



Research Article

Mechanical, Tribological and Thermal Properties of Epoxy Based Phenolic Nanocomposites Reinforced with Graphene Nanoplatelet

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Keywords

Graphene nanoplatelet (GNP), epoxy-based phenolic resin, nanocomposite, ball-on-disc, wear.

Abstract

This study aims to investigate the effect of the graphene nanoplatelet (GNP) at different contents on the mechanical, tribological, and thermal properties of epoxy-based phenolic resin (EPhR) nanocomposites. The sliding wear tests of the nanocomposites were performed using ball-on-disc tester at room temperature under a constant load and sliding speed in ambient air. The friction coefficient and wear rate were obtained for 0.5 wt% GNPs addition 0.14 and $5 \times 10^{-7} \text{ mm}^3/\text{Nm}$ with increases of 30% and 74%, respectively, compared to the neat EPhR. The tensile strength and modulus of elasticity were found for the 1.0 wt% GNPs addition 74.0 MPa and 6.2 GPa, respectively. Moreover, the composites were characterized using SEM and TGA. The GNP reinforced composites showed an increase of 8.0–59.2% in thermal stability data when compared to the neat EPhR. The results indicate that GNP content and dispersion in resin have a substantial effect on thermal stability, mechanical and tribological performance of composites.

1. Introduction

Polymeric composite materials, due to their lightweight, low friction coefficient, wear-resistance, and self-lubricating properties, are widely used in aerospace, automotive and chemical industries as well as various structural applications [1]. Epoxy, phenolic, polyurethane, and polyester resins are generally preferred as a matrix in polymeric composite materials. Epoxy resins are more expensive than other thermosetting resins, but they have better mechanical properties, moisture absorption, higher resistance to corrosive liquids, and environmental factors. Another positive aspect of epoxy resins is their low shrinkage during the curing process; in other words, the reduction percentages are low in volume. Because of the lack of styrene, epoxy resins have less toxic emissions during the curing process. This makes the use of epoxy resins with "open die" manufacturing technologies (e.g., hand lay-up or vacuum bagging) possible [2]. Also, the tribological properties of the epoxy resins are limited, but it can be improved by the addition of micro and nano-sized particles into the matrix

[3]. Particularly with nanoparticle additives, it is possible to increase the load resistance of polymer matrix composites, improved thermal properties, reduce the friction coefficient, and wear rate [4-6]. In literature, a wide variety of nanoparticles such as graphene, carbon nanotube, nano clay, Si_3N_4 , SiC, ZnO, Al_2O_3 , TiO_2 , SiO_2 , MnO_2 are used as reinforcing elements to improve the different properties of composite materials [7-13].

Graphene nanoplatelet (GNP) is one of the widely used nanofiller to improve the overall mechanical properties and tribological performance of polymer composites due to their solid lubricant properties and thermal stability. Graphene, known to be 300 times stronger than steel, is much harder and more conductive than diamond [14]. The main superior features of graphene are specific surface area ($2,630 \text{ m}^2\text{g}^{-1}$), mobility of charge carriers ($200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) high thermal conductivity ($\sim 5,000 \text{ Wm}^{-1}\text{K}^{-1}$), high Young's module ($\sim 1,100 \text{ GPa}$), fracture strength (125 GPa) and optical transmittance ($\sim 97.7\%$) [15, 16]. It has been stated in various studies that the addition of nanoparticles leads to a significant increase in the various mechanical properties of

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polymers such as modulus, hardness, strength, and fracture toughness. Khun et al. reported the values of hardness, tensile strength, and Young's modulus of epoxy composites increase with increasing graphene content [17]. It is well known that the percentage and dispersion of graphene within polymers is an important parameter for the improvement of mechanical and tribological properties. Optimum conditions are generally achieved at lower additive rates, whereas as the percentage increases, it is difficult to distribute graphene homogeneously in the polymer, and the resulting agglomerations cause a decrease in properties [14]. Shen et al. reported the addition of graphene at low content into the epoxy matrix is more effective in increasing tribological performance [18].

In this study, the effect of 0.5, 1.0, and 1.5 wt% GNP addition on mechanical, tribological, and thermal properties of epoxy-based phenolic resin (EPhR) was investigated in detail. The hardness measurements, mechanical and tribological tests were performed in accordance with the ASTM standards.

