Advanced Journal of Science and Engineering

Original Research

Comparing Effects of Different Nanoparticles and Compatibilizers on the Properties of Thermoplastic Polyester Elastomer Nanocomposites

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*Received***:** 12 June 2021 / *Revised***:** 25 June 2021 / *Accepted***:** 26 June 2021 / *Published Online***:** 30 June 2021

A B S T R A C T

Reinforced polymer flexible composites, including nanoparticles (titan dioxide, nTiO₂, and Zinc oxide, ZnO), reveal new avenues of engineering that demonstrate better mechanical and chemical features. This paper examines the effects of nanoparticles and compatibilizers (maleated styrene-(ethylene-co-butylene)-styrene, SEBSMA and stearic acid, SA) on the features of poly(butylene terephthalate)-block-tetramethylene ether glycol terephthalate (PBT-TEGT)-based thermoplastic polyester elastomer (TPE). The nanoparticle content in the matrix was varied from 1 to 5 wt%. The surface of the nanoparticles was modified with different compatibilizers such as SA and SEBSMA before melt blending for better surface adhesion and fine dispersion. The effects of modified and unmodified nanoparticles with a varying concentration on the morphological and mechanical features of TPE/nanoparticles nanocomposites were manufactured by a twin-screw extruder followed by a heat press machine. Due to the stiff structure of nanoparticles, all tensile features (yield strength, tensile strength, and tensile modulus) increased while impact strength and elongation at break reduced. Consequently, although nTiO₂ has a higher hardness than nZnO, the elongation of nanocomposites with nTiO₂ was higher than that of nZnO. The presence of SA in TPE/nTiO₂ nanocomposite was more effective than the presence of SEBSMA in TPE/nTiO₂ nanocomposite. On the contrary, the tensile features of SA modified nTiO2 nanocomposites were higher than that of SA modified nZnO nanocomposite. This is probably due to the better compatibility of nTiO₂ with SA and in this case, the more fine structure of nTiO₂ with TPE has been induced, which ensures the result of lower elongation at break.

K E Y W O R D S Thermoplastic polyester elastomer, Nano-TiO2, Nano-ZnO, Nanocomposites, Morphology, Mechanical properties.

C I T E Zaman HU, Khan RA. Comparing Effects of Different Nanoparticles and Compatibilizers on the Properties of Thermoplastic Polyester Elastomer Nanocomposites. Advanced Journal of Science and Engineering. 2021;2(2):86-92.

D O I <https://doi.org/10.22034/advjscieng21022086>

U R L <https://sciengpub.com/adv-j-sci-eng/article/view/advjscieng21022086>

I N T R O D U C T I O N .

Pioneering Thermoplastic elastomers (TEs) are innovative ingredients that have both elastic and plastic features. With TEs, a thermoplastic polyester elastomer (TPE), which consists of poly(butylene terephthalate) (PBT) as the hard part and tetramethylene ether glycol terephthalate (TEGT) as the soft part, has superior mechanical, thermal properties, and elasticity.¹ TPEs in TEs have very good low-temperature flexibility and high performance for mechanical properties at temperatures up to 130°C.² It has excellent oil resistance, impact, creep, and abrasion and is also used for automotive parts such as gears and sprockets, tubing, electronics, electronic parts, and even increasingly substitute

the cross-linked rubbers.³ It has attracted interest because of its low specific gravity and excellent reprocessing, which has been considered an environmentally friendly material that replaces vulcanized rubber and PVC. Consequently, both academically and commercially, many studies related to the modification of TPE have progressed to achieve its more suitable features for various applications such as electronic devices, clothing, and outdoor devices, etc. The chemical structure and hydrogen bonding of the PBT-TEGT based TPE are revealed in scheme 1.

Scheme 1: a) Chemical structure of thermoplastic polyester elastomer (TPE), b) Binding mode of carboxylate with titania surface: hydrogen bonding.

