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REINFORCEMENT OF EPOXY RESIN-POLYIMIDE COMPOSITES USING MAGNETIC-CARBON NANOFIBER AND TITANIUM DIOXIDE AS HYBRID FILLER FOR ELECTROMAGNETIC INTERFERENCE SHIELDING MATERIAL

(Penguatan Komposit Resin Epoksi-Polimida Menggunakan Karbon Nanofiber Magnetik dan Titanium Dioksida Sebagai Pengisian Hibrid Untuk Material Perisai Gangguan Elektromagnetik)

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Abstract

Polymer nanocomposites with hybrid fillers have been used as alternative materials for electromagnetic interference (EMI) shielding applications. The combination of magnetic-carbon nanofiber (Mag-CNF) and titanium dioxide (TiO_2) produces a unique hybrid filler which can improve the physical and mechanical properties of polymer materials. This research focuses on evaluating the effects of adding aminated Mag-CNF-TiO_2 as a hybrid filler in epoxy resin-polyimide composites. Amination was performed by reacting Mag-CNF and TiO_2 with ethylenediamine ($C_2H_8N_2$), sodium nitrite ($NaNO_2$), and sulfuric acid (H_2SO_4). The aminated hybrid filler was then used to reinforce epoxy resin and polyimide composites. The macroscopic appearance of the composites shows increased homogeneity or uniformity. The successful amination was analyzed using Fourier transform infrared (FTIR) spectroscopy, revealing the presence of the amine functional group as indicated by the amine absorption at 3773 cm^{-1} (N-H) and 1336 cm^{-1} (C-N). Then, the covalent reinforcement of epoxy resin-polyimide composite with aminated Mag-CNF-TiO_2 hybrid filler was assessed based on thermal properties, mechanical properties (tensile strength and hardness), and electromagnetic interference radiation. The thermal gravimetric analysis (TGA) profiles showed degradation of the composite because the chemical bonds between the polyimide and epoxy resin have broken. Owing to the stronger covalent crosslinks between the polymer and the filler, composites with amine-modified fillers exhibit higher mechanical properties than those without reinforcement. Furthermore, the epoxy resin-polyimide composite reinforced by aminated Mag-CNF-TiO_2 also demonstrated improved electromagnetic shielding ability.

Keywords: magnetic-carbon nanofiber, titanium dioxide, epoxy resin, polyimide, EMI shielding

Abstrak

Nanokomposit polimer dengan pengisi hibrid telah digunakan sebagai bahan alternatif untuk aplikasi menyerap gangguan elektromagnet (EMI). Gabungan nanofiber karbon magnetik (Mag-CNF) dan titanium dioksida (TiO_2) menghasilkan pengisi hibrid unik yang boleh meningkatkan sifat fizikal dan mekanikal bahan polimer. Penyelidikan ini memberi tumpuan kepada menilai kesan penambahan Mag-CNF-TiO_2 yang diamin sebagai pengisi hibrid dalam komposit resin epoksi/polimida. Aminasi dilakukan dengan bertindak balas Mag-CNF dan TiO_2 dengan ethylenediamine ($C_2H_8N_2$), natrium nitrit ($NaNO_2$), dan asid sulfurik (H_2SO_4). Pengisi hibrid aminat kemudiannya digunakan untuk mengukuhkan resin epoksi dan komposit polimida. Penampilan makroskopik komposit menunjukkan peningkatan kehomogenan atau keseragaman. Aminasi yang berjaya dianalisis menggunakan spektroskopi inframerah transformasi Fourier (FTIR), mendedahkan kehadiran kumpulan berfungsi amina seperti yang ditunjukkan oleh penyerapan amina pada 3773 cm^{-1} (N-H) dan 1336 cm^{-1} (C-N). Kemudian, tetulang kovalen bagi komposit resin-polimida epoksi dengan pengisi hibrid Mag-CNF-TiO_2 yang diaminkan telah dinilai berdasarkan sifat terma, sifat mekanikal (kekuatan tegangan dan kekerasan), dan sinaran gangguan elektromagnet. Profil analisis gravimetrik terma (TGA) menunjukkan kemerosotan komposit kerana ikatan kimia antara resin polimida dan epoksi telah pecah. Disebabkan oleh pautan silang kovalen yang lebih kuat antara polimer dan pengisi, komposit dengan pengisi diubah suai amina menunjukkan sifat mekanikal yang lebih tinggi daripada yang tanpa tetulang. Tambahan pula, komposit resin-polimida epoksi yang diperkukuh oleh Mag-CNF-TiO_2 yang diamin juga menunjukkan keupayaan penyerapan elektromagnet yang lebih baik.

Kata kunci: karbon nanofiber magnetik, titanium dioksida, resin epoksi, polimida, perisai EMI

Introduction

In the development of artificial intelligence in the Industry 4.0 era, 5G wireless technology and high-frequency electronic equipment have caused environmental pollution in the form of electromagnetic interference (EMI), which is harmful to human life, the environment, and the safety of civil applications [1-3]. EMI results in interference or noise caused by electrical current injection through electrostatic coupling or electromagnetic induction originating from external sources, such as lightning, radio transmitters, relay contacts, or changes in electric current. EMI can be conducted and radiated, produced by the high switching frequency of the inverter which can degrade the performance of electrical devices or circuits. In the worst cases, EMI can lead to device malfunctions and create noise in communication signals [4,5]. Applications equipped with radar signal communications and other electronic instruments on aircraft, aerospace, and military vehicles, will also generate strong electromagnetic interference during operation [6]. Therefore, EMI shielding materials or EMI wave absorbers are needed to prevent radiation penetration by reflecting and absorbing it. EMI shielding, whose effectiveness is set by the commercial standard of 20 dB [7,8], is expected to reduce or eliminate electromagnetic radiation.

EMI shielding materials work by reflection through free electric charges on their surface (electrons or holes) which interfere with electromagnetic plane waves in radiation. The presence of electric or magnetic dipoles is necessary for electromagnetic shielding [9,10]. In this regard, the main characteristic required for EMI shielding material is excellent electrical conductivity, such as that of metal-based EMI. However, metal-based materials are generally heavy, costly, and have limited flexibility and manipulation capabilities [11]. Recent fabrication changes in metal-polymer composites have resulted in various advantages, i.e., low specific weight, great corrosion resistance, good plasticity, tunable properties, and inexpensive production. Two widely used types of polymer matrices for EMI absorbers are: (1) thermoplastics, including polycarbonate (PC), polypropylene (PP), polyethylene (PE), polystyrene (PS), polylactide (PLA), polymethylmethacrylate (PMMA), acrylonitrile butadiene styrene (ABS), and polyvinylidene fluoride (PVDF); and (2) thermosets, e.g., epoxy resins, polydimethylsiloxane (PDMS), and polyurethane (PU) [12].

Epoxy resin is a thermosetting polymer known to be superior in chemical and corrosion resistance, thermal stability, as well as mechanical and electrical insulating properties, making it widely used as coatings, composite matrices, adhesives for electronic components, structural materials in construction, and semiconductor capsules for applications in automotive, naval, aerospace, and space industries [13,14]. Nevertheless, epoxy resin is a weak heat conductor and electrical insulator [15]. Meanwhile, polyimide (PI) is a polymer composed of imide monomers with excellent mechanical properties, thermal stability, chemical resistance, electrical resistivity, and dielectric properties because it contains aromatic rings in its backbone [16]. Polyimide is widely used in the microelectronics and aerospace industries. However, this material has low thermal conductivity (0.1 W/mK), which limits the thermal requirements of advanced electronic products and aerospace applications [17]. Polyimide is classified as a thermoplastic polymer with naturally rigid chains, making it an excellent dielectric material for electrical and thermal insulation applications [18]. Epoxy resin and polyimide have been mixed as a composite in the previous research [19]. More recent research has also examined the synthesis of polyimide composites reinforced with epoxy resin. Lee et al. (2023) investigated the blending of polyimide and epoxy resin (bisphenol A diglycidyl ether) with various ratios and thermal post-curing treatments and reported that epoxy resin and polyimide blending could improve flexural strength and impact strength by up to 55.66% and 129.33%, respectively, compared to the neat epoxy [20]. Xing et al. (2022) studied the modification of waterborne polyamic acid (PAA) with epoxy resin by copolymerization to enhance the properties of high-temperature resistance and mechanical strength [21].

Some polymers are known to have brittle properties that limit their applications, thus requiring high impact strength and fracture strength. To improve their properties, polymer matrices need suitable fillers, not only to tune the mechanical and structural properties of the composites but also to provide room to adjust the electrical conductivity, permittivity, permeability, or thickness to obtain the desired EMI shielding performance [22]. In addition to being light, carbon allotropes exhibit numerous outstanding chemical and mechanical properties, i.e., low density, corrosion resistance, and easy-to-form diverse compounds due to their ability to create long carbon-to-carbon chains [3,23]. EMI shielding materials frequently utilize carbon-based conductive fillers, e.g., carbon black, CNF, carbon nanotubes (CNT), graphene, reduced graphene oxide, bulk-graphite, and combinations of carbon allotropes with or without other metallic or non-metallic particles such as carbon-fiber-reinforced polymer (CFRP) [24,25]. Other types of nanofiller material with volume resistivity, direct current breakdown strength, high strength, and in-service lifetime are silicon dioxide (SiO_2), titanium dioxide (TiO_2), aluminum oxide (Al_2O_3), and boron nitride (BN) [18].

