

# On Mechanical and Thermal Properties of Epoxy/Graphene Nanocomposites

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**Keywords:** Graphene, Epoxy, Impact Strength, Hardness, Brazilian Test, Thermal Conductivity, Thermal Gravimetric Analysis.

**Abstract.** In this research, we have prepared epoxy/graphene nanocomposites (graphene content: 1, 3, 5, 7, and 9 wt%) to investigate some mechanical (impact strength, hardness, and Brazilian tests) and thermal properties (thermal conductivity and thermogravimetric analysis). Our results show that the impact strength, hardness, and compression strength values increased to 5.04 kJ/m<sup>2</sup>, 79.8, and 27.85 MPa, respectively, as increasing graphene content up to 5 wt% and then decreased for further increasing of the graphene content. The observed reduction in the hardness could be attributed to the samples brittleness. On the other hand, the thermal conductivity increased with increasing the graphene content because of the high thermal conductivity of graphene and thus the efficiency increase with increasing of graphene content. In addition, the thermal stability of epoxy/graphene composite increase compared with pure epoxy resin, while the activation energy for samples consists of 9 wt% graphene greater than those containing 1 wt% graphene.

## Introduction

Recently, introducing of nanoscale reinforcing fillers into polymers to form a polymeric composite has attracted considerable attention. It well-known, the composite is a combination of two materials in which one of the materials, called the reinforcing phase, is in the form of fibers, sheets, or particles, and is embedded matrix material and the matrix material can be metal, ceramic, or polymer. Typically, reinforcing materials are strong with low densities while the matrix is usually a ductile or tough material. If the composite is designed and fabricated correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties not available in any single conventional material. The downside is that such composites are often more expensive than conventional materials [1]. Nanocomposite represents new boundaries in material science, thanks to the changes in reinforcement size from micrometer to nanometer scale [2]. In fact, the nanomaterials in the nanocomposite system are playing an important role in the final properties of the nanocomposites, such as electrical, optical and thermal properties [2]. The development of a nano level dispersion of graphene particles in a polymer matrix has opened a new and interesting area of materials science. These nanohybrid materials show considerable improvement in physical and electrical properties. For example, an excellent improvement in thermal and mechanical properties can be done with the very small amount of loading of graphene sheets to the polymer matrices. That cannot normally be achieved using conventional composites or pure polymer [3].

Fractures can classify in several ways. For an instance, a fracture is described as ductile or brittle depending on the amount of deformation that precedes it failures may also be described as intergranular or transgranular depending on fracture path. The impact test is often used to assess the toughness of materials. The most common of this is the Charpy test. In this test, a notched bar is broken by a swinging pendulum, and the energy absorbed in the fracture is measured by recoding by how high the pendulum swings after the bar breaks [4]. The polymer composite has small hardness, as a result of which the impact of such composite can cause delamination and cracks. In order to improve the mechanical and electrical properties of the polymer matrix, the reinforcement

in the form of nanofillers such as carbon nanotubes, nanofibers, carbon black, and recently graphene was needed [4].

Advances in the mixing processes of nanoparticles with large surface areas that lead to improved mechanical and rheological properties of epoxy composites have generated a growing interest in inorganic and organic nanocomposites over the past two decades. In the past decade, many research groups have reported on the physicochemical properties of GO and chemically-modified GO-based epoxy nanocomposites. Norhakim et al., prepared graphene oxide (GO) filled epoxy nanocomposites using the hot pressed method [5]. The GO was produced using a modified Hummers method. In this study, the GO of different compositions (0.1, 0.3 and 0.5 wt%) were mixed with epoxy before the addition of hardener using ultra-sonication. The produced epoxy nanocomposites were characterized in terms of mechanical and thermal properties. The mechanical properties of the nanocomposites were significantly enhanced by the addition of GO [6]. In addition, about 50% of increment in the flexural strength of the composite sample filled with 0.3 wt% of GO as compared to the neat epoxy sample. However, only a slight improvement in the impact strength of the composite was obtained by adding 0.1 wt% of GO.

