

The synergistic effect of graphene nanoplatelets-montmorillonite hybrid system on tribological behavior of epoxy-based nanocomposites

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Abstract

Polymer nanocomposites have gained significant attention in wear application due to possessing distinctive wear resistance absent in polymers. In this study, the graphene nanoplatelets (GNPs) and montmorillonite (MMT) nanoclay were used to fabricate the hybrid epoxy-based nanocomposites. The synergistic effect of nanomaterials on and wear behavior of nanocomposites was studied at three different temperatures by using pin-on-disk tests. The most significant wear resistance was obtained at 0.5 wt% MMT-0.15 wt% GNPs nanocomposites at the temperatures below the T_g (25 °C and 60 °C) and at 0.3 wt% GNPs at the temperature above the T_g (95 °C) in comparison to the neat epoxy. It was determined that MMT with high hardness and GNPs with self-lubricant properties and increasing the T_g , improve the wear properties.

Keywords: Polymer matrix nanocomposites, Graphene nanoplatelets, Nanoclay, Tribology

1. Introduction

The usage of polymer composites is increasingly developed in fields of aerospace, automobile, and chemical due to demanding for long life and reliability of machines and their

lightness [1,2]. Some of these applications are tribological parts like gears, bearings, cams, clutches, and seals, working against steel counterparts [3-5]. However, one of the limitations of polymer composites in the application is their inappropriate thermal resistance compared to ceramics and metallic materials. For example, during wear, the mechanical energy dissipates as heat, and it can result in degradation and deterioration of the polymeric matrix. Polymer composites can be tailored with consideration to their creep, wear, and temperature resistance, their load-carrying capacity, and their friction coefficient [3].

Excellent resistance to heat, chemicals, and impact and also high strength, hardness, electrical insulation, and adhesive strength are unique properties of the epoxy resin [6]. Incorporation of reinforcements in nanoscale to polymers can improve the attributes of polymers such as chemical, mechanical, thermal, and tribological properties [7].

Graphene as a popular nanomaterial has attracted the consideration of this research because of its excellent characteristics such as high aspect ratio, high thermal conductivity, high mechanical strength, low shear strength, unique friction and wear properties [8-10].

Besides, clays are aluminosilicates or hydrous silicates and are mainly comprising silicon, magnesium or aluminum, oxygen, and hydroxyl with several associated cations. These OH groups and ions are arranged into two-dimensional constructions like sheets. Nanoclay is an ideal nanoparticle to reinforce polymers due to its excellent chemical behavior, aspect ratio, low cost, and simplicity of accessibility [6,11]. Nanoclay reinforced polymers can show a good mechanical attributes by intercalating the polymer between silicate layers, or by exfoliating the silicate layers in the polymer [12]. The incorporation of nanoclay to polymer matrices like polyester resin [13], nylon 6 [14], polyamide 6 [15], polyvinylidene fluoride [16] and polycarbonate [17] has enhanced wear resistance.

The composition of several useful nanomaterials is a significant way for expanding superior composite that impossible to gain by adding one filler alone [18]. For this purpose, researchers have combined several reinforcements to polymer matrix to improve the properties of composites. Some of these combinations are graphene oxide with montmorillonite [19], montmorillonite with carbon nanotubes (CNTs) [20,21] carbon black with CNTs [22], CNTs with graphitic [23], and graphene with clay [24].

In one of these researches, the mechanical properties of graphene-clay/polyimide composites were surveyed. The storage modulus of the nanocomposite with 12.78 vol% graphene and 4.5 vol% of clay increased by 52.4%. In addition, the damping ability of composite enhanced 52.2%, with the addition of 9 vol% clay [8].

Wetzel et al. [25] studied the impact strength, block-on-ring wear behavior, and dynamic mechanical thermal attributes of hybrid epoxy nanocomposites with varied content of fillers. They demonstrated that the nanoparticles increase the wear resistance, stiffness, and impact strength of the epoxy.

On the other hand, the tribological behavior of composites in different test conditions, e.g., different sliding speed, applied load, and temperature have been investigated. Meng et al. [26] discussed the tribological performance of CNTs/polyamide composites under two sliding conditions (dry and water lubricated) and different normal loads. They revealed that CNTs improve the wear properties under both sliding environments. Also, in lubricated condition, increasing the applied load reduced the coefficient of friction.

Sung Rok et al. [12] studied the tribological attributes of nanoclay reinforced epoxy at three sliding speeds. They reported that nanoclay improves the wear performance of these samples. In the case of PEEK composites reinforced with various fillers, Friedrich et al. [27] reported that wear rates increased with increasing temperature.

Eliezer et al. [28] examined the pin-on-disk test on epoxy polymer and steel. They showed that the initial friction coefficient is approximately independent of temperature until the glass transition temperature (T_g). However above T_g , the friction coefficient rises, due to the increasing the contact region at higher temperatures. Furthermore, Shimbo et al. [29] reported similar results in case of epoxide resins.

As was mentioned above, numerous researches have been investigated about the thermal and mechanical performance of the GNPs-MMT hybrid systems. Nevertheless, as far as we are aware, the synergistic effect of GNPs-MMT on the tribological attributes of the epoxy-based nanocomposites has not been investigated. Hence, in present study, with the aim of forming a dual network structure and improving the wear attributes, the GNPs-MMT/epoxy nanocomposites were investigated. Furthermore, the effective mechanisms on the wear properties of these nanocomposites were discussed.

2. Experimental

2.1. Materials

The composites matrix was considered epoxy resin (KER-828) with the polyamine hardener with a weight ratio of 100:10. The MMT KIO nanoclay and GNPs (Armina Co., Iran) were selected as reinforcements. The surface modification of nanomaterials performed with the silane coupling agent, 3-amino-propyltrimethoxysilane (3-GPTS, Merck Chemical Co., Germany). The materials properties are presented in Table 1.

Table 1: Some properties of materials from data sheets of the company.

Material	Property (unit)	Magnitude
KER 828 epoxy resin	Dynamic viscosity (Pa.s)	12-14
	Density (g/cm ³)	1.16
	Flashpoint (°C)	200
	Boiling point (°C)	200
Montmorillonite nanoclay	Morphology	Powder 200
	Thickness (nm)	1
	Surface covering (m ² /g)	250
GNPs	Diameter (μm)	2-18
	Purity (%)	95

2.2. Fabrication of nanocomposite samples

For the sake of modification of nanomaterials, the GNPs and MMT were separately added into the distilled water and ethanol solution, and then dispersed by an ultrasonic device. Later, 3-GPTS was mixed and, subsequently, the created solution was treated in the reflux system for half a day and a specific temperature. Lastly, they were centrifuged at 4000 rpm to separate the functionalized nanomaterials from the solution. Also, to remove the non-functionalized nanomaterials or silane compounds, the attained material was thoroughly refined by ethanol and completely dried [30].

The nanocomposite specimens were fabricated by the solution mixing technique [31]. Regarding the previous studies, the optimal combination of GNPs and MMT nanoclay against 52,100 steel counter material was considered [32,33]. Table 2 indicates the compositions of nanomaterials in epoxy resin and their density. The surface-modified nanomaterials were dispersed in the polymer by stirring magnetically at 400 rpm and ultrasonicated coincidentally for 1.5 h. Finally, a certain quantity of the hardener was added to resin and cast in a mold with the dimension of 30 × 30 × 5 mm². The specimens cured at 25 °C for a day and post cured at

70 °C for 4 h. Fig. 1 displays the schematic of the incorporation of nanomaterials to the epoxy resin.

Table 2. Compositions of epoxy composites and their density.

