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Thermal and Mechanical Properties of Epoxy Resin Reinforced with Modified Iron Oxide Nanoparticles

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Abstract

Epoxy polymers, having good mechanical properties and thermal stability, are often used for engineering applications. Their properties can be further enhanced by the addition of iron oxide (Fe_3O_4) nanoparticles (NPs) as fillers to the resin. In this study, pristine Fe_3O_4 NPs were functionalized with polydopamine (PDA), (3-glycidoxypopyl)trimethoxysilane (GPTMS), and (3-aminopropyl)trimethoxysilane (APTES). X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to study any changes in the crystal structure and size of the NPs while Fourier-Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA) were used to ensure the presence of functional groups on the surface. The mechanical properties of the Fe_3O_4 -based nanocomposites generally improved except when reinforced with Fe_3O_4 /PDA. The maximum improvement in tensile strength (~34%) and fracture toughness (~13%) were observed for pristine Fe_3O_4 -based nanocomposites. Dynamic Mechanical Analysis (DMA) showed that the use of any of the treated NPs improved the material's initial storage modulus and had a substantial impact on its dissipation potential. Also, it was observed that the glass transition temperature measurements by DMA and Differential Scanning Calorimetry (DSC) were below that of pure epoxy. SEM of the cracked surfaces show that the incorporation of any NPs leads to an enhancement in its thermal and mechanical properties.

Keywords: Epoxy composites, mechanical properties, thermal behaviour, iron oxide nanoparticles, polydopamine, organo-silanes

List of Symbols

θ	Bragg angle (radians)
D	Crystalline size (nm)
$\tan\delta$	Damping factor
T_d	Degradation temperature (°C)
ΔP	Difference in loading (MN)
K_I	Fracture toughness (MPa.m ^{0.5})
β	Full width at half maximum intensity (radians)
T_g	Glass transition temperature (°C)
K	Dimensionless shape factor
α	Ratio of crack length to width in compact tension sample
E'	Storage modulus (MPa)
T	Thickness of compact tension specimen (mm)
λ	X-ray wavelength (nm)
wt%	Weight percentage
W	Width of compact tension specimen (mm)

List of Abbreviations

APTES	(3-Aminopropyl) triethoxysilane
GPTMS	(3-Glycidoxypropyl) trimethoxysilane
DSC	Differential Scanning Calorimetry
DMA	Dynamic Mechanical Analysis
EDX	Energy Dispersive X-Ray Analysis
Fe ₃ O ₄ /Epoxy	Epoxy reinforced with 2.5wt% Fe ₃ O ₄
Fe ₃ O ₄ /APTES/Epoxy	Epoxy reinforced with 2.5wt% Fe ₃ O ₄ /APTES
Fe ₃ O ₄ /GPTMS/Epoxy	Epoxy reinforced with 2.5wt% Fe ₃ O ₄ /GPTMS
Fe ₃ O ₄ /PDA/Epoxy	Epoxy reinforced with 2.5wt% Fe ₃ O ₄ /PDA
Fe ₃ O ₄ /PDA	Fe ₃ O ₄ functionalized with polydopamine
Fe ₃ O ₄ /APTES	Fe ₃ O ₄ functionalized with APTES
Fe ₃ O ₄ /GPTMS	Fe ₃ O ₄ functionalized with GPTMS

FT-IR	Fourier Transform Infrared Spectroscopy
Fe ₃ O ₄	Iron Oxide
NPs	Nanoparticles
PDA	Polydopamine
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis

1. Introduction

Epoxy resin is a thermoset polymer containing epoxide terminal groups. This resin can form a highly cross-linked network either by homopolymerization in the presence of a catalyst or reacting with compounds having terminal amine, carboxylic acid, acid anhydride, phenol, or alcohol groups [1]. The most widely commercialized epoxy resin is based on the reaction between epichlorohydrin and bisphenol A forming Diglycidyl Ether of Bisphenol A (DGEBA) resin shown in Figure 1. When mixed with a polyamine hardener, DGEBA undergoes an exothermic addition reaction leading to a fully cured and crosslinked 3D network.

Figure 1: Chemical Structure of Diglycidyl Ether of Bisphenol A (DGEBA) resin [1].

Epoxy resin has also often presented itself as a strong thermoset with a high modulus of elasticity and good thermal stability. Nevertheless, the rigid chemical structure of this crosslinked polymer causes relative brittle behavior and low resistance to crack initiation and propagation [2, 3]. To resolve these issues, researchers have long been attempting to reinforce the resin with particulate fillers to create a composite material with enhanced properties [4-6]. Researchers have reported the successful incorporation of carbon-based nanofillers such as graphene, carbon nanotubes, fullerenes, and carbon black powder with a respective improvement in mechanical and thermal properties [7-13]. Other researchers have focused on the use of inorganic metallic fillers such as nickel and aluminum and metal oxides such as zinc, silica, and copper oxides to improve the resin's properties [14-18].