Similar to the previous study, Abdullah et al analyzed the effects of GO on composites based on epoxy resin [7]. Various contents of GO (1.5–6 vol%) were added to the epoxy resin. The GO/epoxy composite was prepared using the casting method and was prepared at room temperature (RT). Mechanical tests results (such as tensile test, impact test, and hardness test) show enhancements of the mechanical properties of the GO/epoxy composite. The experimental results clearly show an improvement in Young's modulus, tensile strength, and hardness. However, the impact strength was seen to decrease, pointing to brittleness increase of the GO/epoxy composite. As an application of epoxy composites, Matsuura showed that thermoplastic epoxy composites are commonly used for electronic devices and building repairs [8].

The success in preparing a good nanocomposite depends on the degree and quality of the nanofiller dispersion. As well, nanocomposites exhibiting uniformly dispersed nanofiller would render optimum performance. Nanofiller dispersion is favored by the polymer/nanofiller interaction during mixing. The probability for particle agglomeration increases with decreasing of particle size of the filler [9]. Graphene/polymer nanocomposites can be prepared through three synthesis routes: solution mixing, melt blending, and in-situ polymerization, which are the most common synthesis strategies of the polymer matrix composites [10]. Solution mixing is the most straightforward method for the preparation of polymer composites. It consists of three steps; dispersion of the filler in a suitable solvent by, for example, ultra-sonication, incorporation of the polymer and removal of the solvent by distillation or evaporation [11]. During the solution mixing process, polymer coats graphene sheets and when the solvent is evaporated, the graphene sheets reassemble, sandwiching the polymer to form the nanocomposite. The solvent compatibility of the polymer and the filler plays a critical role in achieving good dispersion. The process is more helpful in making a dispersion of carbon material within the solvent [12]. Melt Blending or melt mixing is a common method, particularly useful for thermoplastic polymers [13]. The technique employs a high temperature and shear force to disperse fillers in the polymer matrix. High temperature softens the polymer matrix allowing easy dispersion of reinforcement phase. This process is free from toxic solvent but less effective in dispersing graphene in the polymer matrix especially at higher filler loadings due to increased viscosity of the composites [14]. In the in-situ polymerization method, the graphene is dispersed through monomers is terminated by polymerization. In this approach, there is the possibility of using a higher percentage of the filler and reach to a strong interaction with the polymer matrixes. This method is useful especially to prepare nanocomposites with polymers which are not soluble in solvents or melt blending and sensible against high temperature [13]. The intercalation of monomers into the layered structure of graphite, during in-situ polymerization, increases interlayer spacing graphene platelets producing well-dispersed graphene in polymer matrix after polymerization. In-situ polymerization technique makes possible the covalent bonding between the functionalized sheets and polymer matrix via various chemical reactions [10].

## Experimental Details

### Chemicals materials and equipment

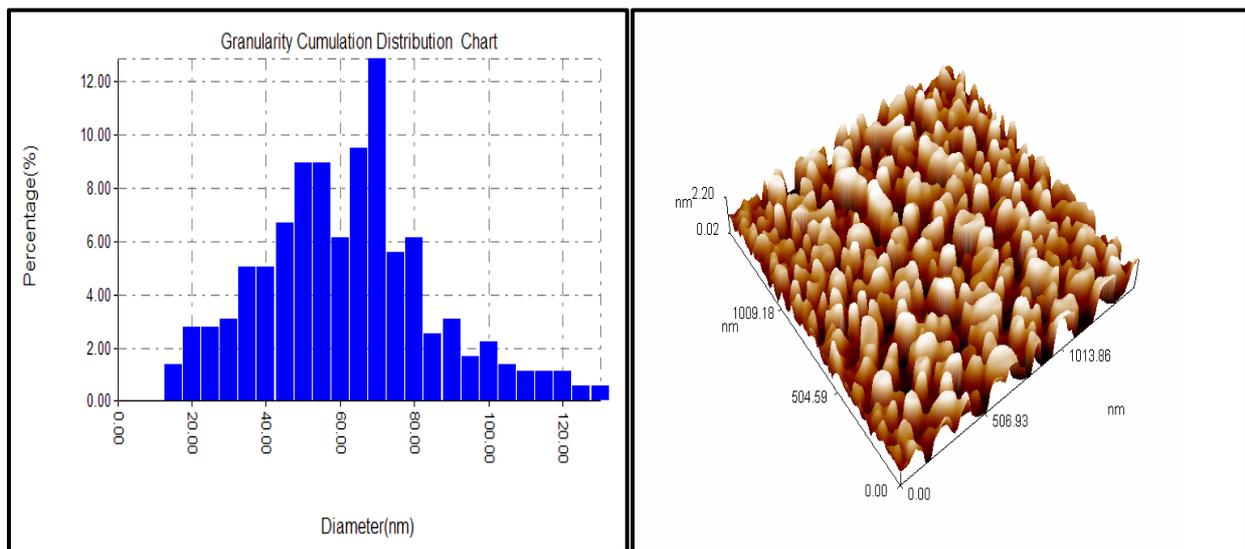
1. Epoxy resin (EP10) with a density of  $1.2 \text{ g/cm}^3$ , Hardener (HY- 956), and Graphene.
2. Sensitive balance, *Mettler H35AR* of accuracy  $10^{-4} \text{ g}$ .
3. Magnetic stirrers, as a device for the purpose of preparation epoxy/graphene nanocomposites.