Symbols of Composition	Composites compositions	Density (g/cm ³)
A	Epoxy	1.168
B	Epoxy-1 wt.% MMT (optimal mass ratio [32])	1.180
C	Epoxy-0.3 wt% GNPs (optimal mass ratio [33])	1.171
D	Epoxy-0.5 wt% MMT-0.05 wt% GNPs	1.1740
E	Epoxy-0.5 wt% MMT-0.1 wt% GNPs	1.1745
F	Epoxy-0.5 wt% MMT-0.15 wt% GNPs	1.1750
G	Epoxy-1 wt% MMT-0.15 wt% GNPs	1.180
H	Epoxy-1.5 wt% MMT-0.15 wt% GNPs	1.185

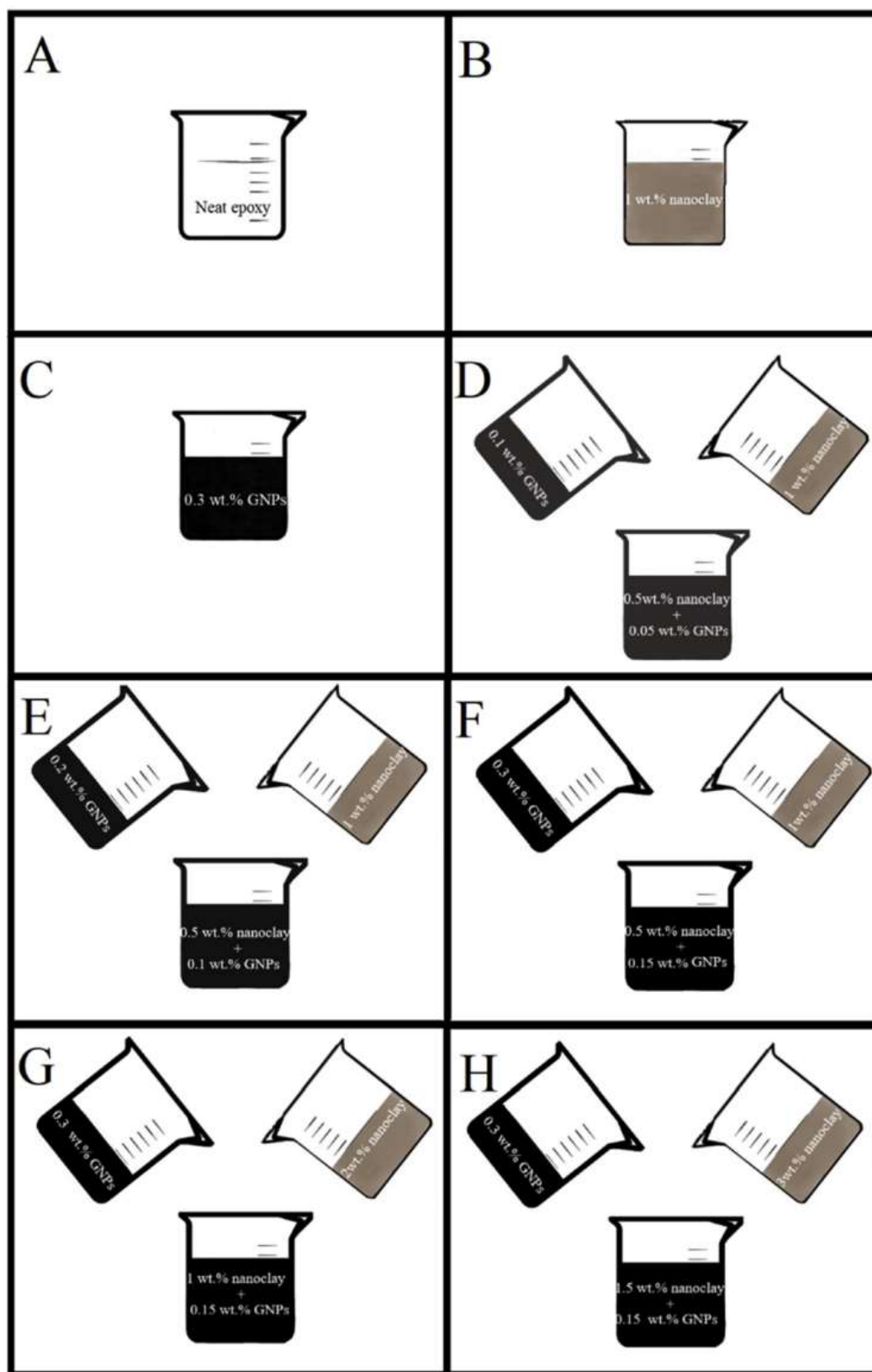


Fig. 1. Schematic combination of nanomaterials in resin.

2.3. Characterization

In order to approve the functionalization of the nanomaterials, Fourier transform infrared spectroscopy (FT-IR) examination (Jasco-460, Germany) was implemented with the wavenumbers range of 400-4000 cm⁻¹. The structural changes of nanomaterials and as well as their composites, were surveyed by X-ray diffraction (XRD, Siemens D500, Germany) with Cu radiation ($\lambda = 0.154$ nm). A differential scanning calorimetry (DSC-200F3 Maia, Germany) with a heating rate of 5 °C/min was employed to identify the T_g of epoxy and its nanocomposites.

To assess the friction and wear, the pin-on-disk tests were implemented on the samples according to the ASTM G99. The wear tests were performed by 52,100 steel pin with a hemispheric tip and sliding distance of 1000 m. Moreover, the rotational speed and load of the pin were adjusted 0.5 m/s and 10 N, respectively. The wear tests were performed at least on three specimens of each nanocomposite type at 25, 60 and, 95 °C and the average and standard deviations of the test results were reported. Fig. 2 displays the schematic of the nanocomposite specimen under the pin-on-disk wear test.

After the tests, the mass reduction of nanocomposites was evaluated and the following equation obtained the wear rate of the samples.

$$W = \frac{\Delta m}{LF\rho} \quad (1)$$

In equation W is wear rate, Δm (mg) is the mass reduction, L (m), F (N) and, ρ (g/cm³) are sliding distance, normal load, and the density of nanocomposites respectively, [26,34].

The Vickers microhardness of nanocomposites by 10 indentation measurements was evaluated using a microhardness device (Buehler MHT-IB, UK). Finally, the surface

morphology of wear tracks was analyzed by field emission scanning electron microscopy (FESEM, MIRA3TESCAN-XMU, Czech).

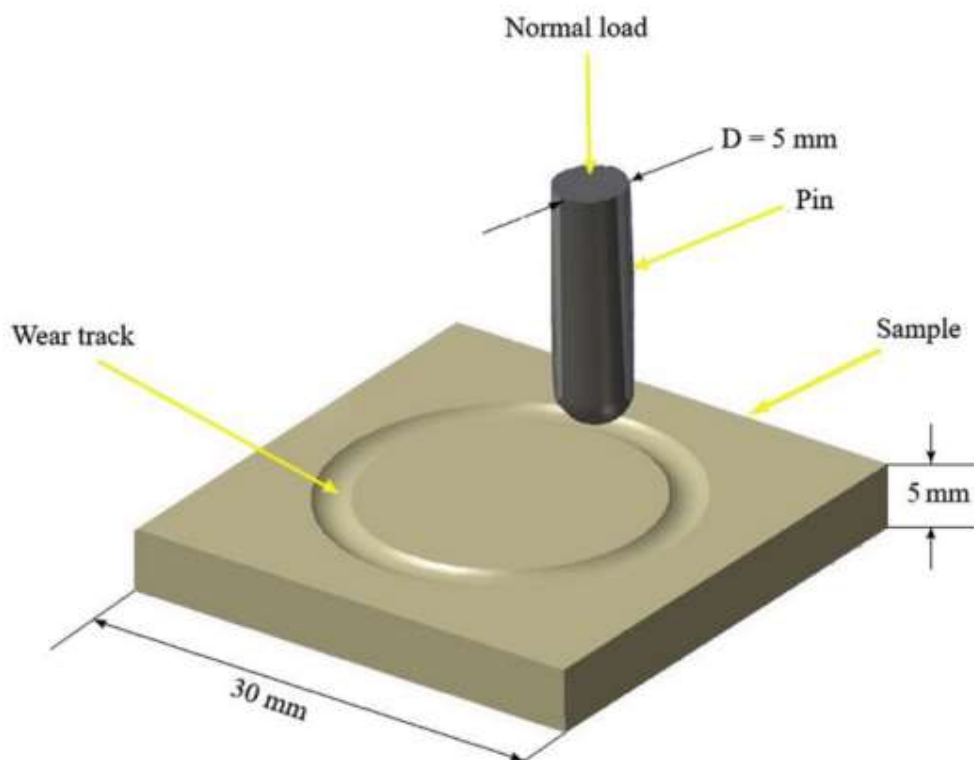


Fig. 2. Schematic of the nanocomposite sample under the pin-on-disk test.

