Chapter 5

A Case Study: Particulate-Filled Polyester Hybrid Laminated Composites

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Abstract

The aim of this work was to develop the novel glass fiber–reinforced polyester hybrid composites (PHCs) filled with micro-sized titania (TiO_2) particles and investigate their functional, mechanical and thermal behaviors. To equip PHCs of unsaturated polyester resin (UPR) with multifunctional characteristics, TiO_2 particles (1–5 wt.%) were dispersed with high disperser homogenizer using hand lay-up process (HLUP), combined with compression molding technique (CMT). The interactions (cross linking and hydrogen bonding) between polymeric chains, styrene, silica contents of glass fiber and TiO_2 particles in PHCs were confirmed by Fourier transform infrared spectroscopy (FTIR). The mechanical and thermal properties increased brilliantly by potential utilization of TiO_2 particles. The 3 wt.% of TiO_2-imbedded PHCs showed remarkable progress in tensile strength (46 MPa) as well as tensile modules (2.9 GPa) relative to unloaded PHCs. The 5 wt.% of TiO_2-imbedded PHCs showed 61 and 64% increase in impact energy and hardness, respectively. Thermo-gravimetric analysis (TGA) showed that controlled PHC-0 had the mass loss up to 50%, which was restricted to 17% by using TiO_2 particles for PHC-5. Hence, it was inferred that micro-sized TiO_2 was encouraging filler for incremental valuation in functional, mechanical and thermal characteristics of PHCs. After finding the marvelous mechanical and thermal properties of PHCs, it is endorsed that these polyester composites can be tested for high strength and high temperature applications.

Keywords: hybrid composites, polyester, titania, functional, thermal, mechanical, cross linking, hydrogen bonding

1. Introduction

Composite material is a blend of at least two components having distinguishable interfaces at point of their junction, to make one macroscopic material. One component is matrix (transmitter), which transfers the load while, other is reinforcement (carrier) that bears the same load. Wood is a natural composite, where lignin (matrix) transmits the load and cellulose (reinforcement) bears stress [1]. Polymer matrix composites (PMCs) are polymer based, where thermoplastic or thermosetting polymers are responsible for matrices and continuous fibers, discontinuous fibers, chopped fibers or fillers (organic/inorganic) are performing as reinforcements [2]. If there are at least two different matrices and single reinforcement or vice versa, these composites are called hybrid composites. Fiber reinforced polymer composites comprise continuous or discontinuous fibers, woven or non-woven fiberics (carbon, glass or Kevlar fiber) as reinforcing phase in polymer resin matrices, are the largest manufactured category of the PMCs [3].

The durability problems related with traditional materials, the needs of higher speeds of construction and increasing functionality demands led to fiber reinforced polyester composites (FRPCs) with higher specific strength, light weight, environmental and corrosion resistant and requiring less maintenance during their service life. FRPCs are basically comprised by a fibrous reinforcement (usually glass, carbon or aramid fibers) embedded in a polyester matrix. These materials have applications in construction, marine, aerospace, automotive and sports industries [4, 5]. Owing to their high in-plane tensile properties, superior receptiveness to impact damage, poor interlaminar properties and compression molding are of foremost issues [6]. To solve these impediments, further research work is required. Particulate-imbedded FRPCs also called polyester hybrid composites (PHCs), with better properties by inclusion of inorganic filler in polyester matrix, is an imperative method to dig out material issues [7], even though several metal oxides are discussed in literature like zirconium oxide, zinc oxide, aluminum oxide, silicon oxide and cerium oxide [8]. However in recent era, titanium oxide/titania (TiO_2) has gained much attraction as inorganic phase for the preparation of PHCs [9], due to its specific properties like photocatalytic, high refractive index and UV radiation absorption that can used to develop new functional organic-inorganic materials [10].

A broad spectrum of polymer matrices are available; polyester, polyimide, polysiloxane, vinyl ester, epoxy, polydimethylsiloxane but unsaturated polyester resin (UPR) is more frequent due to its superior mechanical properties, good process ability and low cost [11]. To dissolve polyester, styrene is mostly used in industry. Styrene containing polyester has relatively low viscosity and can wet the glass fibers properly. The properties of glass fiber like, high electrical and corrosion resistance with good dimensional stability are responsible for its use as reinforcement in FRPCs [12]. Additionally, styrene can crosslink with –C=C– bond of different polyester chains resulting in improved thermal and mechanical properties [13].

The association of inorganic fillers in FRPCs contributes to reduce the void contents by lowering polymerization shrinkage resulting higher mechanical and thermal properties and fillers also increase the viscosity of the matrices leading good handling during fabrication processes. Ferreira et al. studied thermal stability of an aluminized E-glass fiber/unsaturated polyester composites compared to un-metallized E-glass/polyester composites and unreinforced polyester. The residue

content of the aluminized E-glass fiber reinforced composites was greater than that of unmetallized E-glass fiber composites by nearly 26 and 658% than the unreinforced polyester [14].