### Preparation of pure epoxy

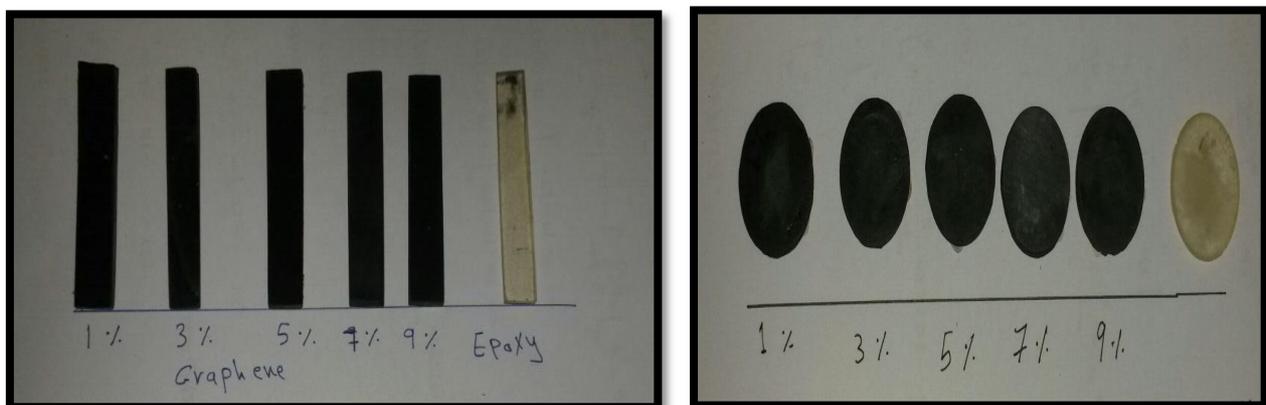
The solution of epoxy and hardener was formed with a ratio of 3:1. The hardener liquid was added slowly to the epoxy resin at RT, this mixture was stirred for 5 min, and the composition was left at RT for 24 h to dry.

### Preparation of epoxy/graphene nanocomposites

To prepare epoxy/graphene nanocomposites, nanographene powder was used as filler material. The surface morphology of graphene nanoparticles was observed with AFM micrographs as shown in Fig. 1. It emerges that average diameter 59.22 nm for graphene particles. Graphene was added to the epoxy resin, and then the resulting solution was put in glass tubes on a magnetic stirrer at a temperature of 50-60 °C for 1 h. After that, the composition was left at RT for 24 h after mixing with hardener for 5 min. The hand-lay-up technique was used to cast the samples in the molded glass.



