

Multi-featured epoxy composites filled with surface-modified PTFE powders treated by Na-naphthalenide system

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Abstract

This study aimed to produce new multi-featured epoxy composites that are advanced in terms of mechanical properties, wear and impact resistance, and glass transition and heat deflection temperatures. Epoxy composites filled with chemically surface-treated poly (tetrafluoroethylene) (PTFE) powders at various ratios were prepared to obtain these improved properties. The chemical treatment was carried out via a Na-naphthalenide system. After this treatment, the x-ray photoelectron spectroscopy results presented the existence of functional groups such as OH, carbonyl groups, and C=C unsaturation points on the surface of the PTFE powders. On the PTFE surfaces, while the atomic ratios of carbon and oxygen were substantially increased, the fluorine ratio presented a significant decrease after the chemical treatment. However, the wear rates of the novel composites were highly advanced despite this large decrease in the fluorine ratio on the surface of the PTFE powders. Moreover, functional groups such as OH, carbonyl groups, and C=C unsaturation points and spongelike or network structures on the PTFE surfaces provided the opportunity to obtain strong adhesion and interfacial bonding between the surface-modified PTFE powders and the matrix. Strength and modulus values showed substantial enhancement besides the IZOD impact resistance. All glass transition and heat deflection temperatures were also substantially improved.

KEYWORDS

epoxy composite, Na-naphthalenide system, surface-modified PTFE particles

1 | INTRODUCTION

Composite are prepared for various purposes such as improving mechanical properties, wear properties, and thermal properties,^{1–4} and obtaining enhanced photocatalytic,^{5–8} antibacterial,^{9–11} hydrogen storage,^{12,13} flame retardation properties,¹⁴ antistatic and electrically conductive materials.^{15,16} Composites with favorable mechanical properties and wear resistance have considerable demand in the industries that include mechanical applications such as gears,

cams, wheels, impellers, brakes, clutches, conveyors, transmission belts, bushes, and bearings.¹ Recently, polymer composites have been studied intensely by researchers to improve their mechanical, wear, and physical properties. This is because lightness and manufacturing costs are key parameters for most industries. In this regard, thermoset polymer materials have become prominent in different sectors due to their high strength. Among these thermoset polymer materials, epoxies have played an important part due to their characteristic properties such as high tensile strength,

stiffness, and hardness. Epoxies have also exhibited good thermal stability and chemical resistance. Epoxies are included in prepolymer (epoxy resin) and hardener systems. There are many epoxy systems consisting of various prepolymer resins and hardeners available in industries based on different application areas. These epoxy systems have a wide range of unique features. These unique properties have been considerably attractive for widespread engineering applications. For example, epoxies with an excellent surface appearance for decorative applications, those with favorable mechanical properties for composite applications, and those with more functional groups for high temperature applications are some variants that used in various sectors such as the coating, marine, aviation, automobile, aerospace, and furniture sectors. However, the low fracture toughness property of epoxies is a very significant restriction for engineering applications in industrial sectors. The desired wear resistance, thermal properties, and mechanical properties of epoxy systems also need to be increased to higher levels for some engineering applications such as gears, cams, wheels, impellers, brakes, clutches, conveyors, transmission belts, bushes, and bearings. Metals, oxides, nitrides, carbides, solid lubricants, and short fibers have been used in epoxy systems to overcome these limitations.^{2-4,17} Moreover, these conventional fillers or reinforcement materials have provided improvements in certain properties. For instance, while strength or modulus values of the manufactured composites increase, impact resistance values substantially decrease or do not show remarkable improvement, or vice versa. In addition to these, by the addition of fillers such as elastomers and soft segments into epoxy systems, strength values can generally be reduced while improving impact resistance substantially. Hence, these segments such as liquid rubbers improve the fracture toughness of epoxy systems substantially but cause a decrease in their rigidity, T_g , and mechanical strength. Furthermore, currently, more efficient filler and reinforcement materials are available for applications to enhance overall mechanical properties, and these have been incorporated into epoxy systems. Some of the prominent examples can be listed as some metal oxides and sulfides such as micro and nano Ta_2O_5 ,¹⁸ TiO_2 , and ZnS ,¹⁹ nano Al_2O_3 ,²⁰ graphene,²¹ graphene oxide,²² carbon nanotubes,^{23,24} mineral fillers such as shungite²⁵ and wollastonite ($CaSiO_3$),²⁶ hollow glass microspheres,²⁷ micro and nano short fibers such as aramid,²⁸ and ultra-high molecular weight polyethylene (UHMWPE).²⁹ Moreover, hybrid systems of these filling and reinforcement materials such as graphene/carbon nanotube nanoplatelets,²³ graphene/alumina particles,²² TiO_2 -filled poly(acrylonitrile-butadiene-styrene) ABS,³⁰ expandable graphite/ammonium phosphate,³¹ multiple fillers such as TiO_2 /short CF/graphite/ ZnS particles.¹⁹ Moreover, various surface treatment and functionalizing processes of these filling and reinforcement materials such as chemically treated

UHMWPE and aramid fibers,^{28,29} silane-treated graphite nanoplatelets,³² cation- π interaction-assisted facile preparation of graphene,²¹ and the grafting of any polymer with functional groups onto graphene oxide³³ have been more efficient in terms of enhancing the desired properties. However, these systems are not practical to implement, and they require complex processes despite the fact that significant improvements have been achieved with these filling and reinforcement materials in epoxy composites.^{17,34,35} Considering the positive and negative aspects of some prominent efficiency studies in detail, Xian et al.²⁶ used short CF and mineral particles such as wollastonite ($CaSiO_3$) to fill an epoxy resin. They used wollastonite in the form of fine and coarse particles. The epoxy composites with fine wollastonite particles were much more efficient compared to those with coarse particles and short CF. Using 10 vol% of fine wollastonite particles substantially improved the flexural modulus, strength, and toughness of the pure epoxy. Moreover, the wollastonite-filled epoxy composites presented much higher wear resistance values compared to the composites filled with short CF and the pure epoxy. Klyuchnikova et al.²⁵ prepared shungite-filled epoxy composites. Shungite is a mineral whose crystals contain fullerene-like structures. It has been known that it increases the oxidation and heat resistance of polymer-based materials. Using 20 wt% of shungite-filled composites presented substantial increases in bending strength and elasticity modulus at rates of 25.9% and 5.4%, respectively. Gupta and Satapathy³⁶ produced borosilicate glass microsphere (BGM)-filled epoxy composites. They investigated the mechanical properties and erosion ratios of the samples. The 30 wt% of BGM-filled composite presented an increase of 56% in impact strength and decreases of 7% and 6.5% in tensile and flexural strength, respectively. In the air-jet type erosion test, the erosion resistance of this composite improved at a rate of 37%. Imran et al.²⁷ formulated hollow glass microsphere (HGM)- and amine functionalized HGM (a-HGM)-filled epoxy composites. They investigated the compressive and thermo-mechanical behaviors of these composites. Compressive strength values decreased at rates of 44% and 42% for the composites filled with 5 wt% of HGM and a-HGM, respectively. Additionally, storage modulus values increased at rates of 27.7% and 32.5% for the composites with 5 wt% of HGM and a-HGM, respectively. Agrawal and Satapathy³⁷ produced hybrid epoxy composites with Al_2O_3 and solid glass microsphere (SGM) fillers. The epoxy composite with 5 wt% Al_2O_3 and 5 wt% SGM presented an increase of 13% in compressive strength and decreases of 2.5% and 10.2% in tensile strength and T_g , respectively. Du et al.²⁸ manufactured epoxy composites filled with well-dispersed aramid nanofibers (ANF). They reported that the tensile strength, bending strength, and impact resistance of the epoxy composites with 0.15 wt% ANF increased consecutively by 28.2%, 81.9%, and 81.8% compared to the pure

epoxy. Li et al.²⁹ created UHMWPE fiber-reinforced epoxy composites. They also treated UHMWPE fibers chemically and produced chemically treated UHMWPE fiber-reinforced epoxy composites. While tensile strength values decreased for both composites, tensile modulus, bending strength, and bending modulus values increased with the addition of the UHMWPE and treated UHMWPE fibers. Moreover, T_g values slightly increased for both composites. Besides, the friction coefficients of both composites substantially increased compared to those of the pure epoxy. Jyotishkumar et al.³⁰ prepared Epoxy/poly (acrylonitrile-butadiene-styrene) (ABS) blend- and TiO_2 -filled ABS/Epoxy hybrid composites. They used 3.6 wt% of ABS in the epoxy resin, and TiO_2 was used up to 6.7 wt% as a filler into the blend mixture. The tensile strength and fracture toughness (K_{Ic}) of the neat blend increased at rates of 25% and 23.5, respectively. However, the tensile modulus and T_g values did not change. Among the TiO_2 -filled ABS/epoxy hybrid composites, the 6.7 wt% TiO_2 -filled hybrid composites presented the most improved mechanical properties. Tensile strength, tensile modulus, and fracture toughness values increased at rates of 56%, 14.8%, and 32.3%, respectively. However, the T_g value decreased at a rate of 10.5%. Besides these studies, the relevant literature includes studies of rigid carbon-based fillers such as graphene, graphene oxide, carbon nanotubes, graphite, and expandable graphite used in epoxy composites due to their intrinsic high performance. Likewise, these fillers have been recently used in treated and functionalized forms to increase the interfacial bonding between the matrix and the fillers such as silane-treated graphite or graphene oxide, phase transferred graphene, and COOH—functionalized multi-wall carbon nanotubes (MWCNT). It was observed that these treated and functionalized fillers showed a more improved performance. In addition to this, the usage of these carbon-based fillers as hybrid fillers in the polymer matrix has recently been prominent like other hybrid fillers such as expandable graphite/ammonium polyphosphate, graphene/carbon nanotubes, Si_3N_4 -functionalized MWCNT, and graphene/ Al_2O_3 nanoparticles. These studies also presented very efficient results. These results are discussed and compared in the results and discussion section of this article.

In light of all this information, epoxy composites that can be candidates for load-bearing applications in the industry, such as plain bearings, must have favorable mechanical properties, high impact resistance, and high wear resistance. For this reason, it was decided to use surface-modified PTFE powders treated with a Na-naphthalenide system as the filling material. This was because poly (tetrafluoroethylene) has excellent heat resistance and wear resistance due to the C—F bonding dissociation energy and the low friction coefficient of

fluorine atoms. Besides, PTFE has excellent thermo-mechanical properties above 150°C. However, it has some drawbacks such as poor strength and hardness at room temperature compared to epoxies. These constraints have limited its application areas.³⁸ In addition to these drawbacks, PTFE has very low surface tension and poor compatibility with different matrices. To increase its compatibility and achieve strong bonding with the matrix, surface modification and functionalization processes are required.³⁹ This way, it will be feasible to obtain more favorable engineering properties such as mechanical strength, wear resistance, and heat resistance with surface-modified and functionalized PTFE particles. On the other hand, it should be kept in mind that PTFE also has high density besides its low surface tension. Hence, incorporating PTFE without surface modification and functionalization into a main resin or solution via mechanical stirring is very difficult. This is because these particles tend to collapse into the matrix resin. Therefore, the surface modification of PTFE powders is becoming popular in attempts to obtain PTFE-filled homogeneous resins easily and achieve an easier process. The surface modification of PTFE has been carried out via various methods such as chemical treatment, plasma treatment, irradiation treatment, corona discharge, flame treatment, and ozone treatment. Clearly, these methods have their own advantages and disadvantages. For example, plasma treatment and irradiation methods usually require expensive and complex equipment, while chemical methods have potential problems in terms of environmental pollution. Among them, the sodium naphthalene solution method has more merits, such as a simple process, low costs, and a good activation effect; thus, this method is widely used.⁴⁰ Moreover, plasma treatment and irradiation methods include degradation reactions due to the bombardment of the polymer surface by electrons and ions. These physical and chemical modifications can change the surface properties of the material. In comparison to the Na-ammonia complex, both of these methods are equally effective. However, the Na-naphthalenide complex is more widely used due to its better stability and ease of handling.⁴¹ In addition to these, Benderly et al.³⁹ reported that a Na-naphthalene solution can be stored and intermittently used without an exhaust device or inert atmosphere, and the activated sample does not need high-temperature treatment. This is an important advantage in terms of practicality. A Na-naphthalenide system is also very effective in promoting the adhesion of fluoropolymers. Ayurova et al.⁴² modified PTFE surfaces with active Na-naphthalenide in THF in atmospheric conditions at room temperature. They reported that hydroxyl groups formed on the surface of the PTFE treated with the Na-naphthalenide system. The wettability of the PTFE substantially increased.

The large decreases in the contact angle values of the surface-modified PTFE in the range between 50° and 60° confirmed this situation.^{41–43} Apart from Ayurova et al.,⁴² other researchers such as Miller et al.,⁴⁴ Borisova et al.,⁴⁵ Dake and Boraska,⁴⁶ Jansta et al.,⁴⁷ and Roina³⁴ reported functional groups such as conjugated C=C unsaturation points, carbonyl groups, and hydroxyl groups available on the surfaces of PTFE treated with Na-naphthalenide systems.

In summary, the purpose of this study is to obtain novel multi-featured epoxy composites with improved mechanical properties, as well as enhanced impact and wear resistance. These composites were prepared by the incorporation of surface-modified PTFE powders into epoxy resin. The surface modification process was carried out by a Na-naphthalenide system. This is because a Na-naphthalenide system is a very efficient chemical surface modification method for PTFE materials, and there is no study on epoxy composites filled with PTFE powders treated by a Na-naphthalenide system in the literature. Important functional groups such as conjugated C=C unsaturation points, carbonyl groups, and hydroxyl groups, as well as spongelike or network structures, were observed on the surface of the PTFE powders after the surface modification of the PTFE powders with the Na-naphthalenide system. It was thought that these modifications would provide strong adhesive bonding and high compatibility with the epoxy matrix. The surface-modified powders were incorporated into the epoxy system at ratios of 5%, 10%, 15%, 20%, 25%, and 30%. Surface-modified PTFE and untreated PTFE powders were characterized by Fourier transform infrared (FT-IR) spectroscopy and x-ray photoelectron spectroscopy (XPS). XPS was specifically carried out to determine the functional groups on the surfaces of the surface-modified PTFE powders. The mechanical properties, wear resistance, and impact resistance of the novel epoxy composites were observed. Moreover, heat deflection temperature and glass transition temperature (T_g) values were determined. The samples were mechanically characterized with tensile, flexural, and IZOD impact resistance tests. T_g values were examined by differential scanning calorimetry (DSC). The morphologies of fractures and worn surfaces were characterized by scanning electron microscopy (SEM). Additionally, the energy dispersive spectroscopy (EDS) technique was used for the chemical analysis of features being observed on the SEM monitor. According to the results of this study, the novel epoxy composites in which surface-modified PTFE powders were incorporated exhibited improved mechanical properties, impact resistance, wear resistance, and thermal properties. Considering these improved properties, these

multi-featured epoxy composites can be important candidates for components in load-bearing applications.