The main focuses of this chapter, were the fabrication of polyester hybrid composites (PHCs) using unsaturated polyester resin (UPR) with woven E-glass fiber sheets and micro-sized TiO_2 particles by hand lay-up process (HLUP) and compression molding technique (CMT), and investigating their functional, mechanical and thermal properties for high strength and high temperature applications.

2. Fabrication of polyester hybrid composites

The unsaturated polyester resin (pre-polymer of maleic anhydride and propandiol) with average molecular weight (Mw = 1500 g/mol) having of 40 ± 2% styrene content and inhibitor hydroquinone (150–200 ppm) was obtained from local commercial market. Cobalt-naphthenate (CN) as an accelerator and methyl-ethyl-ketone-peroxide (MEKP) as curing agent was acquired from Fluka Co. E-glass fiber roving strand mat used was acquired from Toray, Japan. Micro-TiO_2 particles (melting point ~1843°C and 4.23 g/cm^3 density) were purchased from Sigma Aldrich. Then micro-sized TiO_2 in predetermined weight concentrations (1–5 wt.%) were taken and dispersed in the UPR by a high speed mixer, run with 2000 rpm at 40°C for 2 h. The dispersions were cooled to room temperature following by the addition of catalyst MEKP (2 wt.%) and accelerator CN (1.5 wt.%) and then mechanical stirring for 2 min for uniform mixing of curing agent and accelerator. Unidirectional (1D) PHCs laminates were fabricated by a layer-by-layer impregnation using HLUP. Four individual sheets of cross plied woven roving E-glass fiber mat with dimensions (180 × 180 mm^2) were immersed in UPR dispersion for complete impregnation of TiO_2-imbedded UPR matrix including catalyst and accelerator, then stacked on one another by HLUP in compressed die of stainless steel (SS).

The whole assembly of PHCs laminates (along SS die) was kept in a High Temperature Melt Press (HTMP) under 5000 pounds (2.27 metric ton) at 75°C for 2 h for getting complete curing and uniform thickness and this technique called compression molding technique (CMT). Preparation of PHCs laminates was tricky practice so a plain geometry of SS was implemented for sampling. After molding in HTMP, the whole assembly of PHCs (along SS die) was cooled to room temperature at same pressure for avoiding thermal residual stresses. All PHCs were prepared with same number of fiber sheets with changing TiO_2 content from 1 to 5 wt.% and cut for different specimens using respective ASTM standards. **Table 1** shows the codes and compositions of PHCs and one thing should be noted here that we loaded TiO_2 content, MEKP content and CN content in matrix content to make total 100 percent weight of specimens. Schematic illustration of experimental set-up for fabrication of composites using hand lay-up process (HLUP) and compression molding technique (CMT) has shown in **Figure 1**.

2.1. Proposed scheme reaction for the fabrication of TiO_2-imbedded hybrid composites

During the synthesis of PHCs, H-bonding of TiO_2 and SiO_2 contents of glass fiber and cross linking of UPR is revealed with scheme reaction in **Figure 2** Polyester chains were cross-linked

Code names for HCs	Matrix content imbedded with TiO_2 (wt.%)	Fiber content (wt.%)	TiO_2 content in matrix (wt.%)
PHC-0	50	50	0
PHC-1	50	50	1
PHC-2	50	50	2
PHC-3	50	50	3
PHC-4	50	50	4
PHC-5	50	50	5

Table 1. Code names for PHCs specimens along with their matrix, fiber and titania compositions.