**Fig. 1:** AFM analysis images of graphene nanoparticles used in the work.



**Fig. 2:** Optical images of epoxy/graphene nanocomposites samples.

### Characterizations of epoxy/graphene nanocomposites

The mechanical behavior refers to the response of materials to forces. Under load, a material may either deform or break. The factors that give a materials resistance to deformation and very different from those governing its resistance to fracture [15]. The impact test is often used to assess the toughness of materials. The most common of this is the Charpy test. The energy absorbed in the fracture is measured by recoding by how high the pendulum swings after the bar breaks [15]. In order to determine the mechanical performance of impact strength, Charpy tests were carried out using impact testing according to the standard test method of ISO-179, with dimensions of  $5.5 \times 1$  cm. Another important mechanical test is the hardness, and there are different shore hardness scales for measuring the hardness of different materials. Shore A scale measures rubbers and very soft and shore D scale measures the hardness of hard plastics. As well, the Brazilian disk fracture test can be considered as one of the most interesting mechanical tests for materials is the diametrical compression of a solid disk. This test was performed on disk using a compression test device Instron, the sample was fixed between the upper and lower platens of the device to start compressing at a rate (cross-head speed = 0.5 mm/min) until a fracture occurs. By applying equation (1) the flexural strength ( $\sigma_f$ ) was determined [16]:

$$\sigma_f = \frac{2F}{\pi d h} \quad (1)$$

Thermal conductivity coefficient was calculated to the data that measurement by using the lee's disk {manufacture by Griffin and George/England}, thermal conductivity coefficient was calculated by using the following equations [17]:

$$K [T_B - T_A / d_s] = e [T_A + 2/r [d_A + d_s / 4] T_A + 1/2r (d_s T_B)] \quad (2)$$

$$H = IV = \pi r^2 e (T_A + T_B) + 2\pi r e [d_A T_A + (1/2) d_S (T_A + T_B) + d_B T_B + d_C T_C] \quad (3)$$

Where K is the thermal conductivity coefficient, e represents the amount of thermal energy passing through a unit area per second disk material, H represents the thermal energy passing through the heating coil unit of time, d is the thickness of the disks (mm), r is the radius of the disk (mm),  $d_s$  is the thickness of the sample (mm), and T is the temperature of the disk ( $^{\circ}\text{C}$ ).

The efficiency of the thermal filler may be characterized by the thermal conductivity enhancement ( $\eta$ ), and defined as:

$$\eta = \frac{K_{comp} - K_{ep}}{K_{ep}} \quad (4)$$

Here  $K_{comp}$  is the thermal conductivity for nanocomposite and  $K_{ep}$  is the thermal conductivity for epoxy.

In the thermogravimetric analysis (TGA), argon used as an inert gas, at a temperature range of 0 to 1000  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ . The samples were ground into fine powder. The measurements were taken using 15-20 mg samples.

## Results and Discussion

### Mechanical tests

Fig. 3 shows the results of the Charpy impact tests for epoxy composites. The impact strength increased from 2.419  $\text{kJ}/\text{m}^2$  to 5.04  $\text{kJ}/\text{m}^2$  at a graphene content of 5 wt% clearly indicating good compatibility of the graphene with the epoxy resin. It also points to a good dispersion of graphene in the polymer matrix, which makes the stress distribution more uniform and allows graphene to be easily incorporated into the matrix structure. It thus blends in with the matrix structure rather than

remaining in the external filler. It decreased to  $3.48 \text{ kJ/m}^2$  at graphene content of 9 wt%. Graphene incorporated into the epoxy nanocomposite matrix structure by enabling a chemical bond formation with epoxy resin and the filler which is a good agreement with Ref [18].

Fig. 4 shows the Shore-D hardness value of the sample which increased by a very good margin. The good surface finish was observed. The hardness value of 70.7 for the pure epoxy and the samples of nanocomposites epoxy with graphene increased up to 79.8 for the 5 wt %. This indicates that with the increase in the addition of the graphene, better bonding has taken place resulting in an increase in hardness which agrees with Ref [19]. Decreasing hardness values to 75.4 for the ratio of 9 wt%. Fig. 5 shows the compression strength values and it increases with increasing the wet percentage graphene the epoxy pure 8.75 MPa and the samples nanocomposites up to 27.85 MPa to 5wt% graphene. The graphene dispersed in the epoxy matrix may create creased structures that have a tendency to unfold rather than stretch under applied loading; these indicate that graphene is highly effective in suppressing crack propagation in an epoxy matrix; may be due to homogeneity dispersion of graphene inclusions within epoxy matrix [19]. In addition, we observed the decreasing in the compression strength with increasing graphene to 19.75 MPa at 9wt% graphene.