Various inorganic nanoparticles like TiO₂, SiO₂, CaCO₃, and ZnO are being used to develop the mechanical features of polymers.^{4, 5} TPE/nanoparticles nanocomposites continue to arouse great interest in scientists due to their flexibility in design in addition to advanced mechanical features. ⁶ Despite a substantial increase in mechanical properties, nanoparticles may agglomerate, and nanoparticles may exhibit a decrease in toughness due to their stiffness. To overcome this problem, it is necessary to use dispersants and additive agents.^{5, 7} An additional problem studied with nanoparticles is the reduction in impact resistance due to the stiff and rigid structure of the reinforcement. This problem can be solved by incorporating elastomer particles in the polymer matrix.^{8, 9} Huang et al.¹⁰ used stearic acid as a dispersant in PP/nZnO nanocomposite. They acquired structures with finely dispersed particles and they observed an increase in tensile strength, flexural strength, and flexural modulus of the composite. Tjong et al.¹¹ used SEBS-g-MA in PP/montmorillonite composites. The maleic anhydride acted as a compatibilizer between inorganic particles and the matrix, as well as increasing the toughness of the SEBS composite. In this work, we used PBT-TEGT copolymer as a matrix and prepared TPE/nanoparticles nanocomposites by melt mixing method. It is known that metal oxide nanoparticles such as nTiO₂ or nZnO can interact with acidic functionalities of polymers, increasing the particle-matrix interaction. The binding mode can lead to increased interactions between the TPE matrix and nanoparticles. As a result, the features of nanoparticles-filled TPE composites should be significantly changed. In this study, TPE, which is a class of engineering thermoplastic elastomers with a wide range of domestic and industrial applications, is reinforced with SA and SEBAMA coated nanoparticles. The mechanical features of the nanocomposites were investigated according to the inorganic particle content and the surface modifier.

M A T E R I A L S & M E T H O D S .

Preparation

The polymer matrix TPE granules were kindheartedly delivered by M/S Rupal Plastics Ltd, Mumbai, India with a grade was Hytrel 6356. Nanomaterials such as nTiO₂ and nZnO were supplied by China's Nabond Company. Stearic acid (Merck, Germany) and SEBSMA (Kraton, France) were used for modifying particles.

Before modification, nanoparticles were dried under a vacuum oven. The nanoparticles were coated with two different compatibilizers: stearic acid and SEBSMA. For stearic acid coating, stearic acid was dissolved in chloroform at room temperature for one day. Then, pure nTiO₂ or nZnO particles were added to this solution and followed by crushing for mixed 3 h. The quantity of the stearic acid was 4 and 5 % of nTiO₂ and nZnO particles, respectively. The SEBSMA was dissolved in toluene for two days at 50°C and then the nanoparticles were slowly incorporated separately into the solution and mixed with a mechanical mixer (IKA RW 20 digital). The mixer was then crushed after drying for 6 h at a temperature of 50°C. The quantity of the SEBSMA was 3 wt% of the nanoparticles.

The nanocomposite samples were prepared with varying amounts of nanoparticles (1, 3, and 5 wt%), with a fixed amount of 3 wt% of the nanoparticles with two types of compatibilizers (SA and SEBSMA) with a predetermined

amount of TPE. The coding of uncoated and coated nanocomposites was as follows: For uncoated, TPE/1 wt% nTiO₂ (marked as TPE/1UnTiO2), TPE/3UnTiO2, TPE/5UnTiO² and TPE/1UnZnO, TPE/3UnZnO, TPE/5UnZnO and for coated, TPE/SA coated 1 wt% nTiO₂ (indicated as TPE/1SAnTiO₂), TPE/3SAnTiO₂, TPE/5SAnTiO₂ and TPE/SEBSMA coated 1 wt% nZnO (designated as TPE/1SEnZnO), TPE/3SEnZnO, TPE/5SEnZnO. The nanoparticles and the TPE were loaded into a Berstorff twin-screw extruder (ZE-25A UTX, KraussMaffei Berstorff GmbH, Germany) with an L/D ratio of 44. The operation temperature was ranged from 180°C to 220°C and the speed of the screw was 100 rpm. The extruded strands were ground into small pellets and the achieved pellets were used to make thin plates using a hot press machine.

Characterization

TEM and SEM were used to analyze fracture surfaces and the dispersion of nanoparticles. SEM, JSM-6360LV from JEOL, Tokyo, Japan was used to analyze the fracture surfaces of nanocomposites. The samples were gold-coated before imaging. Transmission electron microscopy (TEM, JEM-2100F, JEOL) was used to examine the dispersion of TPE and nanoparticles.

