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Construction of *An Epoxy* **Composite Coating** with **Exceptional** Thermo-Mechanical Properties **using Zr-based** *NH_2-UiO-66* Metal-Organic Framework: Experimental and DFT-D Theoretical Explorations

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Highlights

- A Zr-based *UiO-66-NH_2* MOF was covalently functionalized by glycidyl methacrylate.
- The tensile properties of the *GMA-UiO-66* reinforced epoxy were investigated.
- *80% improvement in* the energy at break of *GMA-Zr-MOF* reinforced epoxy was observed.
- *GMA-Zr-MOF particles could effectively toughen the Epoxy composite.*

Abstract

In this study, for the first time, the influence of the nanoporous Zr-based *NH_2-UiO-66* metal-organic frameworks (MOFs) on the tensile strength and fracture toughness of the epoxy coating was investigated. In addition, the impacts of the UiO particles' functionality (i.e., NH_2 or GMA) on the MOFs/epoxy interfacial bonding and nanoparticles dispersion quality in the epoxy resin were examined by the tensile test, dynamic mechanical thermal analysis (DMTA) and field emission-scanning electron microscope (FE-SEM). The *NH_2-UiO-66* and *GMA-UiO-66* MOFs chemical structures were investigated by FT-IR, BET, and FE-SEM approaches. The FE-SEM investigation of the fracture morphology (at the cross-section of the epoxy composites) and EDS-mapping analysis results evidenced the uniform dispersion of the Zr-based *GMA-UiO-66* particles in the epoxy matrix. TGA achievements revealed that by introducing 0.2 wt.% *GMA-UiO-66 and* NH_2-UiO-66 nanoparticles into the epoxy coating, the thermal stability of the coating was improved about 80% and 48%, *respectively* compared with the neat epoxy sample. *The tensile test results evidenced about 80% and 70% improvements in the energy at the break, and 64% and 41% improvements in the tensile strength, of* the *GMA-UiO-66 and* NH_2-UiO-66 loaded nanocomposites, respectively. *The final results declared that the GMA-UiO-66 could effectively toughen the epoxy coating much higher than the* NH_2-UiO-66 *particles.*

Keywords: Nanoporous Zirconium-based NH_2-UiO-66, *GMA-UiO-66;* Functional Metal-Organic Framework (MOF); Epoxy-composite; tensile properties; FT-IR.

1. Introduction

Epoxy resin is a well-known type of thermosetting polymers *with* excellent moisture, good thermal/mechanical properties, high solvent resistance, and remarkable adhesion properties to most of the metallic/un-metallic substrates. Because of these unique characteristics, it has been extensively used in vehicles, aircrafts fields, electrical appliances, oil/gas storage tanks/pipes, and construction. However, the poor crack deflection performance, as well as the brittle nature of the epoxy, has extremely limited its practical applications [1-2].

The inclusion of nanofillers into the epoxy-based coatings is an advanced strategy for the achievement of high-performance nanocomposites with superior thermal/mechanical properties [3]. Various nanofillers, i.e., carbon-based nanofillers, including fullerene [4], graphene/graphene oxide [5], carbon nanotubes [6, 7], and inorganic nanomaterials like LDH [8], halloysite [9] and clay [10], etc. have been selected for this aim. Recently, the 3D MOFs have been introduced as advance coordination materials with nanosize pore morphology, exchangeable/strong ligands, and large specific surface areas [11-13]. MOFs are advance porous (with pore fraction relatively greater than 40%) functional materials with many potential applications. However, the mechanical characteristics of the MOFs have not been well studied and considered. MOFs, due to controllable pore size, low density, and high surface area, are new types of porous materials that have been widely used in many fields, for example, photocatalysis [14-17], catalysis [18-23] and adsorption [24-26]. Due to these unique inherent features, they are used for the development of advanced composite materials with outstanding thermal/mechanical characteristics [27-29] as well as anti-corrosion properties [30-31]. Ma et al. [32] reported the epoxy composite coating mechanical/thermal properties improvement after the addition of Sn-MOF@PANI. Zhang et al. [33] explored that by the addition of nano-hybrids based on MOF-GO, the fire resistance of the epoxy composite coating was remarkably improved. Recently, the zirconium-based MOFs with high coordination number has attracted the attention of the researchers due to their excellent thermal stability, solvent resistance, high shear strength, nano-scale structures, and large specific surface areas. Because of these unique features, they are used in separation and drug delivery applications [34-39]. Among various MOFs, the Zr-based MOFs have been recently considered due to their much higher elastic moduli (G)/shear modulus (>13 GPa) than other MOFs. Based on the reports, the shear modulus values of this kind of MOF are at least 5-10 times greater than the other MOFs, i.e., ZIF-8. The exceptional mechanical, thermal, structural, and chemical stabilities of the Zr-based MOFs are attributed to the high number (12, the highest number possible connection of the inorganic (Zr)-organic (2-ATA) nodes) of coordination in the Zr-based MOF. Due to these unique characteristics, the Zr-based MOFs have shown much better mechanical properties and structural stability against shear stress than other types of MOFs [37].