3. Results and discussion

3.1. ET-IR spectroscopy

The FT-IR spectra of the pristine GNPs and MMT powder and also the functionalized ones are demonstrated in Fig. 3. The absorption peak at 456 cm^{-1} indicates the Si-O-Si groups bending vibration in the functionalized MMT [35]. The absorption at 1030 cm^{-1} is because of the stretching of Si-O and Si-O-Si groups of the tetrahedral sheet [36]. A peak at 1215 cm^{-1} denotes the epoxide ring vibration [37]. Furthermore, a wide peak at 3402 cm^{-1} indicates the tensile vibrating of hydroxyl groups. In the spectrum of the functionalized MMT a band at 3620

cm^{-1} represents the bonded hydroxyl groups to aluminum atoms that does not exist in the primary MMT spectrum [38]. Since the pristine MMT lacks the declared bonds, this can be determined that the functionalization of MMT performed successfully.

In the case of modified GNPs, a peak at 645 cm^{-1} is related to the creation of C-H bond on GNPs. In addition, a broad absorption occurred at 1125 cm^{-1} implies the stretching vibration of C-O. A sharp peak at 1462 cm^{-1} is related to the CH_2 and CH_3 creation. Furthermore, a peak at the wavenumber of 1650 cm^{-1} shows the bending vibration of H-O-H [36]. These observations approve the successful grafting of the silane agent onto GNPs [39].

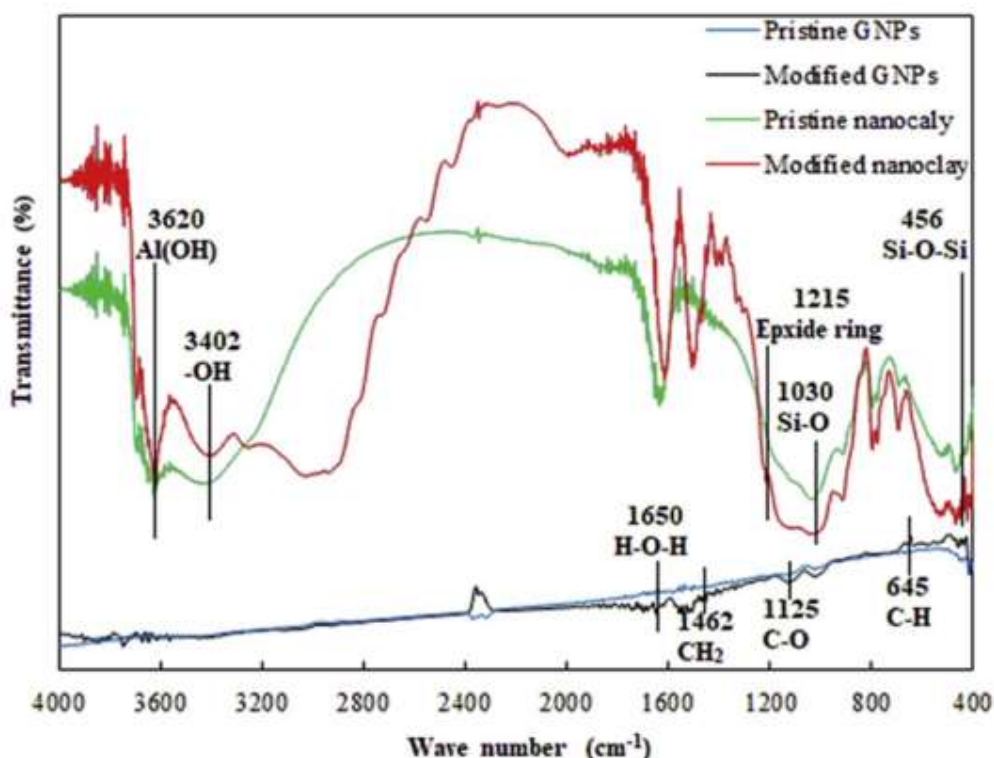


Fig. 3. FT-IR spectra of pristine GNPs, modified GNPs, pristine MMT, and modified MMT.

3.2. Structure of the nanomaterials in nanocomposite

The structures of GNPs, MMT, and MMT-GNPs with various amounts in epoxy were identified by XRD examination (Fig. 4). A broad peak of pure epoxy at 17.9° is attributed to the amorphous essence of the epoxy [40]. Pristine MMT represents a peak at 8.5° , which is related to the 001 reflecting. For sample B, 001 reflecting of MMT is transferred to 4.7° that demonstrates the expanded d001 spacing of MMT [21]. It shows that epoxy or hardener has been inserted into clay's galleries [41]. In sample C, the reflection of GNPs is shifted to lower 2θ (22.2°) from a sharp peak of pristine GNPs in 26.6° , which demonstrates that space of GNPs has expanded. In the case of sample F, there is not any diffraction peak of GNPs, which is due to the exfoliation of graphene nanosheets within the polymer. The XRD results show that the existence of MMT within the epoxy affects the dispersion of GNPs and causes its exfoliation state.

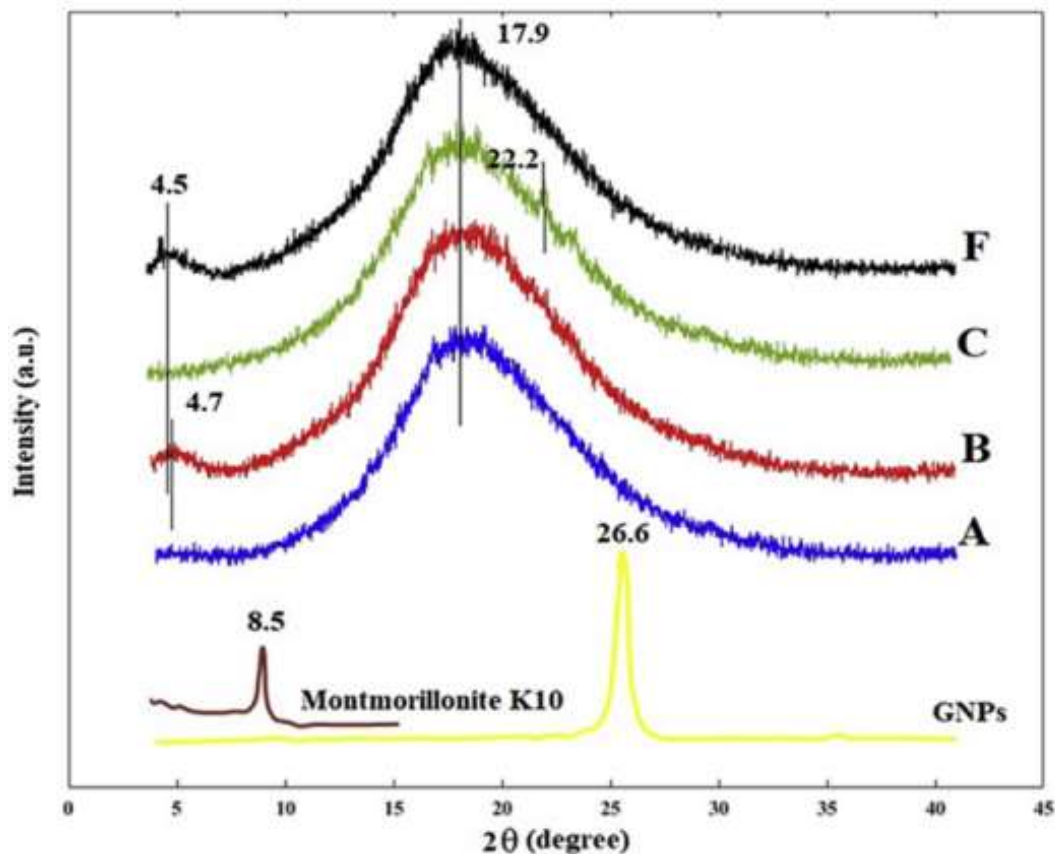


Fig. 4. XRD patterns of nanomaterials, epoxy and its nanocomposites.