2. Experimental

2.1. Material and Production of Polymer Composites

The hardener cycloaliphatic amine (KH-816) and epoxy-based phenolic resin (YDPN-631) were purchased from KUKDO Chemical Co. The graphene nanoparticles (Graphene Nanoplatelet (GNP), 99.5 +%, 6 nm, S.A.: 150 m²/g Dia: 5µm) were obtained from the Nanografi Turkey.

The production procedure of polymer composites is given in schematically in Figure 1. The amount of epoxy resin was determined, and the GNPs were weighed in an amount corresponding to 0.5, 1, and 1.5 wt% of the EPhR. A

tipped sonicator was used to distribute graphene particles homogeneously in epoxy-based phenolic resin. The GNPs were first homogeneously dispersed in acetone by tip sonicating (sonic frequency 20 kHz) for 15 min. After that, the GNP/acetone mixture was added into the EPhR and mixed in a sonicator for 20 minutes. To remove the acetone from the GNP/EPhR mixture, the mixture was degassed in a vacuum oven at 70 °C for 24 h [19]. Following, the curing agent was added into the mixture at the recommended ratio of 100:30 and mechanically stirred for 5 min. The mixture was poured into the tensile test molds and 90 mm circular molds designed for dry sliding wear tests. After the molding process, the composite samples cured at 70 °C for 24h and post-cured 80 °C at 15 h [20].

2.2. Mechanical Tests

Shore Durometer TH 210 tester was used to measure the hardness of composites. Tensile properties were determined using Stretch and Pressing Equipment TST-Mares/TS-mxe. The tests were carried out in three repetitions at a speed of 5 mm/min.

2.3. Dry Sliding Wear Tests

The tribological properties of the specimens were investigated by using a chrome steel ball with 6 mm diameter and 62 HRC hardness in ball-on-disc wear tester (Figure 2). The tests were carried out at a 0.5 m/s sliding speed and 10 N load for 30 minutes at room temperature (25 ± 3 °C). Composite samples were cleaned with acetone before and after the tests, were weighted in 10⁻⁴ grams sensitivity. The specific wear rate, *Ws*, was calculated using the following equation.