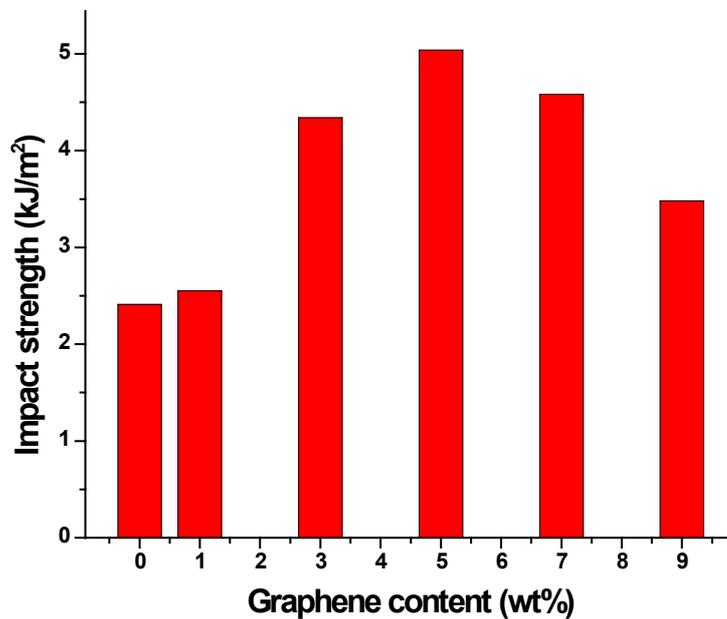


Fig. 3: Impact strength as a function of graphene content.

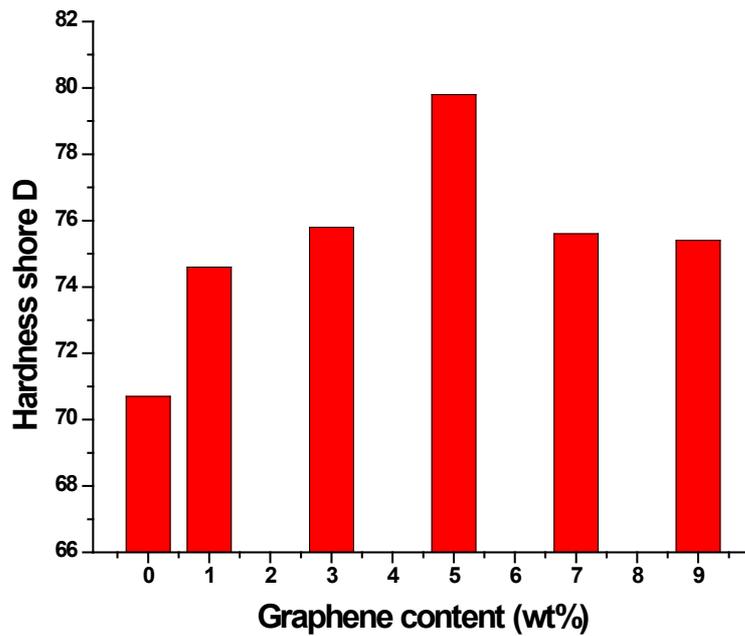


Fig. 4: Values of hardness shore D as a function of graphene content.