3.3. DSC characteristics

At the temperatures above the T_g , polymer properties degrade significantly and the noncrystalline polymer behaves as a viscous fluid, dependent on the amount of crosslinking and the molecular weight. Beneath this temperature, the polymer becomes more or less brittle [42]. In hybrid systems, the T_g of material could be impressed by two factors. First, there can be the nanoreinforcement effect, which is dispersed in the polymer and confines the movement of polymer chains and leads to a rise in T_g . Second, the crosslinking density of epoxy can be decreased by the addition of nanomaterials, which results in T_g reduction [43]. Fig. 5a shows the DSC results of epoxy and its nanocomposites. In order to intensify the transition, the derivative of heat flow is given in Fig. 5b. As can be observed, T_g of sample B is reduced by 8

°C as compared with the pure epoxy (sample A). Interaction of the nano materials surface with the polymer chains can significantly change the kinetics of the chain in the areas surrounding them and causes an inadequate crosslinking density. Also, the interphase formation between the silicate layer and thermal degradation of compatibilizing agents at high temperatures are probable reasons for the reduction of T_g [44,45]. Yasmin et al. [46] studied the effect of clay loading on the T_g of epoxy composites. They revealed that increasing clay content leads to decrease in values of T_g .

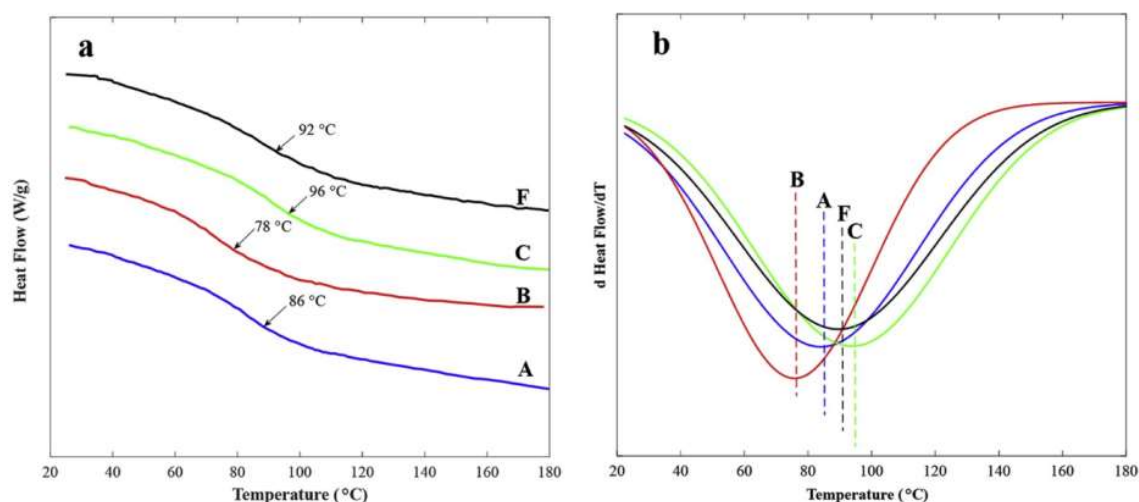


Fig. 5. DSC results of epoxy and its nanocomposites, (a) heat flow vs. temperature and, (b) derivative of heat flow vs. temperature.

In the case of sample C, T_g is elevated 10 °C as compared to the neat epoxy from 86 °C to 96 °C. Embedded GNPs in the epoxy matrix can increase the T_g [47,48]. The main reason which can account for T_g increase is that the sizeable superficial zone formed by the GNPs can change the behavior of nearby polymer matrix and hinder the matrix chains mobility [49]. Furthermore, the T_g of the hybrid nanocomposite (sample F) is increased 6 °C as compared to sample A. It

demonstrates that in sample F, GNPs has significant effect on T_g variation as compared with MMT which can be due to its higher amount and exfoliated state.

3.4. Wear test

The plot of mass reduction and wear rate of nanocomposites vs. weight percents of GNPs and MMT in various temperatures are presented in Figs. 6 and 7, respectively. Room temperature (25 °C) results demonstrate that the addition of GNPs and MMT and their hybrid increases the wear resistance of epoxy nanocomposites. So that, adding 0.3 wt% of GNPs to epoxy (sample C) decreases the mass reduction and wear rate, by 26.1% and 26.3%, respectively with comparison to the pure epoxy. The presence of GNPs in the nanocomposites performs as an efficient obstacle to inhibit much fragmentation of polymer matrix [13,50]. Furthermore, the GNPs incorporation makes the topography of composites surface smoother due to the enhancement of composites embrittlement [51]. Easier fracture of surface asperities and creation of relatively smooth surface results in reduction of mechanical interlocking between pin and disk, and, consequently decrease in friction. On the other side, the increased stiffness and elastic modulus of the nanocomposite by the addition of GNPs decrease the friction by reducing the contact area between the counterparts [52]. A decrease in friction improves the wear properties and consequently, reduces the wear rate and mass reduction of graphene/epoxy nanocomposites.

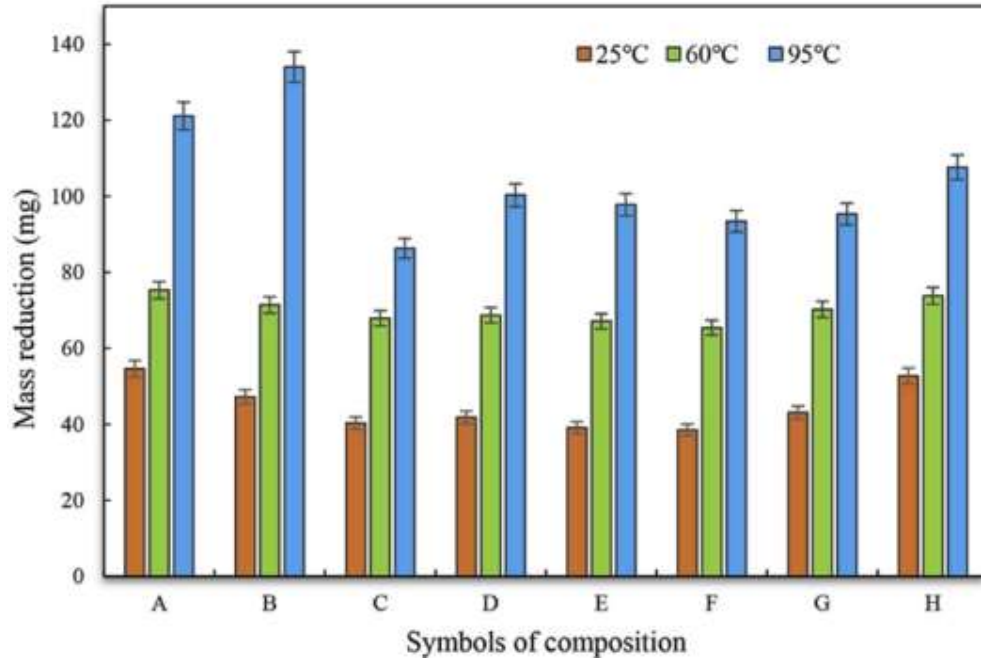


Fig. 6. Mass reduction of samples vs. different wt.% of MMT and GNPs at 25, 60 and 95 °C.