Carbon allotropes primarily consist of aromatic rings with sp^2-hybridization of carbon and can be classified by their dimensions, namely zero-dimensional 0-D (buckminsterfullerene), one-dimensional 1-D (CNF, CNT), two-dimensional 2-D (graphene), and three-dimensional 3-D (graphite). Compared with other carbon allotropes, 1-D nanomaterials (CNT, CNF) attract particular attention because of their extraordinary properties which are applicable in various usages [26]. One-dimensional carbon nanomaterials and two-dimensional graphene materials have shown greater potential as polymer matrix reinforcements due to their larger surface area and better interface with the matrix [27]. CNF exhibits unique properties that enable diverse applications, including selective adsorption, polymer reinforcement, electrochemical catalysis, and hydrogen storage. With a higher aspect ratio of 100:1, CNF's mechanical properties are influenced by the placement orientation of the carbon layer [28]. Based on its general structure, CNF is categorized into three types: herringbone, platelet, and ribbon [29]. Similar to CNT, which is formed by impeccably cylindrical carbon structures with one or more graphene walls, CNF consists of curved graphene structures organized as stacked cones [28]. CNF also reveals simplicity and extraordinary properties, such as being lightweight and having a high surface area and good thermal and electrical conductivity, making it suitable for EMI-shielding material [30].

Another potential filler for EMI shielding materials is TiO_2, a zero-dimensional nanomaterial commonly used as a reinforcing agent in polymer matrix composites due to its mechanical, electrical, thermal, and ultraviolet resistance properties [18]. TiO_2 plays an important role by improving viscosity and obtaining filaments for 3D printing. In addition, this non-toxic and inexpensive material has excellent photocatalytic and chemical inertness properties. TiO_2 also adopts three polymorphs in its structure, namely: rutile, anatase, and brookite [31]. Hybrid filler reinforcement becomes a fascinating way to combine one or more fillers in a composite through chemical or physical means to enhance the composite's performance [32]. Both primary and secondary fillers improve composite properties (electrical or thermal conductivity) by dispersing or bridging the primary fillers or producing a synergistic effect [33]. Zakaria et al. (2015) reported a significant increase in the mechanical properties (flexural strength and flexural modulus) and the dielectric constant properties of epoxy composite reinforced with hybrid filler (CNT-Al_2O_3) [34]. Hybridization of filler or polymer results in a more stable formation that can improve crosslinking and help achieve certain desired characteristics [35]. Both CNF and TiO_2 can be potential hybrid fillers with extraordinary properties.

The addition of filler helps form complex conductive pathways to compensate for the void interface between filler and matrix. However, the van der Waals forces between fillers cause agglomeration of the fillers in the matrix due to the relatively poor interfacial compatibility between the fillers and the matrix, leading to difficulty in forming a uniform dispersion [36]. An alternative method to increase the dispersion ability between filler and matrix is surface modification, which includes covalent (chemical) and non-covalent (physical) functionalization [37].

Nanofillers, such as carbon nanotubes, graphene, nanosilica, and rubber nanoparticles, have been used to reinforce epoxy-polymer composites and enhance their mechanical, thermal, electrical, and chemical properties [38]. Besides epoxy, polyimide has demonstrated comprehensive performance through doping with graphene-based, silica-based, and other nanofillers due to their excellent mechanical properties [39]. Prior research has evaluated thermosetting polymers and thermoplastics in hybrid composites obtained by adding nanofillers to enhance their mechanical properties, bonding strength, electrical conductivity, and thermal properties [40]. However, investigations into the incorporation of epoxy resin and polyimide as base matrix polymers reinforced with carbon nanomaterial and metal oxide filler have not been conducted.

Therefore, this research investigates the reinforcement of epoxy resin-polyimide hybrid polymer composites using Mag-CNF and TiO_2 as hybrid fillers. Mag-CNF and TiO_2 were combined through one-pot amination surface modification to increase the dispersion ability by reacting the mixture with ethylenediamine, sodium nitrite, and sulfuric acid. Meanwhile, the precursor of polyimide, namely poly(amic) acid (PAA), as well as the fillers were synthesized by reactions with oxydianiline and pyromellitic dianhydride. PAA-filler was combined with epoxy resin and polyaminoamide as a hardener by a direct mixing method. The resulting composites were characterized to determine their thermal and mechanical properties, as well as EMI shielding efficiency. The produced composites are shown to have improved mechanical and thermal properties, making them applicable to various industrial applications as electromagnetic interference shielding materials.

Materials and Methods

Materials

The materials used in this research are toluene (Merck, 99.9%), ethanol (Merck, p.a.), ethanol (Merck, 99%), ethylenediamine (Merck), sodium nitrite (Riedel-de Haën), sodium dodecyl sulfate (Merck), sulfuric acid (Merck), dimethylformamide (Merck), 4,4'-oxydianiline (technical grade), pyromellitic dianhydride (technical grade), dimethylacetamide (Merck), bisphenol A diglycidyl ether epoxy resin (Eposchon), and polyaminoamide (Eposchon). The OTF-1200X furnace was used in the vacuum annealing process.

Preparation of Mag-CNF

Mag-CNF was synthesized according to the method proposed in previous research [41]. After that, it was dissolved in 100 mL toluene and mixed with a sonicator for 20 minutes. The mixture was separated by sedimentation for 12 hours and decanted to dry at room temperature. Then, mag-CNF was dissolved in ethanol, centrifuged, and dried using a vacuum desiccator. Lastly, it went through a vacuum annealing process at a temperature of 800 °C for 3 hours to obtain purified Mag-CNF.

Surface amination of Mag-CNF and TiO_2

Ethylenediamine (121.43 mg) was mixed with sodium nitrite (132.86 mg). This mixture is referred to as Mixture A. Then, a combination of purified Mag-CNF (100 mg) and TiO_2 (100 mg) with a weight ratio of 1:1 (w/w) was mixed with sodium dodecyl sulfate (121.43 mg) and sulfuric acid (0.087 mL), forming Mixture B. After that, Mixture A and Mixture B were mixed, stirred, and heated for 1 hour at 60 °C. The resulting mixture was washed with dimethylformamide and distilled water several times to remove unreacted products. The modification of Mag-CNF and TiO_2 was made through a one-pot process by surface amination. The same steps were also carried out for TiO_2 to form aminated TiO_2. The filler variations produced are Mag-CNF, Mag-CNF-

TiO_2 (without amination treatment), Mag-CNF-TiO_2-NH_2, TiO_2, and TiO_2-NH_2.

Preparation of combining the precursor of polyimide (poly(amic) acid) with various fillers

4,4'-Oxydianiline (2.5 g) was dissolved in dimethylacetamide (35 mL) using ultrasonic dispersion for 1 hour at room temperature. The suspension was poured into a 250 mL three-neck flask. Then, the mixture was stirred in an ice bath for 15 minutes under a nitrogen atmosphere. Pyromellitic dianhydride (2.5 g) was gradually added to the mixed solution. After that, the mixture was stirred for 60 minutes to obtain the poly(amic acid) solution. The same procedure was carried out by adding 50 mg of various fillers (Mag-CNF, Mag-CNF-TiO_2, Mag-CNF-TiO_2-NH_2, TiO_2, TiO_2-NH_2) to the initial ultrasonically dispersed oxydianiline.

Preparation of reinforcing the epoxy resin-polyimide composite with various fillers

Various poly(amic) acid fillers (2 mL) were mixed with bisphenol A epoxy resin (6 g) in manual stirring. The mixture was then mixed and stirred for 15 minutes with polyaminoamide (6 g) as the hardener (with the ratio of poly(amic acid)-epoxy resin-hardener of 1:2:2). The mixture was poured into a mold and heated at 60 °C for 12 hours until a composite was formed. This process produced a final epoxy resin-polyimide (ER-PI) composite with various fillers.

Preparation of reinforcing epoxy resin composite with various fillers

Various fillers (125 mg) were added to the tetrahydrofuran (20 wt.%) and sonicated for 1 hour. Epoxy resin (4.5 g) was blended and sonicated into the filler dispersion for 20 minutes. The mixture went through a vacuum process to remove the solvent. Then, polyaminoamide hardener was combined with the mixture for 15 minutes (with an epoxy resin-hardener ratio of 1:1) and gasified for 10 minutes. The mixture was put into the mold and heated at 80 °C for 6 hours.

Characterization

Characterization was conducted on the powder of Mag-CNT before and after purification, modified Mag-CNT, and modified epoxy resin composites. The purified and modified Mag-CNF and TiO_2 were characterized using X-ray diffraction Cu; 40.0 kV; 30.0 mA (XRD Philips Analytical) scanned in the 2θ range of 10-90° and Fourier transform infrared spectroscopy (FTIR, Shimadzu IR Prestige-21). The modified composites with various fillers were characterized using macroscopic testing tool (Olympus stereo microscope SZX7), Fourier transform infrared spectroscopy (FTIR, Shimadzu IR Prestige-21), tensile strength test (JTM-UTS510 Universal testing machine based on ASTM D638), durometer shore A and D, and Thermogravimetry analysis (TGA, Linseis STA PT 1600). The electromagnetic radiation reduction test was carried out by measuring the electromagnetic radiation (Electromagnetic radiation detector DT-1130).

