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Studies on thermal and mechanical behavior of nano TiO_2 - epoxy polymer composite

J. S. Sagar[a], G. M. Madhu[a], Jammula Koteswararao[a,*], Pradipkumar Dixit[b]

[a]*Department of Chemical Engineering, M. S. Ramaiah Institute of Technology, Bangalore 560054, India*
[b]*Department of Electrical and Electronics Engineering, M. S. Ramaiah Institute of Technology, Bangalore 560054, India*

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Abstract

The present study purposely is to study the properties of TiO_2-epoxy composites. TiO_2 was synthesized using the peptization and hydrolysis method and the synthesized powder is in anatase form. The present work aimed to develop the low TiO_2 filler epoxy composites for the improved thermal and mechanical properties. The synthesized TiO_2 was used as a filler along with epoxy composite and the epoxy - TiO_2 nanocomposites were fabricated using the low filler concentration of 0.5, 1.0, 1.5, 2.0, and 2.5% by weight. The glass transition temperature (T_g), regardless of the nanoparticles, was almost the same at 71.23°C. Tensile strength was maximum at 0.5%wt.; further increase in filler loading resulted in a linear reduction of tensile strength. Tensile modulus increased linearly and was found to be maximum at 2.5wt%. Meanwhile, compressive strength was maximum at 0.5%, and compressive modulus increased with filler increase. The present work mainly aimed to develop low filler concentrations

Keywords: Epoxy polymer; titanium dioxide; composites; nanofillers; peptization and hydrolysis method; mechanical properties

1. Introduction

Polymer nanocomposites have emerged as a new class of materials for various applications in construction materials, catalysis, flexible electronics, coatings, or dressings. [1-4]. Due to the incorporated nanoparticles, they show tremendous improvement in their overall properties compared to those without nanoparticle doping [5,6]. These high-performance materials have been proved to resist deterioration arising due to thermal and electrical stress [7,8].

It is reported in literature that the increasing concern about polymer nanocomposites has improved electrical insulating behaviors [9-11]. Epoxy resins are one of the important and widely used thermosets in view of their high strength and good cross-linking and applicability in various applications. Epoxy-based nanocomposites have been reported to demonstrate appreciable thermo-mechanical and dielectric parameters - even with the low concentrations of nanoparticles [11-18]. They are employed for electrical insulations in power requirements such as dry-type transformers and rotating machines, printed circuit boards and generator ground wall insulations systems. The permittivity values of epoxy-based nanocomposites have been proven to significantly decrease a wide range of frequencies, and this trend was mainly dependent on the type and size of the incorporated nanoparticle. Various fillers such as SiO_2, Al_2O_3, TiO_2, MgO, fly ash, and clay with low concentrations in the base matrix have improved mechanical, thermal, and electrical insulating properties [19-22] of the various nanoparticles used for high voltage insulation applications, TiO_2 nanoparticles are worth mentioning due to their versatile properties including high thermo-mechanical stability, wear resistance, corrosion resistance and wide bandgap. With the right filler concentration in the base matrix, these composites are capable of producing the excellent breakdown strength and lowering dielectric conductivity and permittivity.

From the literature, it is observed that researchers worked on TiO_2- epoxy loading with very high weight percentages with procured TiO_2. In the present work, an attempt was made to synthesize Nano TiO_2 – epoxy composites and explore their various properties. Nano TiO_2 was synthesized using the peptization and hydrolysis method. Microstructural changes in the nanocomposites were The Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), and X-ray Diffraction Analysis (XRD). The nanocomposites were subjected to tensile and compression tests to investigate their mechanical stability. Thermal properties were evaluated *via* thermogravimetric analysis (TGA). The effect of nanofiller loading on mechanical properties of nanofiller was studied.

2. Materials and Methods

2.1. Reagents and materials

The epoxy resin Lapox L-12, and hardener Lapox K-6 procured in the study were supplied by Yuje Enterprises,

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* Corresponding author. Tel.: +91 93530 23465;
Email: koteswararao@msrit.edu

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Bangalore, India. L-12 is a liquid epoxy resin of average viscosity that can be employed with many hardeners for manufacturing glass fiber reinforced composites. The hardener used was determined by the processing method and on the properties expected of the finished composite. Hardener K-6 was cured at room temperature and had a low viscosity. Being rather reactive, it had a small pot life and would rapidly cured at ambient temperatures. Titanium(IV) isopropoxide (TTIP), Iso-propanol and NH_4OH used in the study were the AR grade and were procured from Sigma-Aldrich, Bangalore, India.