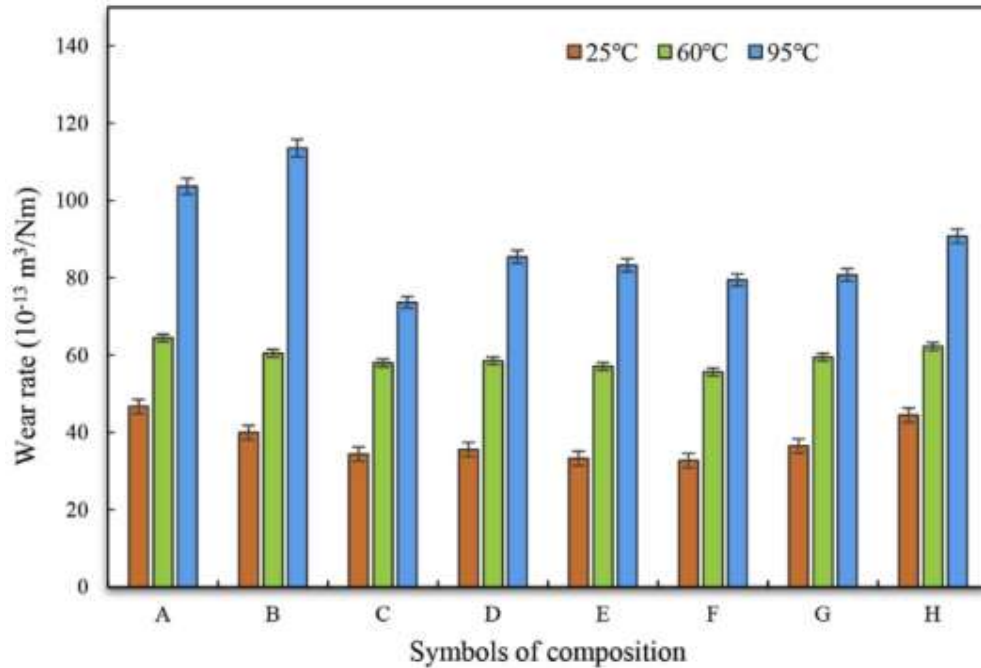


Fig. 7. The wear rate of samples vs. different wt.% of MMT and GNPs at 25, 60 and 95 °C.

Moreover, the pin movement on the polymer composites leads to the creation of the transfer films. The transfer film reduces the wear rate by separating the specimen surface from the pin and decreasing frictional stresses, so it reduces the formation of wear particles. Created transfer films also decrease the friction by creating surface sliding between the counterparts [53]. Self-lubricating property of GNPs enhances the wear attributes of the materials by producing a stable and thin transfer/lubricating film [33]. Also, the GNPs' two-dimensional structure with a high specific surface area is advantageous to stress transfer between GNPs and matrix. The excellent performance of stress transfer in nanocomposites containing GNPs leads to improvement in wear resistance of them [54-56].

Figs. 6 and 7 indicate that the mass reduction and wear rate of the nanocomposite containing 1 wt% of MMT (sample B) is declined, by 13.5% and 14.4%, respectively as compared with the pure epoxy at 25 °C. MMT, as a reinforcing element, endures the load and decreases wear rate [13]. The combination of MMT could raise the modulus and stiffness of the epoxy-based nanocomposite. This phenomenon could be caused by the higher stiffness of MMT, as the comparison with the pure epoxy. Furthermore, the entanglement of the polymer chains and MMT could also raise the modulus [30]. The elastic modulus and stiffness increasing of the epoxy could lead to a decrease of the friction between nanocomposite and the steel pin, and consequently an overall decrease in the mass reduction and wear rate of nanocomposites.

Also, sample F exhibits the lowest mass reduction and wear rate at 25 °C. Recent studies confirmed that clay alters the morphology of nanocomposites to a rough and crumbly structure, including exfoliated clay sandwiched between graphene platelets [8,57]. According to the XRD results, MMT leads to exfoliation of the modified GNPs within the epoxy matrix. In another word, the existence of MMT in epoxy affects the dispersion of GNPs and causes its exfoliation

state. Double network and multiphase structure between the nanofillers and also their interfacial interaction dramatically improves the elastic modulus, toughness and consequently reduces the wear rate and mass reduction.

Regarding Figs. 6 and 7, the mass reduction and wear rate of the nanocomposites rises with increasing the temperature. Furthermore, the friction coefficient and wear rate as functions of temperature both increase with increasing temperatures [58]. The rise in temperature leads to micro-melting in the nanocomposite surface and causes the transfer film rubbed off. Therefore, samples worn away simply and wear rate of them rise [59]. Sample F has the lowest mass reduction and the wear rate at 60 °C as compared with the other specimens. It could be the effect of an appropriate dispersion of nano-fillers and the formation of a double network structure.

Sample C had the lowest mass reduction at 95 °C. The incorporation of GNPs to epoxy leads to raise the T_g above 95 °C so that in sample C, a sharp drop in wear properties is not observed. The existence of the MMT in the epoxy matrix leads to a decrease in the T_g , which deteriorates the wear properties. Moreover, the agglomerated MMT also could reduce the mass reduction and the wear rates, so that sample B had the highest mass reduction and wear rates as compared to the other nanocomposites.

The friction coefficient vs. the sliding distance in wear tests for GNPs-MMT/epoxy composites at multiple temperatures are displayed in Fig. 8. The friction coefficient in all nanocomposites and at various temperatures primary raised dramatically and then kept steady. The distinction between the diagrams is in the primary rise. Regarding each diagram separately, it can be evident that in sample A at 95 °C, the primary growth in the coefficient of friction was higher. It illustrated that the specimens with the large surface area of the graph traversed a

shorter distance to reach a tough frictional situation, and consequently, both wear rate and mass reduction were high and also material did not have a good wear performance.

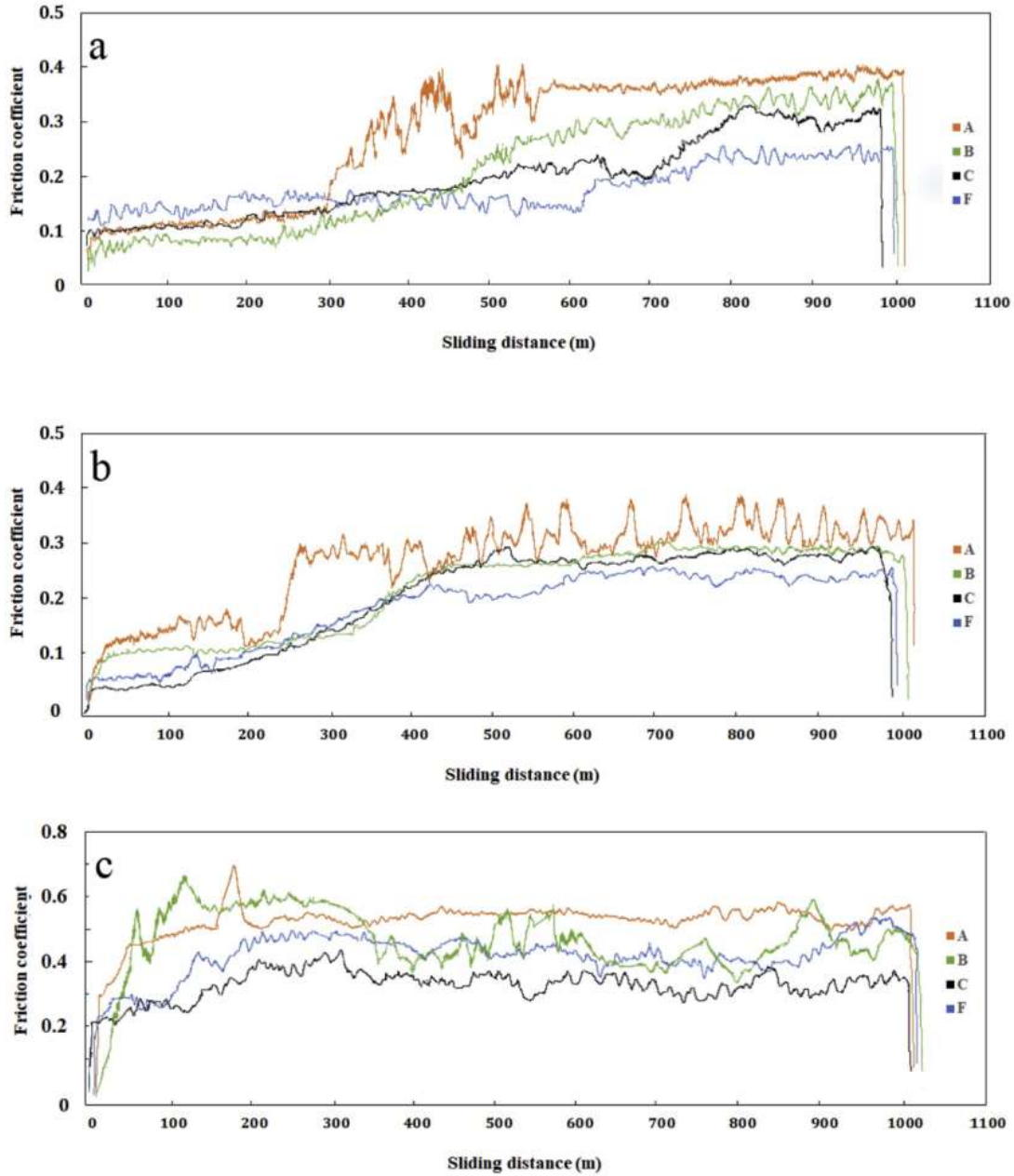


Fig. 8. The friction coefficient vs. the sliding distance for GNPs- MMT/epoxy composites at, (a) 25 °C, (b) 60 °C, (c) 95 °C.