Results and Discussion

Preparation of Mag-CNF and TiO_2 Hybrid Filler

The synthesized CNF carries several impurities in the form of amorphous carbon, metal particles, and fullerene [42]. Amorphous carbon affects both the physical and chemical properties of CNF in its applications. To optimally remove any surfactants, solvents, and amorphous carbonaceous impurities, annealing was conducted at a temperature of 1000 °C for more than 1 hour, leaving the embedded catalyst nanoparticles [43] and improving the graphitic structures. The purified Mag-CNF was modified by amine surface functionalization to enhance the dispersion ability in the polymer matrices. This procedure was conducted in a one-pot medium to incorporate Mag-CNF with TiO_2 as the hybrid filler. Figure 1 shows the result of Mag-CNF and aminated Mag-CNF-TiO_2, where Mag-CNF exhibits the physical characteristics of black powder, while aminated Mag-CNF-TiO_2 shows those of grayish powder. Both fillers still reveal good magnetic and physical properties as indicated by the string attraction with the magnet bar, as shown in Figure 1. The powder attraction to the magnet bar indicates that the amine surface modification and the incorporation of Mag-CNF and TiO_2 do not remove the magnetic characteristics of the materials.

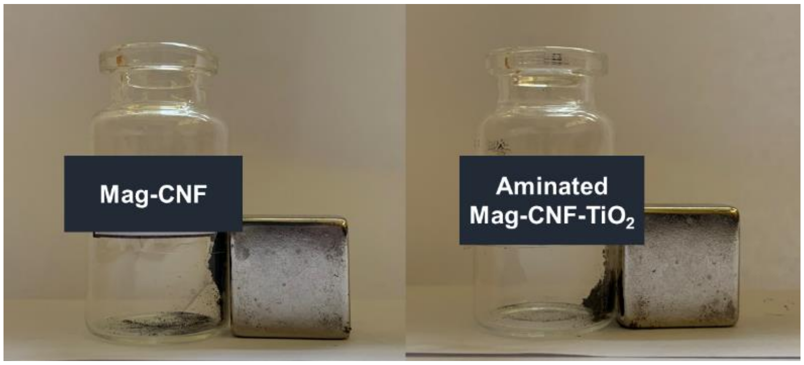

Figure 1. The magnetic test of Mag-CNF and aminated Mag-CNF-TiO_2 with magnet bar

The X-ray diffraction spectra analyses are presented in Figure 2 and Table 1. Figure 2(a) displays the XRD spectrum of Mag-CNF, indicating its three main compositions: carbon, iron oxide, and iron carbide. The C(002) carbon peak, based on PDF #75-1621 (graphite), appears mostly in high intensity at an angle of 2θ 26.27°. Meanwhile, iron oxide generally has three phases: α-Fe_2O_3 (hematite), Fe_3O_4 (magnetite), and γ-Fe_2O_3 (maghemite). Based on PDF #89-0691 (Fe_3O_4), the Fe_3O_4 peaks in Mag-CNF and Mag-CNF-NH_2 appear at angles of 2θ 30.27° (220), 35.75° (311), 43.39° (400), 51.40° (200), 53.90° (422), and 57.34° (511). Based on PDF #39-1346 (γ-Fe_2O_3), the γ-Fe_2O_3 peak in Mag-CNF is observed at an angle of 2θ 63.16° (553), while the Fe_3C peak in Mag-CNF is shown at an angle of 2θ 44.09° (031), based on PDF #77-0255 (Fe_3C).

Figures 2(b) and (c) present the XRD spectra of TiO_2 and aminated TiO_2 (TiO_2-NH_2), where the TiO_2 peak at higher TiO_2 intensity (101) is observable at 2θ 25.47°. Based on PDF #86-1157, the XRD spectra of TiO_2 and aminated TiO_2 (TiO_2-NH_2) reveal the characteristic peaks of TiO_2 at 2θ 25.13° (101), 36.64° (103), 37.68° (004), 38.47° (112), 47.97° (200), 53.69° (105), 54.94° (211), 62.59° (204), 68.59° (116), 70.13° (220), and 74.92° (215). Figure 2 (d) shows the XRD spectrum of aminated Mag-CNF-TiO_2 (Mag-CNF-TiO_2-NH_2), revealing the main composition of TiO_2, carbon, and Fe_3O_4. However, TiO_2 peaks appear more intense due to the dominant crystalline phase of TiO_2 compared to the other components, i.e., TiO_2 peaks at 2θ 25.48° (101), 37.17° (103), 37.86° (004), 38.69° (112), 48.19° (200), 53.96° (105), 55.19° (211), 62.63° (204), 68.82° (116), 70.47° (220), and 75.29° (215). Meanwhile, Fe_3O_4 peaks appear at 2θ 30.30° (220), 35.66° (311), 43.64° (400), and 57.27° (511), whereas the carbon peak with lower intensity is observable at an angle of 2θ 26.38°. The Fe_3C peak also appears in the XRD profile of Mag-CNF-TiO_2-NH_2 overlapped with Fe_3O_4 (400), however in lower intensity. The crystalline phase of all components, including TiO_2, carbon, and Fe_3O_4, as seen in Table 1, indicates that amine surface modification does not defect the crystallinity phase of the materials.

The modification of Mag-CNF and TiO_2 with the addition of an amine functional group aims to increase filler dispersion in polymer matrices to become a homogenous composite. This modification can be made by adding a hydrophilic group (acid or amino agent). Amine modification using ethylenediamine and sodium nitrate is categorized as the functionalization of reactive species with the unstable diazonium salts, causing nitrogen extrusion and resulting in radical species connected to reactive Mag-CNF. This bridging reaction allows for covalent bonding to the polymer. Due to its high nucleophilicity, sidewall functionalization of Mag-CNF occurs by a nucleophilic amine addition reaction [44,45]. The incorporation of Mag-CNF and TiO_2 through amine surface modification generates possible hydrogen bonding interaction and amine group bonding with oxygen atoms from the hydrogen interaction. The possible reaction of amine surface modification in Mag-CNF and TiO_2 is shown in Figure 3.

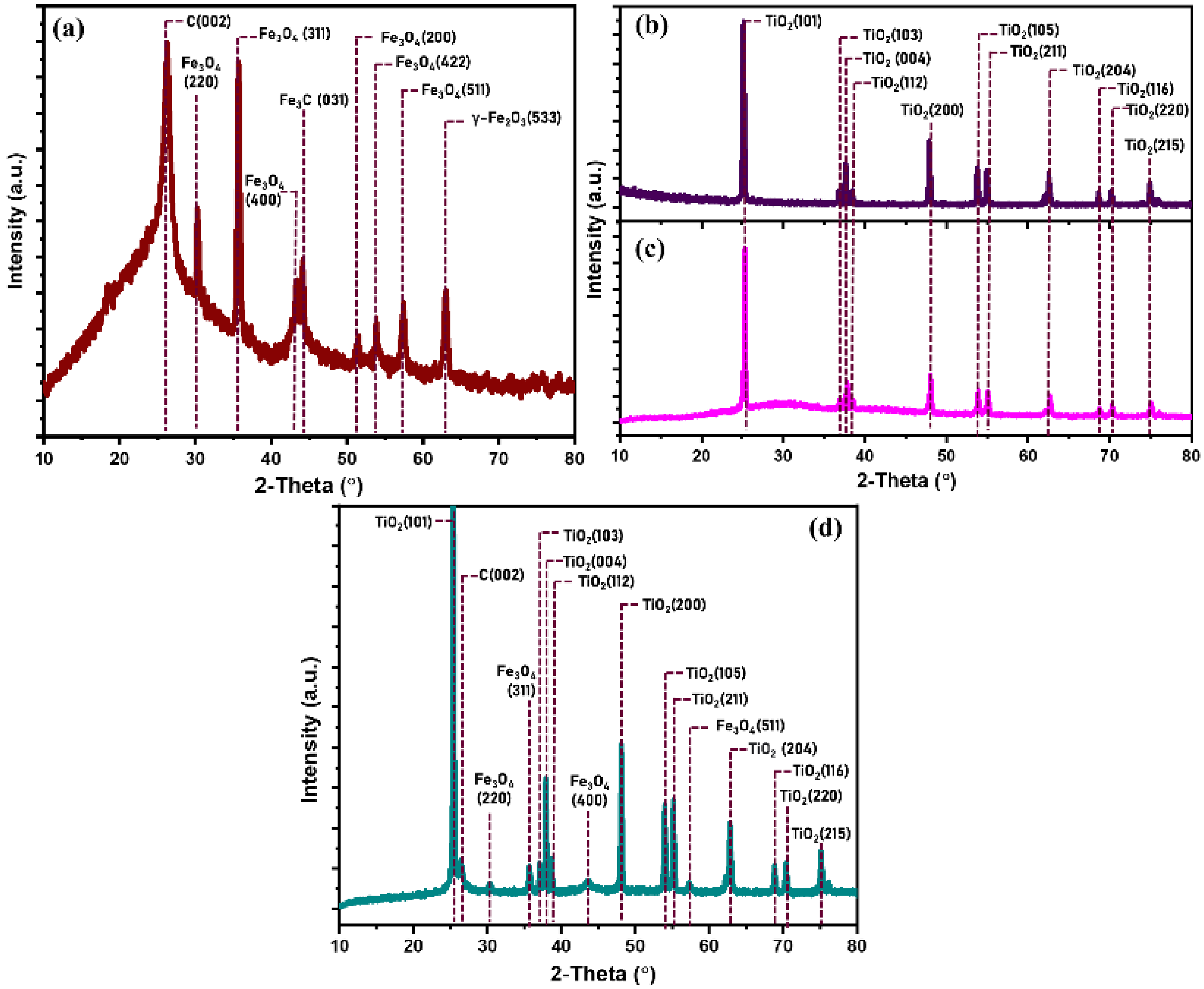

Figure 2. The XRD analysis of (a) Mag-CNF, (b) TiO_2, (c) aminated TiO_2 (TiO_2-NH_2), and (d) aminated Mag-CNF-TiO_2 (Mag-CNF-TiO_2-NH_2)