2.2. Synthesis of TiO_2 nanoparticles

TiO_2 nanoparticles were prepared by peptization and hydrolysis method [23]. A mixture of 5 ml Titanium (IV) isopropoxide (TTIP), and 15 ml isopropanol was mixed at room temperature. A 250 ml solution of distilled water with various pH (9, 10) was used as the hydrolysis catalyst. The desired pH was adjusted by adding NH_4OH. The gel preparation started when both the solutions were mixed. A turbid solution was obtained when heated at 60°C for 18 hours. The prepared precipitates were washed with ethanol and dried for 2-3 hours at 100°C. Finally, the prepared powder was annealed at a temperature of 800°C for 2 hours.

2.3. Preparation of Nano TiO_2 – Epoxy Composites

At various weight %, TiO_2 nanoparticles were added to the epoxy prepolymer (with a particle content of 0.5, 1.0, 1.5, 2.0, and 2.5% by %wt) and subjected to mechanical stirring for 20 minutes. This solution was then sonicated for 40 minutes to obtain a uniform distribution of nanoparticles in the epoxy matrix. After obtaining a uniform solution, the mixture was cured at room temperature and 10% by volume of hardener was added. The as-prepared solution was poured into a suitable mould coated by Teflon sheets and was allowed to cure for 24 hours. The composite laminates of dimensions 150×200×3 mm thick were made [24]. Table 1 presents the laminates of various %wt. of TiO_2 changed compositions, the mass of epoxy, hardener, and TiO_2 filler used.

Table 1. Composition of epoxy, hardener and TiO_2 nanoparticles used for the synthesis of polymer composites

Sl. No.	Wt. of Epoxy (g)	Wt. of Hardener (g)	Wt. of TiO_2 (g)	%Wt. of solution
1	115	10.05	-	0
2	115	10.05	0.63	0.5
3	115	10.05	1.27	1.0
4	115	10.05	1.91	1.5
5	115	10.05	2.56	2.0
6	115	10.05	3.21	2.5

2.4. Characterization techniques used

The synthesized nanocomposite materials were evaluated for their material properties using various characterization techniques such as X-Ray Diffraction (XRD - Bruker D-8; X-ray source: Ni-filtered Cu-Ka radiation (40 kV, 30 mA), X-ray diffraction recorded in the range of 10 – 80° at a speed of 8° per min.), Scanning Electron Microscope (SEM, Carl Zeiss Ultra 55 Model), Fourier-transform infrared (FTIR) spectroscopy (wavenumber range: 4000-500 cm^{-1}, Bruker Alpha FTIR, Speed - 4 cm^{-1}) and Simultaneous Thermal Analyzer – TGA (Model: STA 449 F5 Jupiter; Make: NETZSCH, Geratebau GmbH; Range: 100 to 800°C). The fabricated pristine epoxy and epoxy – TiO_2 nanocomposite were tested for mechanical properties using a universal testing machine (KIPL-PC 2000 UTM; test speed of 5 mm/min; load cell: 20 kN). Meanwhile, the tensile and compressive strength curves were measured from the UTM. The prepared nanocomposites were 2.5 - 3 mm thick and widths in the range of 17–20 mm. The testing machine had an error range of ±0.2 MPa.

3. Results and Discussion

3.1. X-ray diffraction analysis

Figure1 present the XRD profile of TiO_2 nanoparticles [25] showing the strong peaks at 25.47, 30.92, 38.05, 47.99, 54.71, 62.83, 69.71 and 75.44° corresponding to (101), (001), (004), (200), (211), (204), (116) and (215) planes. The peaks agreed with the standard diffraction data of JCPDS No.: 89-4921 reference card [26,27].

