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Fabrication and characterization of nanostructured TiO_2 and turmeric spent incorporated polystyrene hybrid nano composites

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Abstract

A series of polystyrene hybrid nanocomposites have been fabricated with varying amounts of TiO_2 viz., 0, 0.5 and 1 % w/w along with 3% TS by in-situ polymerization method. The influence of surface modified TiO_2 nanoparticles on the thermal properties of PS matrix was examined using thermogravimetry and differential scanning calorimetry. Thermal characteristics of the polystyrene/TS/TiO_2 hybrid nanocomposites were evaluated by using differential scanning calorimetric (DSC), thermal analysis (DTA), thermogravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMA). By comparing the values obtained for the hybrid mixed composites, the thermal properties of 1wt. % TiO_2 along with 3wt.% TS are increased. On the other hand, PS/TS/TiO_2nanocomposites have higher glass transition temperature and better thermal and thermo oxidative stability than the bare PS. The morphological behaviors of the prepared polystyrene/TS/TiO_2 were analyzed using SEM.

Keywords: Hybrid nanocomposites; turmeric spent; TiO_2; DMA; thermogravimetric analysis; thermal degradation behavior.

Introduction

Increasing air pollution, together with climatic change and abundant biological activity, are responsible for the growing deterioration in the last decades of the movable and immovable cultural heritage [1]. Polymer composites reinforced with bio-based materials have raised great interest among material scientists and engineers due to the consideration of developing eco-friendly composites and partly replacing mineral fillers [2]. Natural fillers are widely used due to their inherent advantages such as low cost, low density, high stiffness and high specific strength [3]. Also, the demand for lignocellulosic sources with low cost is on the rise in the composite industries which can decrease overall manufacturing costs and increase stiffness of the materials [4]. The dimension and microstructure of the dispersed phase can significantly influence the properties of polymer composites. Polymer–clay nanocomposites have at least one ultra-fine dimension, typically on the order

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of 1 to 10 nm. Because of the nanoscale structure, polymer–clay nanocomposites possess unique properties. Today's environmental waste and social concerns point out increasing demands on bio resources, and in order to accomplish this the combination of plant products and synthetic polymers producing cheap substitutes for traditional products, provides a promising way. Pashaei incorporated 90 wt% turmeric which spent improvement in tensile modulus and surface hardness with increase in TS content in vinyl ester matrix was noticed [5].The inorganic particles such as clay, silica, $CaCO_3$, layered silicate nanoparticles and titanium dioxide (TiO_2) have attracted a special interest as inorganic materials for inorganic/organic nano-composites. Among them, TiO_2 is one of the most important materials, because of its potential applications in the photo catalytic activity, as well as photoelectric conversion in solar cells. Moreover, TiO_2 nanoparticles possess also antibacterial activity, odor inhibition and self-cleaning mechanism [6-9]. Such advantages make TiO_2 an ideal inorganic reinforcing component in manufacturing nanocomposites material with promising properties and applications: a good polymer nanocomposite with excellent mechanical properties, light density, reduction of UV and thermal degradation (especially the significant impact of high intensity of UV rays of sunlight, high temperature, humidity from the tropical climate of Vietnam). Several polymers have been successfully mixed with TiO_2 nanoparticles including poly (methyl methacrylate), epoxy, polyether sulfonate, poly(ethylene terephthalate), polystyrene by using processing methods such as sol–gel or polymerization insolution[10–13]. In this paperwaste agriculture material which was used to reduce price of nanocomposit made more biodegradable polymer. The influence of TiO_2 along with TS on glass transition temperature (Tg), as well as thermal and thermo oxidative stability of PS matrix was investigated using differential scanning calorimetry(DSC), thermal analysis (DTA), thermogravimetry (TGA) and dynamic mechanical analysis (DMA). The morphological behaviors of the prepared polystyrene/TS/TiO_2 were analyzed using SEM.