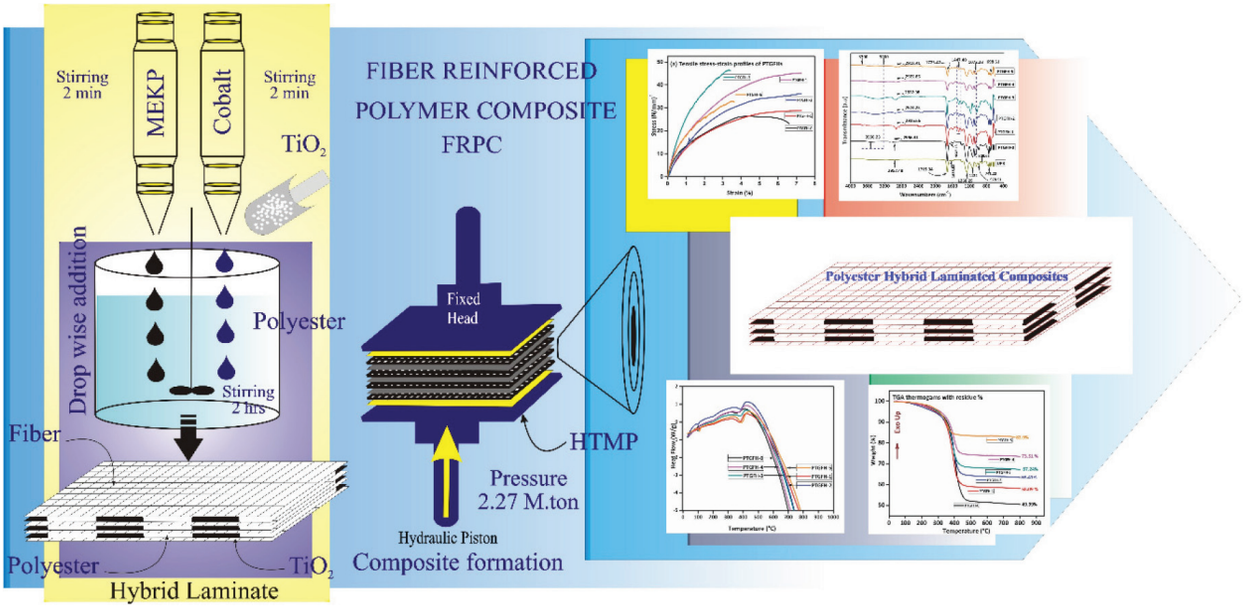

Figure 1. Schematic diagram of experimental set-up for fabrication of composites using hand lay-up process (HLUP) and compression molding technique (CMT).

with –C=C– bonds of styrene in the presence of cobalt naphthenate accelerator and MEKP catalyst. The three dimensional network of PHCs were fabricated resulting from cross linking (physical and chemical) between polyester chains, styrene, TiO_2 and SiO_2 content of glass fiber.

3. Investigation of functional, mechanical and thermal properties of PHCs

3.1. Functional testing

Spectra of PHCs were noted by Fourier transform infrared spectroscopy (FTIR) (IR Prestige-21 Shimadzu), using the attenuated total reflectance (ATR) accessary. The air background was taken before each test sample. The wavenumber range was used from 4000 to 500 cm^{-1} at resolution of 4 cm^{-1} and 100 scans per spectrum.

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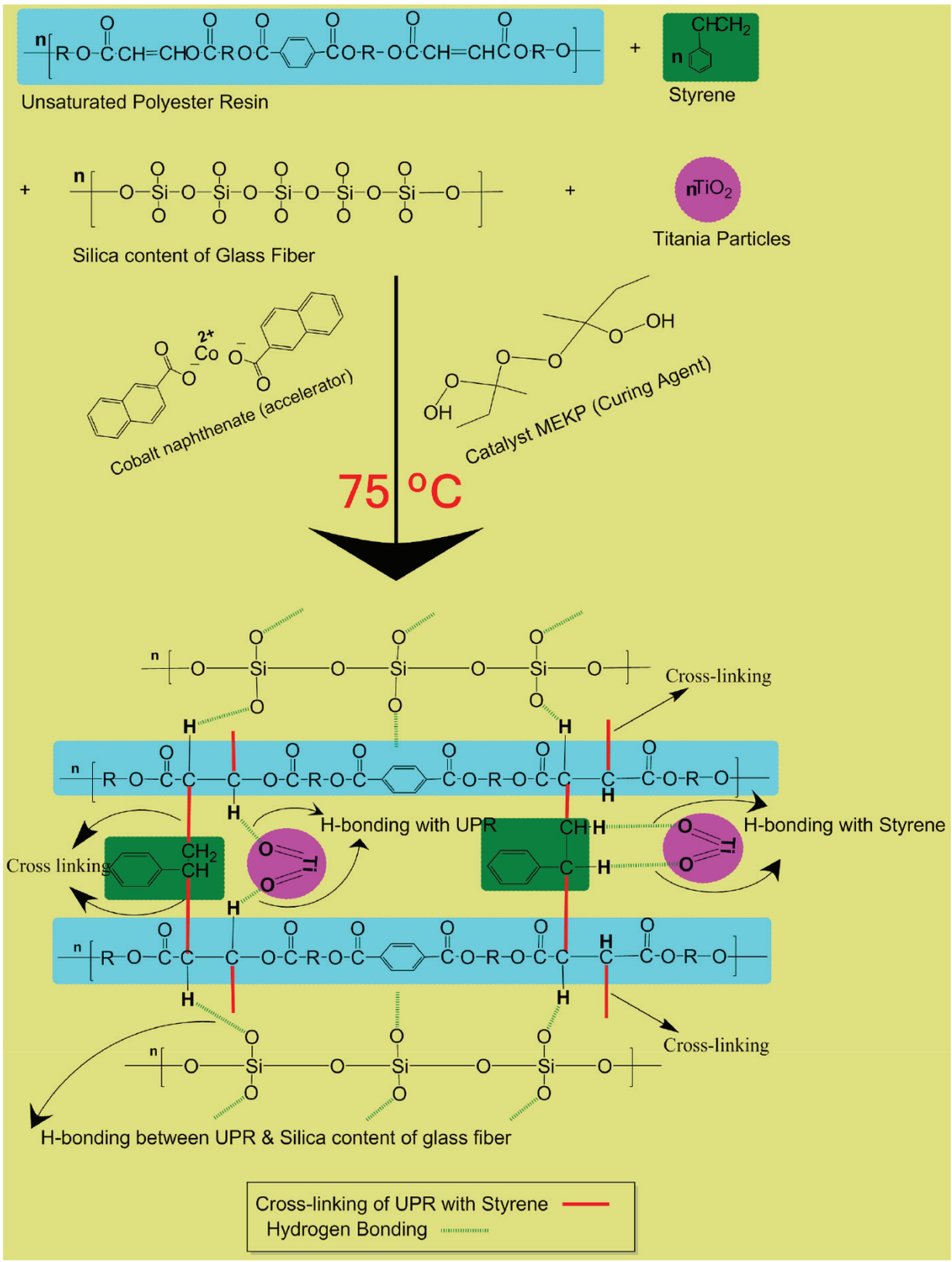

