

Thermal Stability and Dynamic Mechanical Properties of Nano and Micron-TiO₂ Particles Reinforced Epoxy Composites: Effect of Mixing Method

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Abstract

This research work focuses on the performance optimization of composites containing both micron and nano size TiO₂ particles separately in various concentrations and to understand the role of each on the thermal stability and moduli of the composites. Thermal stability of the particle-reinforced composites increased on increasing the concentration of TiO₂, both in nano and micron filled cases, except for the 2.5 wt% nano-filled composite. Storage modulus (E') increased on adding micron-TiO₂ to the epoxy hardener resin system from 1 - 2.5 - 5 wt% respectively and decreased dramatically on further increasing the micron TiO₂ content to 7.5 and 10 wt% respectively. Nano TiO₂ particle-reinforced composites showed an increasing trend of storage modulus for 2.5 - 5 - 7.5 wt% TiO₂ filled composites with respect to the neat resin system. Presence of both micron and nano TiO₂ particles increased the T_g of the composites. Also, the effect of sonication on the modulus and T_g is discussed. As a whole, composites in which the TiO₂ particles were dispersed through the resin matrix by glass rod revealed better results (higher storage moduli and T_g) than those mixed by sonication, due to high viscosity of the epoxy resin used.

Keywords: *Polymer Matrix Composites (PMCs), Nano and Micron TiO₂ Particles, Mechanical Properties, Ultrasonic, Thermal Analysis*

1. Introduction

The transition from micronparticles to nanoparticles yields dramatic changes in physical properties. Nanoscale materials have a large surface area for a given volume [1]. Since many important chemical and physical interactions are governed by surfaces and surface properties, a nanostructured material can have substantially different properties from a larger-dimensional material of the same

composition. In the case of particles and fibers, the surface area per unit volume is inversely proportional to the material's diameter, thus, the smaller the diameter, the greater the surface area per unit volume [1]. There have been some reports on TiO₂ particles being used as pigments in the production of Epoxy-based paints. TiO₂ paints were prepared using the epoxy resins and compared for the weathering characteristics [2-4]. Production of Epoxy-

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TiO₂ paints has also been reported by Sharif Ahmad et al. [5]. TiO₂ has found applications in preparing some epoxy-based composites: The titanium oxide (TiO₂-coated multiwalled carbon nanotube (MWCNT)/ epoxy composite was prepared by coating MWCNTs with a layer of TiO₂ and modified with 3-(amino propyl) triethoxysilane (APTES) in order to improve electrical and mechanical properties [6]. Rusheng Yuan et al. loaded TiO₂ on activated carbon fibers (ACF) with different surface areas by using the residue after epoxy resin being calcined as the link between TiO₂ and ACF, and their surface properties and photo degradations of wastewater from paper mill have been investigated [7]. In another research work the reactive coating of different inorganic model surfaces including TiO₂-substracts with poly (butadiene epoxide) (PBDE) from organic solution has been reported [8]. Also, the study on the pretreatment method of glass-epoxy resin in the presence of TiO₂ sol prepared by hydrothermal method was carried out by Gyung Guk Kim et al. [9]. Dielectric behavior of Nb₂O₅ - doped TiO₂/epoxy thick films have been investigated by Dong-Hau Kuo et al. [10]. Zhang et al. have reported on tribological properties of nano- TiO₂ particles-epoxy nanocomposites whose experimental results indicated that the addition of nano-TiO₂ could apparently reduce the frictional coefficient [11]. The influence of additional short carbon fibers (SCF), aramid and PTFE particles on friction and wear of epoxy- TiO₂ nanocomposites has also been investigated [12]. Optical properties of titana/epoxy nanocomposite coatings have been reported by Joseph Lik Hang Chah et al. [13].

Protective performance of epoxy reinforced with nanometer-sized TiO₂ on 2024-T3 aluminum alloys was investigated by Hongwei Shi and his research team [14]. Epoxy-TiO₂ composites were prepared by solution mixture method using methyl isobutyl ketone as solvent, the effect of solvent on thermo-resistance and some mechanical properties were investigated [15]. Bernd Wetzel et al. studied mechanical properties of nano titanium dioxide (TiO₂) and aluminum oxide (Al₂O₃)-reinforced epoxy composites, focusing on fracture and toughening mechanisms. A controlled dispersion process was achieved by applying high (shear) energy in order to reduce the size of agglomerates and to gain a homogeneous distribution of individual nanoparticles within the epoxy resin [16]. A study was carried out to investigate the effect of different coupling agents on the mechanical properties of TiO₂ particulated-reinforcing epoxy composites, using the adhesion model to explain the experimental data [17]. Internal charge behavior of nanoparticle TiO₂-epoxy composite has been investigated by a variety of diagnostic techniques (including dielectric spectroscopy electro-luminescence, thermally stimulated current and photoluminescence) [18]. Ng et al. worked on the synthesis and some mechanical properties of TiO₂-epoxy nanocomposites to evaluate strain-to-failure and scratch resistance [19]. Chatterjee et al. also worked on fabrication and characterization of TiO₂-epoxy nanocomposites, investigating the thermal, mechanical, morphology and the viscoelastic properties of the samples [20]. Nanocomposites using thermosetting

polymers have not been studied so extensively, particularly using TiO₂ as reinforcing agent. The objective of the present work was to investigate and compare the effect of both nano and micron size TiO₂ particles in varying amounts on thermal stability, flexural and shear storage moduli and glass transition temperature of the corresponding composites. The effect of mixing method on the mechanical properties is also examined and discussed.