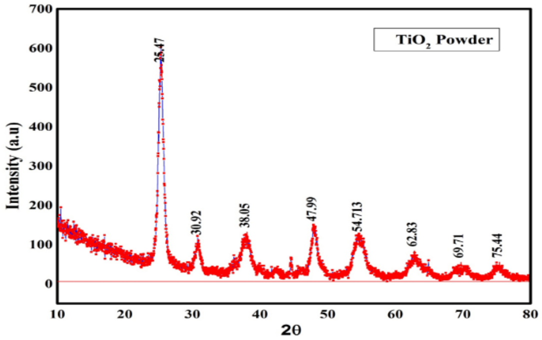

Fig. 1. X-ray diffraction profiles of (a) pure TiO_2

From the XRD it was confirmed that the synthesized TiO_2 is in the anatase phase. The XRD revealed the slightly amorphous nature of epoxy and its profile as presented in figure 2(a). XRD patterns of epoxy – TiO_2 nanocomposites with various concentrations 0.5, 1.0, 1.5, 2.0 and 2.5% %wt. of TiO_2 correspondingly, are displayed in figure 2. All the nanocomposites exhibited a peak at around $2\theta = 19.5^o$ corresponding to (001) crystal plane for epoxy polymer, showing the semi-crystalline nature of epoxy. However, after incorporating the TiO_2 nanofillers, few peaks were observed around 25 and 48°. With the increase in the weight percent of TiO_2 nanoparticles incorporation, these peaks' intensity has increased, whereas the broad peak of the PVA polymer has decreased. It can also be deduced from these observations that there was no structural and phase manipulation.

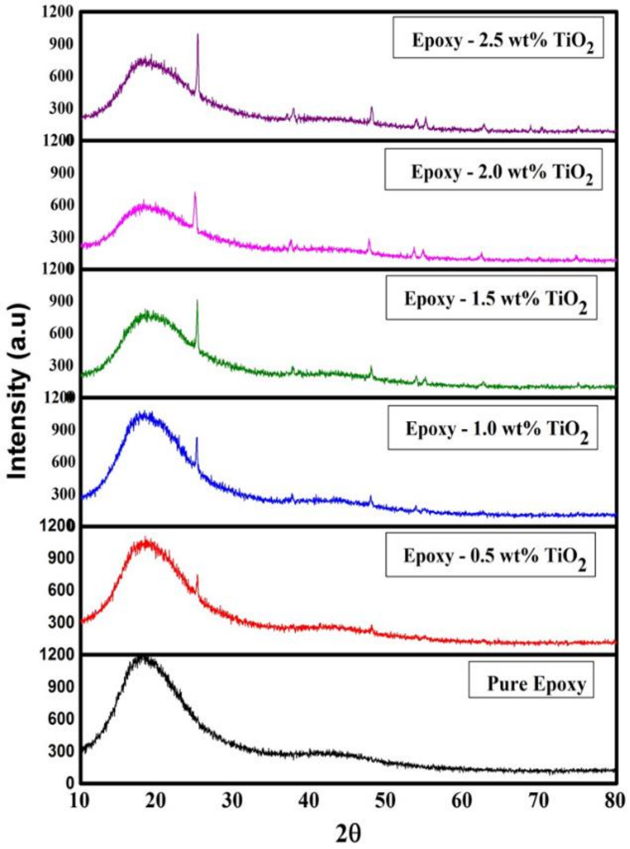

Fig. 2. X-ray diffraction profiles of (a) pure epoxy, (b) epoxy-0.5%wt. TiO_2, (c) epoxy-1.0%wt. TiO_2 (d) epoxy-1.5%wt. TiO_2 (e) epoxy-2.0%wt. TiO_2 and (f) epoxy-2.5%wt. TiO_2

3.2. SEM Analysis

Figure 3 presents the SEM images of Nano TiO_2 and Nano TiO_2 - epoxy composites. In an epoxy polymer, homogeneous dispersion of nanofillers is one of the main challenges in constructing nanocomposites [28]. The epoxy polymer's thermal and mechanical properties would be affected by the agglomeration of nanofillers (typically in micro-meter size clusters). From SEM images, it can be seen that uniform dispersion was attained. This study indicated that the casting method can efficiently disperse the Nano TiO_2 particles into the polymer matrix and avoid the accumulation of TiO_2 nanoparticles. It was observed that no agglomeration of TiO_2 nanoparticles, similar at. The SEM images of TiO_2 nanoparticles presented in figure 3(a) showed spherical shapes with a mean particle size of around 51 nm and diameter of largest particles around 60 nm. The cross-sectional SEM images for various loadings of TiO_2 is shown in figure 3(b) to figure 3 (g). From the SEM images, it can be seen that there was a uniform distribution of filler at 0.5% (figure 3(b)). With the increase in filler loading there was an increased agglomeration (figure 3(c)) to figure 3 (e)). The increased agglomeration then affected the mechanical properties of composites.