Figure 2. Proposed scheme reaction for the fabrication of TiO_2-imbedded hybrid composites in which green dotted lines (⋯⋯) show hydrogen bonding between TiO_2 particles, unsaturated polyester resin, styrene content of UPR, silica content of glass fiber and red solid lines (—) show cross linking of unsaturated polyester resin.

FTIR analysis (**Figure 3**) was based about confirmation of the functional groups of UPR, styrene, silica and titania with the shifting of peaks during H-bonding and crosslinking of UPR with styrene in the fabrication of PHCs. It was determined that the characteristics peaks of UPR: both unsaturated (–C=H) stretching vibrations at 2957 cm^{-1} and saturated aliphatic hydrocarbon (–C–H) stretching between 2957 and 2918 cm^{-1} and unsaturated aromatic out of plane bending deformation at 741 cm^{-1}. In UPR, there can be two or more different sources of aromatic moieties: usually from styrene and Phthalic anhydride. Most characteristics of FTIR spectra of UPR is the strong carbonyl (–C=O–) stretching band between at 1715–1723 cm^{-1} and the two other strong asymmetric bands characteristics for oxygen containing groups (–C–O–C– ester linkages) at 1260.29 and 1122 cm^{-1}. A weak stretching band at 1635 cm^{-1} and out of the plane bending at 978 cm^{-1} were ascribed to –C=C– group of polyester. The band at 698 cm^{-1} (–C–H– out of plane bending in benzene ring) and 909 cm^{-1} (–C=C– group) were typical of styrene. The –Si–O band in PHC-0 was at 1076 cm^{-1} which was shifted to 1072 cm^{-1} in PHC-5 due to hydrogen bonding with –CH group of polyester chain (as in scheme **Figure 2**). Ti–O–Ti stretching vibrations bands were observed at 1447 cm^{-1} in titania-imbedded PHC-1 to PHC-5 (no observed in UPR and PHC-0). The shift in the carbonyl group (–C=O–) from 1715 to 1723 cm^{-1} (from UPR to PHC-5) was due to the cross linking, which increased cross linking density in cured PHC-5 and lead to more brittle behavior during tensile testing. The consumption of styrene during curing process was followed by the disappearance of the peak at 909 cm^{-1} in cured PHC-1 to PHC-5. The consumption of C=C bond in UPR was followed by