2. Experimental

2-1. Materials used

The epoxy resin used, Araldite GY 6010, is a general purpose unmodified diepoxid based on bisphenol-A and epichlorohydrin cured as both room temperature and hot-curing systems. The curing agent, EPIKURE F205 is a low viscosity, modified cycloaliphatic amine. AEROXIDE TiO₂, P 25, used in this work is a highly dispersed titanium dioxide manufactured according to the AEROSIL – process, obtained from the Degussa AG, Germany. Titanium Dioxide P 25 has an average primary particle size of about 21 nm and a specific surface of about 50 m²/g. Micron size TiO₂ used was: Merck KGaA 64271 Darmstadt, Germany. Fig. 1 shows the TEM micrograph of Titanium Dioxide P 25.

2-2. Preparation of epoxy-micron and epoxy-nano particle reinforced composites

Two sets of composites were fabricated by two methods of mixing in order to compare the effect of the type of mixing on mechanical properties:

- By glass-rod
- By sonication

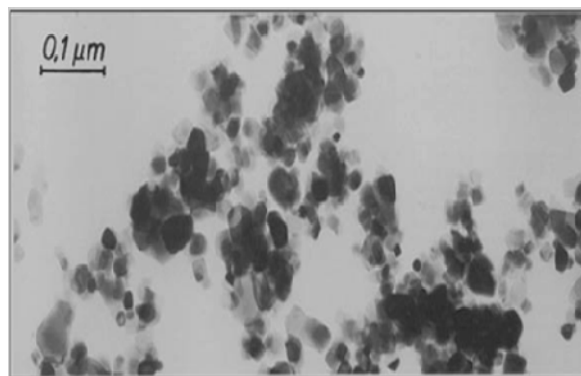


Figure 1. TEM micrograph of Titanium Dioxide P 25 (courtesy of degussa).

2-3. Glass-rod mixing

The resin was heated to 60°C, the respective TiO₂ particles were added to it and mixed thoroughly for 15 minutes by glass-rod, after which the curing agent was added to the mixture and mixed for another 5 minutes (the resin:hardener ratio was 100:40 phr). The sample was immediately poured in to a well-lubricated mould (length 25 cm, width 10 cm, thickness 3 mm), using RENLEASE QZ5101 as the mould-releasing agent. The assembly was then placed in the oven. The oven was preheated to 70 °C. The sample was kept in the oven for 1 hr where the temperature was maintained at 70± 2 °C. The mould was allowed to cool in the oven for several hours and then removed and opened.

2-4. Ultrasonic mixing

The SONREX Digite C ultrasonic bath, DT52 H model made by the Bandelin Company, Germany, was used for the ultrasound mixing. The resin was heated to 60°C, and then the TiO₂ particles were added to it and mixed thoroughly for 15 minutes in the ultrasonic bath, after which the curing agent was added to the mixture and degassed for 5 minutes. The curing cycle is as

mentioned above. Composites studied included the neat resin system as the reference one and those containing 1, 2.5, 5, 7.5, 10 and 20 wt% nano and micron-size TiO₂ particles separately as reinforcing agent. The DuPont 983 Dynamic Mechanical Analyzer was employed for the present investigations. The laminates were cut into the following dimensions:

1. Length: 19.2 ± 0.1 mm
2. Width: 12 ± 1.5 mm
3. Thickness: 3 ± 0.8 mm

Each sample was clamped between two parallel arms and heated at room temperature to 85°C at the heating rate of 5°C/min. in static air, and then the samples were allowed to cool slowly in the drive assembly enclosed by the oven, to room temperature. The 1, 2.5, 5, 7.5 and 10 wt% nano and Micron-size TiO₂ filled composites were subjected to DMA test. TGA experiments were carried out using Dupont Thermal Analyzer, having a 981 TGA module, generating the real time characteristic curves. The cured composites were studied at the heating rate of 10°C/min. sample size/weight varied from 2-8 mg. The initial decomposition temperature-IDT (The temperature where the TG plot deviates markedly from the base line) and the final decomposition temperature-FDT of TGA plots were obtained by extrapolation. The samples were prepared through the same procedure reported above, under the title of glass-rod mixing. The 2.5, 10 and 20 wt% nano and Micron-size TiO₂ filled composites were subjected to TGA test.