Sai et al. [28] studied the significant impact of the Zr-based MOFs synthesized in the presence of the $Zr_6O_4(OH)_4$ (as metal clusters) and 1,4-benzodicarboxylic acid struts (as an organic ligand) on the fire resistance, thermal stability as well as mechanical properties of the polycarbonate matrix. Gue et al. [29] explored the flame resistance of the SiO_2@UiO-66 particles in the epoxy composite. They revealed significant improvement in the thermal resistance of the SiO_2@UiO-66 reinforced epoxy composite. The adsorptive activity of the Zr-based NH_2-UiO-66 MOFs against methotrexate removal from the aqueous solution was studied by Aghajanzadeh et al. [40]. Also, Huang et al. applied the UiO-66 based-MOF as a gas sensor for acetone vapor [41]. Phatake *assessed the catalyst activity of UiO for the N-formylation of amines with* CO_2 *[42]. The Zr-based MOFs, like UiO-66, have been applied for different purposes and numerous applications (i.e., gas storage, catalysis, separation/sensing, etc.) [43]. For example,* Molavi applied NH_2-UiO-66 *[44], and* ethylenediamine functionalized NH_2-UiO-66 *[45] particles for selective adsorption of* CO_2/N_2 *and* CO_2/CH_4, respectively. *However, there is no* systematic study on the estimation of the UiO-66 surface functionality on the particles dispersion quality in the epoxy matrix as well as the particles interfacial interactions with the polymer chains, affecting the thermal as well as mechanical characteristics of the final composite coating [46-48].

In the present study, a novel Zr-based *NH_2-UiO-66* MOF *was synthesized and then covalently functionalized* with Glycidyl Methacrylate (GMA). Then, the structure and morphology of the *NH_2-UiO-66 and* GMA-UiO-66 particles were analyzed by FT-IR, BET, and FE-SEM analyses. *Finally, the* NH_2-UiO-66 *and* GMA-UiO-66 particles were introduced into an *epoxy coating, and the resulting composites' thermal/mechanical characteristics were investigated by TGA, tensile, and DMTA analyses. Also, the MOFs dispersion quality and interfacial bonding with the epoxy matrix were studied by FT-IR (spectroscopy), cross-section EDS-Mapping and FE-SEM analyses. Furthermore, to complement the experiments, fundamental understandings concerning the affinity/interactions of organic/inorganic complexes with epoxy resin chains were achieved by applying a microscopic-scale theoretical method based on DFT-D tools.*

2. Experimental

2.1. Materials

Glycidyl methacrylate (GMA), tetrahydrofuran (THF), zirconium (IV) chloride ($ZrCl_4$), dimethylformamide (DMF) *and* 2-aminoterephthalic acid (2-ATA), *were brought from Sigma-Aldrich Co.* The polyamide hardener (50%) and epoxy resin (type Epiran-01-X75, 75%) were brought from SABA SHIMI ARYA Co.

2.2. Building NH_2-Zr-MOF and GMA-Zr-MOF-based MOFs

NH_2-UiO-66 based MOF was synthesized through mixing the $ZrCl_4$ (0.53 g) and 2-ATA (0.41 g) in 40 mL DMF solvent. The mixture was vigorously agitated (at 25 °C) until getting a homogenous and clear solution. Then, the obtained solution was introduced into a Teflon-lined autoclave (50 mL). The autoclave was placed in the oven with a temperature of 120 °C for 24 h. Afterward, the obtained product (MOF) was centrifuged and carefully washed by DMF solvent for three times. Finally, to remove all remained unreacted reactants, the products were washed with chloroform for 10 min under sonication for another three times. The washed product was dried under vacuum condition (at 100 °C) for 24 h [49]. The obtained product was named NH_2-UiO-66. The procedure is schematically displayed in detail in **Figure 1a**.