2 | MATERIALS AND METHODS

2.1 | Materials

EPIKOTE 828 was used as diglycidyl ether of bisphenol-A-based epoxy resin. It is a medium-viscosity liquid epoxy resin produced from bisphenol A resin and epichlorohydrin. It contains no diluent. The epoxy molar mass of EPIKOTE 828 is 184–190 g/equivalent. Its viscosity at 25°C is 12–14 Pa.s. EPIKURE F205 was used as the curing agent and hardener of EPIKOTE 828. EPIKURE F205 is a low viscosity, modified cycloaliphatic amine curing agent. Its hydrogen equivalent weight value is 102–106. The recommended proportion of EPIKURE F205 to EPIKOTE 828 resin is 58/100. The epoxy formulation process was performed according to this stoichiometric ratio. This epoxy system imparts favorable mechanical properties and good chemical resistance. It was purchased from Hexion. Benzyltrimethylamine (BDMA) was used as an accelerator. PTFE homopolymer powder was purchased from GLEMCO. Its commercial name is Teflon™ PTFE 7B. Its particle size is 24 μm (ASTM D4894). Naphthalene flakes and metallic Na, which were used for the surface modification of the PTFE powders, were purchased from Sigma-Aldrich. Tetrahydrofuran (THF), which was purchased from Aldrich, was used for dissolving the naphthalene flakes. All materials were used as received.

2.2 | Surface modification and functionalization of PTFE powders

Naphthalene flakes weighing 128 g were dissolved in 1 L of THF under atmospheric conditions by the addition of metallic Na in a round bottom flask equipped with a magnetic stirrer. This solution was stirred for a while. As a result of this process, a bath was prepared for the modification of PTFE. The PTFE powders were then added to this bath and mechanically stirred under atmospheric conditions for 5 min. After the stirring process, the powders were washed and rinsed by acetone and distilled water for three times, respectively. After the washing process, the surface-modified powders were dried at 80°C in a vacuum for 24 h. The obtained surface-modified and functionalized PTFE powders were observed to have a light brown color. The FT-IR results of the surface-modified PTFE and untreated PTFE powders are given in Figure 1. The XPS results of the surface-modified PTFE

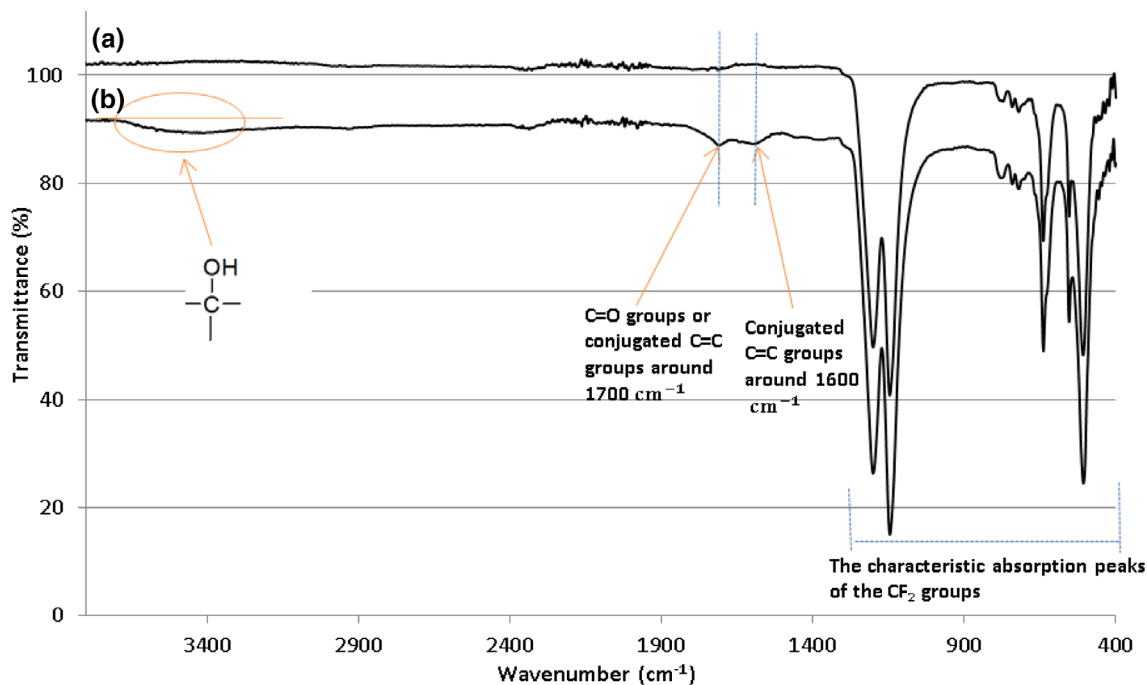


FIGURE 1 The Fourier transform infrared (FT-IR) results of (a) untreated poly (tetrafluoroethylene) (PTFE) powders, (b) surface-modified PTFE powders. [Color figure can be viewed at wileyonlinelibrary.com]

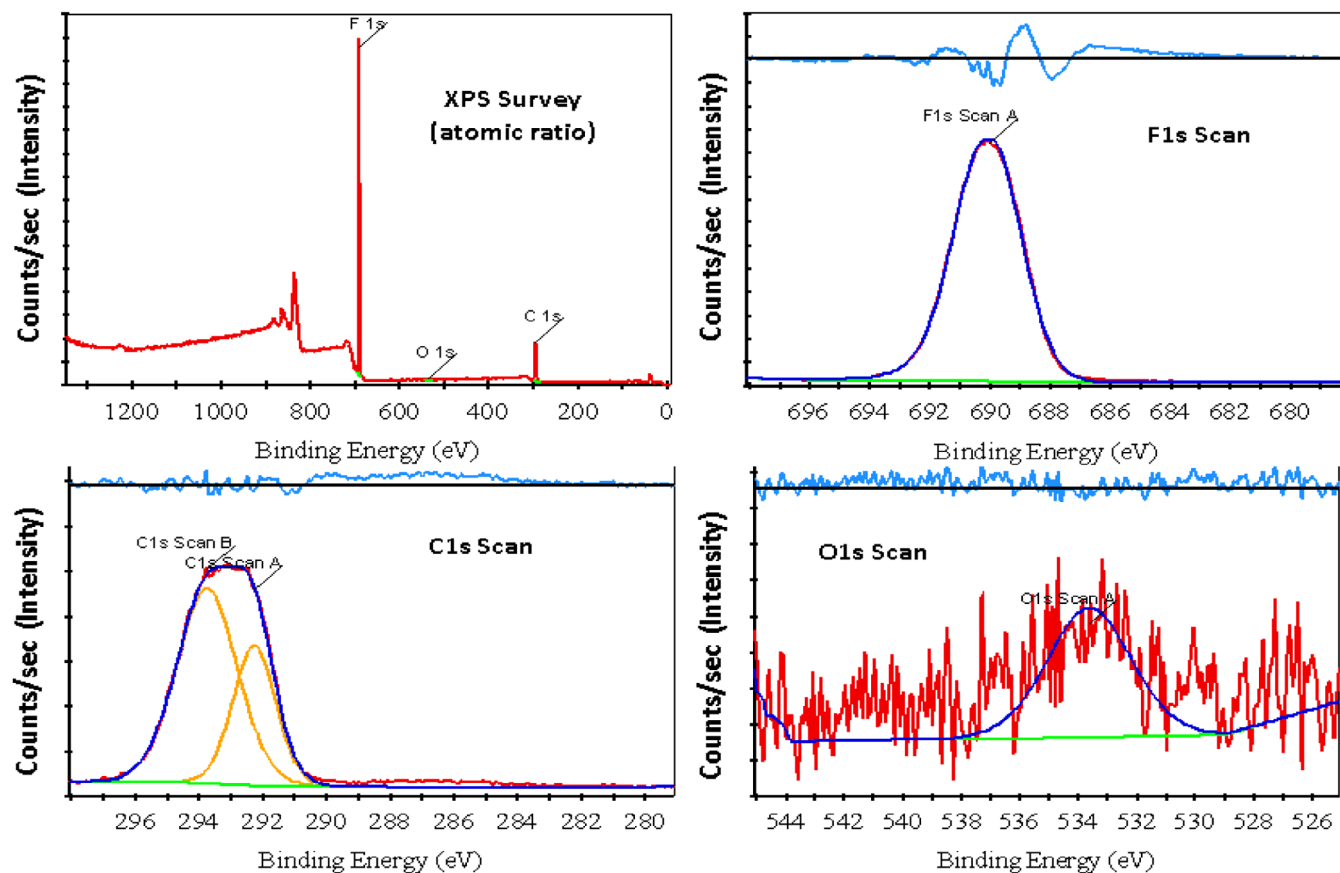


FIGURE 2 X-ray photoelectron spectroscopy (XPS) analysis for the surfaces of untreated poly (tetrafluoroethylene) (PTFE) powders. Atomic ratios on the surface, binding energy and intensity relations of carbon, oxygen, and fluorine atoms. [Color figure can be viewed at wileyonlinelibrary.com]

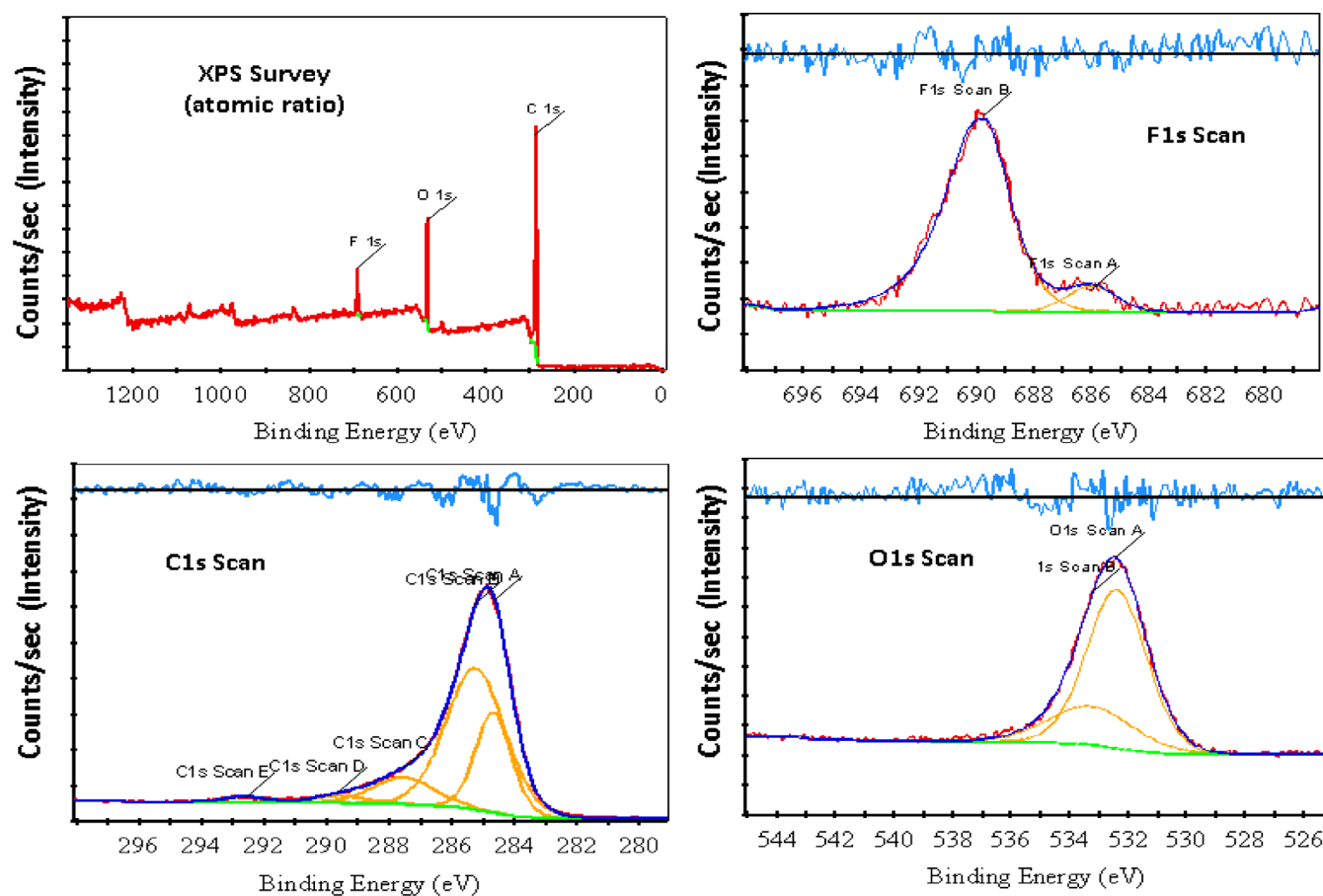


FIGURE 3 X-ray photoelectron spectroscopy (XPS) analysis for the surfaces of surface-modified poly (tetrafluoroethylene) (PTFE) powders. Atomic ratios on the surface, binding energy and intensity relations of carbon, oxygen, and fluorine atoms. [Color figure can be viewed at wileyonlinelibrary.com]

and untreated PTFE powders are given respectively in Figures 2 and 3.

2.3 | Preparation of epoxy nanocomposites filled with surface-modified and functionalized PTFE powders

Before this study, it was observed in previous studies that PTFE powders without any surface treatment or modification precipitated in epoxy resins after mechanical stirring. In contrast, this precipitation behavior was not observed for the surface-modified and functionalized PTFE powders after mechanical stirring. The surface-modified PTFE powders were incorporated into the epoxy resin and mechanically stirred at 300 rpm. The powders were distributed homogeneously in the epoxy resin. First, the surface-modified and functionalized PTFE powders were incorporated into the epoxy resin at ratios of 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%,

and 30 wt% for each sample. Each solution was mechanically stirred, and no precipitation of the surface-modified powders into the epoxy resin was observed. The amine hardener was then added to the solution at its stoichiometric ratio with the resin. These samples were coded as EPTF5, EPTF10, EPTF15, EPTF20, EPTF25, and EPTF30 according to their filler ratios by weight.