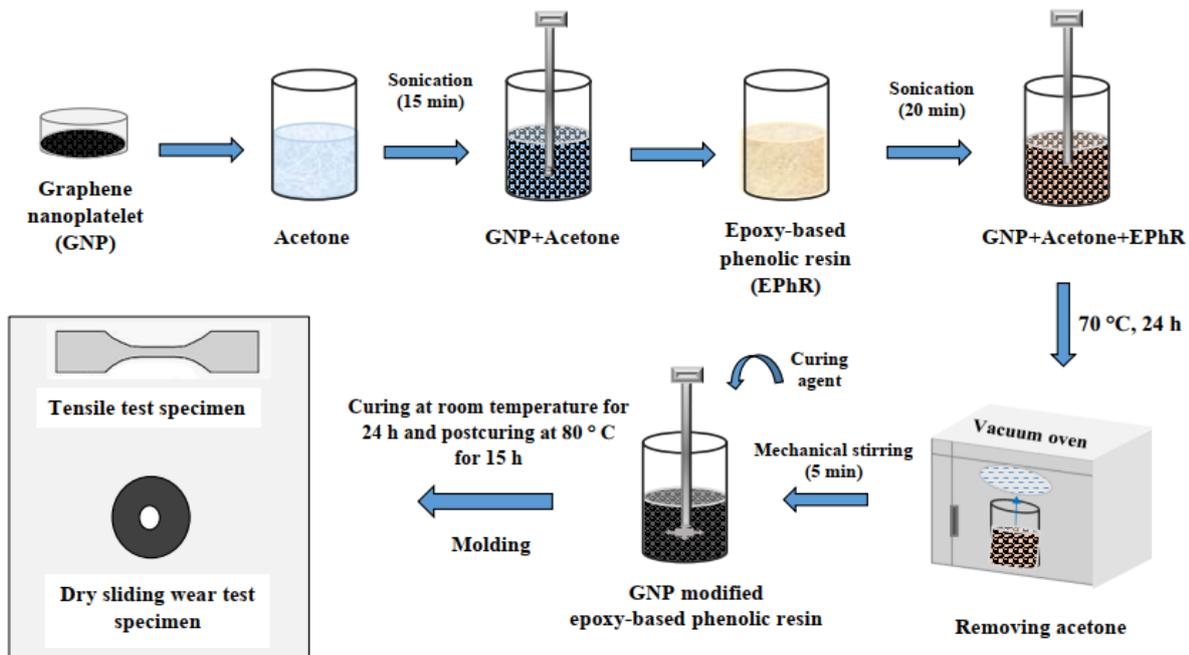


Figure 1. Schematic diagram of GNP/EPhR composites production

$$W_s = \frac{\Delta m}{\rho \cdot F_N \cdot L} \text{ mm}^3 / \text{Nm} \quad (1)$$

Here, Δm represents the weight loss (g) of the worn sample, F_N applied load (N), L sliding distance (m), and ρ density of the specimen in g/mm^3 .

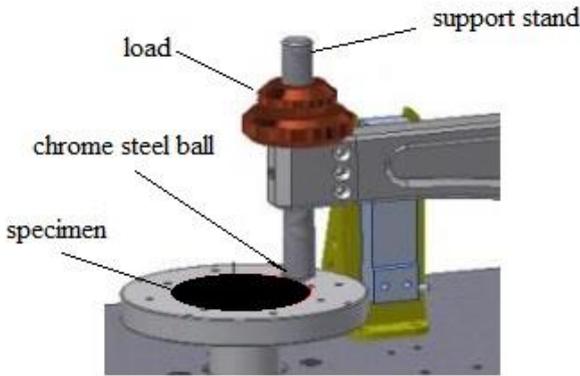


Figure 2. Ball-on-disc test stand

2.4. Analysis

The surface morphology of the interface between nano-additive and matrix was characterized using a Zeiss EVO LS10 scanning electron microscopy (SEM) instrument equipped with a Bruker 123 eV energy-dispersive X-ray (EDX) sensor. Thermogravimetric analysis (TGA) was performed using a thermogravimetry-differential thermal analyzer (Mettler Toledo) in a dry nitrogen atmosphere at the heating rate of $10 \text{ }^\circ\text{C/min}$ using 3–5 mg samples in the temperature range of $0\text{--}750 \text{ }^\circ\text{C}$.

3. Results and Discussions

3.1. Mechanical Characterization

The hardness measurements of composite samples are given in Figure 3. With the increase of the GNP content, the hardness values of the composites showed an average increase of 6%. This increase in the hardness values of EPhR composites can be explained by the inclusion of a secondary hard phase (GNP) in resin. Figure 4 shows that the basic mechanical properties of nanocomposites containing high amounts of GNP decreased, whereas the hardness values increased with the addition of increased nanoparticles. This can be explained by the fact that the hardness of nanocomposites is not sensitive to the presence of agglomerations as much as the basic mechanical properties [6].

The tensile strengths of 0.5, 1.0, and 1.5 wt% GNP/EPhR composites are calculated as 63.5, 74.0, and 60.5 MPa, respectively, whereas the tensile strength of neat EPhR is about 59.6 MPa (Figure 4). The addition of 1 wt% GNPs in EPhR is found to increase the tensile strength up to 74 MPa, which is approximately 19% higher than that of the neat EPhR.