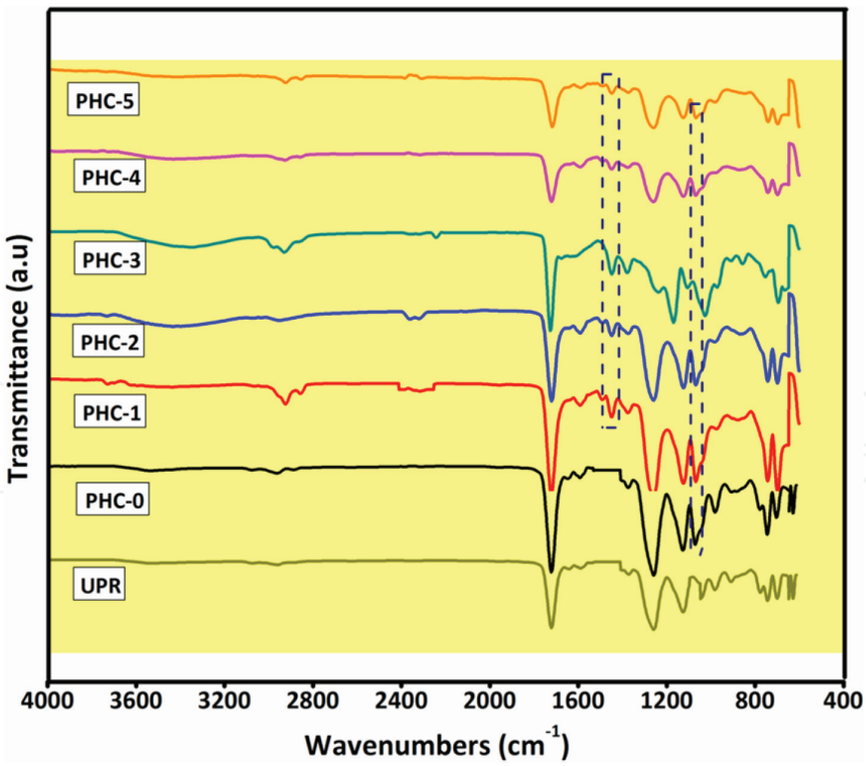

Figure 3. FTIR spectra comparison of cured UPR, controlled PHC-0 without TiO_2 particles and TiO_2-imbedded cured hybrid composites with their relative composition of TiO_2 particles; PHC-1 (1 wt.%), PHC-2 (2 wt.%), PHC-3 (3 wt.%), PHC-4 (4 wt.%) and PHC-5 (5 wt.%).

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the change in the peak area at 978 cm^{-1} in PHC-0 to PHC-3 and vanished up to PHC-5. The –CH stretching band at 2957 cm^{-1} became stronger as observed in cured PHC-0 (2956 cm^{-1}) which was shifted to 2918 cm^{-1} in TiO_2-imbedded PHCs, i.e., PHC-1 to PHC-5 and the shifting of –CH band to lower wavenumber due to H-bonding with the inclusion of silica and titania loading. The stretching band at 1635 cm^{-1} (UPR) was noted at 1645 cm^{-1} in cured PHC-0 and almost vanished in PHCs having concentration of TiO_2 from 1 to 5 wt.% (PHC-1 to PHC-5). This confirms the transformation of this group to alkane through cross-linking which is credited to the contribution of –HC=CH– functional group during curing method. The all spectrum of PHCs were differed from UPR especially in the region 3700–3200 cm^{-1} (most evidently at 3550 cm^{-1}), which were the frequencies associated with –OH stretching and had been almost continuous absorption of moisture from open air [15–17].

3.2. Tensile testing

Testometric universal testing machine (UTM), Model FS100 CT UK, with load cell (100 KN) was employed to evaluate the tensile properties under static force. PHCs specimens with end tabs for the evaluation of tensile behavior were prepared following the ASTM:D 3518-0 with dimensions (200 × 25 × 2.5 mm). The UTM was controlled at room temperature conditions at a speed of 2.0 mm/min. **Figure 4(a)** exhibited tensile stress–strain profiles which showed nonlinear strains with stress on applying force. That non-linearity and asymmetrical behavior was responsible for asymmetric fiber breaking during applied stress. **Figure 4(b)** and **(c)** showed that tensile strength (TS) and tensile modulus (TM) of PHCs increased with increasing TiO_2 contents up to maximum of 3 wt.% TiO_2, which were 46 MPa (TS) and 2.94 GPa (TM) followed decreasing trend beyond that limit. It noted that 3 wt.% TiO_2 was the optimal composition for better tensile properties of TiO_2-imbedded PHCs. The improvement in the tensile properties was the outcome of creation of chemical bonds at the interface between the PHCs and TiO_2 particles [18] and optimized compositions of polyester matrix, & TiO_2 particles were key parameter of marvelous interfacial interaction [19]. When TiO_2 particles and polyester matrix are well bonded, the applied stress can be significantly shifted from the polyester matrix to TiO_2 particles and particles bear the load resulting in high tensile strength. Reduction in tensile properties beyond 3 wt.% TiO_2 was due to crack growth propagation with stress concentrations which triggered by voids in PHC-4 & PHC-5 [20].

3.3. Izod impact test and hardness

Pendulum impact tester (Model CSI-137) of Custom Scientific Instruments, was employed to evaluate the impact strength of developed composite samples in izod mode. Five individual specimens having dimension (63.5 × 12.7 × 2.5 mm) were primed for izod impact testing and notched as per ASTM: D256-10. Hardness of PHCs specimens with dimensions (25.4 × 25.4 × 2.5 mm) was investigated by Bench Rockwell hardness tester (Model NR3-DR) using ASTM:D785-08. A carbide ball indenter having spherical base of 2.5 mm diameter was infiltrate into the sample under applied force F. Applied load was 62.5 kilo pound (kp) while preload was 1000 kp while with ratio HB10. Brinell hardness value was recorded at 10 different positions on each sample. **Figure 5**, demonstrates that the resistance to impact