GMA-UiO-66 particles were synthesized through suspending the NH_2-UiO-66 (60 mg) nanoparticles in 5 mL tetrahydrofuran (THF). The mixture was sonicated for 20 min, and then GMA (1.6 mmol) was added and continually stirred for 36 h at 55 °C. The functionalized *GMA-UiO-66* MOF particles were centrifuged (10 min at 5000 rpm), washed with THF (three times), and chloroform (three times) under sonication (10 min) to eliminate the unreacted GMA molecules. The *GMA-UiO-66* powder was dried (at vacuum condition) for 24 h at 50 °C [49]. The procedure is schematically displayed in **Figure 1b**.

2.3. Preparation of epoxy composites reinforced with NH_2-UiO-66 and GMA-UiO-66 -based MOFs

The prepared MOFs based on *NH_2-UiO-66* and *GMA-UiO-66* (0.2 g) were added to 60 g epoxy resin (with 50% solid content) and then vigorously agitated for about 30 min by a high-speed homogenizer. Then, to ensure the homogeneous dispersion of the MOF particles in the epoxy resin, a proper amount of toluene was added to the mixture. Then, ultra-sonication with 150 W (15 min) was applied to the epoxy/MOF mixture. Finally, 46 g amino polyamide-based hardener was added to the epoxy/MOF mixture. After mixing, the cleaned glass sheets were coated by the epoxy-neat (without MOF), and the epoxy/MOF composites (via a film applicator). The coated samples were placed in a cleanroom for 48 h at 25 °C, and finally, they were transferred into the oven (100 °C, 2 h). The thickness of the cured coatings was 70 μm. The coated glass sheets were then dipped in a water bath for 1 h to remove the free-standing composite films. The obtained free films were stored at 40 °C for 24 h before analysis. The obtained composites were named Epoxy@*NH_2-Zr-MOF* and Epoxy-*GMA-UiO-66*.

2.4. Characterization

Using a Perkin Elmer model FT-IR instrument, the structures of the MOFs were analyzed within the wavenumber range of 400-4000 cm^{-1}. Also, the BET analysis was conducted via BELSORP-mini II instrument in a nitrogen condition at 77 K. The morphology of the MOFs was investigated by MIRA TESCAN model FE-SEM instrument.

DMTA analysis was carried out by 242c/1/G instrument (at 1 Hz, 30-150 °C, 5 °C/min heating rate) to evaluate the thermal and mechanical properties of the composite coatings. The tensile properties of the composite coatings were studied by the EQ-SC1-22 machine (SANTAM) at the speed of 5 mm/min (25 °C). To investigate the MOFs dispersion state in the epoxy matrix, FE-SEM analysis (EDS-Mapping) was carried out on the fractured surface of the films. TGA was carried out on the Epoxy@MOFs composites to investigate the coatings' thermal stability using the Mettler Toledo instrument (in the range of 25-600 °C) with the 10 °C min^{-1} heating rate under N_2 atmosphere. FT-IR analysis was also performed on the Epoxy@MOFs composites to assess the chemistry of the films.

2.5. DFT-D approach

The interactions of the epoxy resin with metal-organic complexes based on zirconium cation (Zr^{+4} or Zr (IV)) were evaluated from a computational perspective applying the DFT-D approach. The zirconium (IV) complexes were built with terephthalic acid (TA) $[Zr(TA)_n]^{+4}$, 2-amino-terephthalic acid (ATA) $[Zr(ATA)_n]^{+4}$, and glycidyl methacrylate (GMA) functionalized 2-amino-terephthalic acid (GMA-ATA) $[Zr(GMA\text{-}ATA)_n]^{+4}$ with n values equal to 2-6. The designed $[Zr(TA)_n]^{+4}$, $[Zr(ATA)_n]^{+4}$, and $[Zr(GMA\text{-}ATA)_n]^{+4}$ complexes represent the *UiO-66, NH_2-UiO-66, and GMA-UiO-66 MOFs*, respectively. All complexes were built through bonding of organic molecules (i.e., TA, ATA, and GMA-ATA) through carbonyl O atom in the carboxylic acid moiety of terephthalic acid to a zirconium (IV) cation. The interactions of all organic/inorganic complexes were inspected with model epoxy resin. For this purpose, complexes were placed near the epoxy molecule. Afterward, the DFT-D equilibration was conducted for epoxy resin and considered complexes and also their hybrid clusters. Within equilibration, the basis set of DNP and the GGA/PBE functional embedded in $DMol^3$ code were utilized [51]. The interactions related to dispersion terms were taken into account by choosing the Grimme method [52]. The structures derived from DFT-D equilibrations of complexes were plotted in **Figure 2**.