A few research studies have reinforced epoxy resin with Fe_3O_4 nanoparticles (NPs) to improve its magnetic and electrical properties [19, 20]. Iron oxide (Fe_3O_4) has proven to be chemically stable, environmentally friendly, cheap, and abundant in nature [21]. These NPs are often added to the matrix along with other reinforcements such as graphene oxide or glass fibers [21, 22]. Some researchers have proven that the incorporation of Fe_3O_4 can lead to an improvement in thermal stability and tensile strength of polymers such as vinyl-ester resins [23].

The challenges faced when manufacturing a polymer-matrix composite lie, not only, in the uniform dispersion of the filler but also in the strength of the adhesion between the filler and the matrix [24]. The improvement of the interfacial region enables efficient stress transfer between the two components of the composite. To do so, the addition of functional groups on the surface of iron oxide NPs was necessary to improve covalent bonding with the resin. The use of organo-silane molecules has gained popularity due to their ability to bind strongly with the NPs and polymer matrix. This coupling agent has often been used to functionalize metal NPs for composite material applications [25-27]. Javidparvar et al. found that the incorporation of 1 wt% Fe_3O_4 NPs functionalized with APTMS into epoxy film and curing with a polyamide could significantly improve the tensile strength and fracture toughness [28]. Sun et al. observed a 150% improvement in the strength of epoxy resin when Fe_2O_3 NPs functionalized with (3-Aminopropyl) triethoxysilane (APTES) were added to epoxy resin [29]. Besides, (3-Glycidoxypropyl) trimethoxysilane (GPTMS) has been used to functionalize the surface of zinc oxide NPs to improve the fracture toughness of epoxy resin [16]. It was explained that the presence of epoxide terminal ends on the NPs improves covalent bonding with the amine-based hardener and strengthens the composite. In addition to the silane-based molecules, 3-hydroxytyramine hydrochloride is a catechol-based molecule that polymerizes into polydopamine, PDA, under slightly basic conditions [30]. Research suggests that the formation of a PDA coating on the surface of metallic NPs could improve their dispersion within a solution [31].

As can be deduced, existing works differ in terms of the type of the filler used, the modifying agent (if any), and the characterization techniques applied. In addition to that, existing research heavily depends on the type of epoxy/hardener system being used and the wt% of filler added [19, 20, 28, 29]. To our knowledge, no work has been done so far on the use of

Fe₃O₄ nanoparticles, in specific, modified with GPTMS or PDA for the improvement of mechanical and thermal properties of epoxy resin with a polyamine hardener.

The present work aims to provide a full analysis of the effects of pristine and functionalized Fe₃O₄ NPs on the thermal and mechanical properties of epoxy resin. In addition to testing pristine Fe₃O₄ NPs, Fe₃O₄ functionalized with polydopamine, GPTMS, and APTES were studied. This paper will layout the detailed methodology for the modification of the pristine nanoparticles, as described in the literature, and the manufacturing process of the filler-based epoxy composites. It will also include the characterization of the produced particles and the results of the mechanical and the thermal testing of the composite materials. As mentioned before, several research papers have studied the effects of Fe₃O₄ NPs on either the mechanical or thermal properties of epoxy resin. However, this paper will provide a comparison between the effects of pristine Fe₃O₄ NPs and those functionalized with amino-terminal groups (APTES), epoxide terminal groups (GPTMS), and PDA on the thermal decomposition, glass transition, and static and dynamic mechanical properties of epoxy.

2. Materials and Methods

2.1 Materials

Pristine Fe₃O₄ NPs and the modifying agents, (3-Glycidoxypyrpyl) trimethoxysilane (GPTMS), (3-Aminopropyl) triethoxysilane (APTES), and 3-hydroxytyramine hydrochloride, as well as toluene, isopropanol, and citric acid used during the functionalization process were purchased from Sigma-Aldrich. The epoxy resin, Araldite LY 564, and its hardener, Aradur 2594, used for preparing the composites were purchased from Huntsman Inc.

2.2 Functionalization of Iron Oxide

Functionalization with PDA. To coat the Fe₃O₄ NPs with a layer of PDA (**Figure 2a**), a solution oxidation method was used where 25 mg of Fe₃O₄ particles were dispersed in 200 mL phosphate buffer solution with a pH of 8.5. The solution was sonicated for 5 minutes after which 2.5 mg of 3-hydroxytyramine hydrochloride was added. The dispersion was stirred for 24 h at room temperature after which the particles were magnetically separated and washed repeatedly by centrifugation at 4,000 rpm using deionized water. Finally, the sample was dried in a vacuum at 50 °C for 17 hours. This procedure was laid out by Zheng et al. with the use of a Tri-hydrochloride buffer instead of a phosphate buffer [32].

Functionalization with GPTMS. A 20 mL of distilled water was added to 100 mg of iron oxide. Then, 1 g of citric acid was dissolved in 10 mL distilled water and was added to the above solution and stirred for two hours. Finally, the solution was sonicated for five minutes to obtain a stable suspension. On the other hand, a pre-hydrolyzed GPTMS solution was prepared by adding a 10 mL mixture of water and isopropanol (1:2) to 107 mg of GPTMS with stirring for 1 hour [33]. A 1 mL of the prepared solution was, then, added to 20 ml of the previously prepared suspension and stirred constantly for 6 hours. The NPs were magnetically separated and washed/centrifuged with distilled water three times at 4,000 rpm. Finally, the particles were dried under vacuum for 16 hours at 50 °C (**Figure 2b**).