As is evident in Fig. 8, sample F have the lowest surface area of the graph and maximum friction coefficient at 25 °C and 60 °C. In other words, this nanocomposite traversed a longer distance to reach a maximum friction coefficient. Therefore, sample F has the lowest friction coefficient at the low temperature as compared to the other samples which is related to double network and multiphase structure between GNPs and MMT and consequently, increased elastic modulus and toughness. The friction coefficient of sample F is less than sample C at 25 °C and 60 °C. It shows that the synergetic effect of GNPs and MMT is more impressive than GNPs self-lubricating effect. However, the friction coefficient of sample C is lower than sample F at 95 °C. As was expressed above, the presence of GNPs can increase the T_g of the nanocomposites that in the case of sample C the T_g is higher than 95 °C. On the other hand, the presence of the GNPs reduces the friction coefficient due to self-lubricant properties and increases the T_g .

Fig. 9 displays the average friction coefficient of the nanocomposites at three temperatures. The average friction coefficient of sample C is declined, by 25, 18, and 33% at 25, 60, and 95 °C, respectively, as compared to sample A at the same temperature. The incorporation of GNPs to the epoxy matrix decreases the friction coefficient because the GNPs act as a solid lubricant on the surfaces [60]. Furthermore, the GNPs can act as a gap to limit the direct interaction between the counterparts [61].

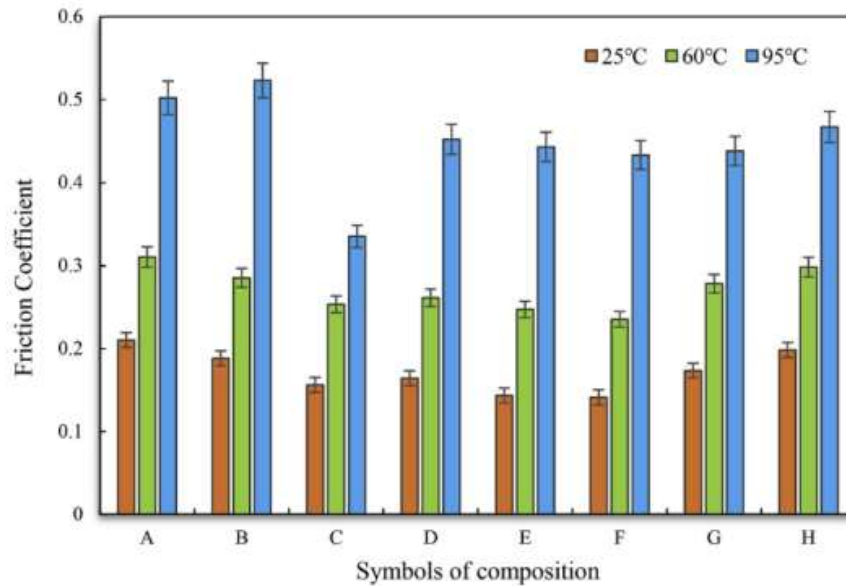


Fig. 9. Friction coefficient vs. different wt.% of MMT and GNPs at the temperatures of 25, 60, and 95 °C.

As it has been exhibited, the friction coefficient of sample B is declined, by 10, 8, and 4% at 25, 60, and 95 °C, respectively, as compared to sample A. During sliding at the contact area, the frictional force could pull out the MMT. The pulled out MMT on the counterface area might serve as three-body roller bearings, which limits the direct interaction of the nanocomposites with pin and leads to a decrease in the friction coefficient. In addition, the reduction in friction coefficient can be because of the combined of the thin transfer film formation on the counterface and influence of three-body roller bearing action of both MMT and MMT-reinforced wear debris [13].

At high MMT content, inappropriate dispersion leads to its agglomeration. The agglomerated MMT might easily detach from the surface and increase wear rates. In the samples with higher than 0.5 wt% of MMT, the created transfer films are unstable and have a tendency to detach from the surface and consequently decreasing the wear resistance.

In general, the friction coefficient of the samples increases with increasing the temperature because the nanocomposites soften in higher temperatures. It impresses the transferring and adhesion performances of the nanocomposites, and so causes the decline in shear strength of the epoxy polymer and the reduction in friction coefficient amount [59].

3.5. Microhardness test

Fig. 10 displays the microhardness of the epoxy and its nano composites. The microhardness value of the neat epoxy (sample A) is 10.2 HV, which is the lowest value as compared to other samples. The microhardness of samples B and C is increased, by 22.5% and 44.1%, respectively, as compared with the pure epoxy. The enhancement in microhardness of nanocomposites was predictable since the MMT and GNPs have a higher intrinsic hardness than the neat epoxy. Moreover, the increase in microhardness of sample B is due to the fact that, the presence of the MMT protects the matrix from being defected by an external force and prevents the growth of cracks inside the epoxy to the surface of the sample [62]. Also, the interaction between GNPs and epoxy, efficient stress transfer, 3D and internal stresses which were created by GNPs leads to an increase in microhardness of the nano composites [18,63]. The maximum hardness of 15.1 HV was achieved for sample H which is 48% higher than that of neat epoxy. In the case of the hybrid samples, the exfoliation of GNPs layers by MMT, and the mechanical interlocking happened in the epoxy can intensify the enhancement of microhardness. Therefore, all of the nanocomposites containing different wt.% of MMT and GNPs, have higher microhardness than the neat epoxy.

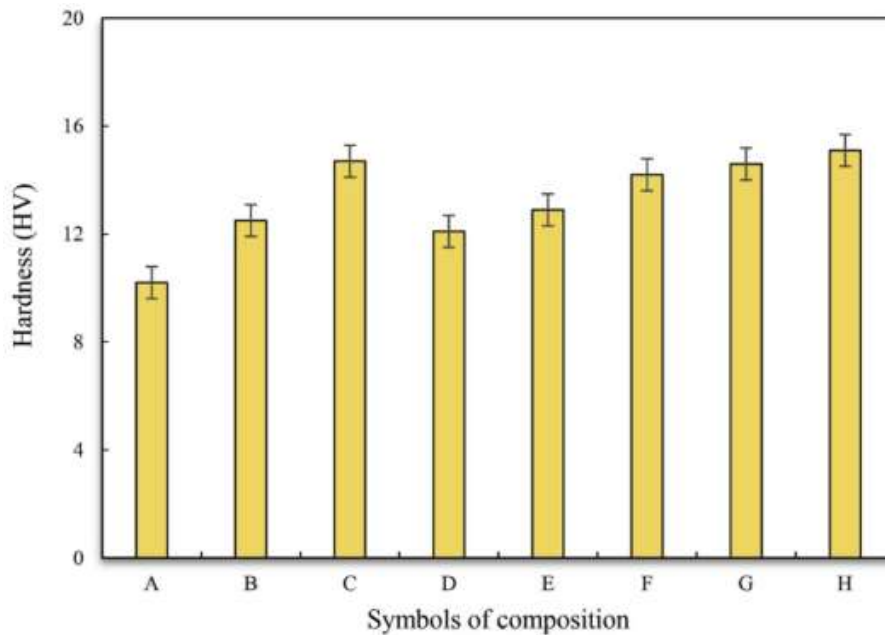


Fig. 10. Microhardness test results for the epoxy and its nanocomposites.