Table 1. The corresponding phases of the observable peaks in XRD spectra

Sample	**Phase**				
	Carbon	**Fe_3O_4**	**γ-Fe_2O_3**	**Fe_3C**	**TiO_2**
Mag-CNF	√	√	√	√	-
TiO_2	-	-	-	-	√
TiO_2-NH_2	-	-	-	-	√
Mag-CNF-TiO_2-NH_2	√	√	-	√	√

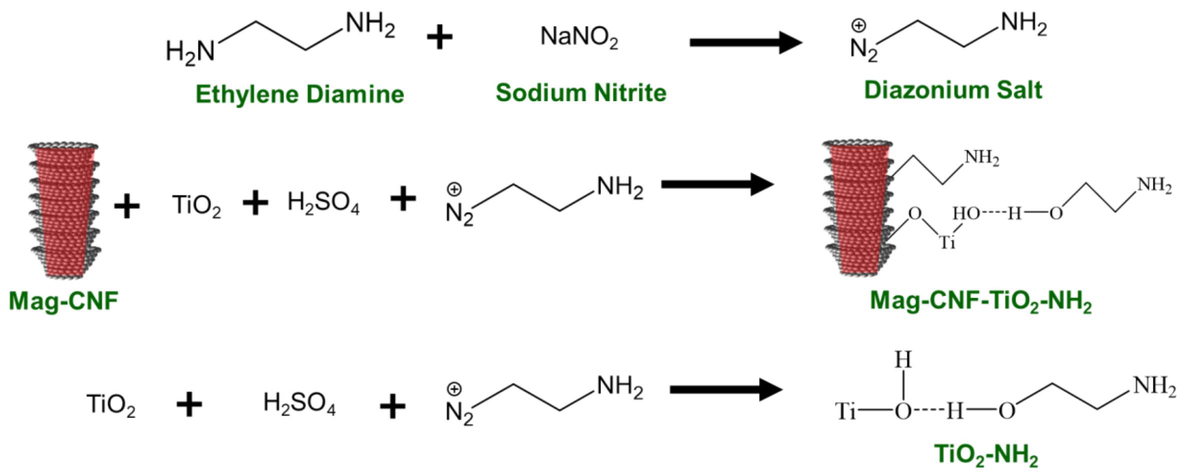

Figure 3. The possible reaction of amine surface modification with Mag-CNF and TiO_2 filler

Testing the dispersion behavior by dissolving the modified material in polar distilled water is done to estimate the success of amine modification. Figure 4 shows the results of the dispersity test, signifying better dispersion of aminated TiO_2 and Mag-CNF-TiO_2 in distilled water compared to unmodified materials. This may occur due to the addition of hydrophilic amine groups, thus allowing the filler to have polar groups that make them dispersible and homogenous in water.

Figure 5(a) displays the Fourier transform infrared (FTIR) spectrum of Mag-CNF that produces vibration peaks of Fe‒O (~500-600 cm^{-1}); C‒C (~874 cm^{-1}); C‒O (~1050 cm^{-1}), C=C (~1667 cm^{-1}), C‒H (~2890cm^{-1}); and O‒H (~3436 cm^{-1}). The FTIR spectra of pure TiO_2 and aminated TiO_2, as shown in Figures 5(b-c), reveal TiO_2 characteristic peaks at Ti‒O (~600 cm^{-1}), Ti‒OH (~1622 cm^{-1}), O‒H (~3414 cm^{-1}), and N‒H (3715 cm^{-1}); the latter vibration is confirmed in the infrared spectrum of aminated TiO_2. Meanwhile, as seen in Figure 5(d), the aminated Mag-CNF-TiO_2 indicates the presence of amine bonding, signifying successful amine surface modification through covalent bonding to carbon, i.e., vibration bonds of Ti‒O at ~500 cm^{-1}, N‒H (3773 cm^{-1}), C‒N bond (1336 cm^{-1}), and shifting peak of C=C at 1762 cm^{-1}.

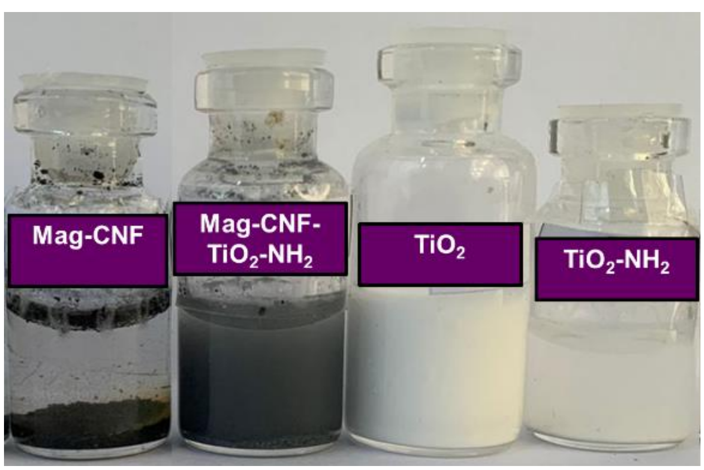

Figure 4. The dispersity test in the water of Mag-CNF, aminated Mag-CNF-TiO_2 (Mag-CNF-TiO_2-NH_2), TiO_2, and aminated TiO_2 (TiO_2-NH_2)

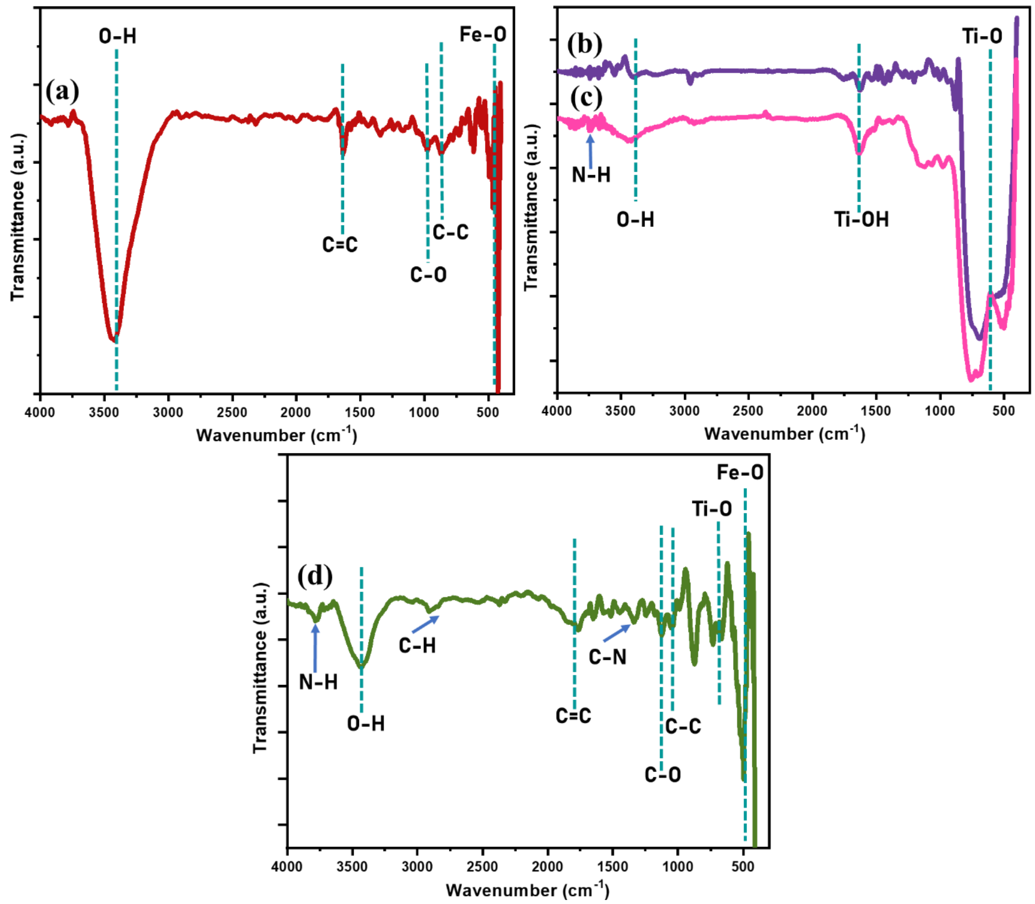

Figure 5. The FTIR spectra of (a) Mag-CNF, (b) TiO_2, (c) aminated TiO_2 (TiO_2-NH_2), and (d) aminated Mag-CNF-TiO_2 (Mag-CNF-TiO_2-NH_2)

Preparation of epoxy resin-polyimide composite with various fillers

The prepared aminated materials, including Mag-CNF-TiO_2-NH_2 and TiO_2-NH_2, were then used as fillers to form poly(amic) acid (PAA) as the precursor of polyimide through the reaction between oxydianiline (ODA) and pyromellitic dianhydride (PMDA). For comparison, the reaction was also performed using non-aminated materials (Mag-CNF, TiO_2, and Mag-CNF-TiO_2). The reaction between cyclic anhydrides and primary diamines occurs as an SN_2Ac (bimolecular nucleophilic acyl substitution) mechanism. The reaction takes place in two stages. The first step is to attach the nucleophilic reagent to the electrophilic carbonyl C atom. PAA is an intermediate formed by a nucleophilic attack of the amine group on the carbonyl carbon of the anhydride group. This process is irreversible because the amine group is a strong nucleophilic agent. In addition, the anhydride cycle has poor resonance stability and charge delocalization as the oxygen atom has the same electronegativity and electron structure. The second step is the closure of the nucleophilic ring due to dehydration and the formation of an imide ring.