2.4 | Characterization of test specimens

Three samples were prepared for each wt% value. The average of these three values was used for the results. Analyses were conducted based on the average results. The coefficients of variation (CoV) are presented in figures and tables. CoV is the ratio of the standard deviation to the mean of the results of a sample multiplied by 100 that is given in Equation 1. In this equation, s is the standard deviation, and μ is the mean of the values of a sample.

$$\text{CoV} = \frac{s}{\mu} \times 100. \quad (1)$$

CoV is a measure of relative event dispersion and is generally used for comparing relative risk. It can also be used to evaluate quantitative likelihood or probability distributions. CoV measures the spread of values like standard deviation. While standard deviation measures distance from the mean, CoV measures the ratio of the standard deviation to the mean.

The samples were mechanically characterized by tensile and flexural tests. Moreover, the IZOD impact resistance test was performed. The samples were also thermally characterized by determining their glass transition temperatures (T_g) in DSC and heat deflection temperatures. Abrasive wear tests were carried out by using the pin on disc method. Density and water absorbance measurements were performed. SEM examinations were also performed to characterize the morphologies of fractures and worn surfaces.

The Fourier transform infrared spectroscopy (FT-IR) spectra of the PTFE powders and surface-modified PTFE powders were recorded using a Shimadzu 8303 FT-IR device to identify the bonds as bulk compositions. To characterize the bonds on the surface, XPS was performed by measuring the binding energies of atoms.

To characterize the mechanical properties of the samples, standard tensile tests were performed to measure Young's modulus, ultimate tensile strength, and elongation at break according to ASTM D638. The tensile tests were carried out at a crosshead speed of 5 mm/min. Moreover, the flexural tests were carried out in the form of three-point bending according to ASTM D790. The crosshead speed of the flexural tests was adjusted to 2.5 mm/min. The tensile and flexural tests were performed using Zwick Z010 equipment at room temperature. The IZOD impact resistance was measured by using unnotched samples according to ASTM D 4812-99 (ASTM D 256). This test was performed with Zwick B5113.30 equipment with a hammer of 5.4 J at a striking rate of 3.96 m/s.

Abrasive wear analyses were carried out using pin-on-disc equipment according to the ASTM G-99 standard that is used for dry sliding wear experiments. The details of the pin-on-disc machine have previously been discussed in literature. Abrasion samples were identified as pins. Prior to the experiment, the dimensions of the pins were adjusted as 10 mm × 10 mm × 4 mm. These pins were abraded with waterproof 1200-grit SiC paper to obtain uniform contact. This abrasion process was followed by cleansing with isopropyl alcohol, drying, and weighing. All pins were tested at room temperature, with a constant load of 20 N, a sliding speed of 8.75 m/s, and a track

radius of 0.05 m. Each experiment was repeated at least three times to ensure the reliability of the test results. The average of the repeated test results was taken. The test was performed up to the distance of 2000 m. After running the sliding distance, the test was stopped, and the weight was measured following the careful cleaning of the samples. The specific wear rate was calculated using the following formula:

$$W_s = \frac{\Delta m}{\rho L F_n}, \quad (2)$$

where W_s is the specific wear rate (mm^3/Nmm), Δm is the mass loss (g), ρ is the density of the material (g/cm^3), L is the sliding distance (mm), and F_n is the load applied to the pin (N). The sliding distance was monitored using an auto-recorder.

Density is mass per unit volume and is usually expressed in g/cc. The densities of the composites were determined using the Archimedes principle. Distilled water at room temperature was used as the immersion fluid, and mass was measured using a high-precision digital weighing balance (Shimadzu Japan, 0.1 mg accuracy). The density tests were performed according to ASTM D792.

During the water absorption analyses, the specimens were dried (in a vacuum oven) for 24 h at 50°C just before immersion. All samples were immersed in distilled water at room temperature. At the end of the immersion time, the specimens were removed from the water, all water on the surfaces was wiped off, and the specimens were weighed and placed back into the water at a different time point. The percentage of increase in weight during immersion in all cases was calculated by dividing the weight gain by the initial dry weight.

The T_g values of all samples were determined by using a TA Instruments DSC 250 model device. The samples were run from 30°C to 120°C at a heating rate of 10°C/min under a nitrogen atmosphere.

The heat deflection temperature corresponds to the temperature that results in a deflection of 0.320 mm at the mid-span of the samples during the three-point bending test at 1.80 MPa. This temperature was measured using a custom-built setup. The test was carried out according to ASTM D648. The samples were prepared at dimensions of 80 × 10 × 4 mm³.

The morphologies of fractures and worn surfaces were observed with a Carl Zeiss Ultra Plus SEM device at an acceleration voltage of 20 kV. The specimens were coated with 2–4 nm of Au/Pd in an ion beam sputtering system using a Quorum Q150R device before the SEM analyses.

3 | RESULTS AND DISCUSSION

In this study, surface modification treatments were applied to PTFE powders using a Na-naphthalenide system, and these surface-modified PTFE powders were incorporated into an epoxy system at ratios of 5 to 30 wt %. It was thought that PTFE would be integrated into the epoxy system as a reinforcement component. Hence, these surface-modified PTFE powders would be more efficient and compatible with the matrix due to their strong interactions with the epoxy system.

To create strong interactions between the epoxy matrix and surface-modified PTFE powders, functional groups must be available on the surface of the surface-modified PTFE powders. These functional groups were identified by the FT-IR and XPS characterization techniques. It is well-known that XPS is carried out for surfaces with a depth between 5 and 10 nm. XPS has been one of the most suitable characterization techniques to measure the surfaces of samples. FT-IR is also well-known as IR spectroscopy, and it is more suitable for higher depth values. Its measurement depth varies from 0.5 to 5 μm , and this depth is expressed in units of wavenumber/cm. It is carried out to determine the bulk composition of materials. According to the IR spectroscopy results in Figure 1, strong bands due to CF vibrations were observed at 1200–1350 cm^{-1} for both the untreated PTFE and surface-modified PTFE powders. Fluoropolymers are immersed into Na-naphthalenide or Na-ammonia solutions for 1–5 min. The polymer surface is treated up to a depth of about 1 μm for these periods, and the surface is darkened. Therefore, it is expected that functional groups such as OH, C=C unsaturation points, and carbonyl groups would be more dominant at lower depths. For this reason, XPS was performed to identify these groups at the surface up to a depth of about 10 nm. Borisova et al.⁴⁵ presented the FT-IR peaks of PTFE etched with a Na-naphthalenide solution. The bands of conjugated C=C bonds, carbonyls, and hydroxyl groups were observed at 1600 and 1700 cm^{-1} , 2150 cm^{-1} , and 3300 cm^{-1} , respectively. Moreover, Dake and Boraskar⁴⁶ reported that when PTFE surfaces were etched by a Na-naphthalenide complex, bands at 1550–1800 cm^{-1} in IR spectroscopy were distinctively changed. Roina et al.³⁴ etched PTFE with a Na-naphthalenide diglyme solution and revealed that the bands that occurred at 1700 cm^{-1} were due to carbonyls. The IR peaks in our study were observed at similar bands to those in the literature as shown in Figure 1. To identify these peaks of important functional groups such as C=O, C=C, and OH, XPS was also used. This was because the FT-IR spectra contained noise commensurate with the signals of functional groups, and it was needed to identify the surface of the surface-modified PTFE powders.

Considering the surface examinations of the untreated and Na-naphthalenide-etched PTFE powders as a whole, the XPS analysis substantially contributed to the determination of the functional groups on the polymer surface. These XPS peaks are shown in Figures 2 and 3, and all values of the XPS peaks are given in Table S1. The C1s main peaks of the untreated PTFE were at 292.26 eV and 293.75 eV, which successively corresponded to $-\text{CF}_2-$ and $-\text{CF}_3-$ bonds. On the contrary, the surface-modified PTFE powders exhibited two major C1s peaks at 284.66 eV and 285.25 eV successively corresponding to sp² ($-\text{C}=\text{C}-$) and sp³ ($-\text{C}-\text{C}-$) carbons. It was thought that the lower C1s peaks at 287.55 eV and 289.59 eV could be related to $-\text{C}-\text{CF}_x-$ bonds and carbonyl groups.^{34,35} The F1s peak of the untreated PTFE powders was single and had a much higher intensity compared to that of the surface-modified PTFE powders. This peak was at 689.97 eV, which corresponded to $-\text{CF}_2-$ bonds. The surface-modified PTFE powders also exhibited a small peak that corresponded to $-\text{CF}-$ bonds besides $-\text{CF}_2-$ bonds. This peak was at 686 eV.³⁵

The O1s peak intensity of the untreated PTFE powders was negligibly low. It was thought that this could be due to contamination. The surface-modified PTFE powders exhibited two O1s peaks that had much higher intensities. It was thought that these peaks belonged to C–O and C=O groups that formed after the Na-naphthalenide system treatment.⁴⁸ Moreover, the XPS curves that are given in Figures 2 and 3 provide the opportunity to compare the atomic ratios of F, C, and O between the untreated and surface-modified PTFE powders. The XPS results of the untreated PTFE powders showed fluorine and carbon atoms. Fluorine atoms had a much higher ratio than carbon, as expected. On the other hand, the XPS results of the surface-modified PTFE powders showed a much higher carbon ratio, and their fluorine ratio was substantially lower. Moreover, oxygen atoms became prominent and had a high ratio in the surface-modified PTFE powders. The order of the atomic ratios of the examined elements was as follows: $\text{C} > \text{O}_2 > \text{F}$.

Ayurova et al.⁴² modified PTFE surfaces with an active Na-naphthalenide system in an air conditioned setting, and they observed various functional groups such as radicals on C atoms, as well as hydroxyl groups. They reported that peroxy-radicals formed when the powders were exposed to O_2 in the air during the surface modification process. They also reported these peroxy-radicals were converted to hydroxyl and other functional groups by the process of washing with H_2O .⁴²

Like Ayurova et al.'s⁴² study, this study also showed similar reaction mechanisms as shown in Figure 4. A bath with the Na-naphthalenide system in THF was prepared under atmospheric conditions, and the PTFE

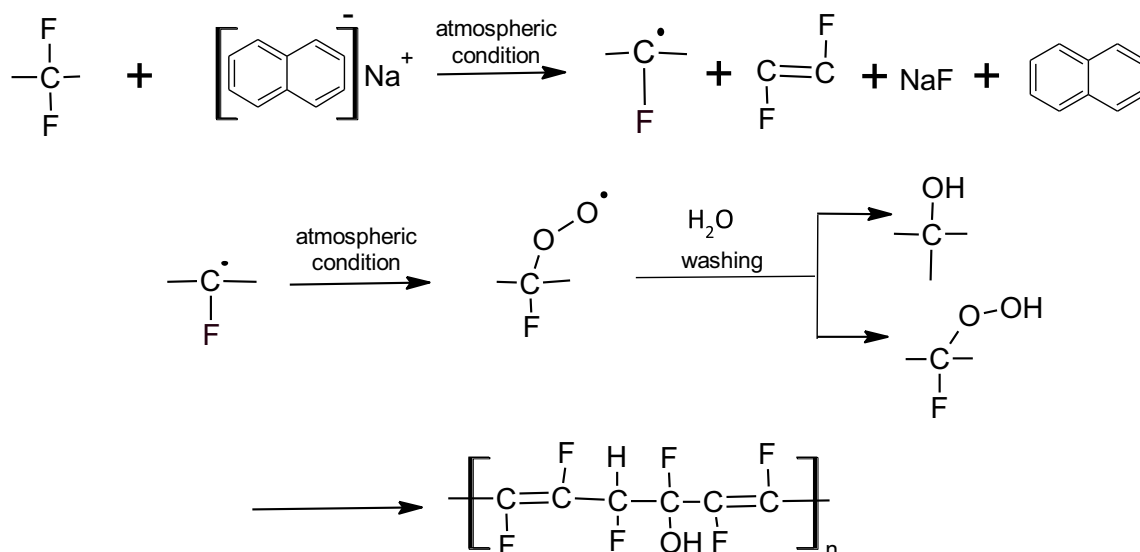


FIGURE 4 The reaction mechanism of surface modification of poly (tetrafluoroethylene) (PTFE) powders with Na-naphthalenide system.^{34,42,46} [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54947)]

powders were added into the bath and mechanically stirred for the surface modification process. After this stirring process, the powders were filtered, washed with acetone and distilled water, and rinsed. As a result of these steps, it was thought that the aforementioned functional groups were obtained on the surface of the PTFE powders.⁴² The occurrence of these functional groups such as unsaturation points of C=C, C—C, C—F, and carbonyl and OH groups on the surfaces of PTFE was reported by Roina³⁴ and Dake and Borshakar,⁴⁶ and while it was also in the textbook of Polymer Interface and Adhesion book⁴⁹ and the study conducted by Ayurova et al.⁴² The XPS results identified these functional groups on the surfaces of the powders as mentioned. Additionally, the occurrence of carboxyl groups was also reported in Ayurova's⁴² study and the textbook of Polymer Interface and Adhesion⁴⁹ as shown in Figure 4. However, it was not possible to be sure that these bonds were formed on the surface of the PTFE powders in this study after the characterizations. Due to functional groups such as OH and carbonyl groups, it was thought that strong interactions were created between the surface of the treated PTFE powders and the epoxy matrix. This was because epoxy has a substantially high amount of OH groups to form strong hydrogen bonds. This situation was thought to be an important factor in the development of these properties. In this regard, Benderly³⁹ treated Teflon and improved the bondability of PTFE with an increase in interfacial energy derived from a Na-naphthalenide system in THF. Benderly³⁹ stated that the adhesive bond strength values of the modified surface of Teflon with epoxy adhesives were very high, and they varied from 1000 to 2000 psi.

Benderly³⁹ also reported that there were some military application areas for surface-modified PTFE surfaces. In their review study, Kang and Zhang¹¹ revealed that a Na-naphthalenide system was highly efficient in promoting the adhesion of fluoropolymers to epoxide adhesives.