Experimental

Materials

General purpose polystyrene was used. Polystyrene is a thermoplastic and aromatic polymer made from the aromatic monomer styrene, a liquid hydrocarbon that is (merckchemical, germany) was purified by distillation under vacuum. It has many desirable properties and one of the most widely used kind of plastic. Polystyrene is outstandingly easy to process. Commercial polystyrene (PS, Pars Petrochemical Company, Iran) was used.ItsTiO_2 powder (rutile and anatase crystal forms) with diameter of about 40–100 nm was provided by Sigma-Alderich. Turmeric which spent (TS) (moisture content 5.7%, bulk density 1.42 g cm^{-3} and ash content 3.5% with diameter of about 100- 250 µm was obtained from Sami Labs, India as gift sample. Benzoyl Peroxide (BPO) was dried in vacuum and storage under nitrogen atmosphere that obtained from Sigma-Alderich. All other chemicals used in this study are AR grades.

Preparation of TS filler

Turmeric spent was used as reinforcing filler in the fabrication of green composite. The spent obtained was thoroughly washed with water to remove sand and other foreign impurities, dried in sunlight and grinded to fine powder. The particles were sieved through ASTM 80 mesh to obtain the required range of sizes of the TS particles. This powder was dried again in an oven with air circulation for 24 h at 50°C to adjust it to a moisture content of 2–3% and stored over desiccator in sealed polystyrene covers until further use.

Preparation of PS/TS/TiO_2hybrid nanocomposite

The synthesis of new inorganic hybrid nanocomposite materials was achieved by in-situ polymerization method. TiO_2wasinitially dissolved in 50 ml of methyl ethyl ketone (MEK) and placed in a three-necked round bottomed flask. PS hybrid nanocomposites were prepared by solvation of the TiO_2along with 3wt. % of TS. The content was stirred for 10–20 min or until the uniform mixture was obtained. This solvation was followed by adding the 1 wt. % of BPO as catalyst. The reaction mixture of the flask was stirred continuously for about 7 h under oxygen free nitrogen gas purge at 60–70°C. The reaction mixture was poured into a cleaned and releasing agent coated glass mold and allowed to stand for 12 h at room temperature. Then the mold was kept in a preheated circulating hot air ovenat90°C for 8–10 h. The toughened PS composite sheet thus formed was cooled slowly and removed from the mold. The above procedure was repeated for different weight percent of TiO_2 contents, viz., 0, 0.5 and 1 wt.% with along 3% of TS. It was found that the percentage of yield in the hybrid nanocomposites is higher than the yield percentage of neat polystyrene.

Techniques

The transition temperatures of the samples were examined by using differential scanning calorimeter (DSC) model DSC-Q 200, DuPont TA instrument, USA. All samples were sealed in hermetic aluminum pans. The dynamic DSC scans were recorded at the heating rate of 10 °C/min from ambient to 300 °C under nitrogen gas flow of 60mL/min. The thermal stability of the PS/TS/TiO_2hybrid nanocomposites has been evaluated using thermogrametric analysis (TGA) DuPont TA instrument, USA with TGA-Q 50 module. The reference sample for all compositions was Indium. The instrument was calibrated using pure calcium oxalate sample before analysis. About 6-8 mg of sample was used for dynamic TGA scans at a heating rate of 20 °C/min in the temperature range of ambient to 700 °C in nitrogen gas purge. The oxidation index (OI) was calculated based on the weight of carbonaceous char as related by the empirical equation;

$OI \times 100 = 17.5 \times 0.4CR$

The storage modulus(E´), loss modulus (E´´)and the mechanical loss factor (Tanδ(E´´/ E´) as a function of temperature (T), were assessed by dynamic mechanical thermal analysis (DMA),DuPont TA instrument, USA, with model 2980-DMA.DMA thermograms were recorded in tension mode at 5Hz frequency at a heating rate of 3 °C/minin the temperature range 30–150°C.

The fractured surfaces of polystyrene/TS/TiO2hybrid nanocomposites were performed using SEM (Hitachi S-2150). The cryo-fractured samples were glued on the aluminum sample holders in order to observe the microstructure of the hybrid systems. The SEM was used to study the micro phase separation and morphology of the hybrid nanocomposite.