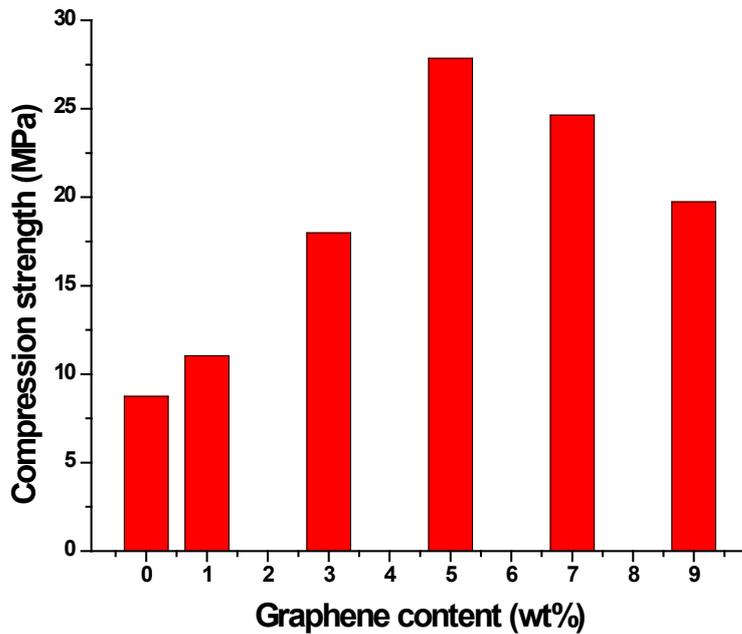


Fig. 5: Compression strength of Brazilian test as a function of graphene content.

Fig. 6 shows the thermal conductivity as a function of the weight fraction of nanographene the thermal conductivity increases with increasing the weight percentage of nanographene because of the high thermal conductivity of graphene. The in-plane thermal conductivity of graphene at RT is among the highest of any known material, about  $2000\text{--}4000\text{ Wm}^{-1}\text{K}^{-1}$  for freely suspended samples [20] which agree with [21]. Fig. 7 shows the efficiency of the thermal filler. The increase of thermal conductivity follows approximately linear dependence without revealing any clear signature of thermal percolation threshold since both filler and matrix contribute to the heat flow through acoustic phonons shows in Table 1 [21].

Thermal stability is very important for polymeric materials. In the present study, the thermal stability of the graphene/epoxy nanocomposites has been investigated by TGA by using a heating rate of 10 °C /min. Epoxy thermosetting resins are a three-dimensional network of bonds (cross-linking). The macromolecules resulting from this architecture are made of oxirane groups, resulting from the reaction between the resin and the hardener [22]. Graphene influence on polymers during TGA tests result in a charred layer which covers the surface of the polymer [23]. Table 2 and Fig. 8 shows Thermal degradation of the graphene represents a massive weight loss around 100-300°C, because of functional groups degradation which contains oxygen, hydroxyl, and a carboxyl group. The second weight loss, occurring from 300-500 °C, shows the decomposition of the main polymer chain which agrees with Ref. [24]. The calculation of activation energy is a measure of the stability of the polymer. The higher the activation energy, the more stable the polymer. The activation energy was calculated by using floss equation [25].

$$E = \frac{R T_i^2}{W_i} (dW_i / dT_i) \quad (5)$$

Where E is the energy activation disintegration, R is general gas constant, T<sub>i</sub> is the temperature of the beginning of disintegration, W<sub>i</sub> is the weight at the beginning of disintegration, and dW<sub>i</sub>/dT<sub>i</sub> is the slope of the tangent at the point of disintegration.

**Table 1: The values of thermal conductivity and the efficiency of the thermal filler of epoxy and epoxy nanocomposites.**

Samples	K ( W/m.K)	η
Ep	0.14	
1% Gr.	0.16	0.142
3%Gr.	0.21	0.5
5%Gr.	0.27	0.92
7%Gr.	0.39	1.78
9%Gr.	0.47	2.35

**Table 2: Activation energy for epoxy and epoxy nanocomposites.**

Samples	Activation energy (kJ/mole)
Ep	5.94
Ep+1wt% graphene	17.58
Ep+9wt% graphene	25.96