Particle size change is another factor that affects the properties of composites apart from the molecule interactions between the surfaces of the fillers and the matrix. Figure 5 shows the SEM images of the untreated PTFE and surface-modified PTFE particles. While the image of a₁ and b₁ presented the surfaces of surface-modified PTFE and the untreated PTFE particles, a₂ and b₂ presented the shapes and sizes of the particles. Both types of particles appeared to not have a distinct shape, and they were very similar in size. The surface of the surface-modified PTFE particles had a spongelike appearance compared to the surface of the untreated PTFE particles. It was thought that this spongelike surface could be efficient in obtaining improved mechanical properties. According to the SEM views of the composites, while the particle size of EPTF10 varied from 20 to 30 μm, the samples with higher ratios than EPTF10 had particles sizes ranging from 40 to 60 μm. Some degree of agglomeration was observed for the samples with higher filler ratios than EPTF10. However, the samples with higher filler ratios than EPTF10 also presented stable agglomerated behaviors.

The tensile, flexural, and IZOD impact resistance test results of all samples are given in Tables S2 and S3. Figures 6 and 7 also present all strength and modulus values by changes in the filler ratios of the surface-modified PTFE powders. The incorporation of the surface-modified PTFE powders into the epoxy system enhanced its mechanical

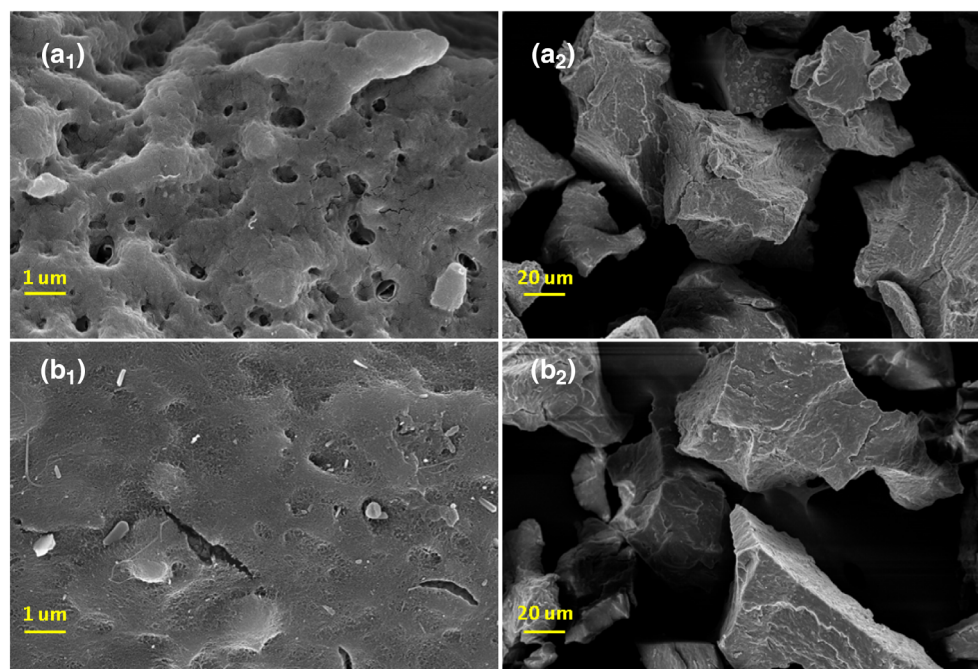


FIGURE 5 Scanning electron microscopy (SEM) morphologies of (a) surface-modified PTFE particles and (b) untreated poly (tetrafluoroethylene) (PTFE) particles. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54947)]

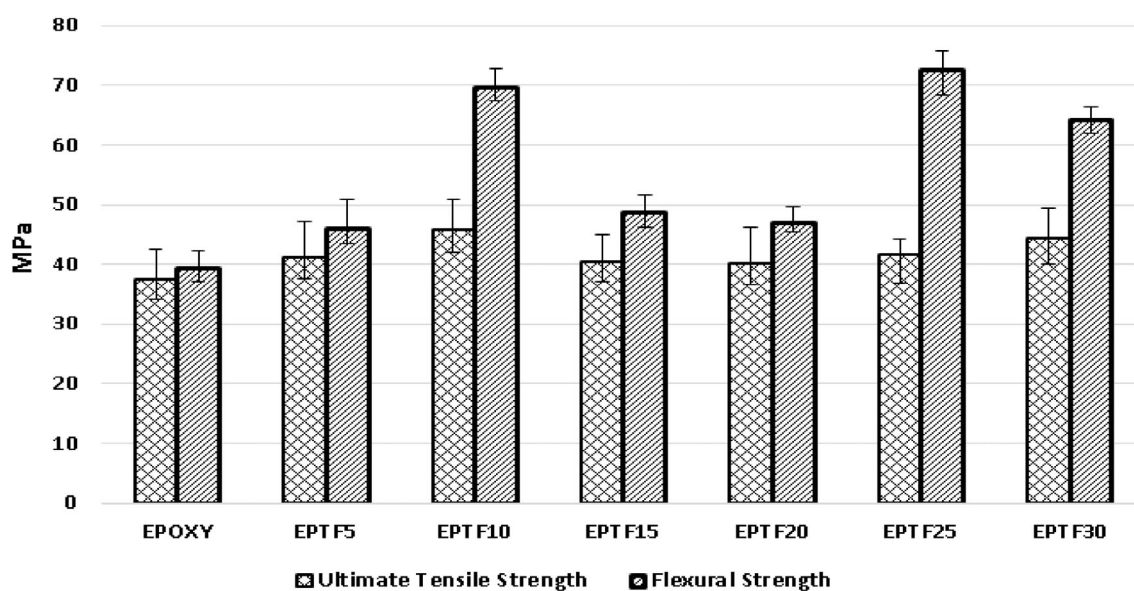


FIGURE 6 Tensile and flexural strength values of surface-modified poly (tetrafluoroethylene) (PTFE) filled epoxy composites.

properties and IZOD impact resistance. As shown in Figure 4, the addition of the surface-modified PTFE powders into the epoxy system increased both the ultimate tensile and flexural strength values by up to 10 wt%. The degrees of increase were measured as 22.8% and 77.2% for the ultimate tensile strength and the flexural strength, respectively.

Figure 7 shows the trend of the tensile and flexural modulus values along with changes in the ratios of the surface-modified PTFE powders. The results of both tensile strength and modulus values showed a decreasing trend between 10 and 20 wt%, and an increasing trend

was observed from 20 to 30 wt%. In the literature, PTFE powders have generally reduced the tensile strength and modulus values of samples due to their low rigidity and modulus, but the surface-modified PTFE increased these values in this study.^{43,50,51} Functional groups such as OH, carbonyl groups, and C=C unsaturation on the surfaces of the PTFE powders could show strong interfacial interactions with the epoxy pre-polymer. Hence, the degree of strong interfacial interactions could show an increase up to a certain incorporation ratio. It was thought that the increase in strong interfacial interactions could

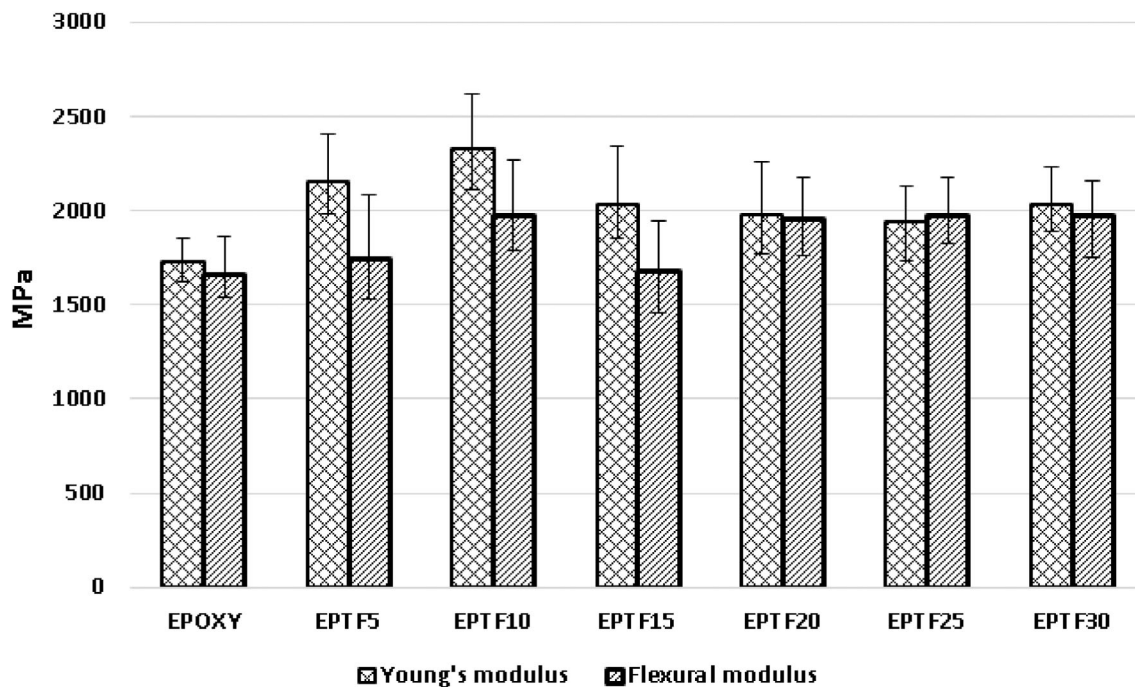


FIGURE 7 Tensile and flexural modulus values of surface-modified poly (tetrafluoroethylene) (PTFE)-filled epoxy composites.

increase the Young's modulus and tensile strength values. The decreases at higher ratios than 10 wt% could be attributed to the debonding of the PTFE powders due their high proportion.

In this study, flexural strength and modulus values showed a similar trend to tensile strength and modulus values. The increasing trend of these values had two peaks at 10 and 25 wt% along the curve. The maximum degrees of increase in flexural modulus and strength were respectively 19.2% and 84% compared to the pure epoxy system.

The effect of the surface-modified PTFE powders on the IZOD impact resistance values of the samples was positive, and they showed a similar trend to their mechanical properties. The maximum degrees of increase were found at ratios of 10 and 30 wt%. The percentages of these increases were 76% and 95%, respectively. The fluctuated behavior of impact test values could be attributed to the increase in strong interfacial interactions due to the surface modification of the PTFE powders and the softer behavior of the debonding powders at higher ratios than the epoxy structure.^{52,53} The excessive debonding of the PTFE powders at high ratios could have caused a fluctuating mechanical behavior due to the possibility of preventing the strong interfacial interactions of the epoxy system.

In the literature, composites filled with PTFE powders without surface treatment were found to have inferior mechanical properties than the neat epoxy. Shen et al.⁵⁰ studied the friction wear and mechanical performance of

PTFE-filled epoxy composites at high ratios of PTFE powders. While the wear resistance of the samples improved, their mechanical properties and hardness values decreased. Moreover, Xian et al.⁵¹ investigated the friction and wear of epoxy/TiO₂ nanocomposites with the influence of some additives such as carbon fibers, aramid, and PTFE. PTFE affected the flexural properties of the epoxy/TiO₂ composites.

Wear properties were determined using the pin-on-disc test system as described previously. The wear properties of the samples were highly influenced by the presence of the surface-modified PTFE powders in the epoxy. Wear rates were determined for a sliding distance of 2000 m. The changing trend of the wear rate values with the ratios of PTFE is shown in Figure 8, and all parameters and results related to wear rates are given in Table S4.

As is well-known, fluoropolymers exhibit very low friction coefficients, and a decrease in this parameter also reduces their wear rate.

The wear rate was dominantly affected by the low friction coefficient of fluorine atoms on the surfaces of the PTFE powders. While the content of the surface-modified PTFE powders increased, the wear rate of the samples decreased continuously. The maximum degree of decrease at the wear rate of the samples was found in EPTF30, and this degree was calculated to be around 96%. Considering studies on PTFE-filled epoxies and polymers in the literature related to wear rates and tribological properties, the EPTF composites in our study showed more favorable wear rate values and lower

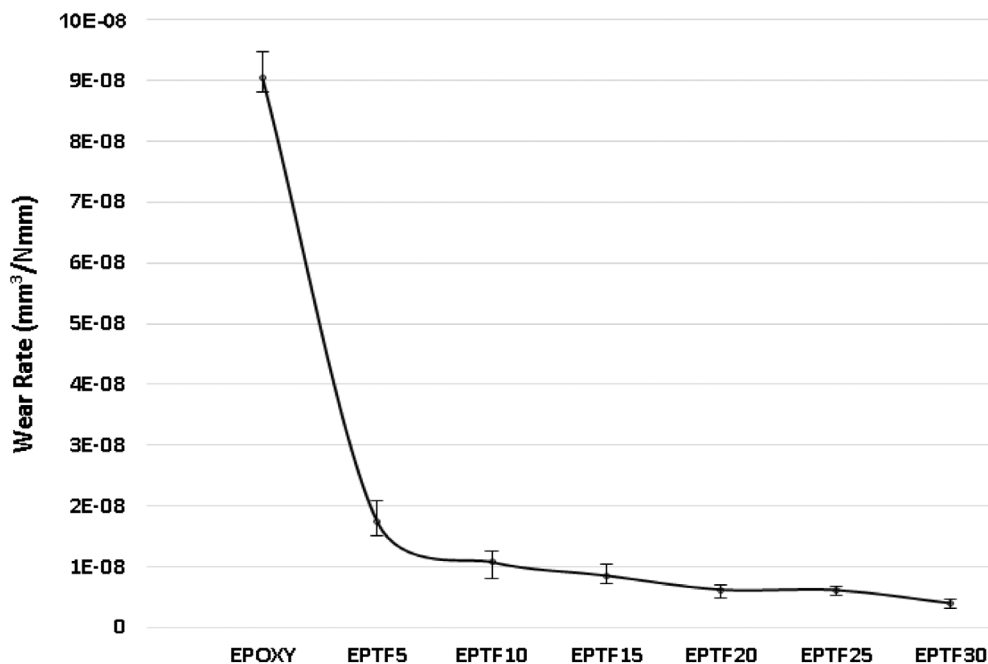


FIGURE 8 Wear rate values of surface-modified poly (tetrafluoroethylene) (PTFE)-filled epoxy composites.

friction coefficients. Shen et al.⁵⁰ studied the wear friction performance of PTFE-filled epoxy composites at high PTFE concentrations. They produced a new composite material containing epoxy and SiO₂ that was filled with PTFE at ratios in the range of 0–30%. The wear rates of the filled samples were compared to those of the neat epoxy, and a decrease of 95% was observed. However, the mechanical properties and hardness values of the samples worsened in their study. McCook et al.⁵⁴ examined ZnO- and PTFE-filled epoxy composites. They obtained highly improved friction coefficients and wear rates in the epoxy samples filled with 0.1% ZnO and 15% (vol.) PTFE. Srinivas et al.¹⁵ reported that 5% SiC- and 35% graphite-reinforced epoxy composites showed decreased wear rates, but these results were less improved than those in studies conducted with PTFE additives. Shen et al.⁵⁰ researched SiO₂/epoxy composites with graphite and PTFE reinforcements. The composites filled with PTFE at ratios ranging between 10% and 15% showed the most improved wear rates. However, graphite contents affected the wear rates negatively.