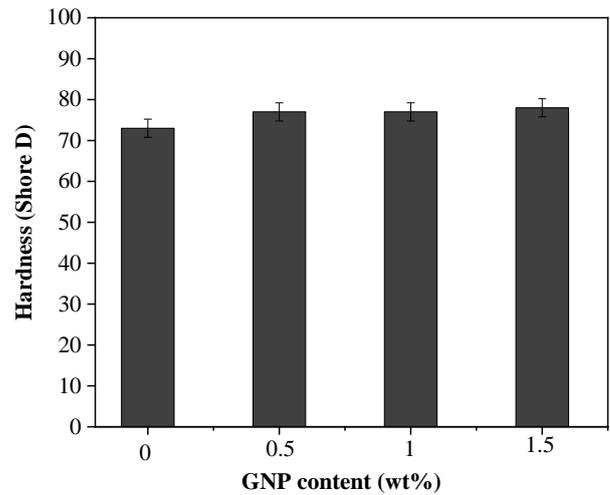


Figure 3. Hardness of neat EPhR and EPhR composites with different GNP contents

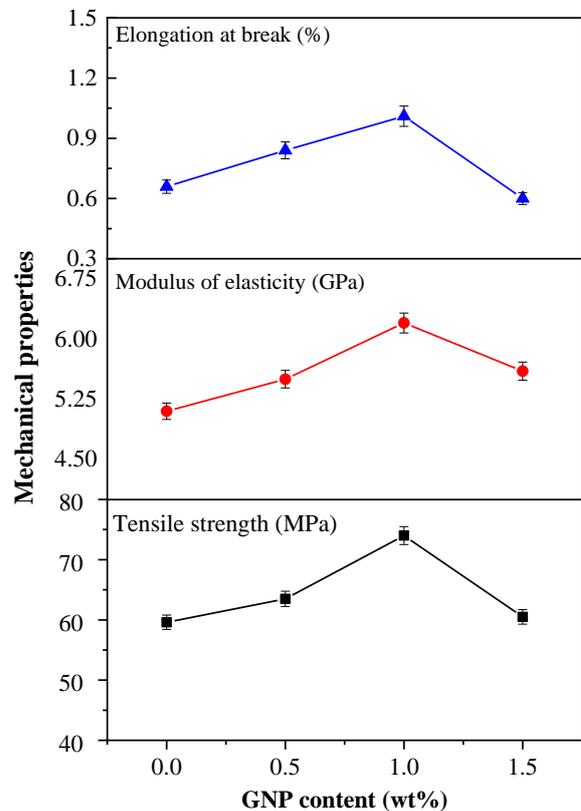


Figure 4. Tensile strength, modulus of elasticity and elongation at break of neat EPhR and GNP/EPhR nanocomposites

The highest modulus of elasticity is calculated as 6.2 GPa for 1 wt% GNP/EPhR composite with a 22% increase compared to neat EPhR. The strain values indicated that the GNP addition improved the ductile behavior of EPhR. The neat EPhR is more brittle compared to GNP/EPhR composites; its resistance to crack initiation and propagation is weaker. Homogeneously dispersed GNP can bridge growing cracks, inhibit crack propagation, and thereby improve the properties of nanomaterials [21].

However, as the additive ratio increases, it is difficult to distribute the nanoparticles homogeneously in the matrix. The nanoparticles, which are not well dispersed in the matrix, tend to agglomerate in the structure. Aggregate zones appear as a defect in the structure and cause a reduction in mechanical properties. The decrease in mechanical properties of 1.5 wt% GNP addition is attributed to these agglomerations.

The surface morphologies of the EPhR matrix and the GNP composites are shown in Figure 5. When the SEM micrograph of the neat EPhR is examined, it shows that there is only one phase that is a regulative crack in the fracture surface, indicating a brittle fracture surface, which is accounted for the poor toughness of the neat EPhRs (Figure 5a). Compared to neat EPhR in general terms, it was noted that GNP has a good distribution in composites. The micro-cracks, which was an indication of the homogeneous dispersion of GNP in the EPhR were seen from Figure 5c. Figure 5d shows fracture lines belonged to EPhR, and smaller agglomeration originated. Homogeneity in the composites continued to rise up to 1.0 wt% GNP loading,

following which heterogeneity increased at 1.5 wt%, causing a weakening of the mechanical properties (see Figure 4). It is believed that such aggregations are due to the interaction between the matrix and the structure and amount of the filler material [22].

3.2. Tribological Characterization

The variation of the friction coefficients of the neat EPhR and GNP/EPhR nanocomposites is given in Figure 6. It is seen that GNP content decreases the friction coefficient of EPhR composites at all additive ratios. This supports that graphene-modified composites have lower friction than neat EPhR. The 0.5 wt% GNPs addition is highly effective at stabilizing the friction coefficient curve and reducing the friction coefficient compared to other additive ratios. It is well known the GNPs act as a solid lubricant between friction surfaces. Besides, the increase in hardness and modulus of elasticity of EPhR composites with GNP content (see Figure 4) decrease friction by reducing contact between steel ball and composites [17].