3.3. Thermal properties

The synthesized were tested for nano TiO_2 - polymer composites glass transition temperature (Tg) and degradation temperature. The highest T_g value was observed for pristine epoxy (71.23°C) with addition of TiO_2 nanoparticles no much deviation was observed. The resulting trend might be due to the poor dispersion of the nanoparticles in the epoxy matrix. The T_g value of a polymer closely relates to its cross-linking density and the degree of polymer chain motion. The incorporation of TiO_2 nanofillers might obstruct epoxy's curing process, resulting in a stoichiometric imbalance of the polymer. This generally leads to low cross-linking, which lowers the T_g. The might the aggregation of fillers in the polymer matrix reduces the filler-resin interface and creates unnecessary free volume promoting segmental chain motion. This phenomenon has been observed in earlier studies dealing with epoxy composites [29,30]. The TGA thermograms of the nanocomposites are presented in figure 4. T_{onset} is taken as the onset of degradation (weight loss), and its values can be seen in the inset figure. From figure 4, it can be concluded that the epoxy systems underwent multi-step thermo-oxidative degradation with a maximum amount of weight loss occurred between 250 and 450°C. The T_{onset} after incorporation of 0.5 wt.% TiO_2 increased by 24 %, improving the thermal stability of the nanocomposite; however, further increase in the nanoparticle wt.% decreased in onset temperature of degradation. This results in anomalous trend resulted in the irregular dispersion and aggregation of nano TiO_2 in the polymer matrix. Although the T_{onset} values of nanoparticle incorporated composites were higher than the T_{onset} of pristine epoxy, it seemed to be no obvious trend. The multistage thermo-oxidative degradation of epoxy systems has been reported in previous studies [31]. It is reasoned that several complex chemical reactions involving epoxy chains, such as aromatization and dehydrogenation of alkyl groups occurred [32]. Incorporating inorganic fillers tends to delay the volatilization of several by-products originating during thermal decomposition, thus giving a way to multistage degradation.