3. Results and discussion

3.1. Analysis of the constructed Zr-based MOFs

The structure of the Zr-based MOFs was analyzed via FT-IR. The *FT-IR* spectrum (**Figure. 3a**) of both MOFs showed characteristic bands related to the C-N stretching at 1250 and 1380 cm^{-1}.

Also, the characteristic peaks observed at 658 and 768 cm^{-1} in the MOFs spectra correspond to the N-H bond [53]. The stretching vibrations related to C=C (1570 cm^{-1}) and C=O (1660 cm^{-1}) absorption bands are observed in the MOFs FT-IR results. The weak absorption bands detected at 2780-2970 cm^{-1} in the spectra of two Zr-MOFs correspond to the C-H bond vibration in the aromatic and aliphatic modes. The broadband, indicating the presence of the NH_2 group in the MOF structure, can be observed at the wavenumbers of 3340 and 3430 cm^{-1} [54]. It should be noted that the second peak related to the NH_2 absorption (at 3430 cm^{-1}) overlapped with the O-H bond absorption vibration. In both MOFs, the Zr-O bond absorption, indicating the coordination between the $ZrCl_4$ and 2-ATA, was observed at 523 cm^{-1}. Generally, the GMA modified MOF particles show similar absorption peaks with slight differences compared with NH_2-UiO-66 NPs. From the GMA modified MOF absorption spectrum, it can be evidently seen that a weak absorption peak related to the unreacted C=O groups appeared at 1720 cm^{-1}, reflecting the GMA reaction with UiO-66 particles. The NH_2 peak intensity at 660 cm^{-1} in GMA modified UiO particles is less than the NH_2-UiO-66 NPs, and the N-H peak intensity at 3430 cm^{-1} is greater than the NH_2-UiO-66 NPs, all disclosing the NH_2 reaction with the epoxide ring of GMA.

The NH_2/*GMA-UiO-66* NPs morphology and particle size were investigated by FE-SEM analysis (**Figure.3b**). This figure displays smooth surfaces with the triangular pyramid-shaped (with symmetrical crystalline) morphologies with the average sizes between 80-280 nm for *GMA-UiO-66* and *NH_2-UiO-66*. Both MOFs represented similar crystal morphology, which is in accordance with the literature [55].

The specific surface area, mean pore diameter, and total pore volume of the *GMA-UiO-66* NPs were evaluated by BET through N_2 adsorption/desorption isotherms at 77 K, and the obtained results are presented in **Figure 4** and **Table 1.** The surface area, mean pore diameter, and total pore volume of 576 m^2/g, 2.99 nm, and 0.42 cm^3/g were calculated for the *NH_2-UiO-66* NPs, respectively. These values for the *GMA-UiO-66* NPs were 568 m^2/g, 2.85 nm, and 0.40 cm^3/g, respectively. These results reveal lower surface area, mean pore size, and pore volume of the *GMA-UiO-66* NPs than *NH_2-UiO-66* NPs. This may be attributed to the partially pores blocking of the *NH_2-UiO-66* particles by GMA. According to **Figure 4**, the hysteresis loop was observed in the N_2 isotherms in the relative pressure (introduced by P/P_0) between 0.8 and 1.0, which is due to the presence of mesopores (in range of 2-50 nm) in the MOFs [56, 57].

3.2. Analyzing the tensile properties of the MOF based epoxy-composites

In this study, the *NH_2-UiO-66* particles were covalently bonded with the GMA molecules to improve the compatibility between the MOF particles and epoxy, leading to better MOF particles dispersion in the epoxy resin and greater improvement of the coating tensile properties. To show this, the stress (δ)-strain (ε) plots of the Epoxy-Neat, Epoxy@*NH_2-UiO-66*, and Epoxy@*GMA-UiO-66* samples are provided in **Figure 5a**. The breakpoint energy, yield stress, and ultimate strain values are depicted in **Figure 5b, c,** and **d.** The *outcomes from this figure represent about 80% and 70% improvement in* the epoxy composite *energy at the break* after incorporation of *NH_2-UiO-66* and *GMA-UiO-66 particles, respectively. Also, in the presence of NH_2-UiO-66* and *GMA-UiO-66* particles, *the tensile strength of the epoxy coating was improved by* about *64% and 41% compared with the Epoxy-Neat sample, respectively. Results also demonstrate a significant increase in the breakpoint elongation compared with the unfilled epoxy matrix*. **Figure 5a** illustrates the increase in Young's modulus of the epoxy-based nanocomposites in the presence of nanoparticles.