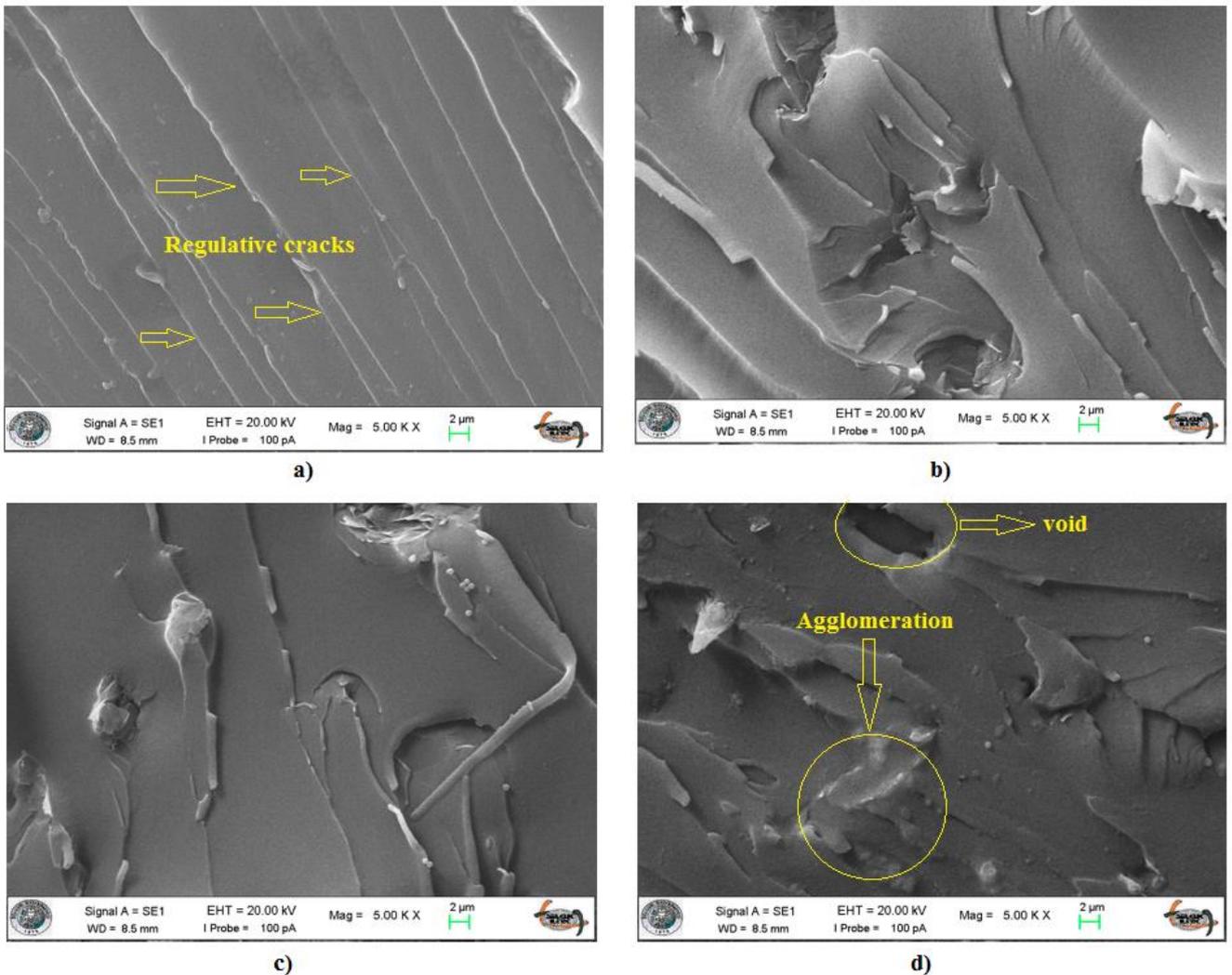


Figure 5. SEM images of a) neat EPhR; b) 0.5 wt% GNP/ EPhR; c) 1.0 wt% GNP/ EPhR; d) 1.5 wt% GNP/ EPhR.