3.6. Microscopic analysis and wear mechanisms

Fig. 11 displays the worn surface of the samples at 25 °C. Pin sliding on the surface of the specimens creates the wear track on the surface of the nanocomposites. As could be observed in Figs. 11a and 11b the wear track of sample A is wider than the wear track of the samples containing nanomaterials (samples C and F). The cracks in sample A are more than those in sample F (Figs. 11b and f). This is reasonable because wear will be more severe in the absence of nanomaterials. Also, coarse scuff is visible on sample A's worn surface at 25 °C. Epoxy is known as a brittle polymer, which the major wear mechanism of epoxy and steel pin is abrasive wear [64]. Moreover, cracks perpendicular to the sliding tracks of samples can be seen in Figs. 11b and f.

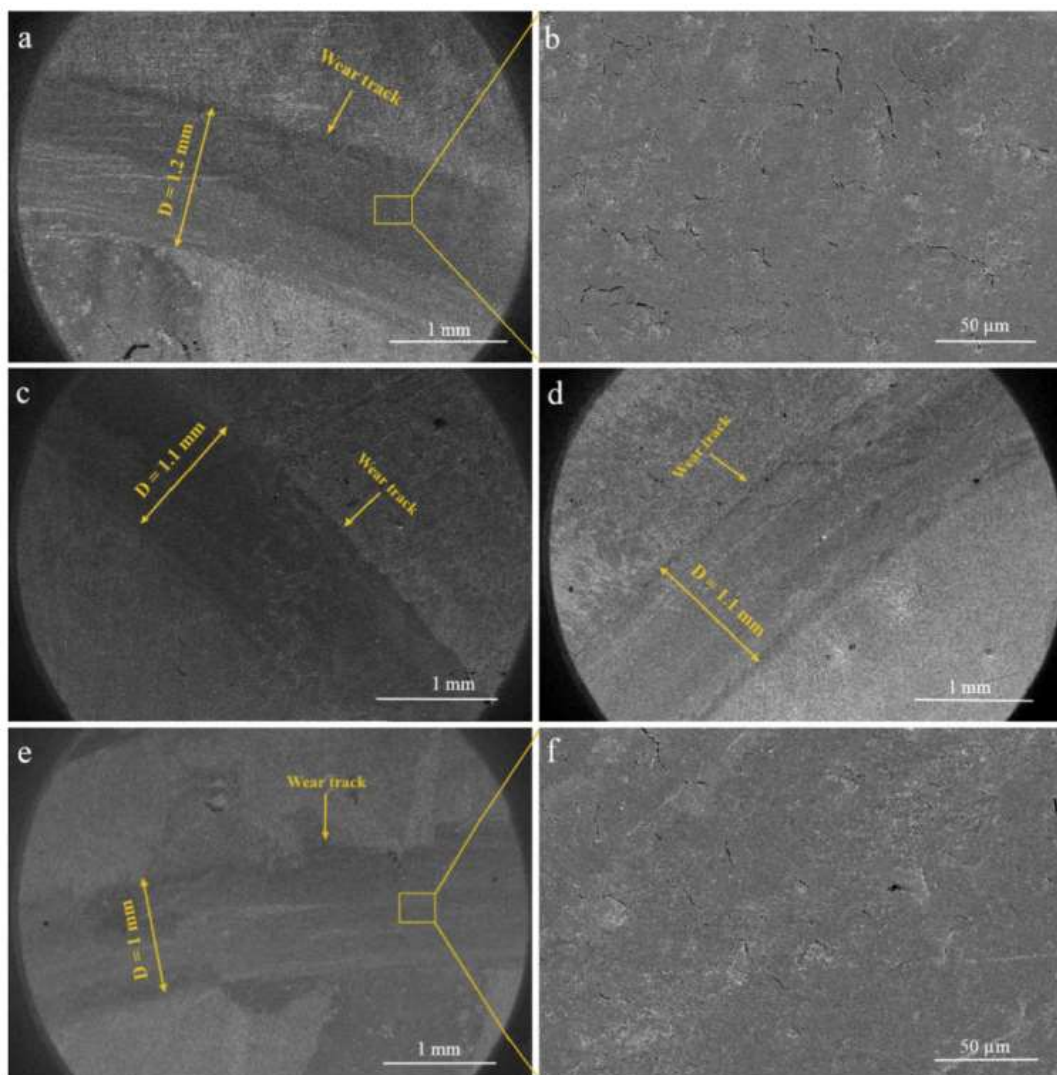


Fig. 11. FESEM micrographs of the worn area of samples, (a) and (b) A, (c) B, (d) C, (e) and, (f) F at 25 °C.

Fig. 12 illustrates the worn area of the samples at 60 °C. A narrower wear track of the nanocomposite samples as compared with the pure epoxy approves that the incorporation of nanomaterials improves the wear properties of the nanocomposites.

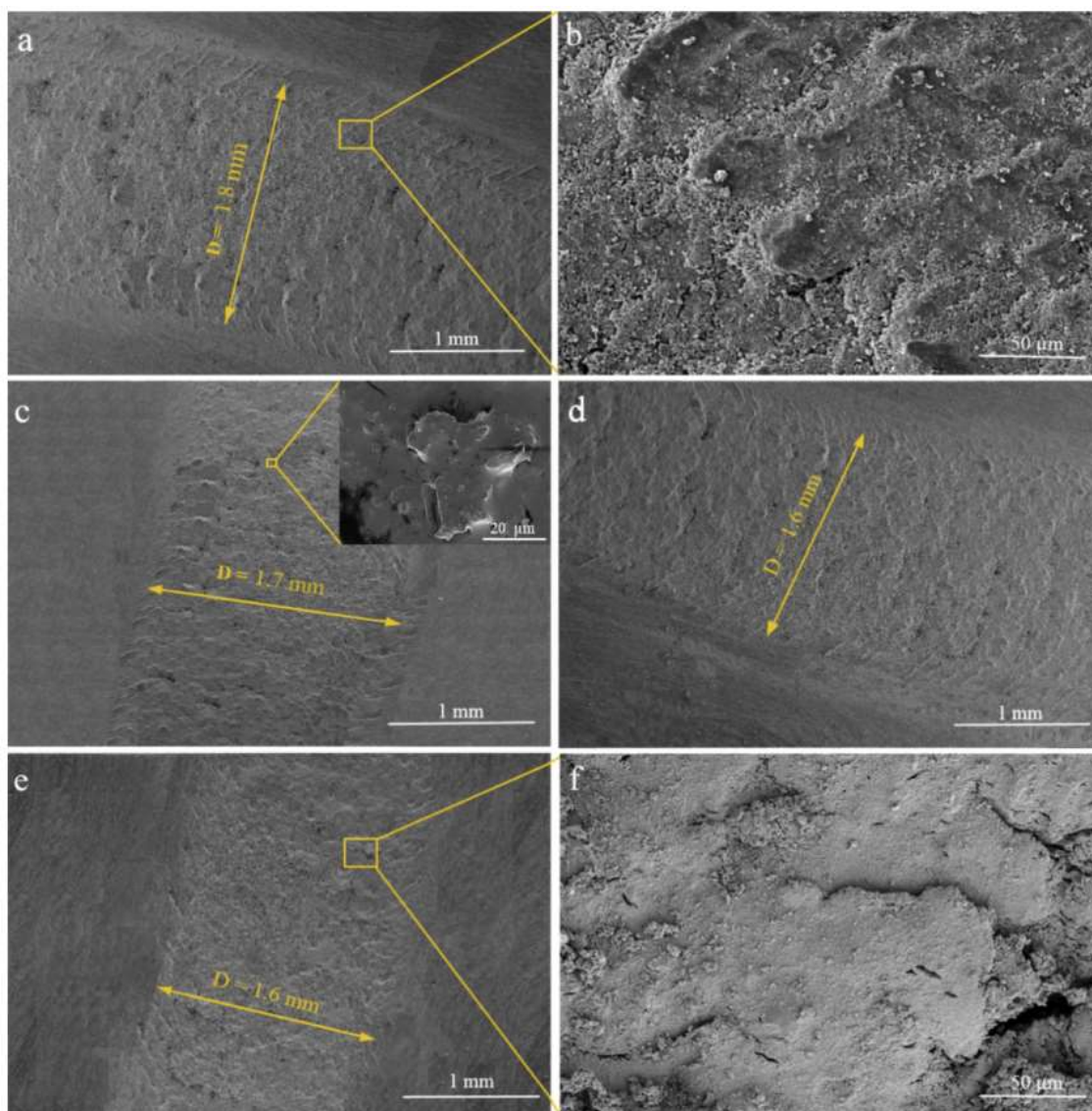


Fig. 12. FESEM micrographs of the worn area of samples, (a) and (b) A, (c) B, (d) C, (e), and (f) F at 60 °C.