It is evident from **Figure 5** results that *the best impact of MOFs on the mechanical properties of the epoxy-based composites was achieved in the case of GMA-UiO-66 particles. This is clear evidence on the toughening effect of the* particles on the epoxy composite through *the strong interfacial interactions between the NH_2-UiO-66* particles and epoxy. *The NH_2 groups of UiO-66 particles could react with the epoxy groups of the polymer by a ring-opening mechanism, leading to the chemical bonding. In the case of GMA modified MOFs, the major mechanism affecting the coating toughness* *properties is the particle dispersion improvement in the epoxy structure.* The tensile properties of the studied samples can be ordered as Epoxy@*GMA-UiO-66*> Epoxy@*NH_2-UiO-66*/EP>Epoxy-Neat.

3.3. Dispersion/morphology analysis of MOF-based epoxy composites

To better discuss the toughening mechanism of the MOF particles on the epoxy coating tensile/fracture performance, the morphology of the fracture surface at the cross-section of the composite coatings was investigated by the FE-SEM method (**Figure 6**). Furthermore, FE-SEM images and EDS-Mapping at high magnifications were provided in **Figures 7** and **8** to investigate the MOF particles dispersion in the epoxy structure. FE-SEM images obviously declare mirror-like and highly rough fracture surfaces for the Epoxy-Neat and MOF-based nanocomposites, respectively. The flat surface area with a brittle edge of the Epoxy-Neat sample proves the poor stress-damping properties of this sample. It is apparent from the images that the pure epoxy did not show evident plastic-type deformation. With the inclusion of Zr-MOFs, more roughness and less flat areas were recorded. According to the images, it is clear that the crack propagation direction lines are more crowded together in the *GMA-UiO-66* reinforced epoxy than the *NH_2-UiO-66* loaded sample. Also, the distance between two river/crack lines become closer in the former, demonstrating the higher stress damping properties and resistance to crack propagation of the *GMA-UiO-66* loaded composite coating. *The* excellent crack deflection and stress damping properties of the Epoxy@*GMA-UiO-66* sample are due to the better dispersion of the particles in the epoxy structure [58]. To show this feature, the high-magnification images and EDS-Mapping results were collected from the cross-section of the films, as illustrated in **Figure 8.** The EDS-Mapping reveals uniform Zr element distribution in the whole surface area, disclosing the presence of the UiO particles in the entire coating structure. However, the high magnification images obtained from the FE-SEM analysis declare the agglomeration of the *NH_2-UiO-66* particles and uniform distribution of the *GMA-UiO-66* particles in the coating matrix**.** In the case of the NH_2-*UiO-66*, the particle surface nature is less hydrophobic than the *GMA-UiO-66* and also the interactions between the epoxy and NH_2-*UiO-66* NPs is chemical bonding. The better tensile results and toughening effect of the *GMA-UiO-66* based MOF than NH_2-*UiO-66* particles can be attributed to the better dispersion of the former due to the GMA molecules' role in the MOF particles agglomeration prevention as well as the weaker interaction between the particles and epoxy matrix. The GMA modified UiO particles interactions with the epoxy chains are almost in the form of hydrogen/van der Waals interactions that promote the *stress damping capability of the* MOF/epoxy interface *[59-60]. The uniformly distributed GMA-UiO-66* particles in the epoxy matrix provide many stress damping sites, causing better tensile strength and more toughness properties of the coating. *The GMA-UiO-66 particles encapsulated polymer matrix includes many weak regions with a high potency of releasing the triaxial stress and damping the energy. Despite the good dispersion and weak interface with high-stress damping power, the highly improved tensile strength properties of the Zr-MOF loaded epoxy composite can be ascribed to the exceptional mechanical stability, arising from the* high shear stability and shear modulus (>13.75 GPa) *of the UiO particles [61]. The* high coordination (inorganic-organic) number of 12 in Zr-based MOF, i.e., UiO-66, describes the great mechanical stability and excellent resistance against shear stress due to the high inorganic-organic nodes connection in the framework (**Figure** 9). According to literature, the strong Zr-O bonds and C (in carboxylate group)−C (in phenyl ring) bridging in the UiO-66 based-MOF show elongations and/or compressions degrees approximately 5 to 10 times higher than other kinds of MOFs due to the high (12) network connections [62]. All of these could explain the high tensile strength and Young's modulus of the epoxy composite reinforced with *GMA-UiO-66*.