Results and discussion

The DTA graphs of the investigated glasses are shown in Figure1in which the DTG peak temperature is the same for all examined samples. The obtained results show that the presence of turmeric spent (TS) has been thermo oxidative degradation of the PS at the lower temperatures, but affects degradation of PS/TS/TiO_2 at the higher temperature. It may be due to the interactions of the fillers with the polymer matrix and these depend on the nature of the fillers, time, pressure and purity of the fillers [14]. According to the mechanism of thermo oxidative degradation of PS [15], it is well known that 6-palmitate ascorbic acid possess antioxidant properties and could act as radical scavenger [16]. Thus, in the case of thermo oxidation of PS/TiO_2nanocomposites, the present TiO_2 nanoparticles interact with generated oxygen containing radicals forming more stable compounds than those formed during the thermo oxidation of pure PS. The examined samples have maximal decomposition rate at the same temperature, i.e. they have the DTG peak at 405 °C, it is so because the formed radicals are no more stable at higher temperature and the degradation rate of PS matrix is controlled by unzipping mechanism.

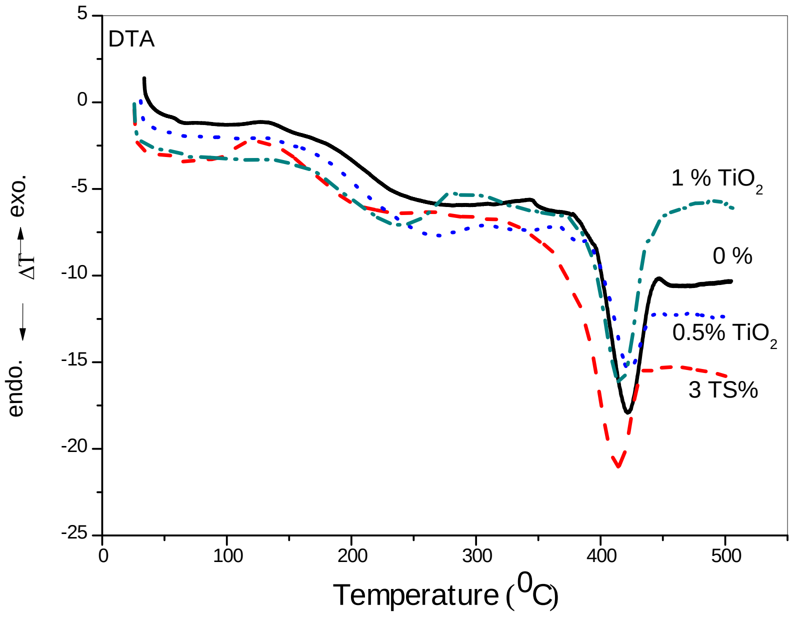

Figure 1. DTA Patterns of the PS/TS/TiO2 and nanacomposites

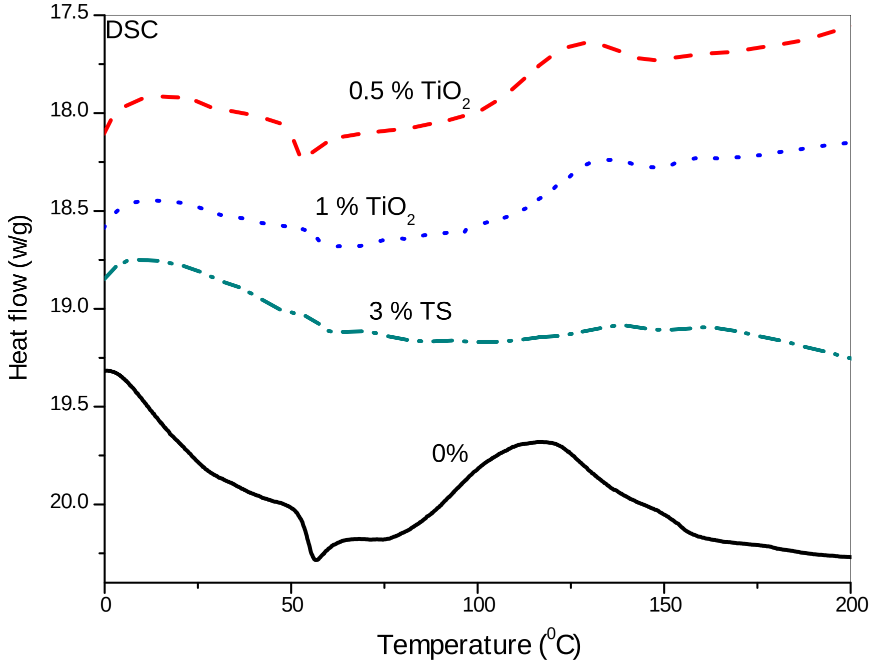

Figure 2. DSC curve of PS and its hybrid nanocomposites

The glass transition behavior and delta heat capacity of the synthesized PS/TS/TiO_2 samples were investigated by DSC (Fig. 2). The values of glass transition temperature (T_g) and delta heat capacity were listed in Table 1. The heat capacity was the highest for pristine PS (0.688 J/g.°C) and it was significantly reduced from 0.688 to0.079 (J/g.˚C) after incorporation of TS and TiO_2. It can be noticed that T_g is increased after incorporation of the TiO_2 nanoparticles in the PS matrix. It reduced that free volume of green composites have been increased. T_g increased after incorporation of TiO_2 and the observed effect can be explained by interaction between nanoparticle and PS segments; moreover, it consequently leads to restriction of mobility of the PS chains. It means that the loading additive interacted with the polymer increases its T_g.

Table 1. Data obtained of PS/ TS/TiO_2 hybrid nanocomposites

Sample	**T_g**	**ΔC_p (J/g. ˆC)**
0	51.4	0.688
3% TS	48.36	0.298
0.5	54.47	0.079
1 %	55.06	0.169