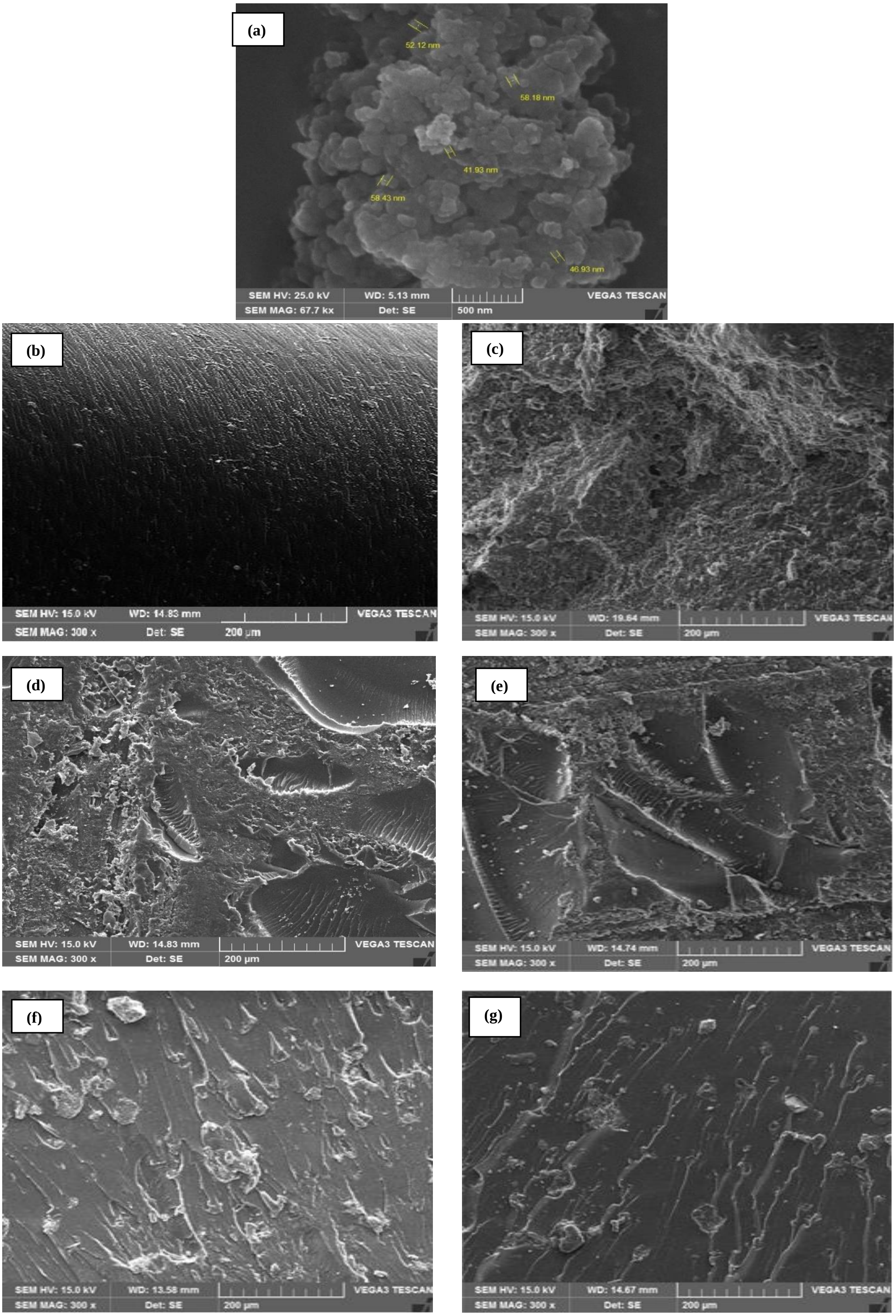

Fig. 3. SEM images of (a) TiO_2 powder and various concentrations of TiO_2 nanofiller (b) Pure Epoxy (c) 0.5 (d) 1.0 (e) 1.5 (f) 2.0 and (g) 2.5 %wt. of nanoTiO_2-epoxy composites

Table 2. Tensile properties of nanocomposites synthesized

% of TiO_2	Width (mm)	Thickness (mm)	Tensile strength (N/mm^2)	Tensile Modulus (N/mm^2)
0	16.2	4.82	6.8	159
0.5	16.3	2.71	14.0	241
1.0	17.1	2.4	12.6	287
1.5	19.1	2.6	5.8	295
2.0	14.12	2.14	4.2	308
2.5	16.32	3.23	5.4	323

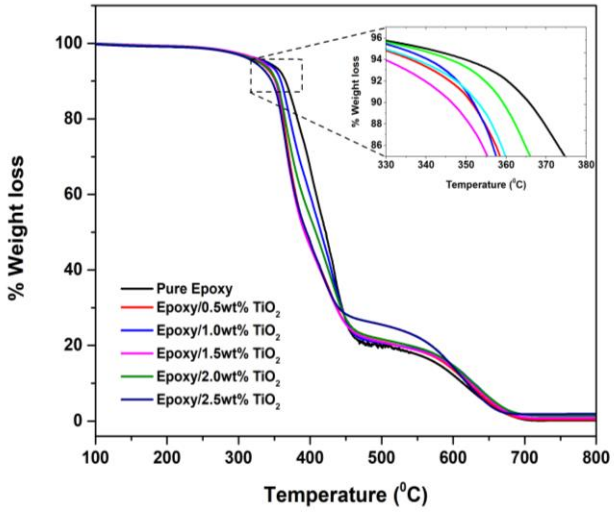

Fig. 4. Thermogravimetric analysis of epoxy and epoxy-TiO_2 nanocomposites

3.4. Mechanical properties

The mechanical properties were tested using UTM and the results for tensile and compressive strength were tabulated in table 2 and table 3, respectively. The tensile and compression strengths were measured in the Energy and Research Institute (TERI), Bangalore and the results were represented in figure 5, figure 6, figure 7 and figure 8. The effect of filler concentration in the polymer matrix was studied for mechanical properties. The effect of titanium dioxide filler on tensile properties of polymer matrix composite was studied for 0 to 2.5 %wt.