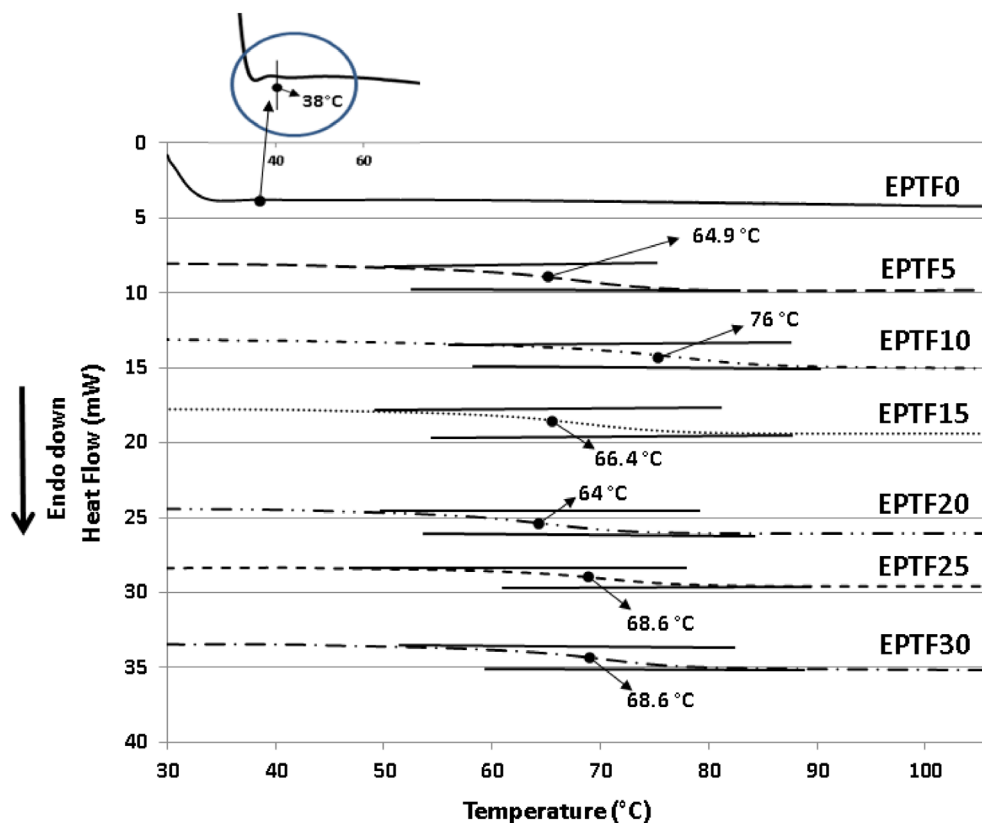
The glass-transition temperature (T_g) is the temperature at which molecular mobility begins to take place. The T_g values of the surface-modified PTFE-filled epoxy composites were observed to be highly improved. These values are given in Table S5, whereas T_g curves are shown in Figure 9.

Fluoropolymers are not compatible with organic structures without any covalent bonding. They show high interfacial energy levels with organic structures or polymers. Hence, they display weak adhesion properties due to the incompatibility of the two materials. In this study,

the surface-modified PTFE powders showed high compatibility and strong interfacial bonding with the epoxy system due to the Na-naphthalenide system that was utilized. Moreover, fluoropolymers can increase the vacancies around crystals, and the amorphous proportions in the structure can also increase.³ However, this situation is more applicable to crystalline systems rather than epoxy systems. In this study, when the surface-modified PTFE powders were incorporated into the epoxy systems, the T_g values of the samples showed substantial enhancements. The maximum T_g value was found to be 76°C for EPTF10. This corresponded to an increase of 100%. At higher ratios than 10 wt%, the T_g values of the samples decreased, but these values were still significantly higher than that of the pure epoxy.

These results demonstrated that there were strong adhesions and interactions between the matrix and the filler powders. This could be explained by the functional groups on the surface-modified PTFE powders such as OH groups, carbonyls, and C=C unsaturation points. Moreover, it was thought that these functional groups could have caused crosslinks between the surface-modified powders and the matrix. It was considered that the crosslinks that formed and the interactions between the functional groups of the surface-modified powders and the matrix restricted the segmental motion of the polymer chains and caused strong interfacial strength. In turn, the T_g values were improved. On the other hand, the neat epoxy did not exhibit a distinct T_g curve. In the comparisons of the neat epoxy to the samples incorporated with the surface-modified PTFE powders, the incorporated samples exhibited much more distinct T_g curves.

FIGURE 9 Glass transition temperatures in differential scanning calorimetry (DSC) curves of surface-modified poly (tetrafluoroethylene) (PTFE)-filled epoxy composites. [Color figure can be viewed at wileyonlinelibrary.com]



However, these T_g curves were substantially higher than the T_g of the neat epoxy sample, as mentioned. In this regard, it was thought that the surface-modified PTFE powders could have affected the network structure of the epoxy and reduced the crosslinking degree of the epoxy structure. However, the surface-modified PTFE powders caused strong interactions with the epoxy matrix due to the functional groups that were formed on the surface. Moreover, this commercial PTFE powder product had a T_g value of 120°C. It was thought that the higher T_g value of this commercial PTFE powder product than that of the epoxy substantially increased the T_g of the novel composites. On the other hand, it is well-known that filler powders added at high ratios reduce the rate of crosslinking due to the physical prevention of the interactions among molecules. The decreases in the samples in our study with higher filler ratios than 10 wt% could be explained by this result.

Besides, T_g values are related to mechanical properties due to the properties of adhesion between the filler powders and the matrix. T_g values changing with the ratios of the surface-modified particles had a similar trend to the changes in their mechanical properties.

The heat deflection temperature is an indicator of the short-term temperature resistance of materials which was also observed for all samples. The surface-modified PTFE powders were found to have a positive influence on the

heat deflection temperature of the neat epoxy. These values are given in Table S5. The relationship between heat deflection temperatures and glass transition temperatures can also be observed in Figure 10. The effect of the ratio of the surface-modified PTFE powders was similar in terms of both heat deflection temperatures and mechanical properties. The maximum degree of increase was observed at the filler ratio of 10 wt%, and it was an increase of 60%. The other results were also higher than those of the pure epoxy. An increase in heat deflection temperatures shows that EPTF composites have high thermal stability.¹

The water absorption values (wt%) of the samples are shown in Figure 11, and all related data are presented in Table S6. Water absorption measurements were taken in various periods, namely 3, 14, 75, 250, and 300 days. Indeed, polymer chains with fluorine molecules display a hydrophobic character due to their impelling effect toward water molecules. For this reason, it was expected that increased filler ratios would reduce water absorption values. However, the surface-modified PTFE powders slightly but significantly increased the percentage of water absorption compared to the neat epoxy.

It is well-known that functional groups such as OH and carbonyl groups have strong interactions with water molecules due to their hydrophilic nature. For this reason, it was expected that the increase in the functional

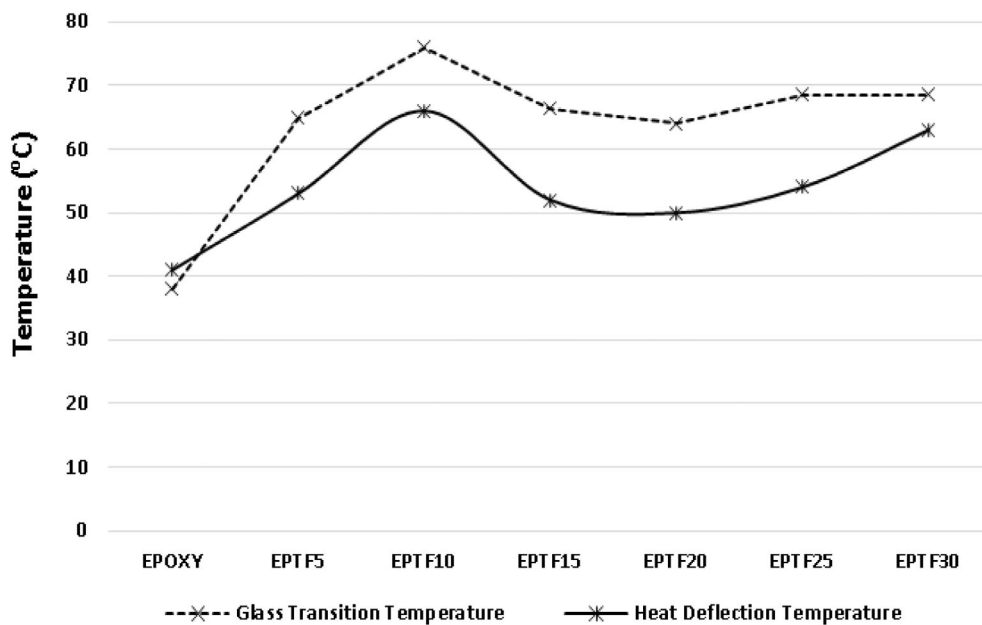


FIGURE 10 Glass transition and heat deflection temperature values of surface-modified poly (tetrafluoroethylene) (PTFE)-filled epoxy composites.

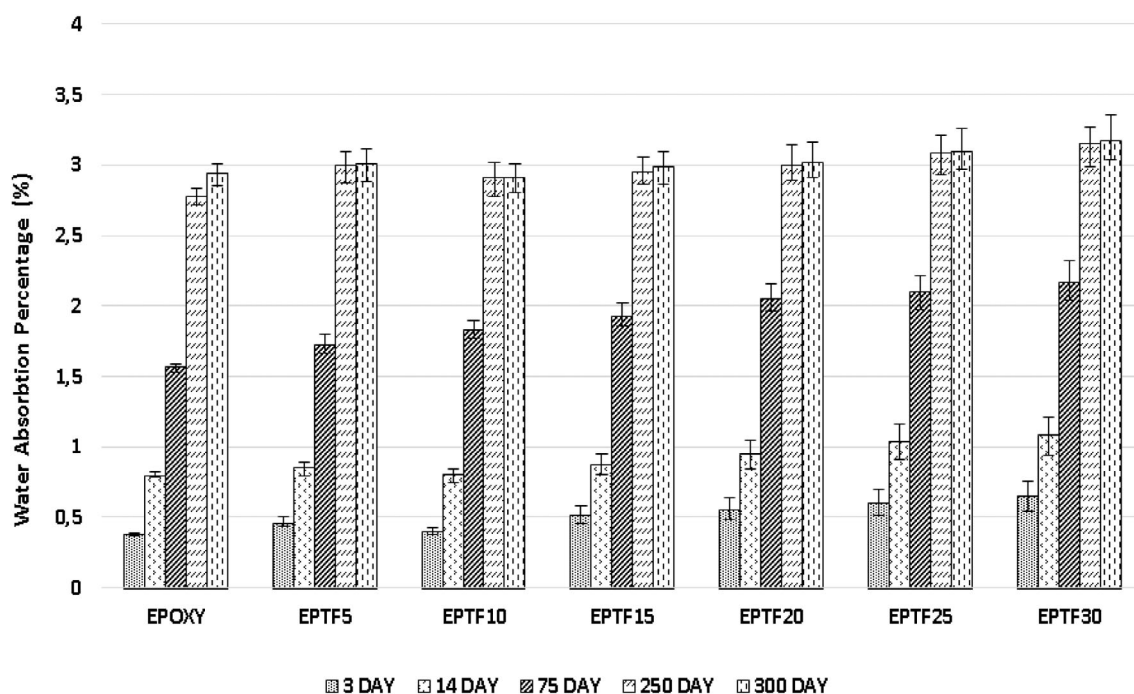


FIGURE 11 Water absorption rates of surface-modified poly (tetrafluoroethylene) (PTFE)-filled epoxy composites at different time points.

groups on the PTFE powders could raise the ratio of water absorption.⁵⁵

Considering the comparisons of the properties of the samples to those of samples reported in the literature in Table 1, PTFE powders that were surface-modified with the Na-naphthalenide system became prominent as a significant filling material for epoxy-based composites in terms of wear, mechanical, and thermal properties. In the evaluation of these properties as a whole, EPTF10

and EPTF30 were the most prominent samples of this study. Moreover, it was an important finding that EPTF10 required a much lower manufacturing cost than EPTF30 due to the usage of a lower amount of PTFE powder. In terms of wear properties, EPTF10 and EPTF30 showed high decreases in wear rate values compared to the neat epoxy. These wear rate values, which were 88.1% and 95.5% for EPTF10 and EPTF30, respectively, were substantially improved compared to those

TABLE 1 Comparison of the mechanical and wear properties of EPTFE samples to the properties of other materials reported in similar reinforcement and wear studies about epoxy-based composites in the literature.