Functionalization with APTES. A 500 mg of Fe_3O_4 NPs were dispersed in 50 mL dry toluene by sonication for 10 minutes. Then, 473 mg of APTES was added dropwise to the suspension and the mixture was refluxed at 110 °C overnight. The NPs were recovered using a magnet and washed 5 times with acetone to remove all traces of unreacted silanes. Then, the NPs were dried under vacuum for 16 hours at 50 °C [34] (**Figure 2c**).

Figure 2: Schematic representation of the experimental procedures used to produce (a) $\text{Fe}_3\text{O}_4/\text{PDA}$, (b) $\text{Fe}_3\text{O}_4/\text{GPTMS}$, and (c) $\text{Fe}_3\text{O}_4/\text{APTES}$ nanoparticles.

2.3 Composite Manufacturing

Before the preparation of epoxy composites, the NPs were gently pulverized to create a finer powder. The required amount of NPs (to be discussed in Section 3.2) were, then, dispersed in 100 g of epoxy resin, Araldite LY 564, by ultrasonication for 30 minutes. The dispersion was further mixed at a high shear rate for one hour and left to cool down to room temperature. 35 g of the hardener, Aradur 2594, was added to the dispersion which was, then, degasified under vacuum for two hours in the beaker followed by another two hours in the tensile-test and compact-tension aluminum molds. According to the manufacturers' recommendations, the samples were cured at 80 °C for one hour and post-cured at 140 °C for 8 hours, after which they were demolded and sanded to remove the oxidized layer from the surface (**Figure 3**).

Figure 3: Schematic of the composite manufacturing process.

The optimum quantity of NPs was chosen based on a series of experiments performed during the first stage of the project. Fe₃O₄/epoxy samples were produced having 1, 2.5, and 5 wt% pristine Fe₃O₄. Based on the results of tensile testing, the use of 2.5wt% Fe₃O₄ NPs led to the greatest increase in tensile strength. Therefore, for the remaining experiments, it was decided to use 2.5 wt% NPs in the epoxy resin.

2.4 Characterization

The mechanical properties and thermal stability of the modified NPs and the manufactured composite materials were studied using a variety of characterization techniques.

Chemical Bonding. Fourier Transform Infrared Spectroscopy (FT-IR) was used to ensure the successful functionalization of Fe₃O₄ by monitoring the formation of new covalent bonds between the NPs and the modifying agents. The data were collected on a Nicolet Nexus 4700 Thermo Spectrometer using the KBr pellet method at wavelengths between 500 and 4000 cm⁻¹.

Mechanical Properties. The mechanical properties of the composites were investigated using tensile testing performed on a universal testing machine (UTM) in compliance with the standard test method ASTM D638 [35]. A laser extensometer was used to measure the strain with a crosshead speed of 1 mm/min using a 100 kN load cell. The dog-bone specimens were cast in aluminum molds such that the gauge length was approximately 50 mm and the cross-sectional area was 13 x 7 mm (**Figure 4a**). At least 5 specimens were tested for each sample at ambient conditions. To study the effect of reinforcements on the fracture toughness of epoxy resin, compact tension testing was performed. Square samples were prepared with a width and a thickness of 40 and 10 mm respectively (**Figure 4b**). A 24 mm notch was introduced in the middle of the sample based on ASTM D5045 and a crack of about 1mm deep was induced at the notch tip by gently tapping in a fresh blade [36]. The test was conducted at a crosshead speed of 0.5 mm/min with a 100 KN load.

Figure 4: Shows the dimensions of (a) tensile testing and (b) compact tension testing specimens for Fe₃O₄/epoxy composites with a thickness of 10 mm according to ASTM D638 and D5045 respectively

To calculate the plain-strain fracture toughness of the samples [37]:

$$K_I = \frac{\Delta P}{B\sqrt{W}} \frac{2+\alpha}{(1-\alpha)^{\frac{3}{2}}} (0.886+4.64\alpha-13.32\alpha^2+14.72\alpha^3-5.6\alpha^4)$$

Where, ΔP is the difference between the maximum and minimum applied load applied, W and B were the specimen's width and thickness respectively. α is the ratio of the crack length to the specimen width.

Dynamic Mechanical Testing (DMA) was performed using a DMA8000 by Perkin Elmer to study the effects of stress and temperature on the properties of the manufactured composites. DMA was performed in a single cantilever mode at a frequency of 1 Hz. The samples were rectangular having a width and thickness of 12 mm and 4 mm, respectively, and were tested between 0 °C and 220°C at a rate of 10 °C/min.

Thermal Properties. The thermal stability of the composites and NPs was studied using a TA Instruments Q500 Thermogravimetric Analysis (TGA) machine between 25 and 800 °C at a rate of 10 °C/min using nitrogen as a purge gas. The T_d was considered as the temperature at 5 % weight loss. Differential Scanning Calorimetry (DSC) was performed between -50 and 200 °C at a rate of 10 °C/min using a TA Instruments Q100 DSC machine in a heat/cool/heat mode.

