynamic and isothermal curing of an epoxy resin modified with oligomeric siloxanes," *J. Therm. Anal. Calorim.*, vol. 122, no. 1, pp. 215–226, 2015, doi: 10.1007/s10973-015-4703-0.

[4]   D. B. Bender, T. Centea, and S. Nutt, "Fast cure of stable semi-pregs via VBO cure," *Adv. Manuf. Polym. Compos. Sci.*, vol. 6, no. 4, pp. 245–255, 2020, doi: 10.1080/20550340.2020.1869891.

[5]   M. A. Khan, C. Pasco, N. Reynolds, and K. Kendall, "Shear deformability characteristics of a rapid-cure woven prepreg fabric," *Int. J. Mater. Form.*, vol. 14, no. 1, pp. 133–142, 2021, doi: 10.1007/s12289-019-01532-0.

[6]   A. Keller, K. Masania, A. C. Taylor, and C. Dransfeld, "Fast-curing epoxy polymers with silica nanoparticles: properties and rheo-kinetic modelling," *J. Mater. Sci.*, vol. 51, no. 1, pp. 236–251, 2015, doi: 10.1007/s10853-015-9158-y.

[7]   A. Keller, C. Dransfeld, and K. Masania, "Flow and heat transfer during compression resin transfer moulding of highly reactive epoxies," *Compos. Part B Eng.*, vol. 153, no. May, pp. 167–175, 2018, doi: 10.1016/j.compositesb.2018.07.041.

[8]   E. F. Sukur and G. Onal, "Long-term salt-water durability of GNPs reinforced basalt-epoxy multiscale composites for marine applications," *Tribol. Int.*, vol. 158, no. November 2020, p. 106910, 2021, doi: 10.1016/j.triboint.2021.106910.

[9]   M. A. Downey and L. T. Drzal, "Toughening of aromatic epoxy via aliphatic epoxy copolymers," *Polymer (Guildf).*, vol. 55, no. 26, pp. 6658–6663, 2014, doi: 10.1016/j.polymer.2014.10.052.

[10]   E. F. Sukur, S. Kocaman, and G. Önal, "Mechanical, tribological and thermal properties of epoxy based phenolic nanocomposites reinforced with graphene nanoplatelet," *Comput. Res. Prog. Appl. Sci. Eng. CRPASE Trans. Mech. Eng.*, no. Special Issue, pp. 2–9, 2020, [Online]. Available: https://www.researchgate.net/publication/344041047.

[11]   U. Szeluga, S. Pusz, B. Kumanek, K. Olszowska, A. Kobyliukh, and B. Trzebicka, "Effect of graphene filler

structure on electrical, thermal, mechanical, and fire retardant properties of epoxy-graphene nanocomposites - a review," *Crit. Rev. Solid State Mater. Sci.*, vol. 46, no. 2, pp. 152–187, 2021, doi: 10.1080/10408436.2019.1708702.

[12] J. S. Monfared Zanjani, B. S. Okan, Y. Z. Menceloglu, and M. Yildiz, "Nano-engineered design and manufacturing of high-performance epoxy matrix composites with carbon fiber/selectively integrated graphene as multi-scale reinforcements," *RSC Adv.*, vol. 6, no. 12, pp. 9495–9506, 2016, doi: 10.1039/C5RA23665G.

[13] B. Saner Okan, "Fabrication of multilayer graphene oxide-reinforced high density polyethylene nanocomposites with enhanced thermal and mechanical properties via thermokinetic mixing," *Turkish J. Chem.*, vol. 41, no. 3, pp. 381–390, 2017, doi: 10.3906/kim-1608-53.

[14] E. C. Senis, I. O. Golosnoy, J. M. Dulieu-Barton, and O. T. Thomsen, "Enhancement of the electrical and thermal properties of unidirectional carbon fibre/epoxy laminates through the addition of graphene oxide," *J. Mater. Sci.*, vol. 54, no. 12, pp. 8955–8970, 2019, doi: 10.1007/s10853-019-03522-8.

[15] M. Nonahal *et al.*, "Design, preparation, and characterization of fast cure epoxy/amine-functionalized graphene oxide nanocomposites," *Polym. Compos.*, vol. 39, no. S4, pp. E2016–E2027, Dec. 2018, doi: 10.1002/PC.24415.