Samples	Reference	Product detail	Wear rate			Change (%)			Impact strength or K _{IC}	
			%	Wear rate (mm ² /N)	Distance, velocity, load	σ	E	σ_F		E _r
EPTFE10	This study	Surface-modified PTFE (10 wt %) filled epoxy composite	-88.1	1.07×10^{-8}	2000 m, 8.75 m/s, 20 N	+22.8	+33.2	+77.2	+18.9	+76.4
EPTFE30	This study	Surface-modified PTFE (30 wt %) filled epoxy composite	-95.5	0.4×10^{-8}	2000 m, 8.75 m/s, 20 N	+18.7	+17.6	+63.8	+18.9	+95
Epomet-PTFE10 Epomet-PTFE15	50	PTFE (10–15 wt%)-filled epoxy composites with SiO ₂ particles (48–63 wt%)	-	1×10^{-6}	1000 m, 60 N	-	-	-	-	-
TiO ₂ + graphite + PTFE + SCF	56	5 vol% graphite- + 5 vol% PTFE-filled epoxy nanocomposite	-77.4	0.89×10^{-6}	1 MPa, 1 m/s	-	-	-	-	-
EPX-GNPOX	57	Epoxy-PTFE (20 wt%) coating modified with oxidized graphene nanoplatelets	-37	1.4×10^{-6}	150 N, 400 mm/s, 1500 m	-	-	-	-	-
POM-PTFE particles	58	PTFE particle (20 wt%)-filled POM	-98	1.04×10^{-3}	7.6 MPa, 4.7 m/s	-28	-8.8	-13.6	-	-30
Epoxy + 10% PTW	1	Potassium titanate whisker (10 wt%)-reinforced epoxy composite	-	-	-	+14	+3.6	+24.3	+9.6	+13.4 (HDT)
L22-S0	59	Core shell rubber (9.66 vol %)-filled epoxy composite	-	-	-	-29.6	-21	-	-	+3.3 (T _g)
POSS-Epoxy	60	POSS nanoparticle (1.5%)-reinforced epoxy	-	-	-	+23.7	+29.1	-	-	-7.2 (T _g)
POSS-Rubber Epoxy	60	POSS-rubber core shell nanoparticle (1 wt %)-reinforced epoxy	-	-	-	+43.8	0	-	-	-6.5 (T _g)
Shungite/Epoxy	25	Shungite mineral (20 wt %)-filled epoxy	-	-	-	-	-	+25.9	+5.4	-
Wollastonite/Epoxy	26	Fine wollastonite mineral particle (10 wt%)(CaSiO ₃)-filled epoxy	-96.3	4×10^{-6}	1 MPa, 1 m/s	-	-	+50	+87	+52
Borosilicate glass microsphere/Epoxy	36	Borosilicate glass microsphere (30 wt%)-filled	-	-	-	-7	-	-6.5	-	+56
Hollow glass microsphere/Epoxy	27	Amine functionalized hollow glass microsphere-filled epoxy composites	-	-	-	-	-	-	-	-
TiO ₂ -ABS/Epoxy	30	TiO ₂ (0.7 wt%)-filled poly (acrylonitrile-butadiene-styrene) (ABS) (3.6 wt %)/epoxy hybrid composite	-	-	-	+56	+14.8	-	-	+10.5
ABS/Epoxy	30	ABS (3.6 wt%)/epoxy blend	-	-	-	+25	0 (stable)	-	-	0 (stable)

(Continues)

TABLE 1 (Continued)

Samples	Reference	Product detail	Wear rate			Change (%)					Impact strength or K _{1c}
			%	Wear rate (mm ² /N)	Distance, velocity, load	σ	E	σ _F	E _f	T _g or HDT	
Multiple fillers (TTG7C-TTG7-TTGCS5)-Epoxy	19	TiO ₂ (4 wt%), short CF (10 wt %)-, graphite (7 wt%), and ZnS (5 wt%)-filled epoxy	-89 (TTG7), -96 (TTGCS5)	1.1×10^{-4} (TTG7) 0.35×10^{-4} (TTGCS5)	100 m, 36.1 N, 60 mm/s	+7.5	+78.4	-	-	+17.8 (TTG7) (T _g)	-
Aramid nanofiber-Epoxy	28	Well-dispersed aramid nanofiber (0.15 wt %)-reinforced epoxy	-	-	-	+28	-	+81.9	-	-	+81.8
UHMWPE fiber-Epoxy	29	Ultrahigh molecular weight polyethylene (0.3 wt%)-reinforced epoxy	-	Friction coefficient: +39.1	-	-21.4	+7.5	+1.1	+21	+1.3 (T _g)	-
Treated UHMWPE fiber-Epoxy	29	Treated ultrahigh molecular weight polyethylene (0.3 wt %)-reinforced epoxy	-	Friction coefficient: +43.5	-	-15.2	+55.2	+26.2	+26	+2.3 (T _g)	-
GrNP-Epoxy	32	Silane-treated graphite (0.25 wt %)-filled epoxy	-	-	-	+22.7	+26.4	-	-	+4.2 (T _g)	-30.7
EG/APP-Epoxy	31	Expandable graphite/ammonium polyphosphate (0.25 wt%)-filled epoxy	-	-	-	+13.1	+7.8	-	-	-1.9	+15
rGO/Py-PEG-Py-Epoxy	22	Thermally reduced graphene oxide with pyrene-functionalized PEG (0.03 wt %)-reinforced epoxy	-	-	-	-	-	+56	-	+5.6	+55
GO/PA-Epoxy	34	Epoxy reinforced with poly acrylate chains grafted onto graphene oxide (1 wt%)	-	-	-	+12.6	-	-	-	-0.2	+40.3
K-graphene-Epoxy	21	Cation-π interaction-assisted facile preparation of graphene (reinforced epoxy)	-	-	-	+116.5	-	-	-	-	(elongation: +126.5)
Graphene/nano-Al ₂ O ₃ -Epoxy	20	Graphene nanoplatelet (0.2 wt %)-/ nano-Al ₂ O ₃ particle (0.8 wt%)-reinforced epoxy hybrid composite	-	Friction coefficient: -20 Micro-hardness: +10	-	-	-	-	-	-	-
GNP/CNT-EPOXY	23	Graphene nanoplatelets/carbon nanotube (1 wt%)-reinforced epoxy hybrid composite	-	-	-	+28.9	-6.8	-	-	-	+47 (K _{1c})
n-Si ₃ N ₄ /COOH-MWCNT-Epoxy	24	n-Si ₃ N ₄ (0.25 wt%)-/carboxylic acid-functionalized multi-wall carbon nanotube (0.5 wt %)-reinforced epoxy hybrid composite	-68.4	28.1×10^{-7}	50 N, 1.6 MPa, 7 m/s	159+	129+	368+	-	-	-

Note: “-” means decrease in properties, “+” means increase in properties.

Abbreviations: σ, tensile strength; E, Young's modulus; σ_F, flexural strength; T_g, glass transition temperature; HDT, heat deflection temperature; K_{1c}, fracture toughness.

reported in other studies in the relevant literature. For instance, Shen et al.⁵⁰ studied the wear properties of PTFE-filled epoxy composites with a high concentration of SiO₂ particles (48–63 wt%). They reported a wear rate of approximately 1×10^{-6} mm²/N in the PTFE (10–15 wt%)-filled epoxy composites with SiO₂ particles by applying a load of 60 N and a distance of 1000 m. In another noteworthy study, Chang et al.⁵⁶ focused on a synergized effect for epoxy composites. They used PTFE powders and graphite flakes to fill epoxy composites and investigated the transfer film derived from these filling materials. They obtained a substantial decrease in wear rate by 77.4% by filling PTFE powder at a ratio of 5 vol% and graphite flakes at a ratio of 5 vol%. In addition to these studies, Bandeira et al.⁵⁵ prepared epoxy composite materials filled with 20 wt% of PTFE powder and modified with oxidized graphene nanoplatelets. These composites displayed a decrease of 37% in wear rates. Zhang et al.⁵⁸ produced polyoxymethylene (POM) composites filled with PTFE particles at a 5- μ m particle size. They obtained a substantial decrease of 98% in wear rates for the 20 wt% PTFE particle-filled POM composite. However, they could not obtain any improvement in mechanical properties due to poor interfacial interactions between the PTFE particles and the POM.

The PTFE powders etched with the Na-naphthalenide system in our study presented highly improved wear results. The wear rate of EPTF30 showed a substantial decrease of 95.5%. The surface-modified PTFE-filled samples also showed improved mechanical properties, impact resistance, and thermal properties besides their improved wear resistance. There are also some studies about particle-filled epoxies conducted for the purpose of improving mechanical properties and toughness, which are presented in Table 1. For instance, Sudheer et al.¹ studied potassium titanate whisker (PTW)-reinforced epoxy composites. The 10 wt% potassium titanate whisker (PTW)-reinforced epoxy composite was the most improved one, and it had increased tensile strength, Young's modulus, flexural strength, and flexural modulus values. Moreover, the heat deflection temperature increased at the PTW reinforcement ratio of 10 wt%. However, impact resistance decreased by the filling of these rigid PTW particulates.

Another noteworthy system is known as core-shell rubber particles. Quan and Ivankovic⁵⁷ studied the effects of core-shell rubber (CSR) nanoparticles on the mechanical properties and fracture toughness of an epoxy polymer. This CSR was made of an acrylic rubber core surrounded by a poly methyl methacrylate (PMMA) shell, and its particle size was 300 nm. The authors obtained the most improved result with the incorporation of CSR at 9.66 vol% into the epoxy resin. They reported

an increase in fracture toughness of 125%, while tensile strength and Young's modulus values decreased at rates of 29.6% and 21%, respectively. Moreover, they obtained an increase in T_g at a rate of 3.3%. Thitsartar et al.⁶⁰ used octa polyhedral oligomeric silsesquioxane (POSS) in an epoxy matrix and synthesized a new reinforcement and filling material by using POSS and poly (n-Butyl acrylate) rubber. They designed this material in three layers. POSS was used as the first layer (inner core), and poly (n-Butyl acrylate) rubber that was covalently bonded to the inner core was used as the middle layer. Functional groups that were in the third layer were bonded to this middle layer, and a new rubber material was obtained with functional groups. This new rubber material was the outer layer of this newly synthesized POSS-rubber core shell nanoparticles. Therefore, they used both rigid and soft segments for this synthesized filling material. The researchers reported the properties of the composites with POSS and POSS-rubber core shell nanoparticles separately. The composites with POSS nanoparticles at a ratio of 1.5% (the most improved one among the POSS/epoxy composites) showed increases in tensile strength and Young's modulus at 23.7% and 29.1%, respectively. However, the impact resistance value decreased at a rate of 50%. In addition to these, T_g values decreased at a rate of 7.2% despite the increase in tensile strength and modulus values. Contrary to the epoxy composites with POSS, the epoxy composites with POSS-rubber core shell nanoparticles showed a simultaneous enhancement of strength and toughness. The authors demonstrated increases in tensile strength and impact resistance results at rates of 43.8% and 76.8%, respectively. The Young's modulus value did not change significantly. Klyuchnikova et al.²⁵ prepared shungite mineral particle-filled epoxy composites and investigated some of their mechanical properties. Shungite crystals contain fullerene-like structures, which increase the oxidation and heat resistance of polymer-based composites. They reported that the 20 wt% shungite-filled epoxy showed increases of 25.9% and 5.4% in bending strength and modulus, respectively. Xian et al.²⁶ produced epoxy composites filled with fine and coarse wollastonite mineral particles. Wollastonite is a calcium metasilicate (CaSiO₃). They investigated the mechanical and wear properties of the composites they prepared. They reported that the filling of 10 vol% of fine wollastonite into the epoxy composite resulted in significant increases of 50%, 87%, and 52% in flexural strength, modulus, and impact resistance values, respectively. Moreover, the wear rate substantially decreased by 96.3% compared to the neat epoxy. The wear rate value decreased from 111×10^{-6} to 4×10^{-6} for the epoxy composite filled with 10 vol% of fine wollastonite particles. Gupta and Satapathy³⁶ prepared borosilicate glass

microsphere-filled epoxy composites to investigate their mechanical and erosion resistance. They reported that the 30 wt% filling of borosilicate glass microsphere results in decreases of 7% and 6.5% in respectively tensile and flexural strength while it led to 56% of increase in impact strength. The authors also applied a standard air-jet type erosion test to this sample. Silica sand particles were crashed into the surface of the samples at 32 m/s. The erosion rate of the 30 wt% borosilicate glass microsphere filling showed a decrease of 32% compared to the neat epoxy. Imran et al.²⁷ manufactured amine-functionalized hollow glass microsphere-filled epoxy composites. They examined the compressive and thermo-mechanical behaviors of these composites. While the 5 wt% amine-functionalized hollow glass microsphere filling resulted in an increase 32.5% in storage modulus, it showed a decrease of 43.4% in compressive strength. Jyotishkumar et al.³⁰ prepared an ABS/epoxy blend using 3.6 wt% of ABS. Moreover, they filled TiO₂ particles into this blend. As a consequence, they obtained TiO₂-filled ABS/epoxy hybrid composites and observed their mechanical and thermo-mechanical properties. While the neat blend showed increases of 25% and 23.5% in tensile strength and fracture toughness (K_{1c}), respectively, its tensile modulus and T_g values did not show any change. Furthermore, the TiO₂-filled ABS/epoxy hybrid composites showed more improvement than the neat blend. The 0.7 wt% TiO₂-filled ABS/epoxy hybrid composite showed substantial increases of 56%, 148%, 10.5%, and 32.3% in tensile strength, tensile modulus, T_g, and impact strength, respectively. Tian et al.¹⁹ studied epoxy composites with multiple fillers such as TiO₂, short CF, graphite, and ZnS to investigate their mechanical and wear properties. Epoxy composites were prepared by creating different combinations of these fillers. The epoxy filled with 4 wt% TiO₂ and 7 wt% graphite showed increases of 7.5%, 78.4%, and 17.8% in tensile strength, tensile modulus, and T_g values, respectively. The wear rate of this composite showed a substantial decrease of 89%, and this wear rate improved further by incorporating 5 wt% of ZnS into the epoxy filled with 4 wt% of TiO₂ and 7 wt% of graphite. Du et al.²⁸ produced well-dispersed aramid nanofiber-filled epoxy composites. They investigated the mechanical and thermo-mechanical properties of these composites. They reported that the 0.15 wt% aramid nanofiber reinforcement caused respective increases of 28%, 81.9%, and 81.8% in tensile strength, bending strength, and impact resistance values compared to the neat epoxy. This situation was attributed to the interface enhancements between the aramid nanofibers and the epoxy matrix. Lie et al.²⁹ prepared improved epoxy composites with treated and as-received ultra-high molecular weight polyethylene (UHMWPE) fiber fillers. They obtained