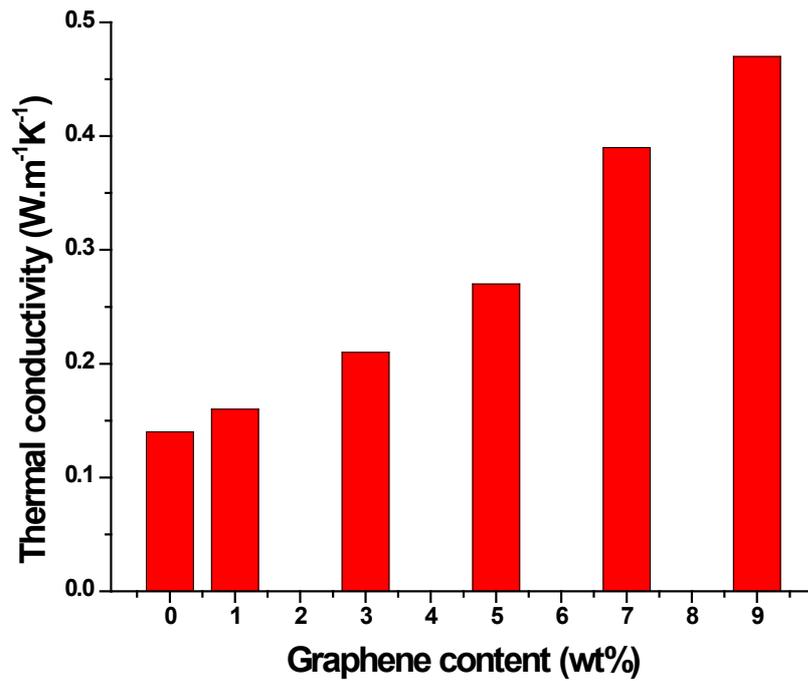


Fig. 6: Thermal conductivity as a function of graphene content.

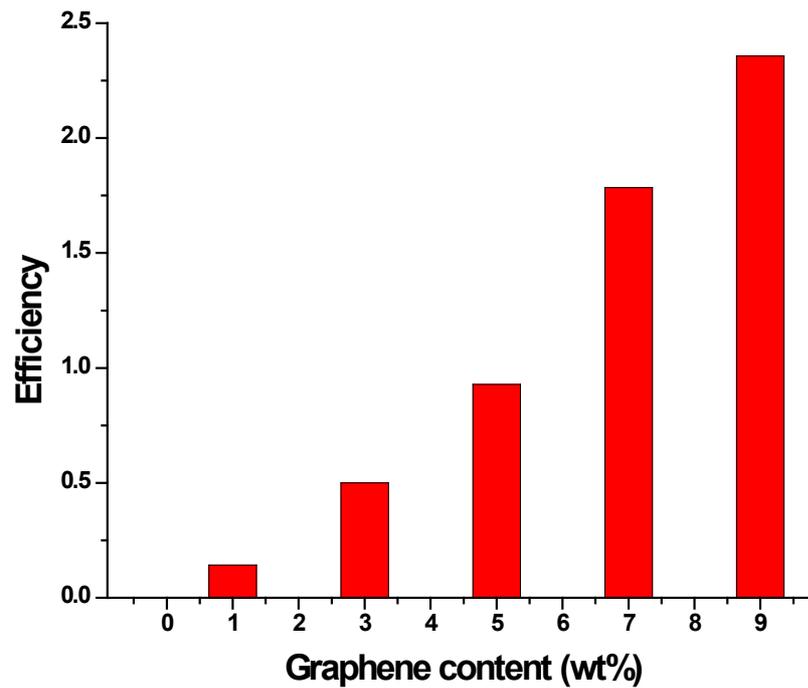
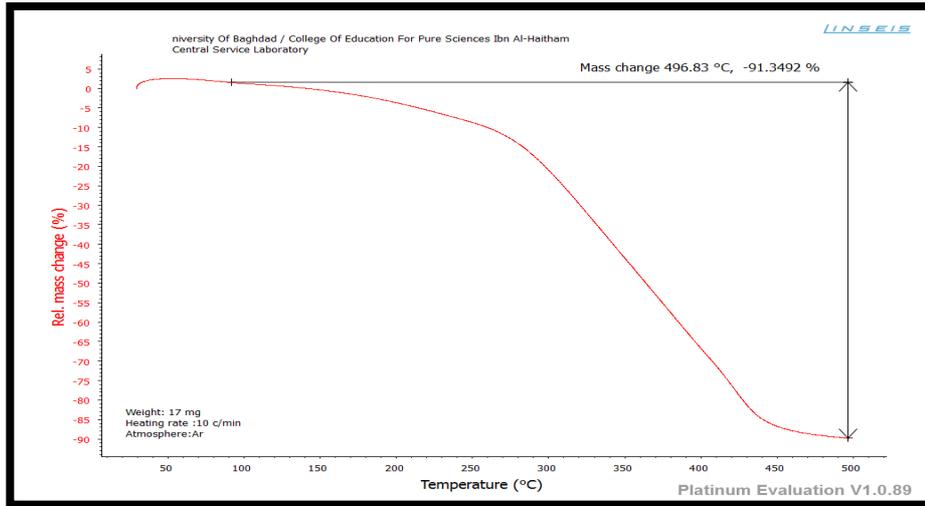
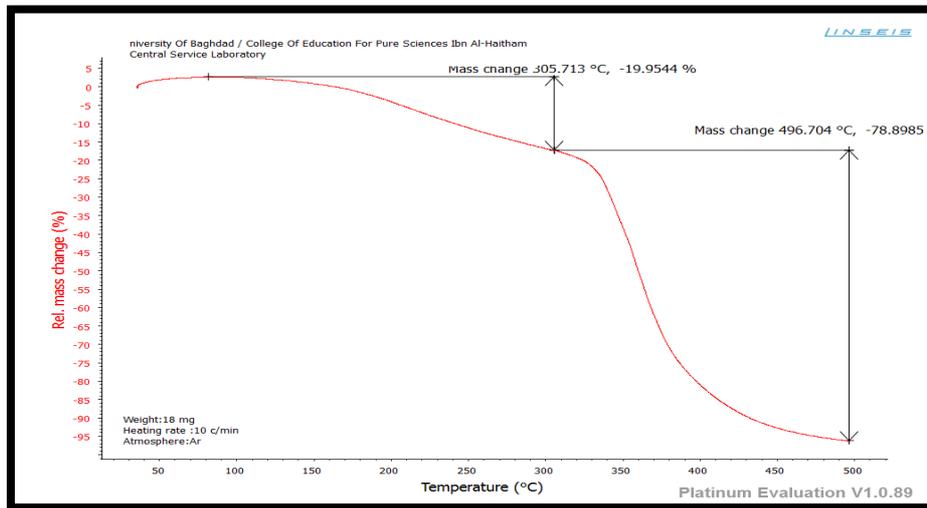