3. Results and discussion

3-1. Thermal stability of the epoxy-nano and epoxy-micron TiO₂ particle-reinforced composites

The thermogravimetric analyzer (TGA) is the most powerful tool used to determine the thermal behavior of materials. Figure 2 is the comparative TGA heating profiles of epoxy-micron and epoxy-nano TiO₂ particle-reinforced composites. The graphs show that, increasing TiO₂ concentration increases the thermal stability of the resin systems in both the micron and nanoparticle containing composites except for the 2.5 wt% nano-filled composite which shows decrease in thermal stability compared to all other systems studied. Figure 3 shows the comparison of variation of decomposition temperatures with respect to weight loss for the epoxy-micron and epoxy-nano TiO₂ composites. The 1% weight loss for the 0, 2.5, 10 and 20 wt% epoxy-micron TiO₂ composites has occurred at 113.2, 114.3, 121.8 and 112.8 °C respectively, whereas 2.5% weight loss happened at the decomposition temperature of 146.1, 153.1, 151.8 and 140.7°C respectively. The trend of decomposition temperature, where 5% weight loss has been observed is 180.7, 195.1, 188.3 and 176.3°C respectively. The composite containing 2.5 wt% of micron TiO₂ shows higher thermal stability at 2.5, 5 and 10% weight loss compared to the 0, 10 and 20 wt% resin systems. Fig. 3 also indicates that the 1% weight loss for the 0, 2.5, 10 and 20 wt% epoxy-nano TiO₂ composites occurred at 120.0°C, whereas 2.5% weight loss happened at decomposition temperatures of 146.1, 132.3, 144.9 and 152.2°C respectively. However, the

decomposition temperature for the composites containing 20 wt% nano-TiO₂ are 191.1 and 262.6 °C for the 5 and 10% weight loss respectively. Obviously the composite containing 20 wt% of nano TiO₂ shows higher thermal stability as compared to 0, 2.5 and 10 wt% nano TiO₂ composites, whereas

the 2.5 wt% nanocomposite shows the lowest thermal decomposition temperature at various percentages of weight loss. In the latter set of composites increasing the concentration of TiO₂ nanoparticles from 2.5, 10 and 20 wt% shows an increasing trend of thermal stability.

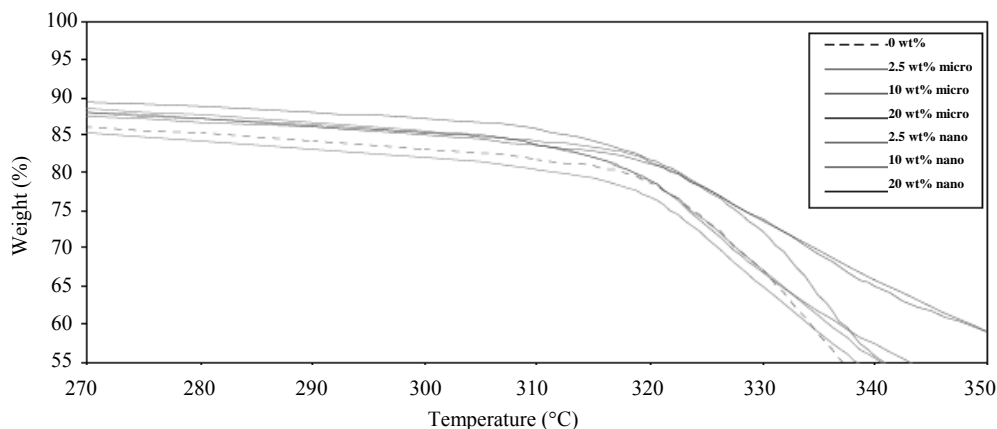


Figure 2. Comparative TGA heating profile of epoxy-micron and epoxy nano TiO₂ particle-reinforced composites.

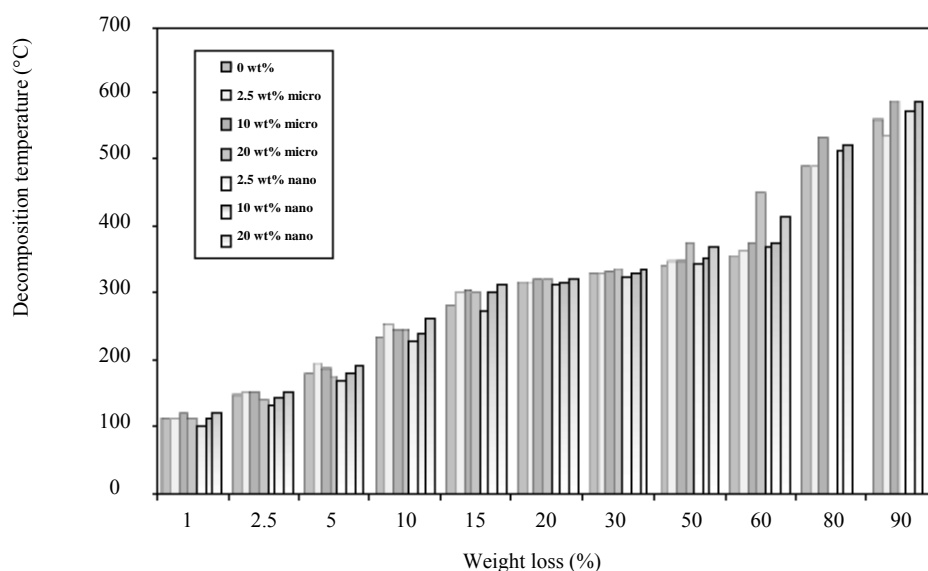


Figure 3. Comparative variation of decomposition temperature with respect to weight loss% for epoxy-micron and epoxy-nano TiO₂ particle-reinforced composites.