Figure 6 shows the possible reactions that occur when polymerizing the formation of PAA with Mag-CNF-TiO_2-NH_2 filler through amine groups connected directly to CNF or TiO_2-bonded CNF. The resulting PAAs in the form of solutions with various fillers are displayed in Figure 7. All filler-reinforced PAA materials were mixed with bisphenol A (epoxy resin). The product was further combined with the polyaminoaminde hardener to produce composites with a curing process at 60°C. The possible reactions between PAA combined with Mag-CNF-TiO_2-NH_2 and epoxy resin, as well as the resulting products and the polyaminoaminde hardener, are presented in Figures 8 and 9, respectively.

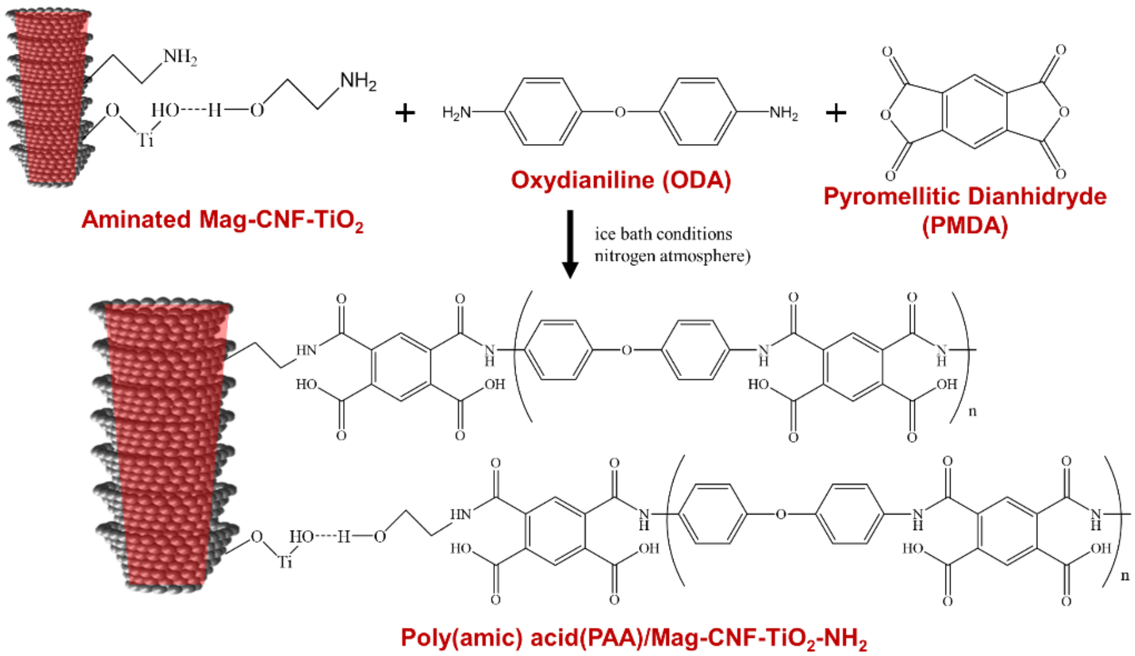

Figure 6. The possible reaction between aminated Mag-CNF-TiO_2 and poly(amic acid) as polyimide precursor

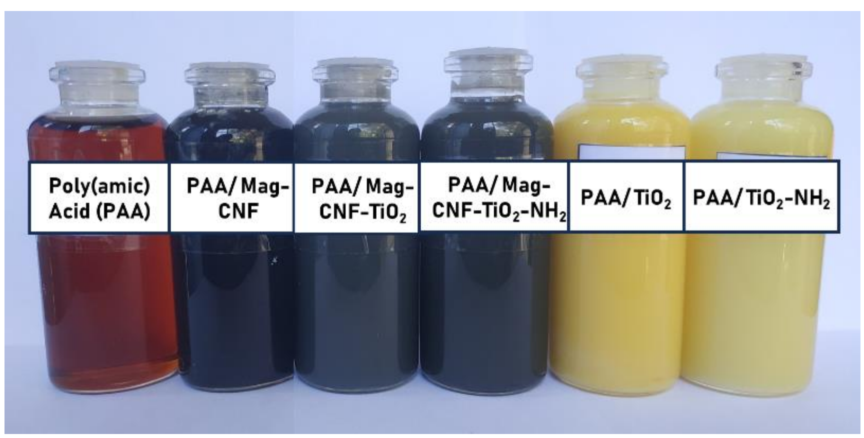

Figure 7. The resulting synthesis of poly(amic acid) (PAA) as polyimide precursor with various fillers

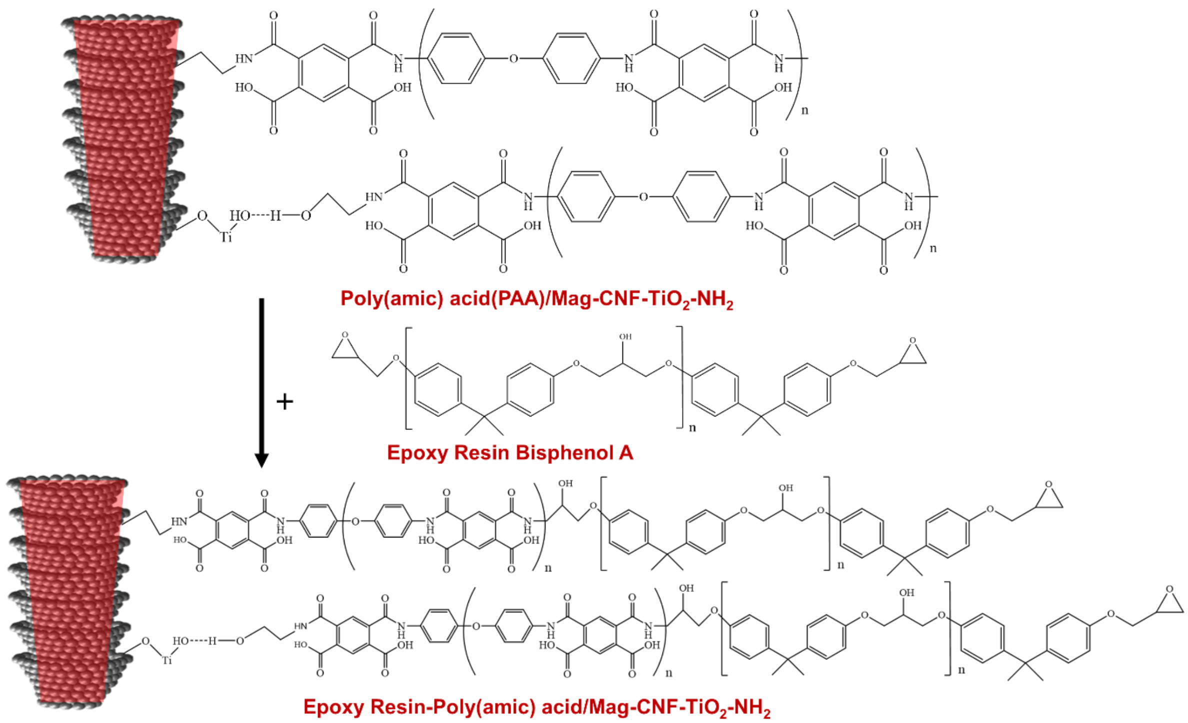

Figure 8. The possible reaction between PAA/Mag-CNF-TiO$_2$-NH$_2$ and epoxy resin