Structure and Surface Morphology. X-ray diffraction (XRD) was performed using a Bruker D8 Advance in the 2θ range between 5 and 70°. *The obtained diffractograms were analyzed using the Fullprof suite using the Rietveld method by comparing them to spectra from the Crystallography Open Database (COD) [38]. Also, to calculate the crystalline size of the pristine and modified NPs, the Scherrer equation was used:*

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where D is the crystalline size (nm), K is a dimensionless shape factor taken to be 0.9, λ is the X-ray wavelength (nm), β is the full width at half maximum intensity (FWHM) in radians, and θ is the Bragg angle (radians) [39].

Scanning Electron Microscopy (SEM) using a Tescan MIRA3 FESEM was first used to study collect data about the size and shape of the pristine and modified Fe₃O₄ nanoparticles. Then, after performing mechanical testing, it was used to study the fracture morphology of pure and reinforced epoxy resin. The samples used were coated with 15 nm platinum before being tested. ***Energy Dispersive X-Ray (EDX) was performed on the modified NPs to study their elemental composition using the SEM micrographs. The presented results are an average of ten measurements.***

3. Results and Discussion

3.1. Modification of Fe₃O₄ Nanoparticles

Figure 5a displays the obtained FTIR spectra of the modified and pristine Fe₃O₄ NPs. The spectrum for pristine Fe₃O₄ NPs shows an absorption band at around 3438 cm⁻¹ representing the stretching vibrations of hydroxyl functional groups on the surface. The sharp band 1629 cm⁻¹ corresponds to the bending vibration of the H-O-H group [40, 41]. After coating the NPs with PDA, it appeared that the large band corresponding to the hydroxyl groups diminished in intensity suggesting possible bonding between the hydroxyl groups on the surface on Fe₃O₄ and the dopamine. The additional peaks at around 2523.5 cm⁻¹ correspond to C-H stretching vibrations.

Observing the spectra of Fe₃O₄/GPTMS and Fe₃O₄/APTES, the peak at around 3438 cm⁻¹ seemed to decrease in intensity and broaden signifying the possible functionalization of Fe₃O₄ NPs [42]. ***The peaks observed between 1100-900 cm⁻¹ indicate the presence of Si-O-Si vibrations in the structure GPTMS and APTES molecules [43].*** Absorption bands at approximately 1250 and 912 cm⁻¹ in 3 (see Figure 5a) are ascribed to the symmetric and asymmetric stretching vibration of the C-O-C the epoxy ring of GPTMS [44] while the bands at 1020 cm⁻¹ were attributed to the Si-O stretching vibration in APTES found on the magnetic

NPs [41]. The absorption bands at 1563.56 and 1499.12 cm^{-1} may be ascribed to N-H vibrations from amino groups on APTES [45].

Figure 5: (a) FT-IR spectra and (b) XRD diffractograms of 1: Pristine Fe_3O_4 , 2: $\text{Fe}_3\text{O}_4/\text{PDA}$, 3: $\text{Fe}_3\text{O}_4/\text{GPTMS}$, 4: $\text{Fe}_3\text{O}_4/\text{APTES}$ nanoparticles.

To study the effect of the functionalization process on the crystal structure of Fe_3O_4 nanoparticles, XRD analysis was performed on the powders, the results were displayed in **Figure 5b**. The diffractogram of pristine Fe_3O_4 NPs shows characteristic peaks at 18.24° , 30.18° , 35.54° , 43.17° , 57.08° , 62.67° corresponding to (220), (311), (400), (511), and (440), respectively, *indicating a cubic crystal system belonging to $Fd3m$ (227) space group (COD ID 9005839 [46]) in accordance with the literature [45, 47-49]*. The XRD pattern for the modified NPs showed the same peaks as with pristine Fe_3O_4 suggesting that there was no **significant** change in the materials crystal structure once modified. The peak intensities for $\text{Fe}_3\text{O}_4/\text{GPTMS}$ and $\text{Fe}_3\text{O}_4/\text{APTES}$ were slightly less than that of Fe_3O_4 with slight shifts in the peak locations suggesting possible surface modification but a stable crystal structure.

To further highlight the effect of surface modification on the Fe_3O_4 NPs, Rietveld Refinement was performed on the obtained diffractograms using the Fullprof suite. The lattice parameter for pristine Fe_3O_4 was calculated to be $8.36 \text{ \AA}$, similar to what has been reported in the literature [50]. While the lattice parameter for the pristine and modified nanoparticles did not vary significantly ($\sim 8.38 \text{ \AA}$), the crystalline sizes calculated using the Scherrer's equation from the broadening of the (311) peak suggest a possible effect of modification on the pristine NPs. The average crystal size for pristine Fe_3O_4 NPs was

calculated to be 68.21 nm. On the other hand, this value decreased to 54.56, 54.56, and 54.55 nm for $\text{Fe}_3\text{O}_4/\text{PDA}$, $\text{Fe}_3\text{O}_4/\text{GPTMS}$, and $\text{Fe}_3\text{O}_4/\text{APTES}$, respectively. A decrease in the crystalline size is an indication of the broadening of the corresponding peak due to defects in the material [51].