A recent work [20] on a type of Diepoxid [DGEBA (SC79)] loaded with 0.5, 1 and 2 wt% of TiO₂ nanoparticles reported the highest Thermal stability at 1% loading and that further increment in particle loading decreased the thermal stability. They suggested that the increase in thermal stability might be due to the higher crosslink density of the nanoparticle-reinforced epoxy composites. Their experimental data indicated that the 2 wt% nanocomposite showed the lower decomposition temperature rather than the 1 wt% loading. Our result indicates lower decomposition temperature for the 2.5 wt% nanocomposite than the neat resin system at 1% weight loss; however, the two higher concentrations of nano TiO₂ particles showed increased decomposition temperature at 1% weight loss level. It has been reported that the crosslink density is maximized when the complete stoichiometry of the epoxy is maintained. As soon as the stoichiometry of the epoxy matrix is broken with an addition of nano-loading [21], the crosslink density is reduced and lower crosslink density results in lower decomposition temperature as is the case with 2.5 wt% TiO₂ nanocomposite, which agrees with the result of Amit Chatterjee et.al., who related lowering the decomposition temperature to just above 1% by weight of nano-epoxy system to colligative thermodynamics effect of an impurity on a bulk solution, where Microscopically, it may be seen as the result of the perturbation that the nanoparticles of TiO₂ are introduced to the three dimensional structure of the polymer. This perturbation weakens the Van Der Waal's interaction between the polymer chains, thus affecting

the thermal stability (by lowering it) of the polymer. This perturbation begins at a point where the number of particles reaches a certain level and particle-to-particle interaction initiates, leading to agglomeration of particles into lumps, which acts as an impurity in the system. However, with the increased concentration of nanoparticles of TiO₂ to 10 and 20 wt% in the composites, the experimental data change towards the increase in thermal stability of the composites with respect to 2.5 wt% composite and the neat resin system both.

3-2. Dynamic mechanical properties of epoxy TiO₂ particle-reinforced composites

Figure 4 is the plot of the comparative DMA heating profile of flexural storage modulus (E') of epoxy-micron and epoxy-nano TiO₂ Particle-Reinforced Composites, illustrating the large drop in storage modulus at the respective glass transition regions. Figure 5 shows the variation of storage modulus on varying the amount of TiO₂ particles for both micron and nano systems. Figure 6 is an indication of the characteristic maximum tan δ , characteristic of the α -transition which occurs at, or slightly above the glass transition temperature (T_g) of the micron and nano-filled composites studied. Our experimental data indicates that, storage modulus (E') increased on adding micron-size TiO₂ particles (1 and 2.5 wt %) to the epoxy-hardener resin system respectively. Further increase of TiO₂ content of the composite to 5 wt% decreased the modulus with respect to the previous two, but still showed slightly higher modulus than the TiO₂-free formulation. However, for the 7.5 wt% TiO₂ composite the modulus fell to

about 1.55 GPa, which increased to about 1.9 GPa for 10 wt% epoxy micron TiO₂ composite.

The glass transition temperatures reported in this study were obtained from the flexural storage modulus curves at declining point. Fig. 7 clearly indicates the increasing effect

of micron-TiO₂ particles on glass transition temperature of the composites, where the 2.5 wt% TiO₂ containing sample shows 12°C increase of T_g (63.3° C) as compared to the resin system without any TiO₂ content (51.3°C).