The TGA and DTG (the first derivative curves of the TGA) curves of pristine polystyrene and PS/TS/TiO_2nanocomposites are shown in Figures 3. TGA thermograms of all composites are shown in Figure 4. From TGA thermograms indicate that all green composites have undergone single step thermal degradation in the temperature range 335 – 460 °C. From TGA plots, the measured T_0, T_{10}, T_{20}, T_{30}, T_{50} and T_{max} were listed in Table 2. From Figure 3 the values of onset (T_o) and degradation temperature (T_p) of pristine and PS/TS/TiO_2hybrid nanocomposites were obtained (Table 3). The presence of TS and TiO_2 increases the T_{max} for the hybrid nano composite systems. For neat polystyrene the weight loss starts at 335 °C which reduces slightly by the addition of TiO_2 and TS. Table 3 indicates that, ash content increases with increase in filler loading. This can be attributed to the synergistic effect of TS/TiO_2 and matrix present in the composite.

Table 2. Thermal data obtained from TGA thermograms of PS/TS/TiO_2 hybrid nanocomposites

Sample	**Temperature at different weight loss (± 2 °C)**				
	T_0	**T_{10}**	**T_{20}**	**T_{50}**	**T_{max}**
0	319	360	377	405	440
3% TS	315	355	385	410	455
0.5	320	380	390	412	455
1	320	385	390	415	460

From Figure 3, the values of onset (T_o) and maximum degradation temperature (T_p) of pristine polystyrene and PS/TS/TiO_2hybrid nanocomposites were determined and presented in Table 3. The presence of TS decreases T_0, T_p and T_{max} for the green composite systems. For nanocomposites temperature degradation, this gradually increases by the addition of TiO_2 along with 3% of TS. Table 3, indicates that, ash content increases with increase in filler loading [17]. This can be attributed to the synergistic effect of TS and matrix present in the composite. Higher the values of oxidation index (OI), higher will be the thermal stability [18]. From Table 3 it was observed that the oxidation index values increases with increase in TiO_2 along with 3% TS content and it lies in the range 6.3–0.43. Annuity reported that, the char yield is directly correlated to the potency of flame retardation [19]. From the aforesaid investigation, it can be concluded that the flame resistance of PS/TS/TiO_2hybrid nanocomposites was slightly enhanced as the filler content increases.

Table 3. Temperature range obtained from derivative TGA curves of PS/TS/TiO2 nanocomposites

Sample	**Temperature (˚C ±2)**			**Ash content (%)**	**Oxidation index (OI)**
	T_0	**T_p**	**T_c**		
0	340	415	450	0.9	0.06
3 % TS	335	411	445	2.2	0.15
0.5%	343	418	455	2.3	0.16
1%	344	420	460	6.2	0.43