more improved results for the epoxies filled with the treated UHMWPE. While these composites showed increases of 55.2%, 26.2%, 26%, and 2.3% in tensile modulus, flexural modulus, flexural strength, and T_g values, respectively, their tensile strength value decreased by 15.2%. On the other hand, the friction coefficient values of the composites showed substantial increases. Lavoratti et al.³² examined silane-treated graphite-filled epoxy composites to increase the interfacial strength between the graphite filler and the epoxy matrix. They reported increases of 22.7%, 26.4%, and 2.3% in tensile strength, tensile modulus, and T_g values, respectively. However, the impact strength of the composite decreased substantially, at a rate of 30.7%. Yuan et al.³¹ prepared expandable graphite and ammonium polyphosphate (EG/APP)-filled epoxy hybrid composites to investigate their mechanical and thermal properties. The epoxy filled with 0.25 wt% EG/APP presented increases in tensile strength, tensile modulus, and impact strength at rates of 13.1%, 15%, and 7.8%, respectively. However, T_g values slightly decreased, at a rate of 1.9%. Xu et al.²² synthesized uniformly dispersed graphene oxide (GO) with pyrene-functionalized polyethylene glycol. They prepared epoxy composites by using these GO particles. The epoxy composite filled with 0.03 wt% thermally reduced GO showed increases of 56%, 5.6%, and 55% in flexural strength, impact resistance, and T_g values, respectively. Xie et al.³³ synthesized GO particles grafted with poly acrylate (PA) chains. They prepared epoxy composites by filling these particles into the epoxy matrix. The epoxy composite filled with 1 wt% PA-grafted GO showed respective increases of 12.6% and 40.3% in tensile and impact strength values. Huang et al.²¹ created epoxy composites filled with graphene modified using potassium ions. They obtained substantial increases of 116% and 126% in tensile strength and elongation, respectively. Kesavulu and Mohanty²⁰ prepared epoxy hybrid composites reinforced with graphene and nano-Al₂O₃ particles. While the friction coefficients of the composites decreased, their micro-hardness values increased. Kopsidas and Olowjoba²³ prepared graphene and carbon nanotube-filled epoxy hybrid composites. They obtained increases of 28.9% and 47% in tensile strength and fracture toughness (K_{1c}), respectively, but the tensile modulus values showed a decrease of 6.8%. Bhagavatula et al.²⁴ produced another epoxy hybrid composite with n-Si₃N₄ and carboxylic acid-functionalized multi-wall carbon nanotube (COOH-MWCNT) fillers. They obtained substantial improvements in mechanical and wear properties. The composite filled with 0.25 wt% n-Si₃N₄/COOH-MWCNT had 159%, 129%, and 368% increased tensile strength, tensile modulus, and flexural strength values, respectively. The wear rate of this composite showed a substantial decrease of 68.4% compared

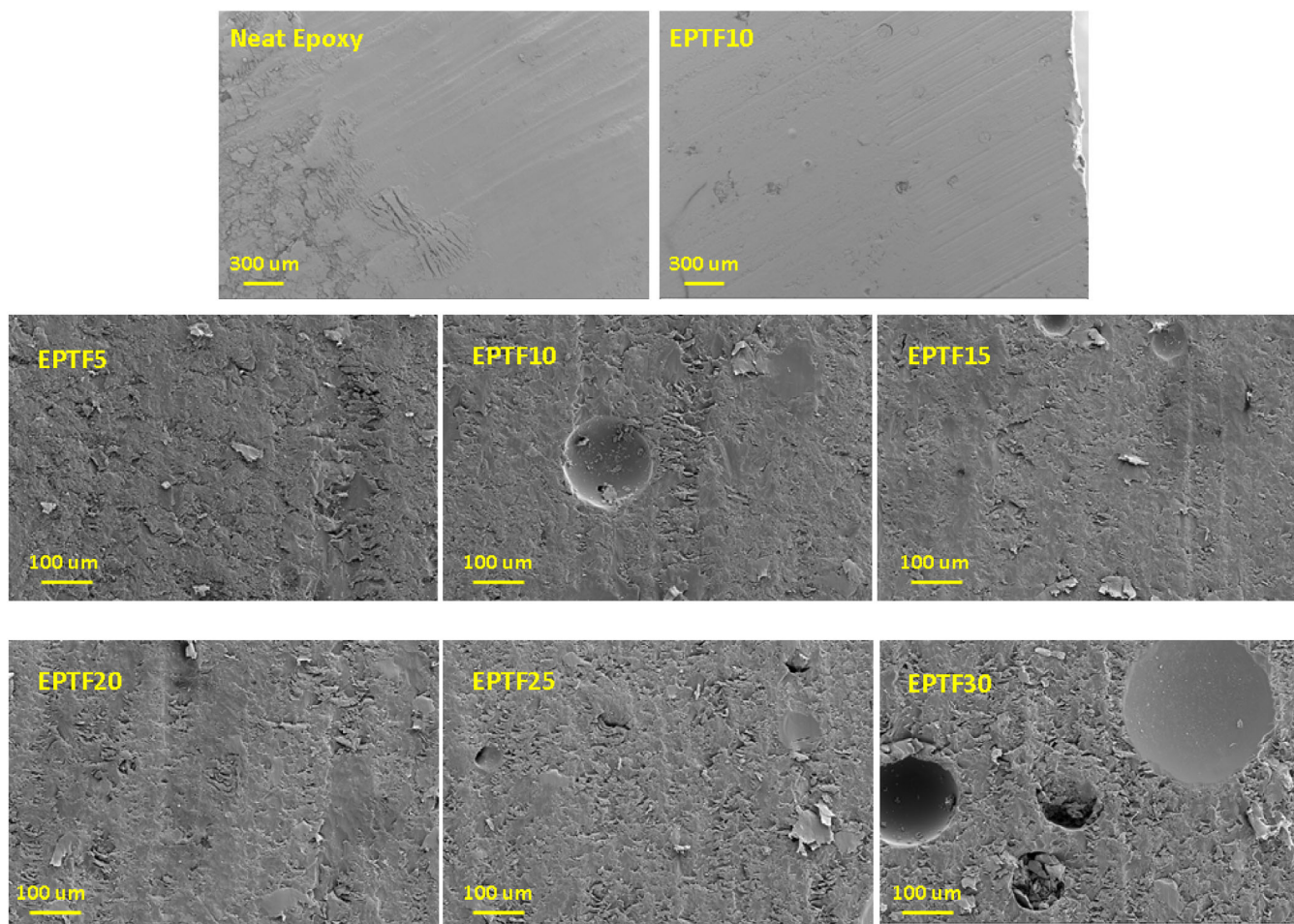


FIGURE 12 Worn surface morphologies of surface-modified poly (tetrafluoroethylene) (PTFE)-filled epoxy composites. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54947)]

to the neat epoxy. The results of these studies are summarized in Table 1 and compared to the results of the prominent samples in this study. Table 1 presents many different types of studies on filled epoxy composites. Considering properties such as mechanical strength, impact strength, wear, and glass transition temperatures, the results in this study are noteworthy.

It is difficult to incorporate PTFE powders into polymer resins without any precipitation and homogeneously due to their high density. It requires mechanical stirring with very high rotational speeds. Likewise, this situation causes the formation of high amounts of bubbles in the resin, and it becomes difficult to eliminate these bubbles before the epoxy cures. The pores that are caused by these bubbles would affect the composite adversely. Hence, the usage of surface-modified PTFE powders in this study also allowed the usage of an easier process. The surface-modified PTFE powders in this study were incorporated into the epoxy resin and mechanically stirred at 300 rpm. Bandeira et al.⁵⁷ used a rotor-stator system at 16000 rpm to disperse unmodified PTFE powders.

They also used a solvent to obtain PTFE solutions and dispersed PTFE powders into the solvent at 6000 rpm with a fluoro-surfactant before mechanical stirring. In this regard, the PTFE powders that were surface-modified with the Na-naphthalenide system in this study were easily dispersed into the resin due to their functional groups and spongelike or network structures on their surfaces without any precipitation. Therefore, epoxy composites were obtained with success.

The worn and fracture surfaces of the samples were characterized by SEM, and the worn surface of EPTF30 was analyzed by EDS. Figure 12 shows the worn surfaces of the samples after a sliding distance of 2000 m, and the EDS results of EPTF30 are shown in Figure 13. The neat epoxy had a wavier morphology with more cracks in its wear track profile compared to the composite samples filled with the surface-modified PTFE powders. The worn surfaces were much smoother for the filled composite samples. The morphologies of the composite samples filled with the surface-modified PTFE powders revealed that their structures had high compatibility for the

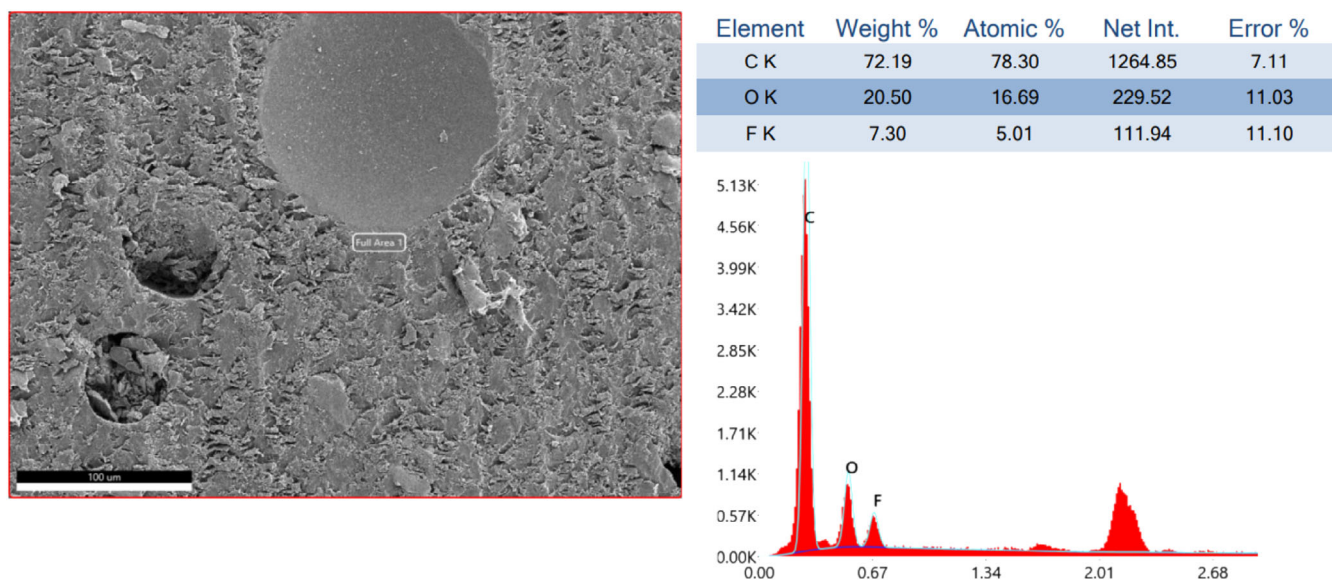


FIGURE 13 Energy dispersive spectroscopy (EDS) result of the worn surface of EPTF30. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54947)]

interface between the surface-modified powders and the matrix. The morphology of the neat epoxy had transverse microcracks to the direction of sliding.

The neat epoxy showed a wavier and deeper wear track than those on the filled composite samples. This result can be related to its mechanical properties. Samples with higher wear depths can have inferior mechanical properties.⁴⁴ Moreover, the ratio of the surface-modified PTFE powders in the composites plays an important role in their tribo-performance. It is known that samples with PTFE powders have low friction coefficients. This parameter could be one of the causes of the differences among the morphologies of the neat epoxy and the filled composite samples. Moreover, PTFE has self-lubricating properties. However, it has a tendency to cold-flow or creep easily. Even at room temperature, PTFE can show large deformations over a long period with the continuous application of force. Additionally, it hardly presents any resilience.⁶¹ Therefore, a PTFE layer or a PTFE transfer layer forms on wear tracks and the sliding steel when sliding over time with a continuous load, and PTFE displays a creep behavior. This polymer layer generally prevents the direct contact between the sample and the abrasive counter.^{44,58} In this regard, the image of EPTF30 shows a similar behavior. The composite samples filled with the surface-modified PTFE powders had thick polymer layers due to the cold-flow or creep behavior of the PTFE powders on the worn surfaces. The PTFE layers can be seen in the image of the filled composite samples in Figure 14. Moreover, these layers filled the voids of the composite samples filled with the surface-modified PTFE powders. These behaviors

reduced the wear rates of the sample. It was thought that the wear tracks of the composite samples filled with the surface-modified PTFE powders originated from indentations like rolling, and minimal mass loss occurred. These wear tracks originating from indentations like rolling can be easily seen in Figure 14. Zhang et al.⁵⁸ prepared polyoxymethylene (POM) composites filled with untreated PTFE particles to investigate the mechanical and tribological properties of these composites. They reported that the PTFE layer that formed on the wear tracks and the sliding steel substantially reduced the wear rate. The specific wear rate decreased from 51×10^{-3} to 1.04×10^{-3} mm³/m for the composite filled with 20 wt% PTFE, and this composite showed a substantial decrease of 98%. This considerable decrease was similar to the decreases in the wear rates of the surface-modified PTFE-filled samples in this study. This could be attributed to the creep behavior of the PTFE particles due to sliding over time with a continuous load as mentioned above. It was thought that Zhang et al.'s⁵⁸ study and this study showed similar tribological behaviors. However, mechanical properties such as tensile, flexural, and impact strength values decreased because of the poor interfacial interaction between the untreated PTFE particles and the POM matrix in the study conducted by Zhang et al. The improvement in the mechanical properties of the filled samples in our study was attributed to strong interfacial interaction created by the means of the surface-modified PTFE particles. Additionally, Figure 15 presents the fractured surface morphologies of the neat epoxy and the filled composite samples for the observation of the fracture modes of the samples. In the views of the filled composite samples, dark nodular voids were attributed to the surface-modified PTFE