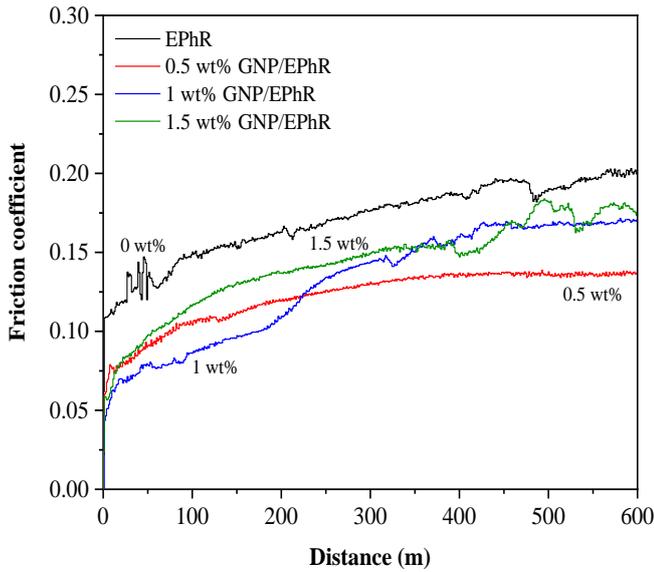


Figure 6. The change of friction coefficient as a function of the sliding distance for neat EPhR and EPhR composites with different GNP contents

Figure 7a shows the mean friction coefficients of neat EPhR, and GNP/EPhR nanocomposites with different ratios of GNP tested at a sliding speed of 0.5 m/s. In the specified test conditions, the friction coefficient of the neat EPhR is 0.2, whereas the 0.5, 1.0, and 1.5 GNP/EPhR are 0.14, 0.17, and 0.18, respectively. The 0.5 wt% GNP addition resulted in a 30% decrease in the friction coefficient. The friction coefficient of GNP/EPhR nanocomposites decreased compared to neat EPhR. More agglomeration is likely to occur when the amount of nanoparticles increases. As the size of the aggregate zone increases, the matrix cannot completely penetrate and wet the particles. Therefore, a weak interface develops between the matrix and nanoparticles in these regions. Nanocomposites containing high rates of nanoparticles cannot fully benefit from the outstanding properties of nanomaterials. The decrease in mechanical properties and the deterioration in tribological properties in the increasing percentages of GNPs reveal the accuracy of this statement [6]. During the wear test, the weight of composites decreases with removing material from the contact surface due to friction. It is known that the friction properties of the materials have effects on the wear rate results.

The wear mechanism of neat EPhR and GNP/EPhR nanocomposites that occurred during the dry sliding wear tests are given schematically in Figure 8. The addition of GNPs into the structure results in a transfer film of low shear strength on the sliding surfaces, which leads to a decrease in the friction coefficients, which in turn reduces wear rates. GNPs acts as a solid lubricant and improve tribological performance by reducing contact between friction surfaces during sliding. Since the transfer film reduces the coefficient of friction, the frictional heat on the contact surface also decreases, which leads to a decrease in the thermal softening of the polymer [23].

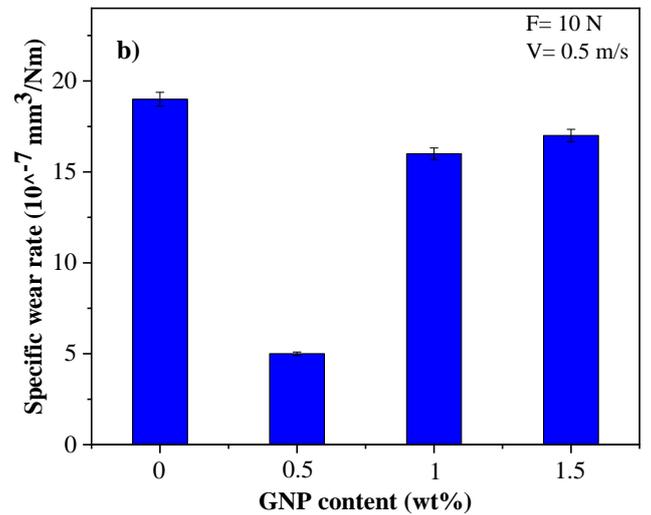
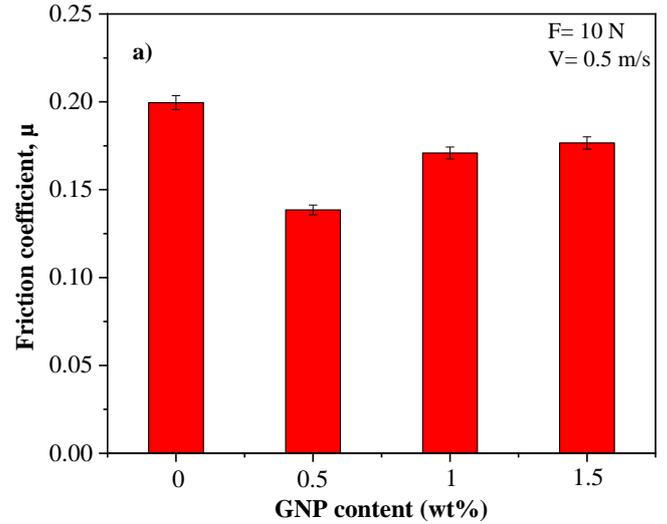