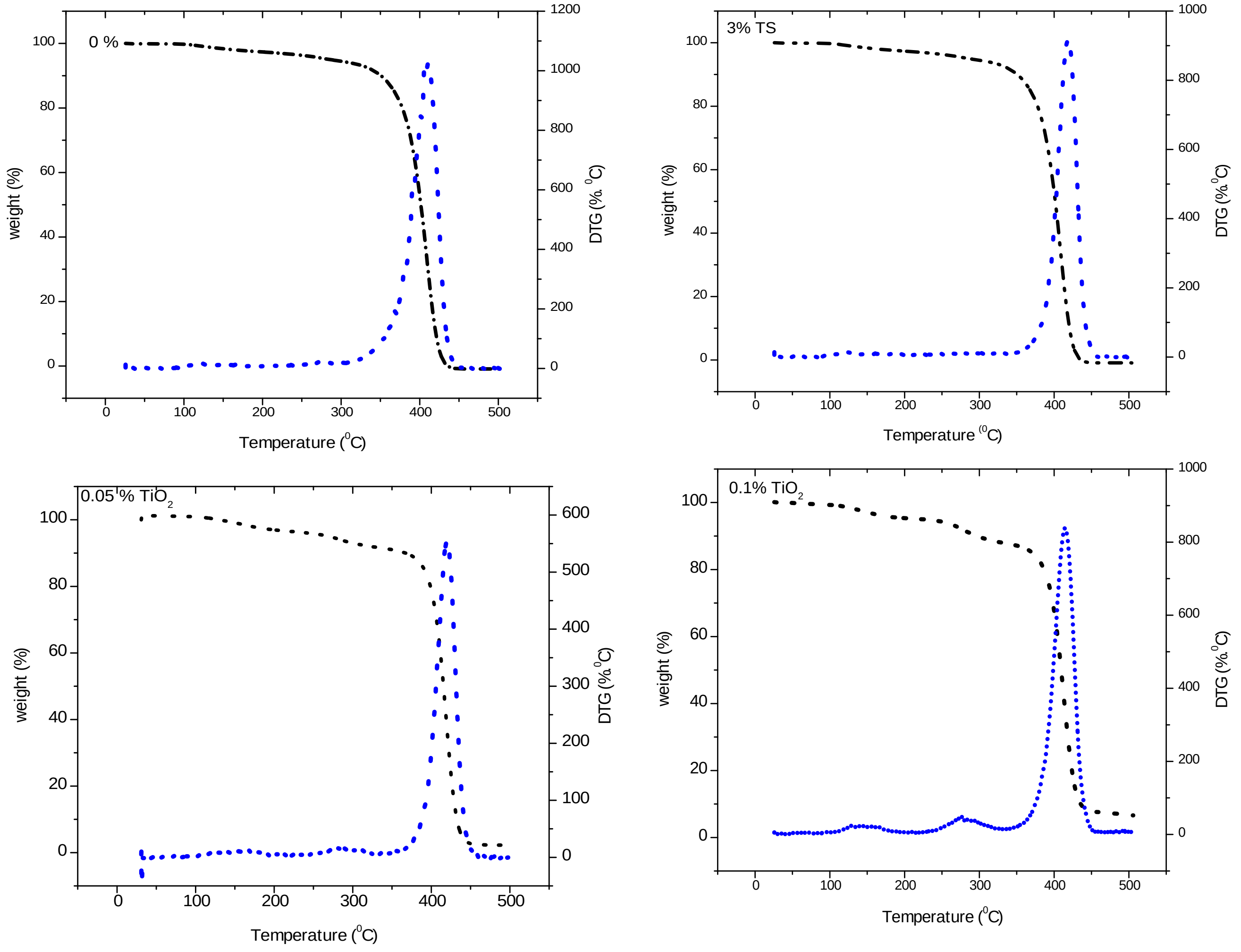

Figure 3. TGA and derivative thermograms of, (a) 0%, (b)3% TS,(c) 0.5% TiO2 and (d)1% TiO2 pristine polystyrene and its hybrid nanocomposites