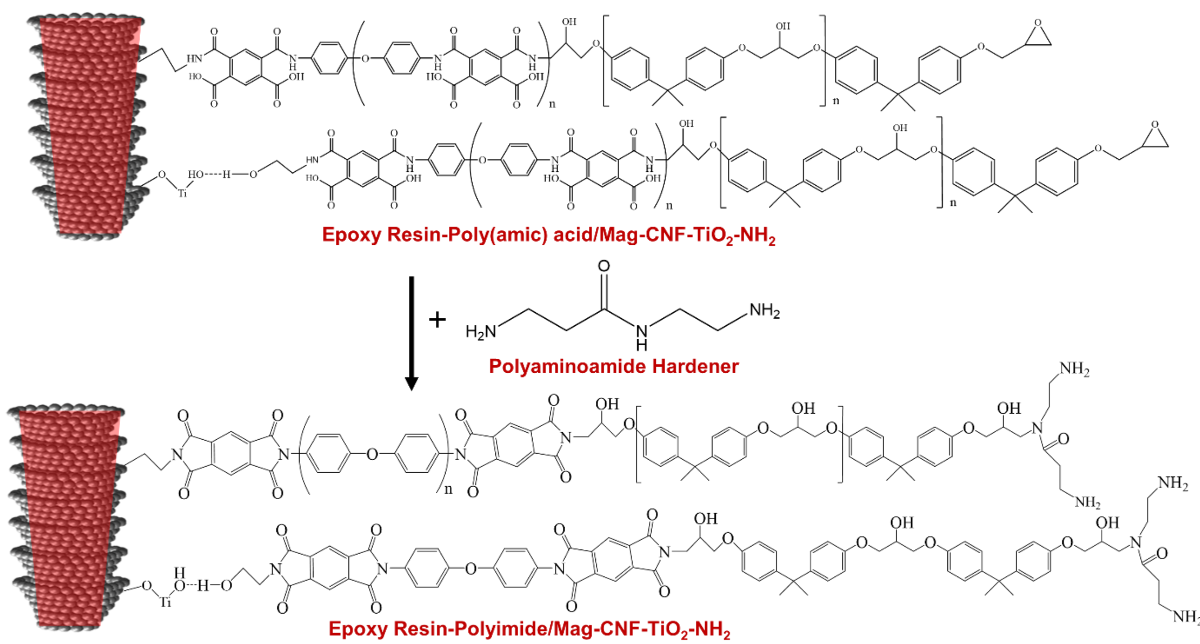

Figure 9. The possible reaction between Epoxy Resin-PAA/Mag-CNF-TiO$_2$-NH$_2$ and polyaminoamide as the hardener

Epoxy resin-polyimide composites reinforced with various fillers were successfully synthesized through direct mixing and heating treatments. The physical color of composites depends on the color of the filler used. Figures 10 and 11 reveal the macroscopic images of epoxy resin and epoxy resin-polyimide composites with various fillers (Mag-CNF; Mag-CNF-TiO_2; Mag-CNF-TiO_2-NH_2, TiO_2; TiO_2-NH_2). As shown in Figures 10 and 11, the amine surface modification of filler results in better dispersion or distribution of the filler in the polymer matrices. The more homogenous the composite compound, the higher the interaction and performance of its mechanical, electrical, and thermal properties.

The FTIR spectra of epoxy resin composites with various fillers as seen in Figures 12 (a-b) show a reduction in intensity around the 1000 cm^{-1} wavenumber region, indicating the opening of the epoxy group on the epoxy resin (C-O-C), which binds to the amine group (-NH_2) on the modified Mag-CNF. The FTIR spectra of epoxy resin-polyimide composites with various fillers as shown in Figures 12(c-d), including the spectra after the addition of Mag-CNF and Mag-CNF-TiO_2, provide increasingly sharp intensity for the amide C=O, C−H, and N−H functional group at wavenumbers ~1637cm^{-1}, ~2925 cm^{-1}, and ~3761 cm^{-1}, respectively. These increases are caused by the blending of epoxy resin-polyimide with Mag-CNF which is connected by N−H and C=O amide groups. The increases in the intensity of the C−H group may originate from C−H in the carbon material (Mag-CNF). The appearance of Ti−O is also uptake around the wavenumber of 444 cm^{-1}.

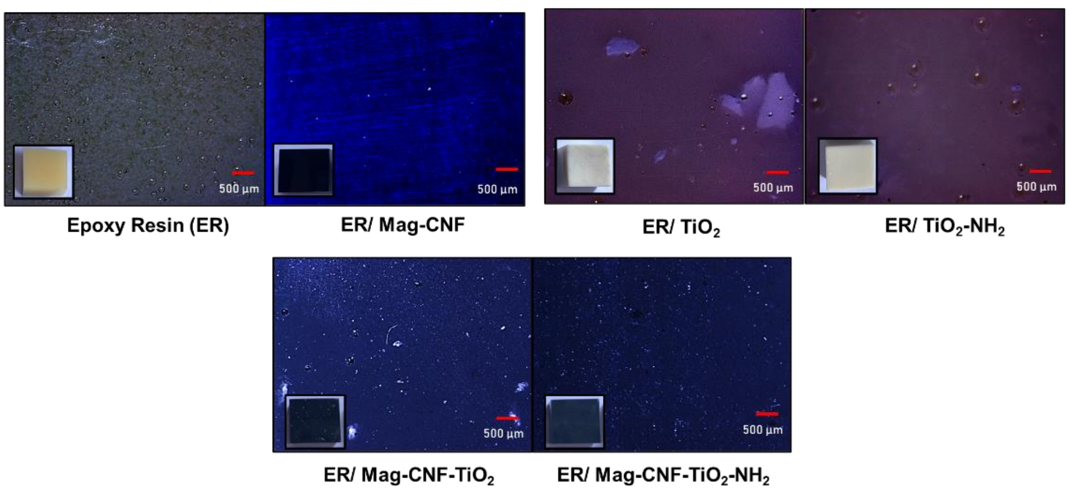

Figure 10. The macroscopic image of epoxy resin composites with various fillers (Mag-CNF, Mag-CNF-TiO_2, Mag-CNF-TiO_2-NH_2, TiO_2, TiO_2-NH_2)

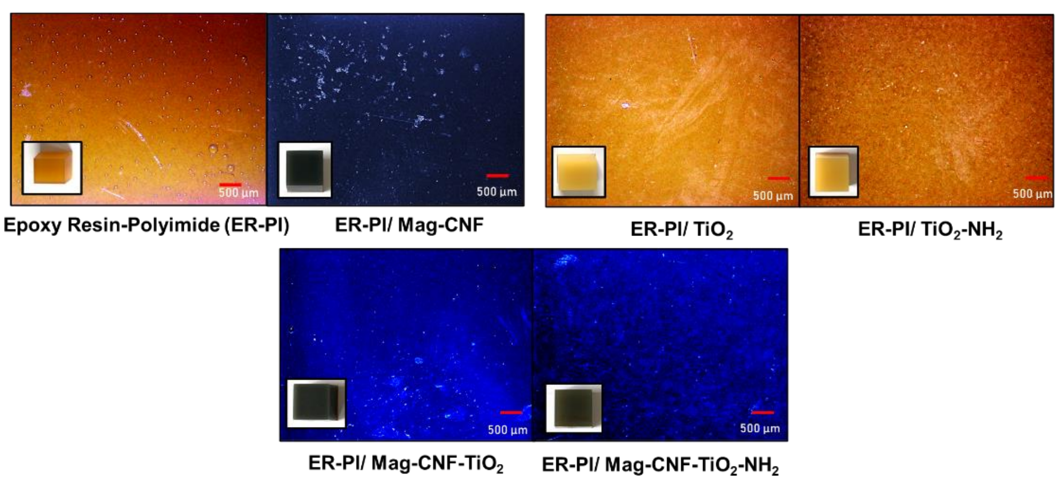

Figure 11. The macroscopic image of epoxy resin-polyimide composites with various fillers (Mag-CNF, Mag-CNF-TiO_2, Mag-CNF-TiO_2-NH_2, TiO_2, TiO_2-NH_2)

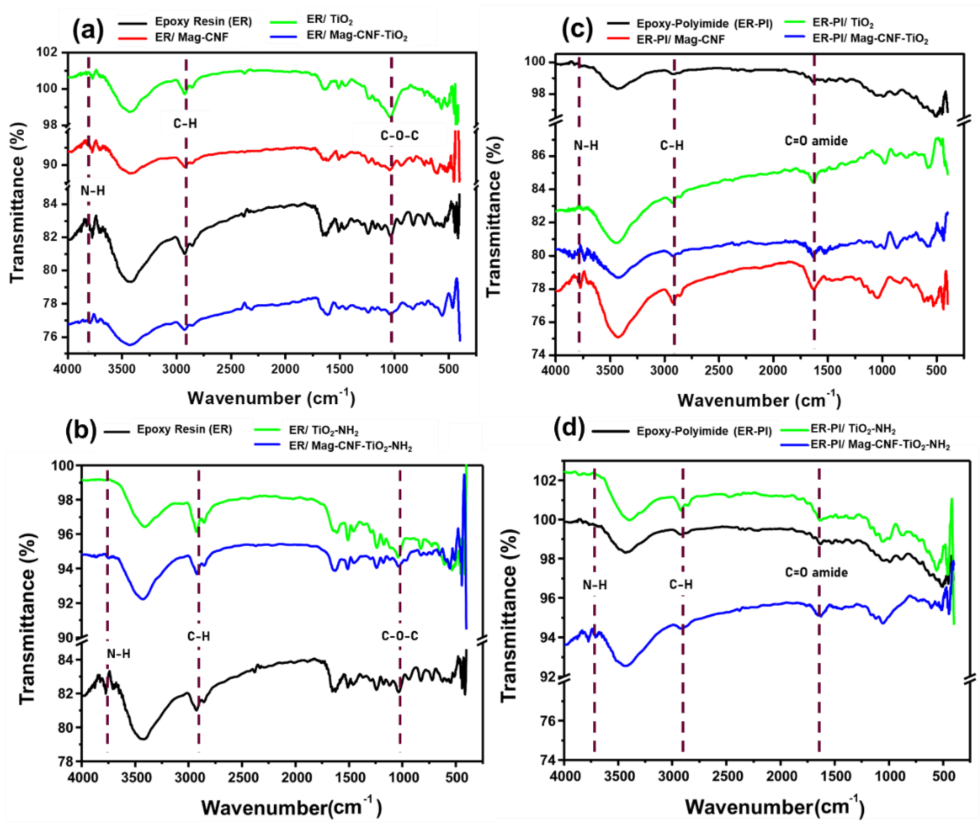

Figure 12. The FTIR analysis of composites with various fillers: (a) epoxy resin, epoxy resin/Mag-CNF, epoxy resin/Mag-CNF-TiO_2, epoxy resin/TiO_2 (without amine modification), (b) epoxy resin, epoxy resin/Mag-CNF-TiO_2-NH_2, epoxy resin/TiO_2-NH_2 (with amine modification), (c) epoxy resin-polyimide, epoxy resin-polyimide/Mag-CNF, epoxy resin-polyimide/Mag-CNF-TiO_2, epoxy resin-polyimide/TiO_2 (without amine modification), (d) epoxy resin-polyimide, epoxy resin-polyimide/Mag-CNF-TiO_2-NH_2, epoxy resin-polyimide/TiO_2-NH_2 (with amine modification)