Figure 6 shows the SEM images for pristine and modified Fe_3O_4 nanoparticles. *As indicated using XRD, the NPs appear to have a cubic shape that does not vary much before and after the chemical modifications. The SEM images appear to be in good agreement with XRD since the morphology of the NPs appeared to remain the same before and after modification with no significant difference.*

Figure 6: SEM images of (a) Pristine Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4/\text{PDA}$, (c) $\text{Fe}_3\text{O}_4/\text{GPTMS}$, (d) $\text{Fe}_3\text{O}_4/\text{APTES}$ nanoparticles.

Table 1 summarizes the average particle diameter and elemental composition of the modified NPs. The average particle size, *from the SEM micrographs*, increased from 116 ± 20 nm to around 164 ± 11 nm when functionalized with PDA. This increase in size may signify the formation of a polymeric layer of PDA as a coating on the surface of the NPs. The size also increased to 150 ± 14 nm and 155 ± 13 nm when functionalized with GPTMS and APTES, respectively. This change may be attributed to the presence of silane molecules on the surface of the NPs. *In terms of elemental composition, as expected $\text{Fe}_3\text{O}_4/\text{PDA}$ NPs did not show the presence of any Si atoms. The percentage of C atoms was the highest signifying the presence of a polymeric later of PDA on the surface of the NPs. On the other hand, for $\text{Fe}_3\text{O}_4/\text{GPTMS}$ and $\text{Fe}_3\text{O}_4/\text{APTES}$ NPs, evidence of Si was observed. This was not as clear for $\text{Fe}_3\text{O}_4/\text{GPTMS}$ since GPTMS by nature possesses a bulky epoxide terminal group that can hinder the observation of Si atoms by EDX. In addition to that, N atoms were detected with $\text{Fe}_3\text{O}_4/\text{PDA}$ and $\text{Fe}_3\text{O}_4/\text{APTES}$ NPs due to the presence of amino-terminal groups for both PDA and APTES.*

Table 1: Average particle diameter and elemental composition of $\text{Fe}_3\text{O}_4/\text{PDA}$, $\text{Fe}_3\text{O}_4/\text{GPTMS}$, $\text{Fe}_3\text{O}_4/\text{APTES}$ nanoparticles.

Nanoparticle		$\text{Fe}_3\text{O}_4/\text{PDA}$	$\text{Fe}_3\text{O}_4/\text{GPTMS}$	$\text{Fe}_3\text{O}_4/\text{APTES}$
Average diameter (nm)		164 ± 11	150 ± 14	155 ± 13
Elemental Composition (%)	C	55.2 ± 1.4	12.7 ± 2.1	62.2 ± 4.7
	N	1.10 ± 0.3	-	0.85 ± 0.4
	O	26.8 ± 0.9	26.0 ± 0.7	28.0 ± 2.8
	Si	-	0.006 ± 0.003	0.09 ± 0.02
	Fe	17.0 ± 0.9	61.4 ± 2.3	9.0 ± 2.1

TGA was used to evaluate the thermal degradation behaviour of the NPs and detect the presence of organic matter (**Figure 7**). The inorganic Fe_3O_4 NPs showed a mere 2.1 % weight loss corresponding to the elimination of desorbed water molecules but no significant decomposition up to 800 °C [52]. When the NPs were functionalized with PDA, the weight loss increased to 13.2 %. The decrease in weight of $\text{Fe}_3\text{O}_4/\text{PDA}$ up to 400 °C corresponds to the degradation of the PDA coating on the surface of the NPs [53].

The thermograms of $\text{Fe}_3\text{O}_4/\text{GPTMS}$ and $\text{Fe}_3\text{O}_4/\text{APTES}$ both display two decomposition steps. For temperatures up to 200 °C, the decomposition is due to the elimination of water molecules and solvents used during the synthesis of the nanoparticles. In the second stage of decomposition at temperatures above 200 °C, Si-C bonds begin to break, and the weight loss increases to 9.2 % and 20 % with GPTMS and APTES molecules, respectively.

Figure 7: TGA thermograms of pristine Fe_3O_4 and the synthesized nanoparticles.

3.2. Characterization of the Epoxy Composites

3.2.1. Thermal Stability

The thermal stability of the manufactured composites was assessed using TGA. The obtained curves are illustrated in **Figure 8** and the section depicting the onset degradation temperature (T_d) is shown on the top right corner.

Figure 8: TGA thermograms of pure epoxy and the manufactured composites.

The average T_d of pure epoxy resin was calculated to be around 338.67 ± 0.47 °C. The polymer undergoes the first step in the decomposition process by breaking down the epoxy network at that temperature. Then, the resin undergoes a secondary decomposition in the range of 350–600 °C where the benzene rings of epoxy breakdown until 3.9 ± 0.5 % of its initial weight remains at 750 °C [54].