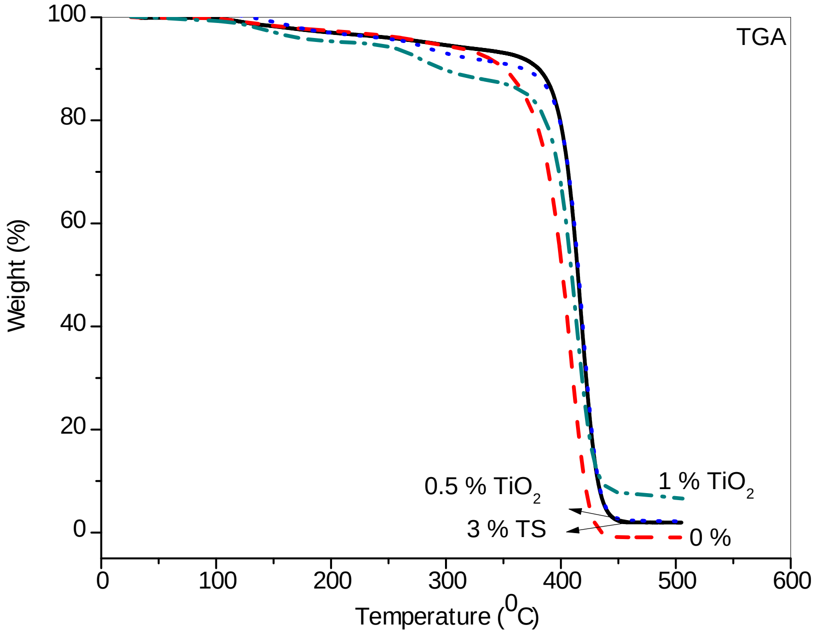

Figure 4. The TG curves of 0%, 3% TS, 0.5% TiO_2 and 1% TiO_2 of neat polystyrene and its nanocomposites

Storage modulus

The study of the storage modulus variation with temperature provides information about the loss of stiffness as temperature increases, and is associated with structural changes. In nanocomposites, the loss in storage modulus has been attributed to weak interfacial compatibility between the matrix and then anaphases where PS/TS shows lower storage modulus values than PS in the whole range of temperatures. Figure 5 shows the variation of the curves of storage modulus, loss modulus Tan δ versus temperature with respect to the different filler loading of the PS nanocomposites. We can see the storage modulus and loss modulus for all composites higher than pristine PS, confirming the evidence that the PS/TS/TiO_2 chains become rigid due to the TiO_2. The curves for the nanocomposites are significantly shifted to higher temperatures with respect to that of the bare PS, which means that the T_g has increased, because of the nanocomposites being made stronger by the nanoparticle. It is noteworthy to mention that by adding up to 1 wt.% nanoparticles to polystyrene, the storage modulus increases all over the measured temperature range.