Figure 7. Tribological properties of neat EPhR and GNP/EPhR nanocomposites a) friction coefficient and b) wear rate.

Wear test results show that the GNP addition reduces wear at all additive rates. In neat EPhR and GNP/EPhR composites with %0.5, 1.0, and 1.5 GNP, the wear rate values are 19×10^{-7} , 5×10^{-7} , 16×10^{-7} , and 17×10^{-7} mm³/Nm, respectively. With the addition of GNP, the decrease in wear rates between 10% and 74% was achieved. Considering the lubrication effect of graphene, as the GNP ratio in the matrix increases, the wear rate is expected to decrease further. However, the results in Figure 7b shows that the wear rate of nanocomposites increases with the GNP content in EPhR increases. This is attributed to agglomerations, which increase with the increase of GNP content. The removed material from the contact surface in the agglomerated regions during wear is higher than which removed in the homogeneous regions (see Figure 8). This increase in weight loss leads to an increase in wear rate under the same conditions when other parameters are constant.

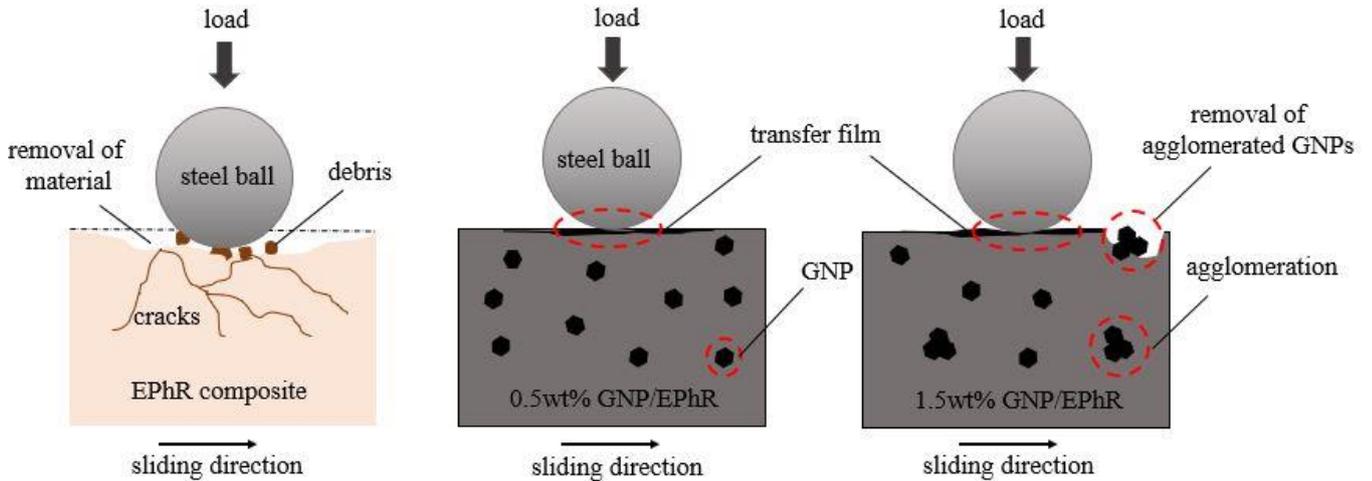


Figure 8. The wear mechanism of neat EPhR and GNP/EPhR nanocomposites

3.2. Thermal Characterization

The TGA curves of neat EPhR and composites reinforced with 0.5, 1.0, and 1.5 wt% of GNPs are shown in Figure 9. The T_5 and T_{50} temperatures where 5% and 50% degradation of the material occurs and char residue at 750 °C are given in Table 1. The decomposition process of EPhR and GNP/EPhR composites are basically the same at low temperatures, but their decomposition processes are different above approximately 450 °C (Figure 9 and Table 1). As have been reported in a study [24], the graphene nanosheets can change the path of thermal degradation at high temperatures and promote ER to form char. The residual weight percentage of the neat EPhR and GNP/EPhR composites at 750 °C was approximately 12.5% and 13.5–19.9%, respectively.

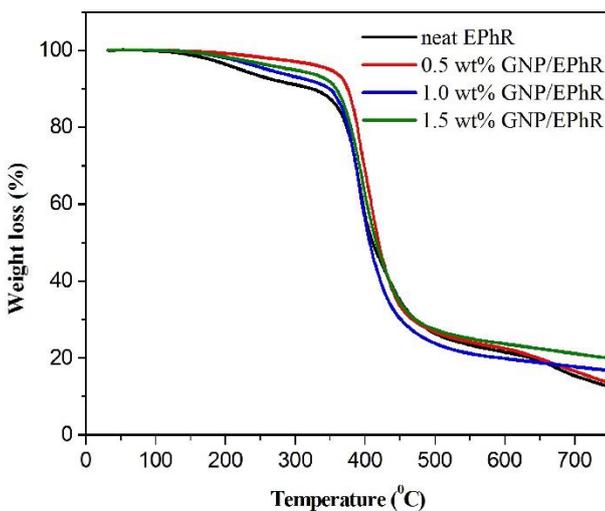


Figure 9. TGA curves of neat EPhR and GNP/EPhR nanocomposites