Figure 5 illustrates effects of TiO_2 loading on tensile strength with epoxy-TiO_2 nanocomposites. From table 2, it can be observed that by adding of nanofiller, the tensile strength values enhanced substantially and confirmed an increase of 51% for 0.5 wt.% TiO_2 of nanocomposite compared to pure epoxy. The good interfacial tension between TiO_2 and epoxy matrix at 0.5 wt.% might have probably been attributed to an increase in the tensile strength values. A further increase in the filler loading resulted in decreased tensile strength. The dispersion of nanofillers affected the mechanical properties of the composites. They found that the good dispersion of filler in the polymer composites exhibited a higher tensile strength. Tensile strength tended to decrease with the increase in filler concentration due to the agglomeration. This indicated that the polymer matrix-nanofiller interface is more effective than the pristine polymer, showing greater intensity associated with the original polymer.

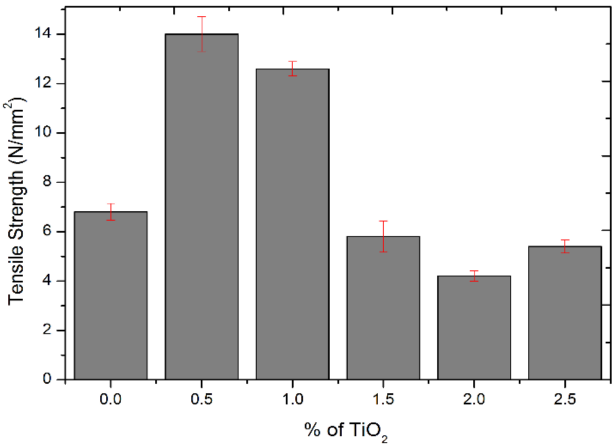

Fig. 5. Tensile strength of epoxy-TiO_2 nanocomposites at different concentrations

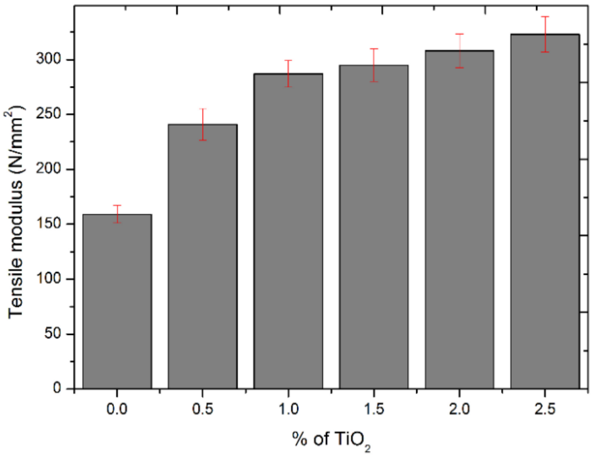

Fig. 6. Tensile modulus of Epoxy-TiO_2 nanocomposites at different concentrations

Figure 6 illustrates a change of tensile modulus with epoxy-TiO_2 nanocomposites. The tensile modulus increased linearly with the increase in filler concentration, and the same is represented in table 2 and figure 6. The highest tensile modulus was observed at epoxy-2.0 %wt. TiO_2. Incorporation of nanoparticles in the epoxy matrix, which enhanced the stiffness of the epoxy composite. This indicated that the polymer matrix-nanofiller interface was extremely effective and has shown greater intensity associated with the original polymer [24,33].

The effect of filler loading on the compressive strength of epoxy polymer is presented in table 3 and figure 7. It was observed that epoxy-0.5 %wt. TiO_2 nanocomposite had greater compressive strength than the pristine epoxy. The epoxy-0.5 %wt. TiO_2 nanocomposite reported an enhancement of around 10% in compressive strength. The compressive strength reduced linearly with the increasing nanofiller loading. This may be due to the release of free radicals during the homo-polymerization between epoxy and nanofiller loading, leading to the weak interactions between the epoxy matrix and nanofiller. The linear decrease in compressive strength above 0.5 %wt. TiO_2

was due to the agglomeration of the TiO_2 nanoparticles [5,33].