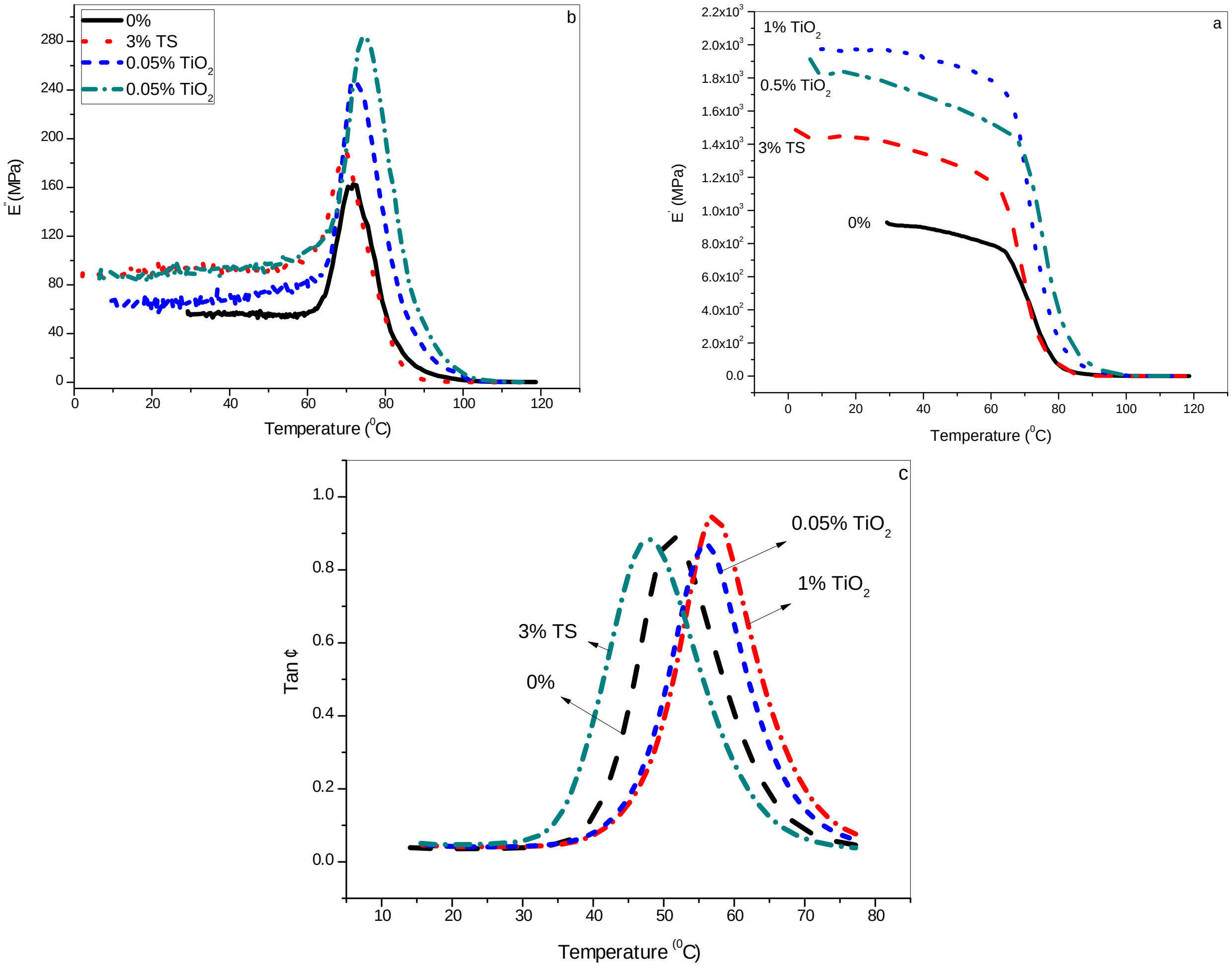

Figure 5. Plots of (a) storage modulus, (b) loss modulus and (c) Tan δ as a functional of temperature of polystyrene/TS/TiO_2nanocomposites

Table 4. Results of DMA analysis of PS/TS/TiO_2 hybrid nanocomposites

Sample	**E´ (MPa) at 40 $^{\text{î}}$C**	**E´´ (MPa) at 40 $^{\text{î}}$C**	**Tan ¢$_{max}$**	**Temperature ($^{\text{î}}$C)**	
				E´´$_{max}$	**Tan¢$_{max}$**
0	898	56	0.89	67	51
3% TS	1345	71	0.88	70	48
0.5% TiO_2	1700	90	0.86	72	56
1% TiO_2	1926	92	0.94	74	58

Table 4 lists the average values of Tan δat T_{max} for different percentage weight of TiO_2 with along 3% of TS. At T_{max}, the Tan δ value is higher for virgin polystyrene indicating the viscous damping because of the segmental motion in the polymer. Tan δ at T_{max} of the hybridnano composites was in general lower than that of bare polystyrene, and it increased as the percentage weight of TiO_2 increased. This reduction in the damping factor was attributed to the restriction to the molecular movements of PS matrix by TiO_2 and TS, which caused reduction in the matrix viscoelasticity. Various mechanisms such as matrix viscoelasticity, filler/filler interfacial friction, etc., could increase the damping capacity of the polymer composite materials. However, the molecular motion at room temperature is frozen, and this may not contribute to the damping mechanisms. However, this did not improve the T_g, in our samples unlike others [20], who reported increase in the $T_g$of the composites. The results indicate that DMA (solids rheology) and DSC were same and similar trends can be observed in Tg of composites. This is somewhat intriguing but literature reports are on both sides.