The incorporation of nanoparticles, whether pristine or unmodified, reduces the resin's thermal stability. As shown in Figure 8, the T_d of the nanocomposites decreases slightly below the benchmark to reach a minimum value of 331.62 ± 2.34 °C when using pristine Fe_3O_4 .

As for the remaining temperature range, the composites undergo a secondary decomposition between 400 and 500 °C associated with further decomposition of the nanoparticle/epoxy/hardener network. The rate of decomposition seemed to decrease when reinforced with APTES and GPTMS since a higher temperature was required to break it down and reach the final residual content (**Table 2**) [16].

Table 2: Decomposition temperature and residual content of the manufactured composites from TGA.

Sample	Onset Td (°C)	Residue (%)
Pure Epoxy	338.67 ± 0.47	3.87 ± 0.48
Fe ₃ O ₄ /Epoxy	331.62 ± 2.35	4.65 ± 0.67
Fe ₃ O ₄ /PDA/Epoxy	337.35 ± 1.18	5.43 ± 0.58
Fe ₃ O ₄ /GPTMS/Epoxy	332.47 ± 1.01	6.68 ± 0.14
Fe ₃ O ₄ /APTES/Epoxy	335.80 ± 0.62	4.62 ± 0.49

It was observed that the residual content of the manufactured composites increased with the incorporation of metallic nanoparticles. As shown in Table 2, Fe₃O₄ NPs did not degrade within the tested temperature range. Therefore, the residue was mainly composed of the inorganic metal content in the NPs by the initial amount dispersed in the matrix. This decrease in the thermal stability of the composite can be attributed to the increase in thermal transport across the composite due to the presence of metallic nanoparticles which, in turn, led to an acceleration in the material's thermal decomposition.

3.2.2. Glass Transition Temperature

The glass transition temperature of the epoxy composites was studied using the DMA and DSC characterization techniques. While DSC is a method that relies on the changes in heat flow to detect the transition temperature, DMA is a dynamic method that relies on sudden changes in the material's storage modulus as it moves from the glassy to the rubbery phase. The T_g of epoxy composites reinforced with metal oxides was proven to be heavily dependent on the interaction between the NPs and the polymeric matrix. The composite manufacturing process, nanoparticle surface modification, and the composite curing process have all played important roles in setting the T_g [55].

The respective DSC curves of the epoxy composites are shown in **Figure 9**. The T_g was determined by noting the midpoint of the shift in the baseline of the curve (pointed out using the arrows). While the T_g for pure epoxy resin was found to be 144.91 ± 1.95 °C, the incorporation of nanoparticles, regardless of their surface modification caused this value to decrease. The lowest recorded value was for the composite reinforced with Fe₃O₄/PDA

(131.62 ± 0.72 °C) and the closest value to the unreinforced epoxy was that with $\text{Fe}_3\text{O}_4/\text{GPTMS}$ (140.35 ± 1.47 °C).

Figure 9: Plots of heat flow versus temperature during the second heating cycle from DSC of pure epoxy and the manufactured composites.

The T_g was also determined by observing the sudden decrease in the curve of the storage modulus, E' , (Figure 10a) as well as the peak in the $\text{Tan}\delta$ curve (Figure 10b) from DMA.

Figure 10: Plots for (a) the storage and loss moduli (logarithmic scale) and (b) $\text{Tan}\delta$ versus temperature for pure epoxy and the manufactured composites.

Both curves show a similar trend, however, the T_g was slightly shifted to a higher value with $\text{Tan}\delta$. While the addition of pristine Fe_3O_4 NPs and $\text{Fe}_3\text{O}_4/\text{PDA}$ did not increase the

composite's T_g , the addition of Fe_3O_4 /GPTMS, and Fe_3O_4 /APTES NPs increased the T_g to 157.43 °C and 152.09 °C respectively from a value of 151.7 °C. This increase was due to the presence of the bulky nanoparticles, covalently bonded to the matrix, restricting the epoxy chain's mobility and decreasing the polymer's free volume. For this reason, the composite required more energy to undergo the thermal transition and, in turn, a higher temperature. A summary of the T_g values gathered from DSC and DMA curves are displayed in **Table 3**.

Table 3: T_g values (°C) of pure epoxy and the manufactured composites from DSC and DMA.

Sample	T_g from DSC	Onset E' from DMA	Peak $\tan\delta$ from DMA
Pure Epoxy	143.37 ± 2.03	151.70 ± 2.57	161.03 ± 1.37
Fe_3O_4 /Epoxy	135.25 ± 2.43	148.73 ± 0.68	157.59 ± 1.76
Fe_3O_4 /PDA/Epoxy	131.62 ± 0.88	146.15 ± 0.23	158.46 ± 0.36
Fe_3O_4 /GPTMS/Epoxy	140.35 ± 1.47	157.43 ± 0.15	167.81 ± 0.61
Fe_3O_4 /APTES/Epoxy	134.04 ± 1.67	152.09 ± 1.23	160.60 ± 0.20