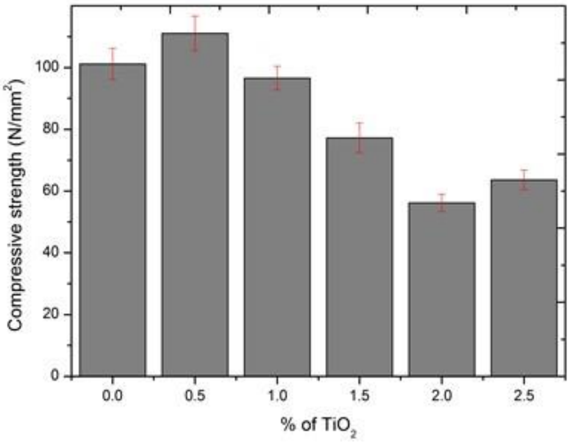

Fig.7 Compressive strength of epoxy-TiO_2 nanocomposites at different concentrations

Table 3. Compressive properties of nanocomposites synthesized.

% of TiO_2	Width (mm)	Thickness (mm)	Compressive Strength (N/mm^2)	Compressive Modulus (N/mm^2)
0	16.2	4.82	101.2	3698
0.5	16.28	2.71	111.1	4034
1.0	17.1	2.4	96.6	4329
1.5	19.1	2.6	77.2	5303
2.0	14.12	2.14	56.2	5360
2.5	16.32	3.23	63.6	5905

Figure 8 illustrates a variation of compressive modulus with epoxy-TiO_2 nanocomposite. An increase in filler loading epoxy-TiO_2 nanocomposite has shown a greater compressive modulus than the pristine epoxy. The epoxy-2.0 %wt. TiO_2 nanocomposite reported an enhancement of around 60% in compressive modulus. It was observed that compressive modulus increased with enhanced TiO2 loading.

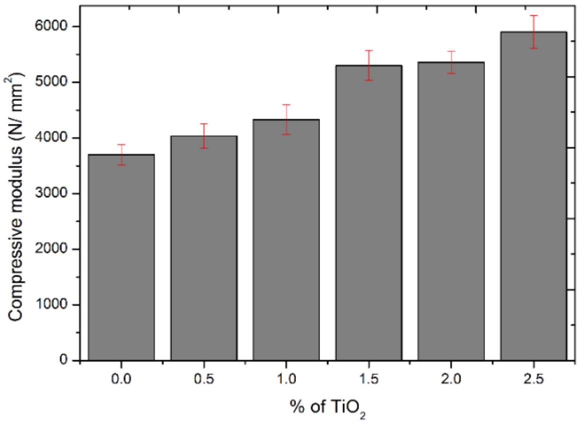

Fig. 8. Compressive modulus of Epoxy-TiO_2 nanocomposites at different concentrations

4. Conclusions

The present work is aimed at synthesis of TiO_2 nanoparticles and incorporating same in Epoxy. TiO_2 was synthesized using peptization and hydrolysis method. The epoxy-TiO_2 loading 0.5, 1.0, 1.5, 2.0 and 2.5 %wt. was synthesized. The ultrasonication method was employed to obtain a uniform distribution of the nanoparticles in the epoxy matrix. XRD confirmed the incorporation of TiO_2 nanofillers, whereas SEM images showed the presence of spherical shape particles without agglomeration 0.5% with the increases in TiO_2 loading there were some increases in agglomeration and the same conformed using SEM and thermal analysis. The UTM analysis found that tensile strength was maximum at 0.5 %wt. of TiO_2 filler loading of filler. The tensile modulus values increased as the percent of filler loading increased. The compressive strength was initially increased but gradually decreased as filler concentration increased. Whereas compressive modulus of the epoxy composites increased linearly with nanoparticle concentration in the matrix. The maximum tensile strength and compressive strength were attained for epoxy - 0.5 wt.% TiO_2, as compared to original epoxy. The highest tensile modulus and compressive modulus was observed for a nanocomposite with epoxy-2.5 %wt. TiO_2, as compared other loadings and pristine epoxy. TGA analysis showed the maximum amount of weight loss occurred between 250 and 450ºC. The T_{onset} increased by 24% with incorporation of 0.5 % wt. TiO2, resulted in higher thermal stability of nanocomposites; however, further increase in nanoparticles loading resulted in decreased onset temperature of degradation.

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