3.4. DFT-D results

The epoxy resin interactions with complexes of zirconium (IV) with terephthalic acid ($[Zr(TA)_n]^{+4}$), 2-amino-terephthalic acid ($[Zr(ATA)_n]^{+4}$) and glycidyl methacrylate functionalized 2-amino-terephthalic acid ($[Zr(GMA\text{-}ATA)_n]^{+4}$) were computationally illustrated via DFT-D methodology. The DFT-D equilibrated clusters of $[Zr(TA)_n]^{+4}$ and $[Zr(ATA)_n]^{+4}$ with epoxy resin were given in **Figure 10**. It is visible that all five complexes of Zr^{+4}/terephthalic acid and Zr^{+4}/2-amino-terephthalic acid remained near the epoxy resin after DFT-D equilibration. These clusters apparently propose the epoxy resin affinity with zirconium (IV) based complexes. Further investigation clarifies that the Zr^{+4} cation in smaller $[Zr(TA)_n]^{+4}$ and $[Zr(ATA)_n]^{+4}$ complexes (i.e., complexes with n values of 2-4) aligned towards the epoxy oxygen (i.e., hydroxyl and ether) atoms. Such an inorganic cation alignment is attributed to its electrostatic attraction with epoxy O atoms possessing negative point charges. In case of larger cationic complexes, it is noted that the -OH fragments in terephthalic acid ligands and the amine and carbonyl moieties in 2-amino-terephthalic acid ones shared hydrogen bonds with the oxygenated centers of model epoxy resin. From the depicted clusters, it is also seen that some phenyl rings of complexes (especially in smaller ones) arranged relatively parallel relative to epoxy rings, which can be evidenced through π-π interactions.

The quantitative inspection of affinity between the above-mentioned Zr^{+4} based complexes and the epoxy molecule was accomplished through estimating the binding energy. For the equilibrated epoxy/$[Zr(TA)_n]^{+4}$ clusters, the binding energies of -158.4, -145.8, -95.0, -85.8, and -76.2 kcal/mol were derived assigned to $[Zr(TA)_2]^{+4}$, $[Zr(TA)_3]^{+4}$, $[Zr(TA)_4]^{+4}$, $[Zr(TA)_5]^{+4}$, and $[Zr(TA)_6]^{+4}$ complexes, respectively. Similarly, epoxy equilibration near the $[Zr(ATA)_2]^{+4}$, $[Zr(ATA)_3]^{+4}$, $[Zr(ATA)_4]^{+4}$, $[Zr(ATA)_5]^{+4}$, and $[Zr(ATA)_6]^{+4}$ coordination complexes accompanied with -156.6, -96.6, -91.4, -51.6, and -64.4 kcal/mol energy, respectively. The binding energies containing negative sing declare the $[Zr(TA)_n]^{+4}$ and $[Zr(TA)_n]^{+4}$ affinity and intermolecular interactions with regards to coating (i.e., epoxy) molecules.

The interactions of the zirconium (IV) complexes with glycidyl methacrylate functionalized 2-

amino-terephthalic acid (i.e., $[Zr(GMA\text{-}ATA)_n]^{+4}$) against considered coating molecule were also examined utilizing DFT-D scheme. The eventual optimized epoxy clusters with Zr^{+4}/GMA-ATA coordination compounds were recorded in **Figure 11**. The clusters with optimized geometries suggest the epoxy localization in the vicinity of the metal/organic complexes. This localization was more ensured by binding energy. It was identified that the interactions of $[Zr(GMA\text{-}ATA)_2]^{+4}$, $[Zr(GMA\text{-}ATA)_3]^{+4}$, $[Zr(GMA\text{-}ATA)_4]^{+4}$, and $[Zr(GMA\text{-}ATA)_5]^{+4}$ happened with binding energies (kcal/mol) equal to -117.8, -109.5, -92.5, -59.3, and -59.3, respectively. Such energy magnitudes quantitatively ensure the stabilization/interactions of complexes with organic coating species. The central zirconium cation of $[Zr(GMA\text{-}ATA)_2]^{+4}$ and $[Zr(GMA\text{-}ATA)_3]^{+4}$ complexes aligned closer to epoxy heteroatoms thanks to electrostatic attraction of cation with negatively-charged heteroatoms. The stronger binding (more negative energy) of smaller complexes likely originates from such strengthened interactions.