[16] M. H. Arikan, F. Eroglu, V. Eskizeybek, E. F. Sukur, M. Yildiz, and H. S. Sas, "A Systematic Characterization Approach for Vacuum Bag Only Prepregs towards an Accurate Process Design," *Materials (Basel).*, vol. 15, no. 2, pp. 1–19, 2022, doi: 10.3390/ma15020451.

[17] C. Monteser, M. Blanco, E. Aranzabe, A. Aranzabe, and J. L. Vilas, "Effects of graphene oxide and chemically reduced graphene oxide on the curing kinetics of epoxy amine composites," vol. 44803, pp. 12–16, 2017, doi: 10.1002/app.44803.

[18] A. Surnova, D. Balkaev, D. Musin, R. Amirov, and A. M. Dimiev, "Fully exfoliated graphene oxide accelerates epoxy resin curing, and results in dramatic improvement of the polymer mechanical properties," *Compos. Part B Eng.*, vol. 162, pp. 685–691, 2019, doi: 10.1016/j.compositesb.2019.01.020.

[19] X. Zhao, Z. Huang, P. Song, H. Yang, and Y. Zhang, "Curing kinetics and mechanical properties of fast curing epoxy resins with isophorone diamine and N-(3-aminopropyl)-imidazole," *J. Appl. Polym. Sci.*, vol. 136, no. 37, pp. 1–10, 2019, doi: 10.1002/app.47950.

[20] L. Li, H. Zou, M. Liang, and Y. Chen, "Study on the effect of poly(oxypropylene)diamine modified organic montmorillonite on curing kinetics of epoxy nanocomposties," *Thermochim. Acta*, vol. 597, pp. 93–100, Dec. 2014, doi: 10.1016/J.TCA.2014.10.008.

[21] "Online Tutorial on Differential Scanning Calorimetry (DSC)." https://www.mt.com/se/sv/home/library/videos/lab-analytical-instruments/dsc-online-training-course-video-28.html (accessed Apr. 04, 2022).

[22] M. Jouyandeh *et al.*, "Curing epoxy resin with anhydride in the presence of halloysite nanotubes: the contradictory effects of filler concentration," *Prog. Org. Coatings*, vol. 126, no. October 2018, pp. 129–135, 2019, doi: 10.1016/j.porgcoat.2018.10.007.

[23] J. B. Robles, L. Hong, M. A. Octeau, and A. Yousefpour, "Material Characterization of Graphene Enhanced Composites for Resin Transfer Moulding," *11th Can. Conf. Compos.*, no. July, pp. 1–7, 2018.

[24] M. Fang, Z. Zhang, J. Li, H. Zhang, H. Lu, and Y. Yang, "Constructing hierarchically structured interphases for strong and tough epoxy nanocomposites by amine-rich graphene surfaces," *J. Mater. Chem.*, vol. 20, no. 43, pp. 9635–9643, 2010, doi: 10.1039/c0jm01620a.

[25] Y. J. Wan *et al.*, "Grafting of epoxy chains onto graphene oxide for epoxy composites with improved mechanical and thermal properties," *Carbon N. Y.*, vol. 69, pp. 467–480, 2014, doi: 10.1016/j.carbon.2013.12.050.

[26] R. Umer, Y. Li, Y. Dong, H. Hj, and K. Liao, "The effect of graphene oxide (GO) nanoparticles on processing of epoxy / glass fiber composites using resin infusion," pp. 1–36, 2015, doi: 10.1007/s00170-015-7427-1.The.

[27] A. J. Kinloch and A. C. Taylor, "The mechanical properties and fracture behaviour of epoxy-inorganic micro- and nano-composites," *J. Mater. Sci.*, vol. 41, no. 11, pp. 3271–3297, 2006, doi: 10.1007/s10853-005-5472-0.

[28] M. S. Saharudin, S. Hasbi, A. Zulkifli, and N. F. Zailani, "The Processing of Epoxy / 1 wt % -graphene Nanocomposites : Effects of Ethanol on Flexural Properties," no. November, 2019, doi: 10.35940/ijitee.A8105.119119.

[29]   R. Eqra, M. H. Moghim, and N. Eqra, "A study on the mechanical properties of graphene oxide/epoxy nanocomposites," doi: 10.1177/09673911211011150.