A thermal property test was carried out using thermal gravimetry (TGA) characterization. Figures 13(a) and (b) show the results of the TGA characterization of the epoxy resin and epoxy resin-polyimide composites with various fillers. The graphs reveal insignificant differences in degradation temperatures, where two degradation points occur at 305-312 °C and 510-515 °C, representing the degradation of epoxy resin and polyimide, respectively. However, the epoxy resin composite (Figure 13(a)) experiences sudden degradation at 312 °C compared to the epoxy resin-polyimide composite (Figure 13(b)). Moreover, the epoxy resin composite reinforced with fillers has lower residues (3-7%) compared to the filler-reinforced epoxy resin-polyimide composite (6-11%). These findings support the previously reported results [20,46], probably due to the unexpected changes in the chemical structures of epoxy resin as predicted in the mechanism reactions in Figures 8 and 9. This may result in unsuccessful reactions, causing the unconnected fragments of the epoxy resin, polyimide, and filler compounds to disturb the polymeric network.

The tensile strength test was done to determine the effects of adding fillers on the mechanical properties of epoxy resin-polyimide composites. This test was carried out using ASTM D638 type 4 equipped with a load cell with a capacity of 50 kN and an operating speed of 5 mm/minute. The specimens of epoxy resin and epoxy resin-polyimide composites with various fillers are shown in Figures 14(a) and (b).

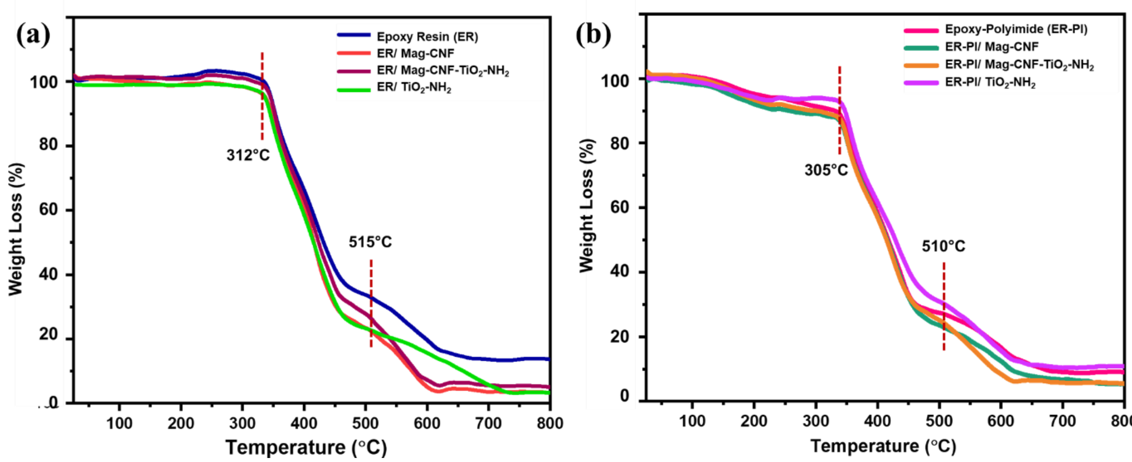

Figure 13. The TGA of composites of (a) epoxy resin (ER) composite and (b) epoxy resin-polyimide (ER-PI) composite with various fillers, Mag-CNF-TiO_2-NH_2, TiO_2-NH_2.

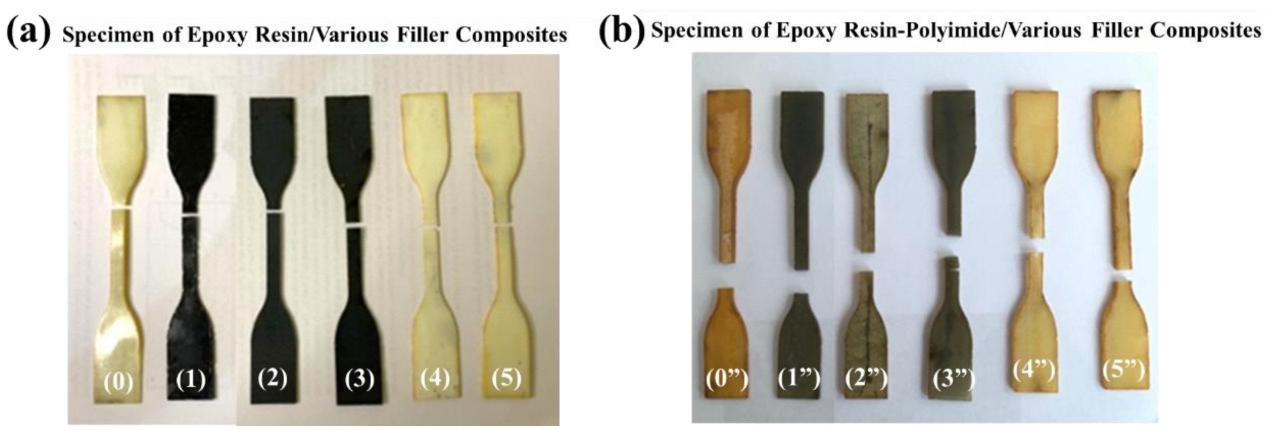

Figure 14. The specimens of composites: (a) epoxy resin composite with various fillers (0) without filler, (1) Mag-CNF, (2) Mag-CNF-TiO_2, (3) Mag-CNF-TiO_2-NH_2, (4) TiO_2, (5) TiO_2-NH_2, and (b) epoxy resin-polyimide composite with various fillers (0") without filler, (1") Mag-CNF, (2") Mag-CNF-TiO_2, (3") Mag-CNF-TiO_2-NH_2, (4") TiO_2, (5") TiO_2-NH_2

As seen in Figure 15 which presents the results of the tensile strength test, the value in the epoxy resin-polymer composite increases after the addition of filler, but the strain value decreases. The addition of filler causes the composite to become stiffer. In the graphic image, the composite reinforced with amine-modified filler has a higher value than the one reinforced with unmodified filler. This is possible because Mag-CNF-TiO_2 attaches to the epoxy matrix through chemical bonds (−NH_2 groups), thus having good interfacial interactions with the epoxy matrix and being better dispersible in the matrix. The maximum performance in the epoxy resin-polyimide composite with various fillers may increase due to the presence of covalent bond interactions between the amine-modified composites compared to the unmodified ones. The aminated Mag-CNF-TiO_2 creates a covalent bond through the N−H groups as the link to the polyimide ends (C−O bonds in the PMDA section), increasing the homogeneity of the mixture which possibly can increase bond interactions.

The hardness test was also performed by durometer on Shore A (for epoxy resin-polyimide composite) and Shore D (for epoxy composite). Figures 16(a) and (b) show the results of the hardness tests. As shown in the graph, there is an increase in the hardness value of the epoxy resin-polymer composite after the addition of filler. The ER-PI/Mag-CNF-TiO_2-NH_2 composite has a higher hardness value than those without amine modification. This indicates that aminated Mag-CNF-TiO_2 increases filler dispersion into the epoxy resin via C−N bonds. The addition of TiO_2 filler increases the hardness value of the composite. Furthermore, the ER-PI/TiO_2-NH_2 composite also has a higher hardness value than the ER-PI/TiO_2 composite, signifying successful surface modification of TiO_2.