3.5. Zr-UiO-filled epoxy composites thermo-mechanical properties analysis

DMTA results (Storage modulus, E', Tan delta, and loss-modulus, E") of the Epoxy-Neat and Zr-based MOF-reinforced epoxy composites are shown in **Figure 12**. **Figure 12b** illustrates that compared with the Epoxy-Neat sample, the composite coatings reinforced with *GMA-UiO-66* and *NH_2-UiO-66 based MOFs show about 4.6 and 10.8 °C increase in T_g, respectively. Despite the significant increase of T_g in the presence of Zr-based MOF (according to Figure 13), the inclusion of the particles caused the storage modulus, E', (in the near glassy region) reduction. The significant increase of the epoxy composite T_g after the inclusion of the* Zr-based *NH_2-UiO-66* particles (with high porosities/*large specific surface area)* can be related to the higher elastic modulus (higher than 20 GPa) of the MOF-based particles than epoxy structure, *and the chemical interactions between the* Zr-based *NH_2-UiO-66* particles *and epoxy structure. The reaction between the* NH_2 groups of *NH_2-UiO-66* particles and the epoxide group of the epoxy film (as schematically proposed in **Figure 14**) results in the epoxy chain mobility restriction and, therefore the increase of T_g.

The thermal stability of the MOF-filled epoxy composites was analyzed by the TGA method. **Figure 15** shows the TGA-DTG plots related to different samples. *According to the TGA plot of the Epoxy-Neat sample, 4.3% loss of weight-related to the evaporation of the adsorbed water can be seen below 100 °C, and a sharp epoxy weight reduction occurred within the temperature range of 280-380 °C, disclosing the* epoxy network degradation. *For this sample, the* decomposition temperatures of 5 wt.% ($T_{d5\%}$)*, 10 wt.%* ($T_{d10\%}$)*, 50 wt.%* ($T_{d10\%}$) and 80 wt.% ($T_{d80\%}$) *occurred at 210, 302, 355, and 368 °C [63-64]. However, results illustrate the significant improvement in the thermal stability of the coating after the inclusion of Zr-based MOF particles. The* $T_{d5\%}$, $T_{d10\%}$, $T_{d50\%}$ and $T_{d80\%}$ *values recorded for the* NH_2*-UiO-66* particles *reinforced epoxy composite were 312, 369, 416, and 447 °C, respectively. In addition, the temperature values of 313, 369, 433, and 551 °C were seen for the* $T_{d5\%}$, $T_{d10\%}$, $T_{d50\%}$ and $T_{d80\%}$, respectively. *These results show significant improvement of the epoxy composite coating thermal stability using the Zr-based MOF particles, especially the GMA modified UiO-66 particles.* The decreased epoxy composite degradation characteristics in the presence of Zr-based UiO-66 particles *is due to the* exceptional thermal and chemical stabilities of the highly inorganic-organic coordinated Zr-based MOF *[61-62].*

3.6. Zr-UiO-filled epoxy composites structure analysis

The epoxy film chemistry changes in the presence of Zr-based MOF were investigated by FT-IR, and the achieved results are presented in Figure 16. The FT-IR spectrum of three epoxy samples showed characteristic bands related to the C-N stretching at 1040 cm^{-1} and stretching vibration of C=C at 1610 cm^{-1}. Also, the peak observed at 810 cm^{-1} corresponds to the N-H peak [53]. The -C-O-C (unreacted oxirane-ring) vibration is detected at 937 cm^{-1} [65]. The absorption bands observed within the range of 2700–3000 cm^{-1} are related to the C-H bond vibration in the aromatic and aliphatic modes. The broadband, indicating the presence of the NH_2 group and O-H bond, was observed at the wavenumbers of 3160 to 3700 cm^{-1} [54]. It should be noted that the second peak related to the NH_2 absorption (at 3430 cm^{-1}) overlapped with the OH groups' absorption vibration. *The ratio of the unreacted epoxide ring intensity to a reference peak (C-H bond stretching) was calculated for all samples. The C-O-C/C-H ratios for Epoxy-Neat,* Epoxy@*NH_2-UiO-66*, and Epoxy@*GMA-66-NH_2* are 5.22, 2.25, and 2.41, respectively, representing the reduction in the epoxide (oxirane) ring deformation intensity after inclusion of Zr-based MOF. The reaction between the MOFs and epoxy through the NH_2 group can be the reason for this observation (see **Figure 1**4).

4 Conclusions

The highly stable and porous Zr-based MOF particles based on NH_2-UiO-66 were covalently bonded with GMA, and the constructed MOFs were then loaded into an epoxy composite. The outcomes of the tensile test depicted that in the presence of Zr-based MOF, the tensile strength and fracture energy significantly increased. By the inclusion of GMA-UiO-66 particles, the epoxy coating thermal stability was increased. The increase of T_g and covalent interactions between the NH_2-UiO-66 MOF particles with the epoxy coating were observed by DMTA results. The uniform dispersion of GMA modified UiO-66 particles in the polymer matrix was observed from the FE-SEM and EDS-Mapping results. Overall, results proved that the Epoxy@Zr-based MOF showed excellent thermal/chemical stabilities, high mechanical properties, and good resistance against shear stress due to the high inorganic-organic nodes connection in the Zr-MOF framework.