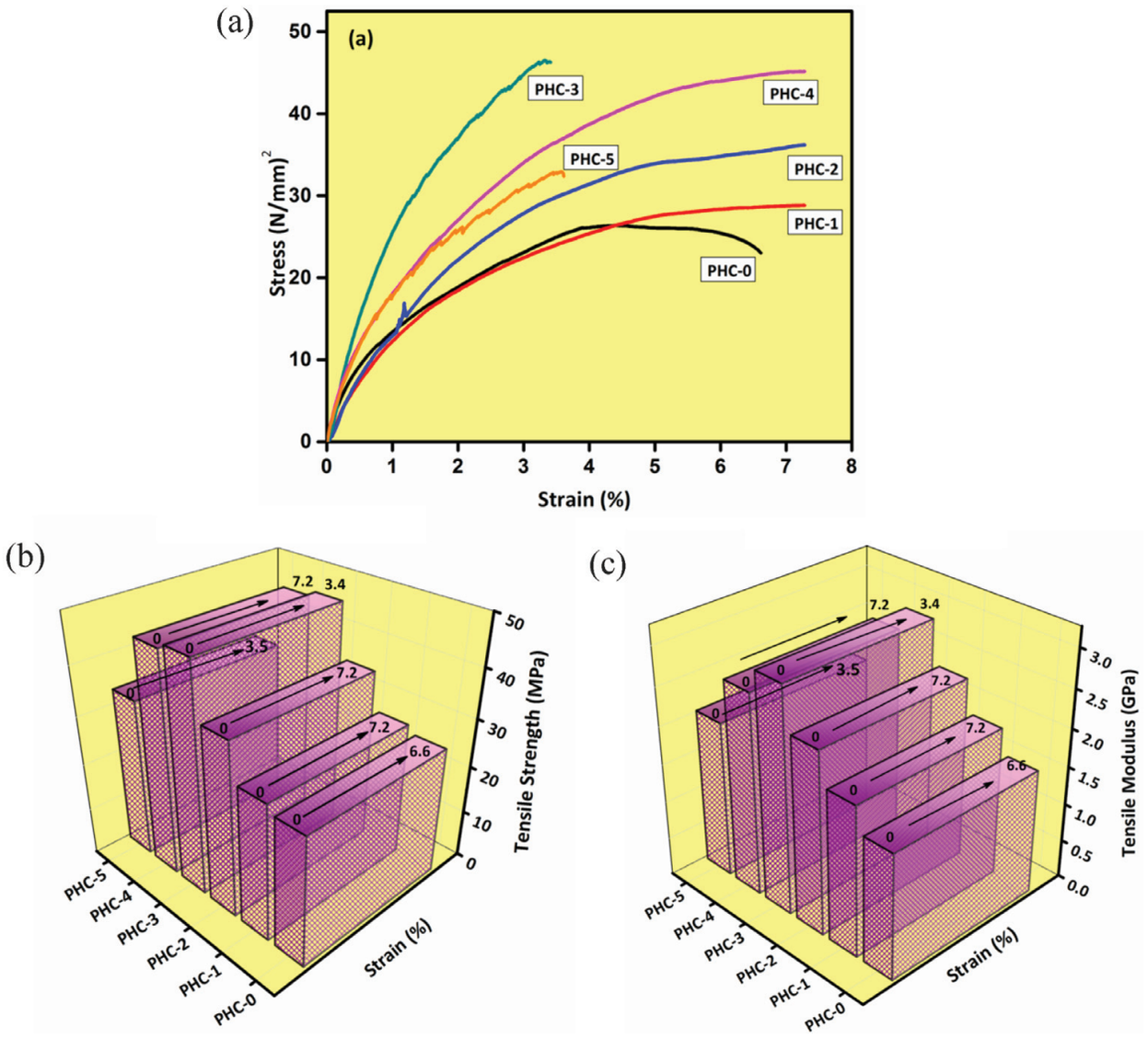

Figure 4. (a) Tensile stress-strain profiles of controlled PHC-0 and PHC-1, PHC-2, PHC-3, PHC-4, & PHC-5. (b) Show tensile strength values in mega Pascal (MPa) of PHC-0, PHC-1, PHC-2, PHC-3, PHC-4, & PHC-5 calculated from stress-strain curves. (c) Tensile modulus values in giga Pascal (GPa) of PHC-0, PHC-1, PHC-2, PHC-3, PHC-4, & PHC-5 calculated from stress-strain curves.

loading of PHCs increased with the addition of TiO_2 particles. The impact strength of PHCs was considerably depended on the particle stiffness, reinforcement strength, matrix fracture, particle-matrix interface adhesion and fiber pullout. The changing in concentration, orientation and distribution of particles in composites were also responsible for changing in physical and mechanical characteristics of resultant PHCs [21]. The level of maximum impact energy, of the order 4.73 KJ/m of PHC-5, was significantly higher with respect to unfilled PHC-0 (0.64 KJ/m). The enhancement of impact energy of PHCs was due to the strong crosslinking and hydrogen bonding (H-bonding) among TiO_2, polyester and SiO_2 content of E-glass fiber and confirmed by Ritesh Kaundal and co-workers [22]. It was noted that both tensile and flexural properties