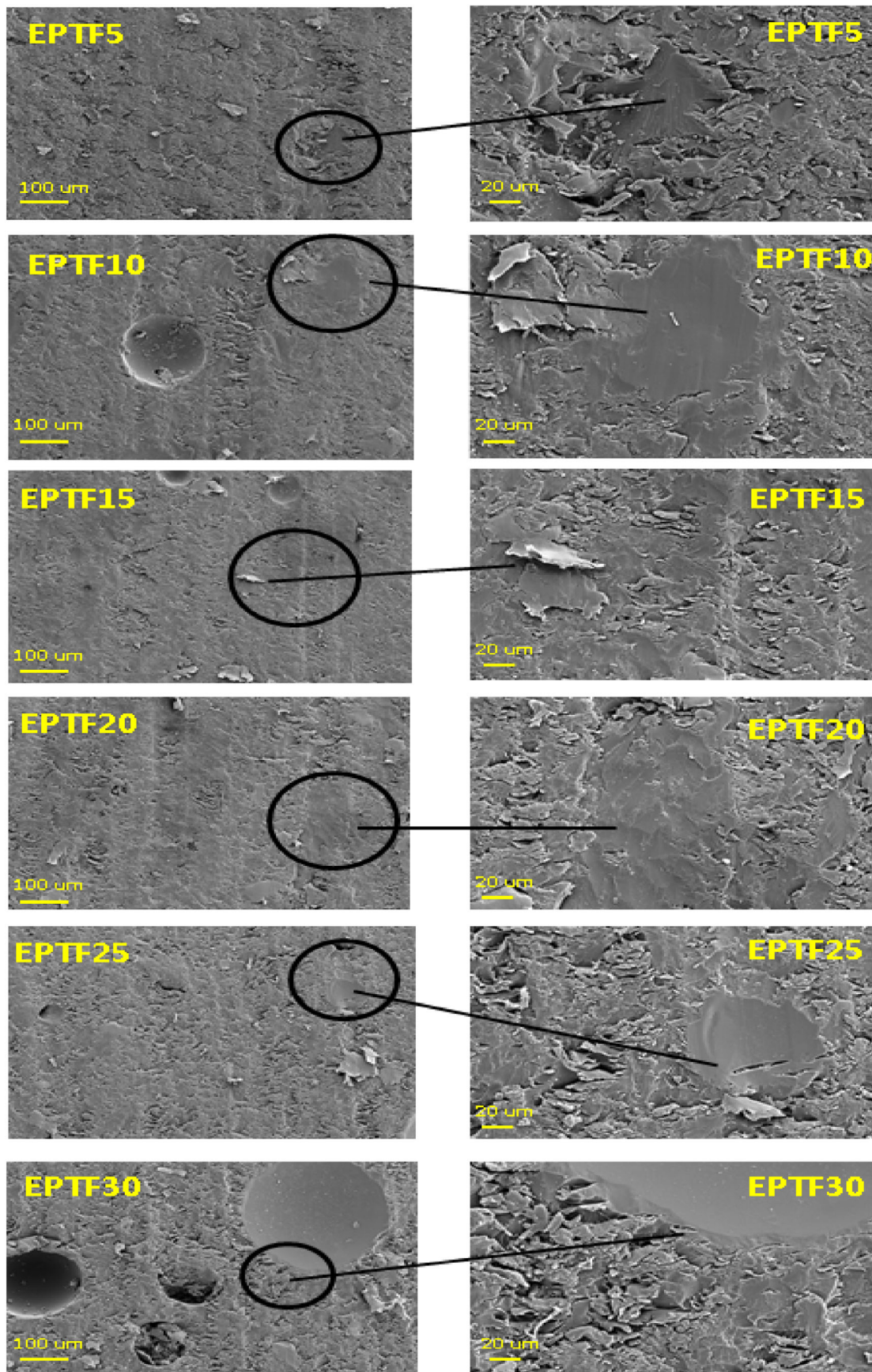


FIGURE 14 Poly (tetrafluoroethylene) (PTFE) layers on the worn surfaces of surface-modified PTFE-filled epoxy composites. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54947)]

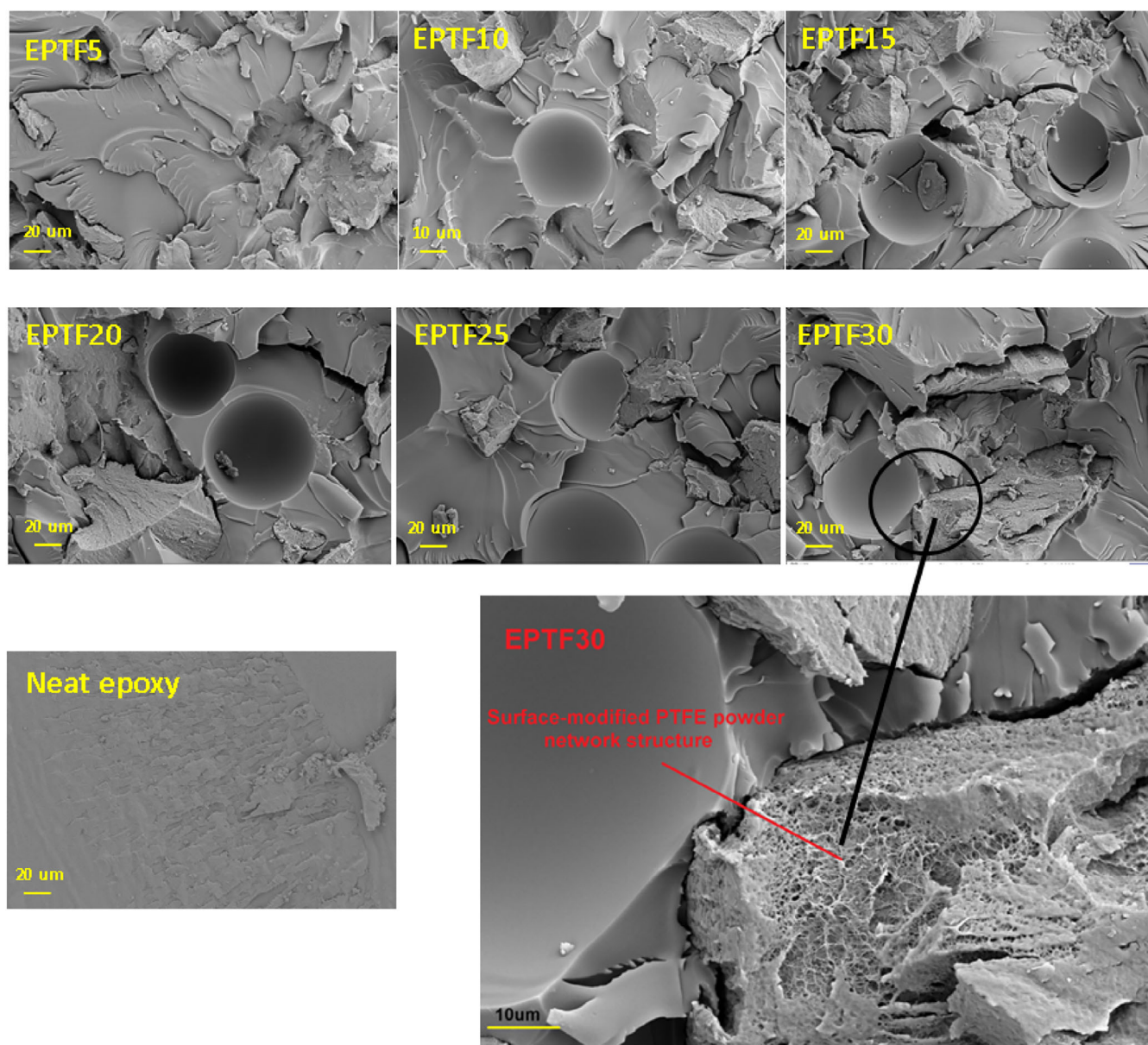


FIGURE 15 Fracture surfaces of the surface-modified poly (tetrafluoroethylene) (PTFE)-filled epoxy composites and the network and spongelike structure of the surface-modified PTFE powders in EPTF30. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/terms-and-conditions)]

powders. Besides, these nodular shapes were also observed in the worn samples. The morphologies of the filled composite samples in Figure 15 seemed to indicate a ductile fracture surface that could be attributed to strong interfacial bonding between the matrix and the surface-modified PTFE powders, while the pure epoxy had a brittle fractured surface.^{50,51} In addition to these, the surfaces of the PTFE powders treated by the Na-naphthalenide system could be a network or spongelike structure as shown in the view of EPTF30 in Figure 14. It is known that PTFE surfaces that are highly modified with a Na-naphthalenide system present spongelike or network structure morphologies.^{34,49} It was thought that the behavior of these network or

spongelike structures on the surfaces of the surface-modified PTFE powders could have increased the adhesion strength and compatibility between the epoxy resin matrix and the powder fillers.

The PTFE powders that were surface-modified with the Na-naphthalenide system provided striking and motivating results for researchers to prepare novel polymer-based composites filled with these surface-modified PTFE powders. This is because the functional groups that are formed on the powder surface such as OH, carbonyl groups, and C=C unsaturation points are highly suitable for obtaining strong interactions between different phases. Moreover, it was thought that this spongelike or

network structure on the surfaces of the modified PTFE powders could provide high interfacial strength and compatibility between the epoxy resin matrix and the powder fillers. It was also considered that these behaviors could affect the mechanical properties of the composites filled with the surface-modified PTFE powders very positively.

Epoxy-based composite materials have a potential for use in load-bearing applications in various industries such as the automotive, aerospace, construction, oil and gas, and marine industries because of their low cost, good mechanical properties, high specific strength, super adhesiveness, as well as good heat and solvent resistance.⁶² They can be used as both bulk and coating materials. They can also play an important role as a coating application for the protection of steel exposed to harsh service environments from wear, besides as bulk materials. For this reason, it is necessary to improve the impact resistance, wear resistance, and mechanical properties of these materials without losing or by increasing their favorable thermal properties.³² Additionally, a high glass transition temperature is a very important property for the material to not lose its mechanical properties when exposed to heat resulting out of long-term wear or operating temperatures. For example, Shen et al.⁵⁰ prepared PTFE-filled epoxy composites with a high concentration of SiO₂ particles. They achieved improved wear properties close to the properties of plain bearings. EPTFs in our study also had favorable wear properties like those reported by Shen et al.⁵⁰ They also showed significant improvements in terms of mechanical properties and impact resistance. Therefore, it is thought that these materials can be important candidates for materials to be used in load-bearing applications in most sectors. In fact, it is thought that if this surface-modified PTFE powder is used as a hybrid with any hard filler such as Si₃N₄, SiO₂, Al₂O₃, and TiO₂ particles, more advanced epoxy composites can be obtained. This powder may be an important candidate for plain bearing materials. Furthermore, continuous fiber fabric-reinforced surface-modified PTFE-filled epoxy composites may be an important research field for critical applications in the aerospace and automobile sectors that require more enhanced mechanical properties and impact resistance in the future. The surfaces of different PTFE-based filling or reinforcement materials such as PTFE fibers can be chemically treated by this Na-naphthalenide system in the future. It is thought that composites with improved results can be obtained with PTFE fibers that are surface-modified by this Na-naphthalenide system. It is known that the surfaces of PTFE fibers can be endowed with functional groups by polarization methods. For instance, Huang and Tseng⁶³ modified the surfaces of PTFE fibers with plasma and improved the compatibility between PTFE and POM.

It is expected that the surfaces of PTFE fibers to be treated by the Na-naphthalenide system in this study will be an attractive research topic for researchers.

4 | CONCLUSION

This study focused on the enhancement of the impact strength, wear resistance, mechanical properties, and thermal properties of epoxy using surface-modified PTFE powders. This was because these multi-featured epoxy composites can be used as materials in load-bearing applications. For instance, plain bearings can be some of the important application areas for the composites that were prepared in this study with improved mechanical properties, wear resistance, impact resistance, and thermal properties. Additionally, it is thought that using hybrid fillers with these surface-modified PTFE powders such as Si₃N₄, SiO₂, Al₂O₃, and TiO₂ or continuous fiber fabric in epoxy systems can provide important composite candidates for bearing and bushing systems or other applications in the future. PTFE is also known for its high flame retardancy. In addition to these features, it is thought that its high flame retardancy property will further expand the application areas of surface-modified PTFE-filled composites and give them a privilege. To prepare these multi-featured epoxy composites, surface-modified PTFE powders were incorporated into diglycidyl ether of bisphenol-A-based epoxy at various ratios, 5%, 10%, 15%, 20%, 25%, and 30%. A Na-naphthalenide system was used to modify the surfaces of the PTFE powders, and functional groups such as OH groups, carbonyl groups, and C=C unsaturation points were formed on the surfaces of the PTFE powders. Moreover, the sponge-like or network structures on the surfaces of the PTFE powders were obtained by the treatment process that included the Na-naphthalenide system. At the same time, the surface-modified PTFE powders treated by the Na-naphthalenide system used as a filler material for an epoxy matrix for the first time in the literature. As a result of this modification, high degrees of compatibility and strong adhesion properties between the particles and the matrix were obtained. The increases in strength, modulus, and impact resistance values can be attributed to these functional groups such as OH groups, carbonyl groups, and C=C unsaturation points, as well as the spongelike or network structures on the surfaces of the PTFE powders. According to the results of this study, the epoxy samples into which PTFE powders whose surfaces were modified using a Na-naphthalenide system were incorporated exhibited improved mechanical, wear, and thermal results. All samples showed improved properties compared to the neat epoxy. Considering all these properties,

EPTF10 and EPTF30 provided more favorable results. The ultimate tensile and flexural strength values of EPTF10 were 22.8% and 77.2% higher, respectively, compared to those of the neat epoxy. Moreover, the flexural and tensile modulus values of EPTF10 showed increases at rates of 33.2% and 18.9%, respectively. The ultimate tensile and flexural strength values of EPTF30 showed increases at rates of 18.7% and 63.8%, respectively. Furthermore, the flexural and tensile modulus values of EPTF30 showed increases at rates of 17.6% and 18.9%, respectively. In addition to these improvements, the impact resistance values of EPTF10 and EPTF30 improved by 76.4% and 95%, respectively. The T_g and heat deflection temperature values of the surface-modified PTFE-incorporated epoxy samples were also substantially enhanced, as expected. While EPTF10 and EPTF30 showed increases in T_g values at rates of 100% and 80.5%, they had increases in heat deflection temperatures at rates of 60% and 53%, respectively. Besides these improvements, the wear rates of all surface-modified PTFE-incorporated epoxy composites decreased substantially despite the decrease in the quantity of fluorine atoms on the polymer surface according to the XPS results. This is also valuable information for designing new materials that include PTFE powders that are surface-modified by a Na-naphthalenide system.

AUTHOR CONTRIBUTIONS

Emre Akin: Conceptualization (lead); data curation (lead); methodology (lead); writing – original draft (lead); writing – review and editing (lead). **Mustafa ÇAKIR:** Formal analysis (lead); supervision (equal). **Halil Demirer:** Project administration (lead).

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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