An excellent surface adhesion between MMT and polymer can be proved by the worn surface of sample B. As shown in Fig. 12c MMT is embedded in the matrix and polymer is attached to MMT. The good interfacial adhesion could be helpful in transferring the stress between MMT and epoxy matrix and subsequently, an appropriate wear resistance of the

material. The plastic deformation, creation of vertical cracks to the sliding track, separation of debris, and material waves because of adhesion are the dominant wear mechanism [32,65].

Fig. 13 demonstrates the worn surface of the nanocomposite samples at 95 °C. As is apparent in Fig. 13d, sample C has the narrower wear track. According to Fig. 13, sample A has a rougher surface as compared to the samples containing nanomaterials. Also the wear track of neat epoxy becomes much thicker and rougher as compared with the nano composites. The wear tracks of samples at 95 °C, are rough with some deep plowing. Fig. 13b illustrates large wear debris as compared to Fig. 13f, which displays the poor wear properties of sample A. These large wear debris come from the cracked area at the vulnerable spots by the adhesive force [66]. Combined adhesive and abrasive wear mechanism leads to the formation of the particle-shaped debris, which can be observed in Fig. 13 [54]. The scoring, gouges, and scratches signs on the wear surface of the composites are related to the abrasive wear, which is created by pin or debris. Also, the ploughing deformation has occurred in Fig. 13. As it is clear, the materials are moved to form grooving in the surface. Moreover, the creation of debris in the counterface of pin and samples causes the three-body abrasive in the worn surface [67].

According to Figs. 11-13, the wear tracks on the specimens at 95 °C, are wider than those at 25 °C and 60 °C. As can be seen, the worn surface of sample C at 95 °C is rougher than that at 60 °C and 25 °C. Also the wear debris of sample C at 95 °C are more and larger as compared to those at 60 °C and 25 °C.

Although the incorporation of GNPs and MMT has reduced the wear track width at 25 °C and 60 °C as compared with the neat epoxy, this reduction is not very drastic. It is clear that there is a direct relation between track width and mass reduction. According to the mass reduction's results the amount of weight loss and wear track width corresponds with each other. In the case of wear tests at 95 °C, the wear track width of nanocomposites containing MMT

(sample B) is increased. However, it is decreased in sample C which is due to the different effects of nanomaterials on the T_g of the epoxy resin.

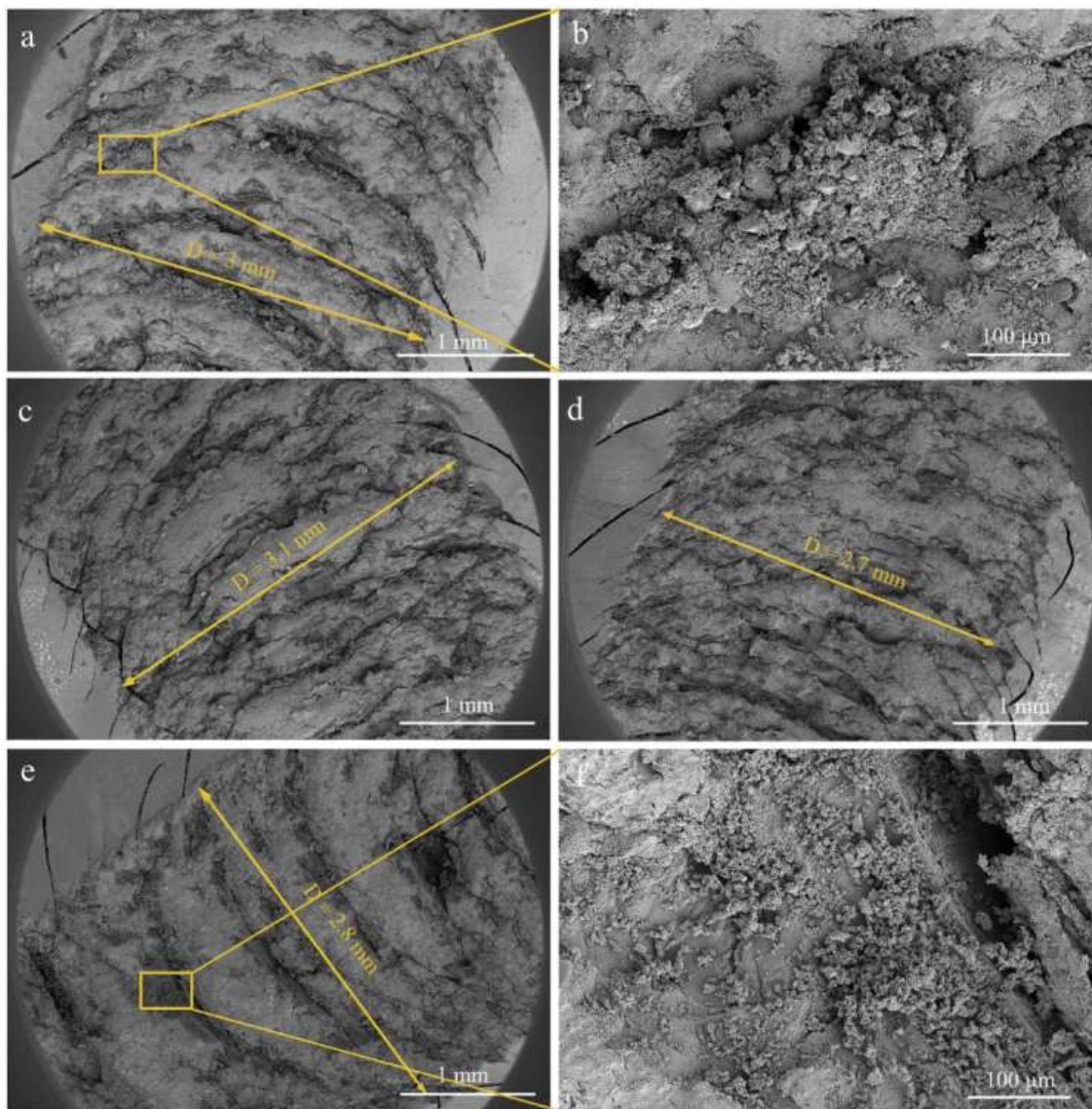


Fig. 13. FESEM micrographs of the worn area of samples, (a) and (b) A, (c) B, (d) C, (e), and (f) F at 95 °C.

4. Conclusions

The influence of incorporating the functionalized GNPs (0-0.3 wt%) and MMT (0 1.5 wt%) on the wear attributes of epoxy-based nano composites at multiple temperatures (25, 60 and 95 °C) and micro hardness of the samples were investigated. The consequences can be drawn as follows:

- The incorporation of functionalized MMT and GNPs enhanced the wear resistance of the nanocomposites drastically. The greatest wear resistance was obtained with 0.5 wt% MMT and 0.15 wt% GNPs at 25 °C; beyond 25 °C, the wear properties deteriorated. At 25 °C, mass reduction, wear rate and friction coefficient of the sample with 0.5 wt% MMT and 0.15 wt% GNPs were decreased, by 29.4%, 29.9%, and 32.8%, respectively, as compared to the pure epoxy.
- The existence of GNPs and MMT in the epoxy matrix improved the wear properties by increasing stiffness and elastic modulus. On the other hand, the high hardness of nanomaterials and self-lubricant attributes of the GNPs decreased the wear rate of nanocomposites.
- Wear properties as a function of the temperature became weak with increasing the temperatures. At the high temperatures, wear tracks of the samples were wider than those at low temperatures.
- The best microhardness result was attained with the sample containing 1.5 wt. MMT and 0.15 wt% GNPs.

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