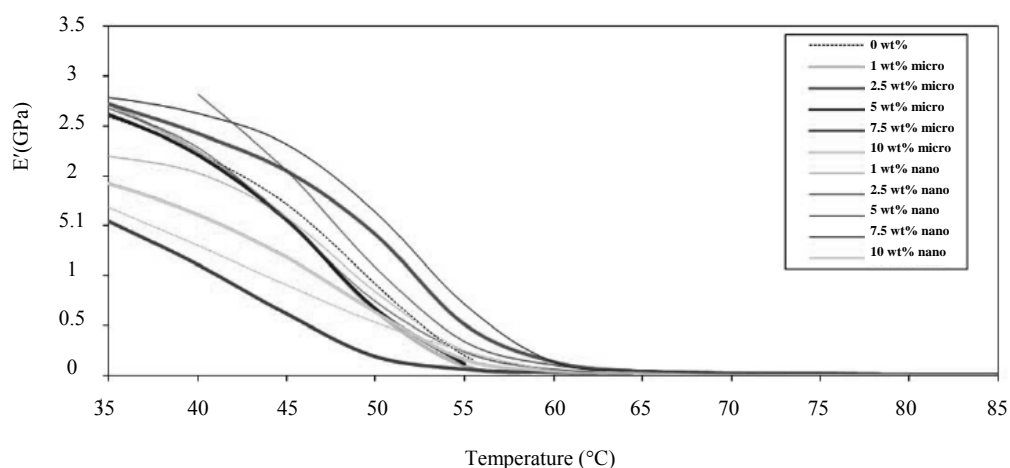


Figure 4. Comparative DMA heating profile of flexural storage modulus (E') of epoxy-micron and epoxy-nano TiO₂ particle-reinforced composites.

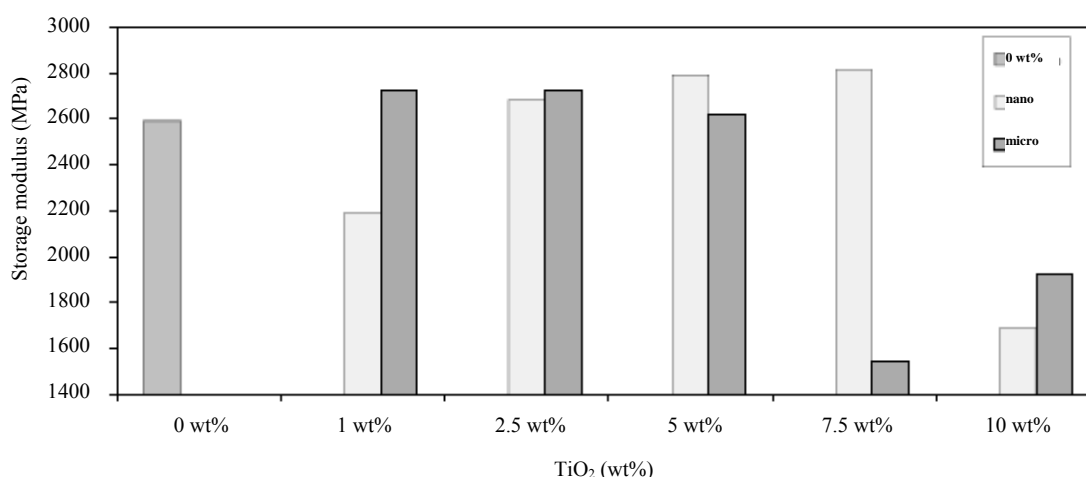


Figure 5. Comparative variation of storage modulus (E') with respect to wt% of TiO₂ for epoxy-micron and epoxy-nano particle-reinforced composites.

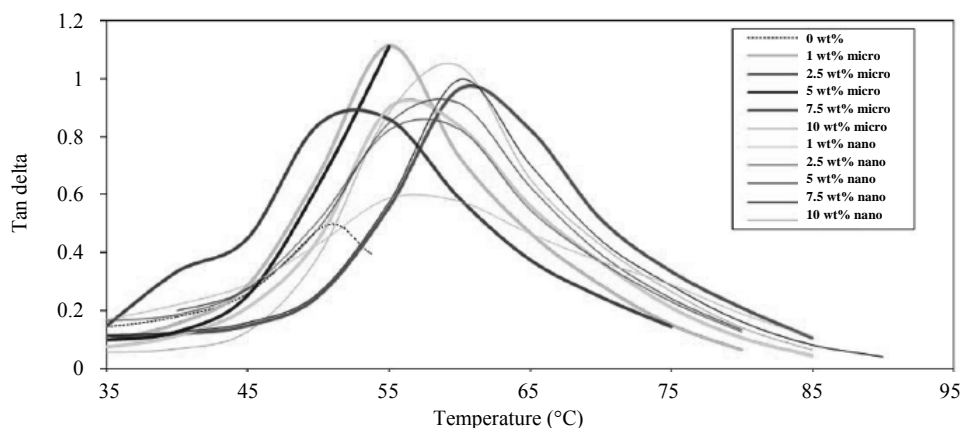


Figure 6. Comparative DMA heating profile of tan delta for epoxy-micron and epoxy-nano TiO_2 particle-reinforced composites.

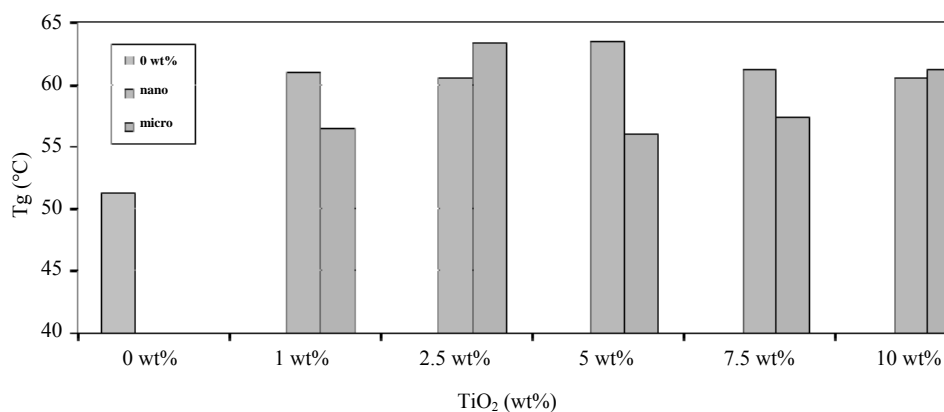


Figure 7. T_g of the composites as a function of TiO_2 content.