Fig. 7: The efficiency of the thermal filler as a function of graphene content.

(a)



(b)



(c)

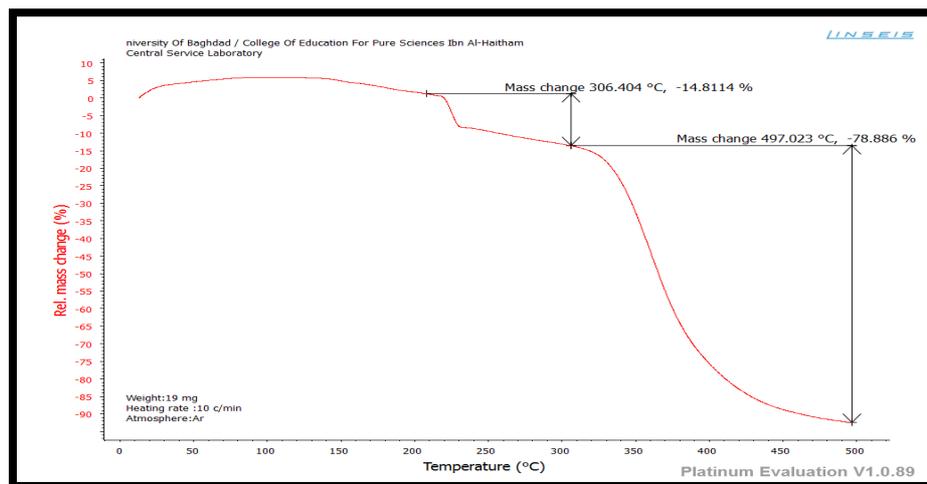


Fig. 8: TGA for (a) pure epoxy, (b) epoxy composite with 1 wt% graphene, and (c) epoxy composite with 9 wt% graphene.

## Conclusion

We have successfully; improve the mechanical and thermal properties of the epoxy composite by adding the graphene to the epoxy resin. The values of impact, hardness, and Brazilian tests increase up to 5 wt% graphene and then decreased again. The decreased in impact strength, hardness, and compression strength could be attributed to the brittleness of the material. Thermal conductivity increases with increasing the weight percentage of graphene. In addition, the thermal stability of polymer increases with increasing graphene content. Moreover, our results show that the prepared epoxy composites contain nanographene more stable compared with the pure epoxy.

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