Although it was expected that the T_g of the produced composites increases with the addition of any of the fillers, this was not the case for all of them. Whether using the DSC or DMA, the T_g of samples with pristine Fe_3O_4 and Fe_3O_4 /PDA decreased beyond the benchmark value. Numerous research papers that deal with epoxy composites have reported a similar trend, however, none of the proposed theories was conclusive [56, 57]. Starr et al. have published one of the few studies that simulate the effect of nanofiller structure and dynamics on the T_g of a polymer. It was proposed that the interaction between the matrix and the reinforcements led to the formation of several layers around the particles. It was stated that a secondary polymer nanolayer formed around the NPs is capable of relaxing faster than the immobile layer bound to the nanoparticles [56]. This portion of the matrix can move freely once subjected to a higher temperature and thus can reduce the T_g of the composite. Nonetheless, since the production of a composite with a completely homogeneous dispersion of NPs is

difficult, any agglomeration will leave sections of the composite with loosely bound changes. This, in turn, might lead to a decrease in the T_g as well [57].

3.2.3. Dynamic Mechanical Analysis

To study the effect of the fillers on epoxy resin under stress and temperature, DMA was performed to gather data about the material's storage modulus (E'), loss modulus (E''), and damping factor ($\tan\delta$). The curves are displayed in Figure 10 (a-b) while the values of the initial E' , E'' at the peak, and maximum $\tan\delta$ were summarized in **Table 4**.

Table 4: The initial value of E' , the peak value of E'' , and $\tan\delta$ for the tested samples

Sample	Initial E' (MPa)	Peak E'' (MPa)	Peak $\tan\delta$
Pure Epoxy	1078.3 ± 70.7	92.93 ± 7.58	0.45 ± 0.015
$\text{Fe}_3\text{O}_4/\text{Epoxy}$	1215.0 ± 42.0	131.1 ± 5.37	0.44 ± 0.011
$\text{Fe}_3\text{O}_4/\text{PDA}/\text{Epoxy}$	1271.7 ± 11.3	150.2 ± 6.33	0.54 ± 0.004
$\text{Fe}_3\text{O}_4/\text{GPTMS}/\text{Epoxy}$	1343.3 ± 75.8	147.0 ± 8.39	0.50 ± 0.004
$\text{Fe}_3\text{O}_4/\text{APTES}/\text{Epoxy}$	1411.0 ± 96.0	167.2 ± 7.02	0.46 ± 0.004

As can be observed in Figure 10a, the value of E' for pure epoxy resin was less than its composites throughout the displayed temperature range. The initial value of E' for the tested samples showed that the biggest improvement was obtained when using the silane-based nanoparticles. The use of $\text{Fe}_3\text{O}_4/\text{GPTMS}$ and $\text{Fe}_3\text{O}_4/\text{APTES}$ resulted in a 25 % and 30 % increase in E' , respectively. This improvement may be attributed to the successful transfer of applied stresses from the matrix to the reinforcements and enhanced covalent bonding [58].

Figure 10a also shows the values of E'' at the peak reflecting segmental motions within the polymer matrix at different temperatures. It was observed that the value increased by as much as 80 % when $\text{Fe}_3\text{O}_4/\text{APTES}$ was used. Therefore, it was deduced that the incorporation of nanoparticles, especially modified ones, increased the viscous response of the composite.

In other terms, the material tends to lose energy during a deformation cycle represented by an increase in damping.

To account for both the elastic and viscous portions of this viscoelastic polymer, the ratio of the two was plotted in Figure 10b as $\tan\delta$. It was observed that the height of the peak increased when the polymer was reinforced with modified Fe_3O_4 nanoparticles. Given that the increase in E'' was larger than that of E' , it is understandable that the height of the $\tan\delta$ curves increased more when epoxy was reinforced. This indicates that the material had more dissipation potential.

The increase in damping may be due to two factors. First, chemical bonding between the NPs and the polymer chains creates an interface with properties different from those of the filler and the matrix. The thickness of this interface, added to the final radius of the NPs, can lead to higher energy utilization [59]. Second, the increase in the loss modulus, or damping signifies ease of NP debonding from the matrix or possible interfacial slippage [60, 61]. This may be caused by the possible agglomeration of the NPs.

3.2.4. Mechanical Properties and Fracture Morphology

To study the effect of the type of nanoparticle on the tensile properties of epoxy resin, tensile testing was performed on the dog-bone specimens and the respective stress-strain curves were plotted in **Figure 11a** and summarized in **Figure 11b**.

(a)

Figure 11: (a) Representative stress-strain curves of the manufactured epoxy composites and (b) a summary of the obtained tensile strengths (MPa) and elastic moduli (MPa) of the manufactured epoxy composites

Regardless of the nanoparticle's structure, the stress-strain curves appeared to show similar brittle-like behavior. There was a clear difference in the tensile strength and elastic modulus of the composites as illustrated in Figure 11b. The addition of pristine Fe₃O₄ NPs increased the tensile strength from 38.50 ± 5.5 to 51.77 ± 1.8 MPa, equivalent to a 34.5 % improvement. The results for epoxy reinforced with Fe₃O₄/PDA showed a decrease in the strength of epoxy to 33.10 ± 0.1 MPa. Tg measurements using DSC and DMA (Table 3) showed a decrease in the value when reinforced with Fe₃O₄/PDA NPs suggesting possible agglomeration with the composite. This was further verified by the decrease in strength of that particular sample. On the other hand, the GPTMS/Fe₃O₄/Epoxy composite showed improved strength (14 %) compared to pure epoxy resin. APTES/Fe₃O₄/Epoxy showed an average strength of 50.19 ± 1.98 MPa i.e. a 30.3 % improvement. As can be observed, Fe₃O₄/Epoxy pertained the highest tensile strength and the lowest damping (Table 4) amongst the composites as it had the smallest particle size and, therefore, better dispersion.