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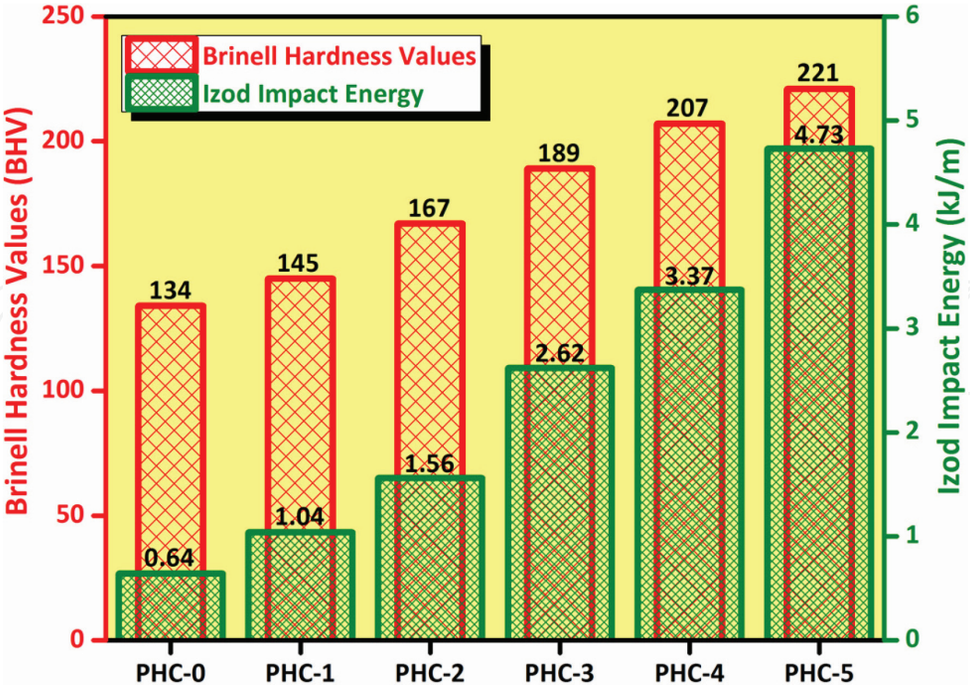

Figure 5. Izod impact strength and hardness results of PHC-0, PHC-1, PHC-2, PHC-3, PHC-4, & PHC-5.

decreased beyond 3 and 4 wt.% TiO_2 loading respectively, but impact energy values increased continuously up to 5 wt.%. It was proposed that higher concentration of TiO_2 particles produced more voids which were responsible of dissipation of impact energy more efficiently in PHC-5 [23].

Figure 5 also demonstrated that the hardness of PHCs augmented linearly with imbedding of TiO_2 particles. The PHC-5 showed 64% increase in hardness compared to PHC-0.

Improved hardness or high resistance to penetration values was due to the fact that when load was exerted on the specimens; fiber, matrix and TiO_2 particles had pressed at once and adhered with each other more effectively and interfaces transmitted pressure more efficiently. During applied compression load, the inter-particle distance got less and hardness became high. It was also considerable that matrix contents lessened on increasing the loading of TiO_2 particles in system and particles induced their intrinsic hardness to PHCs [24].

3.4. Thermal testing

Simultaneous differential scanning calorimetry/thermogravimetric analyzer (SDT) Model (Q600 of TA), was employed to conduct thermos-gravimetric analysis (TGA) of prepared PHCs. Thermal stability of each test specimen (~10 mg) was assessed at a stable temperature ramp of 10°C/min from 40 to 800°C in inert atmosphere with flow rate of 100 mL/min.

Thermal degradation pattern of controlled PHC-0 and TiO_2-imbedded PHCs depicted the weight loss in multiple steps (**Figure 6**). The weight loss from ambient to 100°C was ascribed