The increase in T_g may be attributed to a loss in the mobility of chain segments of the epoxy systems resulting from the particle matrix interaction. Modulus of elasticity increased due to presence of nano TiO_2 particles from 2.5 to 5 and 7.5 wt% respectively. However, for the first formulation, 1 wt% epoxy-nanoparticle composite, the modulus decreased from about 2600 MPa to about 2200 MPa. The last formulation also showed a considerable decrease of modulus with respect to the 0, 1, 2.5, 5 and 7.5 wt% nanoparticle containing composites. Figure 10 also clearly indicates the effect of nano TiO_2 particles on

increasing the T_g of the resin systems where the 5 wt% nano- TiO_2 composite shows the highest glass transition temperature. The mechanical load imposed on the nanocomposites is effectively transferred to the TiO_2 from the matrix. It is well known that good interfacial adhesion between reinforcement and polymer matrix restricts the molecular motions of the polymer networks that may cause the improvement of the flexural properties. However, as indicated by Fig. 9, in 10 wt% nano- TiO_2 composite and 7.5 and 10 wt% micron- TiO_2 composites the particles seem to get agglomerated while processing the samples, therefore, the

dispersion becomes poor and the flexural properties decrease. Modulus is a bulk property of materials that depends on the geometry, particle size distribution and concentration of the filler. Higher particle concentration increases Van Der Waal's forces between the particles and that may lower the dispersion of the particles in the polymer matrix, due to reduced surface area. Effective load transfer lowers, resulting in the lower modulus value. The flexural strength is known to be reduced with raising the filler content [22,23]. The static adhesion on strength as well as the interfacial stiffness usually plays a significant role in transferring stress and elastic deformation from the matrix to the fillers. This is especially true for nanocomposites, because they impart a high portion of interface [20]. If reinforcement-matrix interaction is poor, the particles are unable to carry out any part of external load, (as seems to be the case of 7.5 and 10 wt% micron TiO₂ composites and 10 wt% nano TiO₂ composites in the present study). The gain in mechanical properties is due to the reduction of void content. The reduction in void content in the matrix increases the strength of the nanophase composite. With incremental of particle concentration for 10wt% nano-TiO₂ composite the number of particles increases, which causes particle-particle interaction rather than the particle-matrix interaction. So the particles begin to form agglomerates, which eventually affect the Van Der Waal's interaction between the polymer chains and that may cause decrease in properties. Thus, the large reduction of mechanical properties may be a consequence of a higher level of agglomerated particles that serve as

defect sites. DMA results of epoxy-micron and epoxy-nano TiO₂ particle-reinforced composites are presented in Tables 1 and 2 respectively. Restriction in chain mobility is possible if the particles are well dispersed in the matrix. Good adhesion of nanoparticles with the surrounding polymer matrix (the binder) would additionally benefit the dynamic modulus by hindering molecular motion to some extent. Due to high modulus of TiO₂ particles and good interfacial adhesion, especially between nanoparticles and polymer by physiochemical interaction, mechanical load imposed on the nanocomposites transfers through the stronger interfacial surface to the stronger nanoparticles effectively. The hard particles embedded into the polymer would act as additional virtual network nodes. Mostly, the key factor of controlling T_g for normal thermosetting polymeric systems is crosslink density. Increasing the crosslink density increases T_g. Here increase of T_g is related to the restriction effect of the TiO₂ particles on segmental motion. The interaction of TiO₂ with the epoxy-amine resin system and the formation of the interfacial layers during the curing process will exhibit significantly different segmental dynamics from the bulk resin which is why the epoxy TiO₂ particle-reinforced composites have shown a higher T_g than the neat epoxy-hardener resin system. The smaller the particle size, the greater the surface availability, and thus, increased restriction of the resin networks. Our results are a clear indication of this. However, 25 wt% micron TiO₂ composite exhibits slightly higher T_g than its corresponding nano sample. The reduction of T_g above 5 wt% nano TiO₂ composites may

be due to: 1) On increasing the amount of nano-TiO₂ particles the stoichiometry of epoxy amine system is disturbed, thus shifting the T_g to lower side, which has also

been reported by other authors [21], and 2). The lack of uniform dispersion of nano particles as their concentration increase has been discussed above.

Table 1. DMA results of epoxy-micron TiO₂ particle-reinforced composites, obtained from the glass-rod mixing.