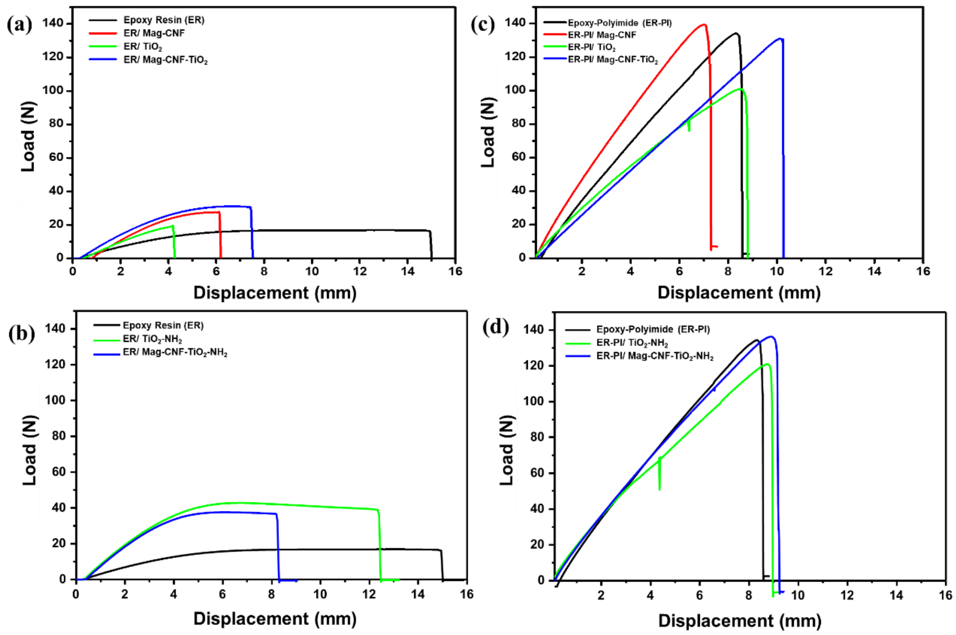

Figure 15. The tensile strength test of composites with various fillers (a) epoxy resin, epoxy resin/Mag-CNF, epoxy resin/Mag-CNF-TiO_2, epoxy resin/TiO_2 (without amine modification), (b) epoxy resin, epoxy resin/Mag-CNF-TiO_2-NH_2, epoxy resin/TiO_2-NH_2 (with amine modification), (c) epoxy resin-polyimide, epoxy resin-polyimide/Mag-CNF, epoxy resin-polyimide/Mag-CNF-TiO_2, epoxy resin-polyimide/TiO_2 (without amine modification), (d) epoxy resin-polyimide, epoxy resin-polyimide/Mag-CNF-TiO_2-NH_2, epoxy resin-polyimide/TiO_2-NH_2 (with amine modification).

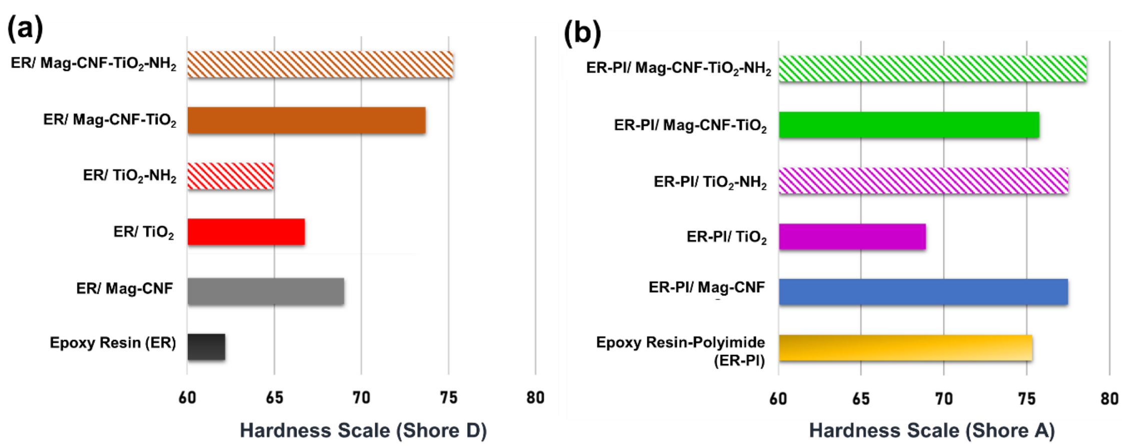

Figure 16. The hardness test of (a) epoxy resin composites with various fillers, and (b) epoxy resin-polyimide composites with various fillers

The increase in the tensile strength and hardness of composites depends on how high the crosslinking density is between the filler and the polymer matrices that form the composite. Similarly, the decrease in these properties is caused by the lower crosslinking density. This is also influenced by the interaction and strength of the crosslinking agent from the filler and polymer matrices in attaching and achieving uniform distribution [47-49].

The hardness value of the ER/TiO_2-NH_2 composite is lower than that of the ER/TiO_2 composite; it is not increased as in the ER-PI composite. This is because the addition of polyimide produces groups containing more oxygen. Thus, aminated TiO_2 has more opportunities to form hydrogen bonds through hydrogen in the amine groups with oxygen in the polyimide network, allowing the epoxy groups to bond with the amine groups with the addition of polyaminoamide hardener. On the other hand, there are not as many oxygen-containing groups in the epoxy resin composite as in the ER-PI composite. Therefore, the amine groups in aminated-TiO_2 compete with those of the hardener to interact with the anime groups in the epoxy resin. Thus, the hardness of ER/TiO_2-NH_2 is not higher than that of ER/TiO_2.

The electromagnetic shielding test was carried out by measuring the ability of the composite to absorb electromagnetic radiation, as shown in Figure 17. In general, non-aminated fillers may result in non-covalent interaction with polymer networks. The ER-PI composite reinforced with non-aminated Mag-CNF shows higher EMI shielding (~50%) properties than the composite reinforced with non-aminated Mag-CNF-TiO_2 (~40%). The addition of non-aminated TiO_2 produces particle agglomeration. Therefore, homogeneous dispersion during the composite preparation process cannot be achieved. Polymer networks with defects caused by unconnected fragments of polymer or agglomerated fillers make the electromagnetic wave more easily transmitted in the composite, resulting in lower EMI shielding efficiency.

As seen in Figures 17(a) and (b), the composites reinforced with aminated fillers have higher EMI shielding induced by better filler dispersion. The ER-PI composite has higher EMI shielding efficiency (>60%) than the epoxy-resin composite (<57%). The results of the EMI shielding test are in line with the results of the hardness and tensile strength analyses.

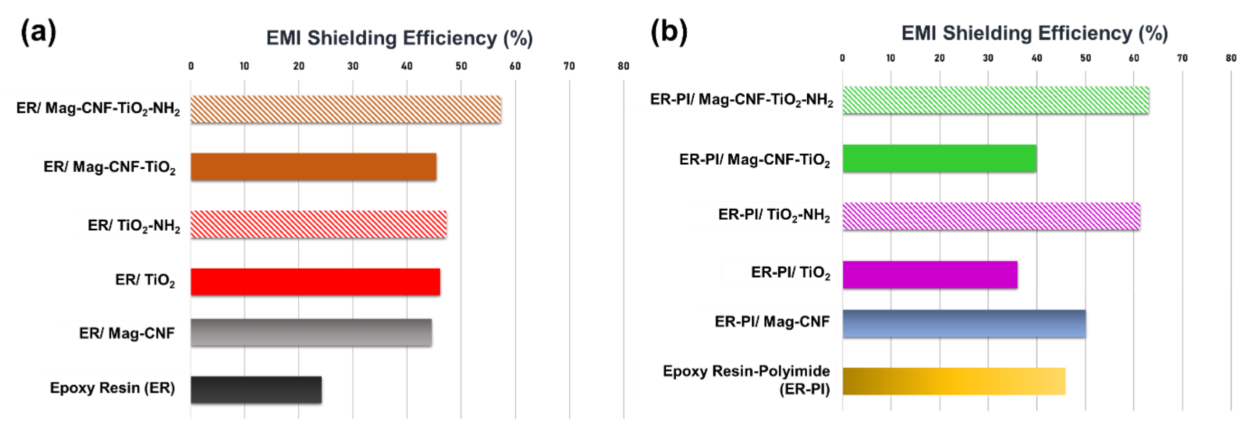

Figure 17. The EMI shielding test of (a) epoxy resin composites with various fillers, and (b) epoxy resin-polyimide composites with various fillers

Conclusion

In this research, Mag-CNF was successfully purified and modified through amine surface modification and incorporation with TiO_2. Based on magnetic physical tests and XRD analysis, the amine surface modification process does not eliminate the magnetic and crystalline phase characteristics of Mag-CNF. The aminated Mag-CNF-TiO_2 shows better dispersion in water, indicating the successful attachment of the C–N and N–H groups as shown in the FTIR spectra of the aminated fillers. Compared to the composites with unmodified fillers, the addition of aminated Mag-CNF-TiO_2 and aminated

TiO_2 fillers into both epoxy resin and epoxy resin-polyimide composites increases their mechanical properties, as proven by better results of the tensile, hardness, and electromagnetic radiation tests. The FTIR spectrum of the epoxy resin composite shows a decrease in the intensity of the C−O−C vibration peak as the opening of the epoxy group will bind to the amine groups of the fillers. Conversely, the FTIR spectrum of the epoxy resin-polyimide composite reveals an increase in the intensity of the N−H, C=O amide, and C−H function groups, where the N−H groups act as a covalent link between the filler and the polymer matrices. Furthermore, the TGA analysis demonstrates two-point degradations in the termination of polyimide and epoxy resin. The hybridization of epoxy resin and polyimide as well as the hybridization of the aminated Mag-CNF-TiO_2 filler increase their mechanical properties (tensile strength and hardness value), which is likely because the materials are well-dispersed by the amine modification, preventing agglomeration and creating covalent crosslinking bonds between the fillers and the polymers. The addition of aminated Mag-CNF-TiO_2 fillers also successfully increases the EMI shielding efficiency.

Acknowledgment

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