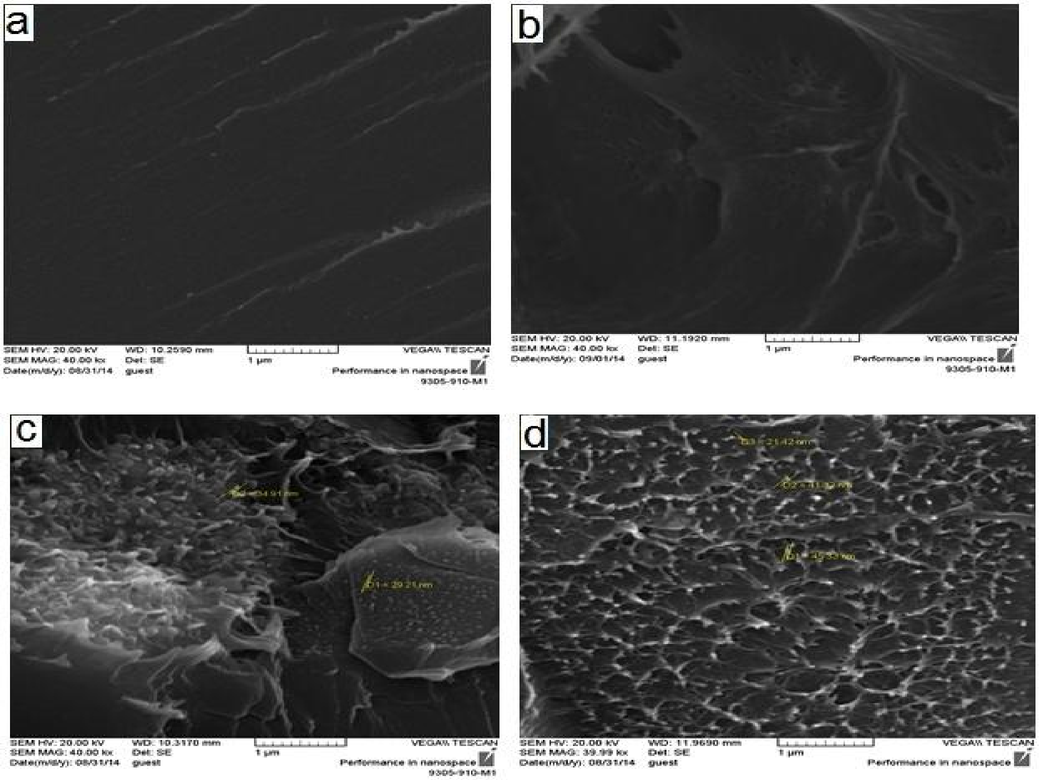

Figure 6. SEM images of (a) bare PS, (b) 3% TS, (c) 0.5%, and (d) 1% of vinyl PS/TS/TiO_2 hybrid nanocomposites

Morphology

Figure 6(a)–6(d) shows the photo micrographs of polystyrene composites with TiO_2 along with TS content ranging from 0 to 1wt.%. Single phase morphology was noticed for bare PS. The SEM images of TS-filled composites showing that TS particles dispersed homogenically in polystyrene matrix. TS particles embedded in matrix. It can be observed that with an increase in the TiO_2 content the surface roughness and whiteness also increases. This could be attributed to the chemical interactions between the polar TiO_2 and the bare PS. This result clearly indicates some physical interaction between the filler and the pristine polystyrene. It was observed that addition of nanoparticles in polystyrene resulted in considerable toughening of the nanocomposites leading to slow crack growth.

Conclusion

PS/TS/TiO_2 hybrid nanocomposites have been fabricated by in-situ polymerization with varying amounts of TiO_2 content along with 3 wt. % of turmeric spent. Incorporation of TiO_2 increases the thermal stability of the composites. TGA thermogram indicates that all polystyrene hybrid nanocomposites are stable up to 315 ˚C and undergo one step thermal degradation. It can be observed that the thermal stability of the TiO_2 loaded polystyrene composites is slightly high as compared to neat polystyrene. Dynamic mechanical measurements have been used to study the viscoelastic properties of polystyrene nanocomposites. The DMA and DSC have been shown that T_g increase by adding TiO_2. The DMA studies confirm good physical interaction between matrix and nanofiller. The storage modulus values increased with the addition of 0.5 and 1 wt.% TiO_2. The E' of PS/TS/TiO_2 is higher than all compositions. SEM images showed the strong interaction between TiO_2 and bare PS. These fillers are portentous materials that can decompose and degrade. So the need to use them as biodegradable fillers incorporated into polymers (plastics which litter the environment and seen at landfills) is strong, to help in keeping the environment clean. Also, they can be used to form bio-plastics due to the mechanical strength property, they displayed; thereby reducing dependence on the polymer resins produced from petrol. Therefore, it is pertinent to channel these fillers into use as fillers for thermoplastic resins and more especially the turmeric spent which are not being used but mainly seen and disposed.

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