Conc. of TiO ₂ (wt. %)	T _g (°C)	Flexural Storage Modulus, E' (GPa) at:				Shear Storage Modulus G' (GPa) at:			
		35	40	45	50(°C)	35	40	45	50(°C)
0	51.3	2.593	2.231	1.713	0.9345	0.9003	0.7748	0.5949	0.320
1	56.5	2.725	2.237	1.566	0.6483	0.9462	0.7768	0.5438	0.2251
2.5	63.3	2.728	2.425	2.047	1.420	0.9473	0.8425	0.7109	0.4931
5	56	2.620	2.214	1.561	0.6677	0.9097	0.7686	0.5419	0.2318
7.5	57.3	1.545	1.113	0.6158	0.1925	0.5366	0.3865	0.2138	0.0668
10	61.2	1.923	1.614	1.183	0.6417	0.6677	0.5605	0.4108	0.2228

Table 2. DMA results of epoxy-nano TiO₂ particle-reinforced composites, obtained from the glass-rod mixing.

Conc. of TiO ₂ (wt. %)	T _g (°C)	Flexural Storage Modulus, E' (GPa) at:				Shear Storage Modulus G' (GPa) at:			
		35	40	45	50(°C)	35	40	45	50(°C)
0	51.3	2.593	2.231	1.713	0.9345	0.9003	0.7748	0.5949	0.320
1	61	2.194	2.024	1.574	0.8398	0.7618	0.7927	0.539	0.257
2.5	60.5	2.681	2.283	1.552	0.7401	0.9308	0.7927	0.539	0.257
5	63.5	2.792	2.622	2.322	1.642	0.9695	0.9106	0.8062	0.5702
7.5	61.2	----	2.814	2.051	1.088	0.9984	0.9771	0.7156	0.3767
10	60.5	1.690	1.298	0.9039	0.5277	0.5869	0.4506	0.3139	0.1832

3-3. Effect of mixing method on dynamic mechanical properties of micron and nano particle-reinforced composites:

Table 3 is a comparison of the dynamic mechanical properties obtained for the four samples, which were prepared by two different mixing methods:

- Mixed by glass rod
- Mixed by sonication

For the composites without any TiO₂ content (the neat resin composites) mixing by sonication has increased the T_g by 1.5 °C, whereas for all the other three systems compared (1 wt% micron, 7.5 wt% nano and 10 wt% nano TiO₂ filled composites) the systems, which have been mixed by glass rod, show higher T_gs (Fig. 8).

Table 3. DMA results of epoxy-micron and epoxy-nano TiO₂ particle-reinforced composites prepared by two different mixing methods: Glass-rod and sonication.

Conc. of TiO ₂ (wt. %)		T _g (°C)	Flexural Storage Modulus, E' (GPa) at:				Shear Storage Modulus G' (GPa) at:			
Micron	Nano		35	40	45	50(°C)	35	40	45	50(°C)
0(S)	0(S)	52.8	1.145	0.5896	0.2214	0.0545	0.3975	0.2047	0.0769	0.0189
0(G)	0(G)	51.3	2.593	2.231	1.713	0.9345	0.9003	0.7748	0.5949	0.320
1(S)		52.5	1.04	0.6282	0.2497	0.0716	0.361	0.2181	0.0867	0.0249
1(G)		56.5	2.725	2.237	1.566	0.6483	0.9462	0.7768	0.5438	0.2251
	7.5(S)	55.8	1.597	1.047	0.445	0.105	0.5545	0.3634	0.1545	0.03645
	7.5(G)	61.2	----	2.814	2.051	1.088	0.9984	0.9771	0.7156	0.2251
	10(S)	55.5	1.381	0.7667	0.3826	0.1914	0.4796	0.2662	0.1329	0.06646
	10(G)	60.5	1.690	1.298	0.9039	0.5277	0.5869	0.4506	0.3139	0.1832

*: Sonication

* *: Glass rod

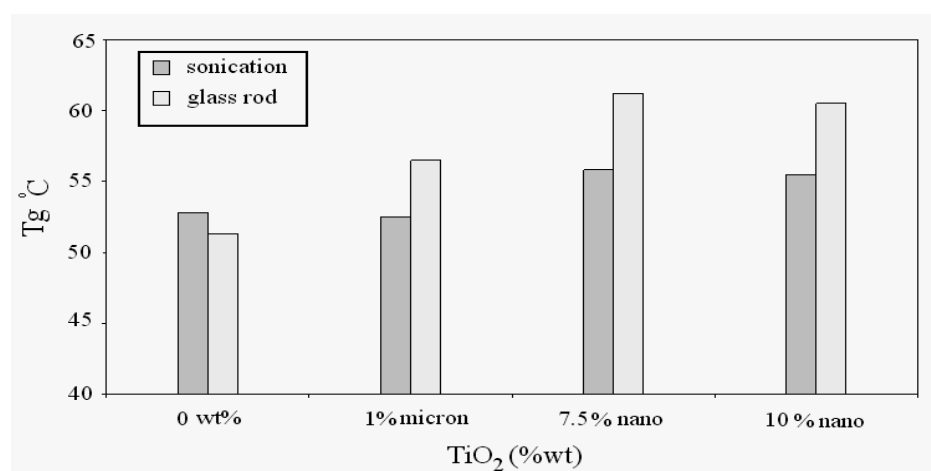


Figure 8. Effect of mixing method on T_g for various micron and nano TiO₂ particle-reinforced composites.