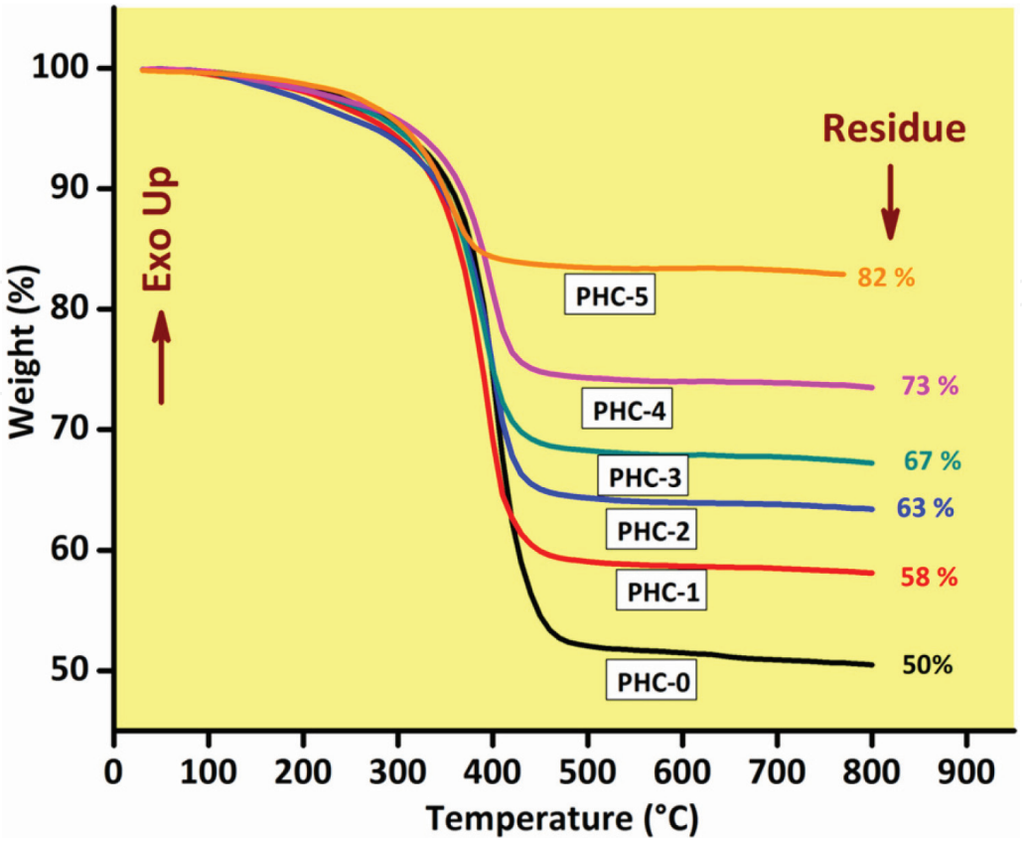

Figure 6. Thermograms of PHC-0, PHC-1, PHC-2, PHC-3, PHC-4, & PHC-5 with their relative residue contents.

to the removal of dampness and after that step dehydration took place in temperature range of 100–250°C. The onset of degradation of PHCs was started at 250°C and high degradation was linked with breaking of weak bonds. The scissoring of highly cross-linked polyester chains were observed above 350°C and transformed in un–cross-linked linear chains [25]. All straight polymer chains went to scission into tiny parts at 400°C near offset temperature [26].

The residual amount at 800°C was accredited to the left behind quantity of glass fiber and TiO_2 particles. It was observed from this result that the control PHC-0 showed the mass loss up to 50%, which was restricted to 17% for PHC-5. The PHC-5 showed 65% increase in residue contents as compared to unfilled PHC-0.

The thermal degradation data of PHCs at different steps of mass losses is given in **Table 2**. This showed that 10 and 15 wt.% loss of PHC-0 was at 352 and 365°C which improved up to 367 and 391°C in PHC-5, respectively. This data also explained that the degradation temperature was improved; overall weight loss of composite samples declined and residual amount were augmented with increasing the loading of TiO_2. The higher thermal stability was attributed to the improved interactions of polyester chains with TiO_2 and SiO_2 content of E-glass fiber and interactions decreased upon heating due to segmental movement of polyester chains [27]. As temperature slowly rose, the interface between particles and matrix started weakening which

PHCs	$T_{10\%}$[a] °C	$T_{15\%}$ °C	Residue[b] %
PHC-0	352	365	50
PHC-1	341	372	58
PHC-2	344	374	63
PHC-3	348	377	67
PHC-4	363	385	73
PHC-5	367	391	83

[a]$T_{10\%}$ and $T_{15\%}$ are the temperatures at 10% and 15% mass losses.
[b]Residue at 800°C.

Table 2. Thermal decomposition data of controlled PHC-O and TiO_2-imbedded PHCs at various percentage mass losses.

caused the motion of polymer chains radically, eventually specimens decomposed at elevated temperatures [28].

4. Conclusions

The TiO_2 embedded glass fiber reinforced polyester hybrid composites (PHCs) had fabricated by hand lay-up process (HLUP) and compression molding technique (CMT) in the presence of methyl-ethyl-ketone-peroxide (MEKP) as cross linker and cobalt naphthenate (CN) as an accelerator. It was evident that functional, mechanical and thermal characteristics of PHCs were enhanced by imbedding TiO_2 particles in unsaturated polyester resin (UPR) with E-glass fiber sheet. The formation of crosslinking of UPR with styrene molecules and hydrogen bonding between O=Ti=O particles and –Si–O content of glass fiber with UPR in PHCs were confirmed by Fourier transform infrared spectroscopy (FTIR). Tensile strength (TS) and Tensile modulus (TM)) of PHCs were improved by loading TiO_2 particles up to 3 wt.%. Impact strength and hardness improved continuously with increasing the TiO_2 loading up to 5 wt.%. TGA showed that 10 and 15 wt.% loss of PHC-0 was at 352 and 365°C, which improved up to 367 and 391°C in PHC-5, respectively. Therefore, it was concluded that TiO_2 particles are good choice as a third reinforcing material in fiber reinforced polyester hybrid composites (PHCs) as they induced the incremental variations in functional, mechanical and thermal trends. From the above conclusions of functional, mechanical and thermal behaviors, it is endorsed that these hybrid composites can be exercised for high strength and high temperature applications.

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