To further test the effect of nanoparticle functionalization on the mechanical properties of epoxy resin, compact tension testing was performed to study the material's fracture toughness. The results are summarized in **Figure 12**.

Figure 12: Fracture toughness of the manufactured epoxy composites.

The results show a similar trend to that collected from tensile testing. While the average fracture toughness of pure epoxy resin was 1.09 ± 0.047 MPa.m^{0.5}, this value reached a maximum of 1.246 ± 0.081 MPa.m^{0.5} when 2.5 wt% Fe₃O₄ were dispersed in the matrix; equivalent to a 13.51 % improvement. The addition of Fe₃O₄/PDA NPs did not deteriorate the properties as with tensile strength but also did not demonstrate any significant improvement in the toughness. While the tensile strength was improved most using APTES as a coupling agent, for toughness, the use of GPTMS proved to enhance the resin the most to 1.17 ± 0.035 MPa.m^{0.5}, approximately 6.85 %. The use of hydroxyl groups at the surface of pristine Fe₃O₄ NPs and silane coupling agents for the other modified NPs led to the formation of a stronger interface with the resin. The binding of the NPs with the polymeric matrix led to the respective improvement in mechanical properties.

SEM was performed on the cross-sectional area of the tensile testing dog bone after fracture to find a correlation between the specimen's morphology and the obtained results. **Figure 13** shows the obtained images for pure epoxy and the manufactured composites.

As reported in the literature, the fracture morphology of a neat epoxy sample appears to be smooth with cracks having a clear direction for propagation as shown in Figure 13a. This is a clear indication of the resin's brittle nature [62]. The location where the crack is initiated was clear, so was the path in which it propagates. The crack lines were relatively smooth and defined with little to no deviations from the main path. It was observed that the incorporation of nanoparticles, regardless of the type, led to morphological differences on the surface of

the samples. As shown in Figure 13(b-e), the crack propagation lines did not appear to have a clear and distinguished path. The surface appeared rougher compared to that of neat epoxy. In Figure 13c, clusters of Fe_3O_4 /PDA NPs were present in the bulk of the specimen creating aggregates in the micro-meter range. This indicates the inhomogeneous dispersion of the NPs and explains the deterioration in the composite's mechanical properties (Figure 11b and Figure 12). On the other hand, the SEM fractography of pristine Fe_3O_4 /epoxy, Fe_3O_4 /GPTMS/epoxy, and Fe_3O_4 /APTES/epoxy did not show any nanoparticle aggregation or cluster formation. Bowing lines as a result of crack pinning were observed in addition to crack deflection in certain areas. These mechanisms decreased the propagation energy of the crack and led to an increase in strength and toughness [16].

Figure 13: SEM of the fracture obtained from tensile testing for (a) pure epoxy, (b) Fe_3O_4 /epoxy, (c) Fe_3O_4 /PDA/epoxy, (d) Fe_3O_4 /GPTMS/epoxy, (e) Fe_3O_4 /APTES/epoxy

4. Conclusions

In this paper, we have chemically modified the surface of Fe_3O_4 nanoparticles (NPs) and used them in the preparation of a series of epoxy-based nanocomposites. The NPs had been successfully modified by monitoring changes in differences in covalent bonding and thermal

decomposition using FT-IR and TGA characterization techniques. Based on the XRD diffractograms, the NPs maintained their crystal structure with surface modification. The tensile strength and fracture toughness of non-modified Fe₃O₄-based epoxy composite increased by 34.5 % and 13.5 %, respectively. While the presence of PDA did not lead to an improvement in mechanical properties, the use of APTES and GPTMS as coupling agents led to an improvement in strength and toughness by as much as 30.3 % (APTES) and 7 % (GPTMS) respectively. DMA testing showed that the material's storage modulus in the glassy region was higher than pure epoxy with more dissipation potential and fewer internal chain restrictions. DSC showed that the T_g of the manufactured samples decreased to a minimum of 131.6 °C. This result was further validated by DMA testing where the T_g was shown to decrease to 157.59 ± 1.76 °C (using Fe₃O₄). Finally, the presence of Fe₃O₄ NPs, pristine and modified, in the composite enhanced the thermal transport as evidenced by the decrease in the T_d (2 % at most). Overall, the addition of pristine and modified Fe₃O₄ NPs led to significant improvement in the mechanical properties of epoxy resin. ***It would be interesting to further explore the effects of Fe₃O₄ NP size and morphology on the surface modification process as well as the thermal and mechanical properties of the manufactured epoxy composites.***

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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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