The tensile test was measured using Shimadzu Universal Testing Machine (model AG-1, Japan). Samples were ~ 10 mm wide, 2 mm thick, with a gauge length of 50 mm. A crosshead speed of 10 mm/min was used to measure the yield strength, tensile strength, tensile modulus, and elongation at break. The Izod impact test was determined on notched specimens using a 5.4 J pendulum hammer on a Zwick impact test machine. All experiments were conducted under ASTM-D 638-03, standard,¹² and five repeat tests were performed to obtain an average value for each sample.

Fig. 1: Tensile features of nTiO₂ and nZnO reinforced TPE nanocomposites; a) yield strength, and (b) tensile strength.

R E S U L T S & D I S C U S S I O N .

Mechanical Properties of the Nanocomposites

Metal oxide nanoparticles progress the mechanical features of the polymer matrix.¹³ Fig. 1 (a) and (b) illustrated the variation of yield strength and tensile strength of TPE, TPE/uncoated nTiO₂ (TPE/UnTiO₂), TPE/uncoated nZnO (TPE/UnZnO), TPE/SA coated nTiO₂ (TPE/SAnTiO2), TPE/SA coated nZnO (TPE/SAnZnO), TPE/SEBSMA coated nTiO₂ (TPE/SEnTiO2) and TPE/SEBSMA coated nZnO (TPE/SEnZnO) nanocomposites with nano-metal oxide (nMO) contents varying from 0 to 5 wt%. It can be observed that increasing the nMO content up to 3 wt% increased the yield strength and tensile strength (yield strength increased by 17% and tensile strength increased by 15% for TPE/UnTiO₂ nanocomposites and yield strength increased by 13% and tensile strength increased by 11% for TPE/UnZnO nanocomposites compared to TPE, respectively) and then decreased by 5 wt%. The addition of nMO particles to the TPE improves the yield and tensile strength of the matrix at 3 wt% nMO due to strong stress transfer from TPE to nMO. At 5 wt% of nMO particles, an improvement in yield and tensile strength was reduced due to the relative low-stress transfer effect of nMO particles. In this case, the agglomerated nanoparticles are easily debonded from the TPE and no fraction of the external load is ultimately allowed to reduce the yield and tensile strength. These outcomes were supported by Zaman et al.¹⁴ To advance the interfacial bonding between nMO particles and TPE, SA and SEBSMA led to the modification of TPE/nTiO₂ or TPE/nZnO nanocomposites. The inclusion of SA in TPE/nTiO2 or TPE/nZnO nanocomposites has created significantly noticeable interfacial bonding between nMO and TPE compared to TPE/UnTiO₂ or TPE/nZnO nanocomposites. The maximum yield strength and tensile strength of TPE/SAnTiO₂ and

TPE/SAnZnO nanocomposite were 22.3, 24.2 MPa and 21.5, 23.3 MPa, respectively, at 3 wt% of nMO content and about 31%, 33%, and 27%, 29% higher than TPE matrix. TPE/SAnTiO₂ gave the highest yield and tensile strength followed by TPE/SAnZnO. The increase in the strength of the compatibilized system is expressed by the better distribution produced by the compatibilizer and an enhanced solid-state adherence, which can transfer more stress from the matrix to the dispersion phase. Although TPE/SEnTiO₂ or TPE/SEnZnO contains the same quantity of nMO as TPE/SAnTiO² and TPE/SAnZnO, it gave lower strength due to the presence of the elastomeric phase of SEBSMA.

Fig. 2: Tensile and impact features of nTiO₂ and nZnO reinforced TPE nanocomposites; a) tensile modulus, b) elongation at break, and c) impact strength.