According to Table 1, the char residue of all composites at 750 °C increased as the amount of the filler increased. This situation was caused by interfacial bonding and the improved interface between the GNP/EPhR composites. In the TGA curve of neat EPhR, the first loss step was started by a slight about 5% around 222.5 °C, which is described as water loss. The T_5 temperature of the GNP/EPhR composites were all higher than that of neat EPhR when the weight percentage of GNP in the composite reached 0.5%, 1.0%, and 1.5%. Also, the T_5 and T_{50} temperatures increased as the weight percentage of GNP in the composite increased.

Table 1. Thermal stability data of neat EPhR and GNP/EPhR nanocomposites

Filler (wt%)	T_5 (°C)	T_{50} (°C)	Residue, % (at 750°C)
For neat EPhR			
-	222.5	406.5	12.5
For GNP/EPhR nanocomposites			
0.5	261.3	410.8	13.5
1.0	298.1	415.8	16.8
1.5	350.1	419.5	19.9

T_5 and T_{50} : degradation temperatures of 5%, and 50% weight loss

4. Conclusions

Mechanical, tribological, and thermal properties of epoxy-based phenolic resin nanocomposites containing different additive ratios (GNP) were investigated. The mechanical, thermal, and tribological performance of the neat EPhR improved with the addition of GNPs. In terms of tribological properties, the best improvement was achieved in 0.5 wt% GNP additive, while mechanical and thermal properties showed the best results in 1.0 wt% GNP/EPhR and 1.5 wt% GNP/EPhR nanocomposites, respectively. At 1.0 wt% GNPs, the hardness, elasticity modulus, and tensile strength values of the nanocomposites were increased by 7%, 22%, and 24%, respectively, when compared to neat EPhR. Friction coefficient and wear rate values were reduced by 30% and 74% by the addition of GNP nanoparticles. The presence of agglomerations prevented

further improvement in tribological properties in EPhR composites containing more than 0.5% by weight of GNP. TGA analysis was performed to illustrate the decomposition mechanism of GNP/EPhR composite. The addition of GNP improved the thermal stability of the GNP/EPhR composite because of molecular crosslinking between the nanofiller and matrix.

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