Considering the effect of mixing method on temperature profile of tan delta for the above mentioned resin systems (Fig. 9), as the concentration of TiO₂ particles increases, the peaks broaden, indicating the increase of inhomogeneity. Figure 10 indicates that the samples, which have been mixed in ultrasonic bath, show a considerable decrease of storage modulus as compared to those mixed by glass rod. This result can be attributed to the high viscosity of the resin

system which probably has not let the cavitation process occur properly during ultrasonic mixing and as a result no proper mixing, thus uniform dispersion of both types of particles has not been done effectively. This failure of mixing has resulted in considerably low modulus composites. It must be mentioned that, the other composite formulations of Table 1 were also prepared by mixing through sonication. But they failed to give any results on DMA testing.

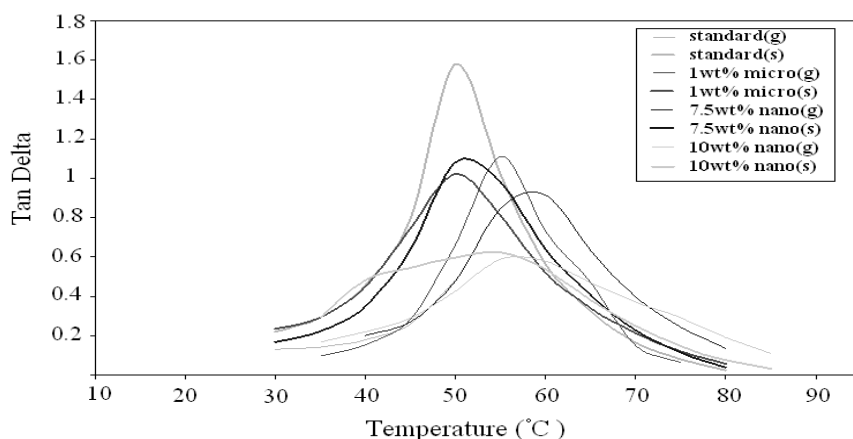


Figure 9. Effect of mixing method on heating profile of tan delta for various micron and nano TiO_2 particle-reinforced composites.

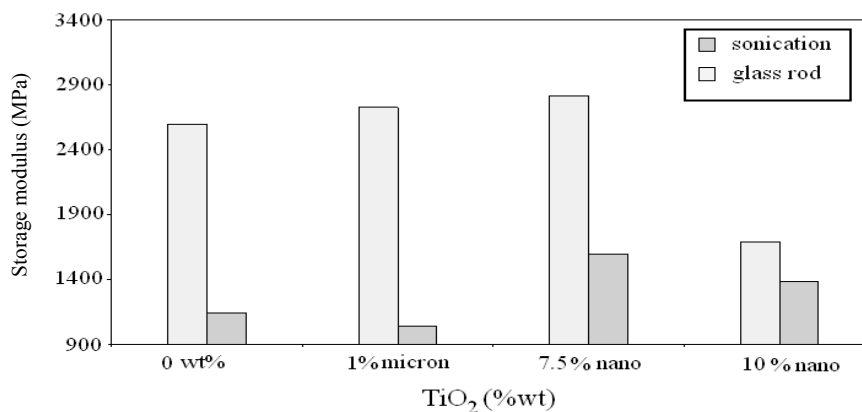


Figure 10. Effect of mixing method on flexural storage moduli (E') for the composites containing varying TiO_2 content.

4. Conclusions

Thermal stability of the particle reinforced composites increased on increasing the concentration of TiO_2 both in nano- and micron-filled cases, except for the 2.5wt% nano-filled composite. The result of this work indicated lower decomposition temperature for the 2.5 wt% nanocomposite than the neat resin system at 1% weight loss; however, the two composites with higher concentrations of nano- TiO_2 particles, showed increased decomposition temperature

at 1% weight loss level. The lower decomposition temperature resulted from lower crosslink density, which in turn could be attributed to the imbalance stoichiometry resulting from addition of nano-loading. Micron-size TiO_2 particles had an increasing effect on storage modulus at lower particle loadings and for the nano- TiO_2 particle-reinforced composites, storage modulus increased as the content of nano- TiO_2 increased from 2.5 to 5 and 7.5 wt% respectively and also with respect to the neat

resin system. Presence of both micron and nanoparticles increased the T_g of the composites. On the whole, composites in which the TiO₂ particles have been dispersed through the resin matrix by glass rod showed better results (higher storage modulus and T_g s) than those mixed by sonication, due to intrinsic high viscosity of the polymer matrix.

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