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Figure 1. Schematic representation of the NH_2-UiO-66 (a) and GMA-UiO-66 (b) synthesis reactions.

Figure 2- DFT-D optimized zirconium cation (Zr^{+4}) complexes with terephthalic acid ($[Zr(TA)_n]^{+4}$) (a_1-a_5), 2-amino-terephthalic acid ($[Zr(ATA)_n]^{+4}$) (b_1-b_5), and GMA functionalized 2-amino-terephthalic acid ($[Zr(GMA\text{-}ATA)_n]^{+4}$) ($c_1$-$c_5$), representing the *UiO-66, NH_2-UiO-66, and GMA-UiO-66 MOFs,* respectively. The atomic color code is: carbon gray, hydrogen white, oxygen red, nitrogen blue, and zirconium pink. All complexes are shown in Stick style.

Figure 3. FT-IR spectra (a) and FE-SEM images of NH_2-UiO-66 (b_1) and GMA-UiO-66 (b_2) nanoparticles.

Figure 4. BET results of GMA-UiO-66 and NH_2-UiO-66 samples.

Figure 5. The stress-strain plots (a), energy at break (b), stress at break (c) and strain at break (d) of Epoxy-Neat, Epoxy@GMA-UiO-66, and Epoxy@NH_2-UiO-66 nanocomposites

Figure 6. The FE-SEM analysis of the cross-section of Epoxy-Neat (a_1, a_2), Epoxy@NH_2-UiO-66 (b_1, b_2), and Epoxy@GMA-UiO-66 (c_1, c_2) nanocomposites.

Figure 7. The high-magnification FE-SEM image (a_1) and (b_1, b_2, b_3) EDS-Mapping results of the cross-section of Epoxy@NH_2-UiO-66 nanocomposites.

Figure 8. The high-magnification FE-SEM image (a_1) and (b_1, b_2, b_3) EDS-Mapping results of the cross-section of Epoxy@GMA-UiO-66 nanocomposites.

Figure 9. Toughening mechanism/lattice shear stability of Zr-Based MOF particles in epoxy matrix composite

Figure 10- The DFT-D (GGA/PBE/DNP) optimized clusters of epoxy resin and $[Zr(TA)_n]^{+4}$ and $[Zr(ATA)_n]^{+4}$ complexes. The H-bonds are shown as a dashed green line. The epoxy resin and complexes are displayed in Ball & Stick and Stick styles, respectively. The atomic color code is: carbon gray, hydrogen white, oxygen red, nitrogen blue, and zirconium pink.

Figure 11- The DFT-D (GGA/PBE/DNP) optimized clusters of epoxy resin and $[Zr(GMA\text{-}ATA)_n]^{+4}$ complexes. The H-bonds are shown as a dashed green line. The epoxy resin and complexes are displayed in Ball & Stick and Stick styles, respectively. The atomic color code is: carbon gray, hydrogen white, oxygen red, nitrogen blue, and zirconium pink.

Figure 12. DMTA analysis of Epoxy-Neat (a), Epoxy@GMA-UiO-66 (b), and Epoxy@NH_2-UiO-66 (c) nanocomposites.

Figure 13. DMTA analysis results for Epoxy-Neat, Epoxy@GMA-UiO-66, and (Epoxy@NH_2-UiO-66 nanocomposites; T_g (a) and storage modulus (b).

Figure 14. NH_2-UiO-66 chemical bonding with epoxy-polyamide chains.

Figure 15. The TGA (a) and DTG (b) plots of the Epoxy-Neat, Epoxy@GMA-UiO-66, and Epoxy@NH_2-UiO-66 nanocomposites.

Figure 16. The FT-IR spectra related to Epoxy-Neat (a), Epoxy@GMA-UiO-66 (b), and Epoxy@NH_2-UiO-66 (c) nanocomposites.

Table 1. BET test results for NH_2-UIO-66 and GMA-UIO-66

MOFs	$a_{s,BET}$	Mean pore diameter (nm)	total pore volumes ($cm^3\ g^{-1}$)

	(m^2 g^{-1})		
NH_2-UIO-66	576	2.99	0.42
GMA@NH_2-UIO	568	2.85	0.40