Fig. 2 (a) and (b) displayed the variation of tensile modulus and elongation at break of the nanocomposites against nMO content. With the inclusion of nMO, tensile modulus steadily increased while elongation at break steadily reduced. Modulus growth offers an effective stress transfer from the TPE to nMO particles. On the other hand, the elongation reduced with the inclusion of nMO-indicated interference or deformability of TPE by nMO. This interference was created by the presence of physical interaction and mechanical restraint of the TPE. SA gave increment of tensile modulus, especially in 5% nMO content. As explained later, the fine dispersion of the SA-coated nMO particles and good adhesion between the TPE and nMO particles enriched the tensile modulus. On the contrary, the nanocomposites with SEBSMA gave high tensile modulus at 5 wt% nMO content. Nevertheless, the tensile test outcomes, SEBSMA coated of nZnO particles were not dispersed as fines as nTiO₂ particles. nTiO₂ has given higher yield strength, tensile strength, and tensile modulus due to its stiff structure, and its higher hardness compared to nZnO was effective in this outcome. In contrast, TPE/nTiO₂ nanocomposites were expected to have lower elongation when compared with nZnOreinforced nanocomposites, but in particular, the opposite was found to be more than 1 wt%. This suggests that the compatibility of SA or SEBSMA was better with nTiO₂ than nZnO. The impact features obtained from the impact test are given in Fig. 2 (c). With the inclusion of nMO, the impact strength was reduced due to the hardness of nMO particles. However, the presence of SA or SEBSMA increased the impact strength when nanocomposites with SA or SEBSMA were compared as follows: TPE/SAnTiO₂ and TPE/SEnTiO₂, TPE/SAnZnO, and TPE/SEnZnO. The presence of SA

provides toughness to the nanocomposite through the molecular flexibility of TPE and induces higher impact strength. With the increment in nMO content, the impact strength reduced due to the presence of agglomerates as discussed later. When the nMO content increased, because the SEBSMA did not provide good dispersion as well as in the SA, agglomerates increased, and the interfacial nMO-TPE adhesion decreased. Depending on it, despite the presence of elastomer phase in the nanocomposite of TPE/SEnTiO₂ and TPE/SEnZnO, low impact strength has been observed. As is well known, each agglomerate induces the effect of cracking and reduces its impact strength.

Fig. 3: TEM photomicrographs; a) TPE/3UnTiO2, b) TPE/3SAnTiO2, c) TPE/3SEnTiO2, d) TPE/3UnZnO, e) TPE/3SAnZnO, and f) TPE/3SEnZnO.

Surface Morphology and Particle Dispersion

Mechanical properties are related to the uniformity of multiple morphologies, domain sizes, and shapes to determine the degree of dispersion of interactions between the two stages, and it is considered to be one of the most important elements.¹⁵ Fig. 3, panels a-c, demonstrated TEM photomicrographs of TPE/nTiO₂ nanocomposites consisting of 3 wt% nTiO₂ (designated as TPE/3UnTiO₂) and TPE/SA coated 3 wt% nTiO₂ (denoted as TPE/3SAnTiO₂) or TPE/SEBSMA coated 3 wt% nTiO₂ (marked as TPE/3SEnTiO₂). Fig. 3 (a) displayed considerably bigger nTiO₂ particles, which were not intercalated and probably form a 'micro composite' structure, possibly due to the absence of SA or SEBSMA. The black shape exhibits the nTiO₂ tactoids and the rest of the region represents an uninterrupted TPE. Nevertheless, some black shapes may indicate some weakly dispersed nTiO₂ aggregates. Fig. 3 (c) on the other hand shows relatively fewer nTiO₂ particles compared to Fig. 3 (a) and the $nTiO₂$ particles were separated into lighter parts by the blending manner. Anyway, a better dispersion can be acquired after the addition of SA as a compatibilizer, which performances as an intercalator between TPE and nTiO₂ (Fig. 3, b). TPE/3SAnTiO₂ systems have better and more uniform dispersion of nTiO₂ in the TPE matrix than in the TPE/3SEBnTiO₂ system because of less black shape in that for SA. Fig. 3, panels d-f, depicted TEM micrographs of TPE/3UnZnO, TPE/3SAnZnO or TPE/3SEnZnO nanocomposites, respectively. Fig. 3 (d) showed remarkably large nZnO particles that are not intercalated and indicate weak dispersion between TPE and nZnO. In the TEM photomicrographs of TPE/3SAnZnO assumed in Fig. 3 (e), nZnO particles were almost embedded in the matrix and dispersed well. This ensures the compatibility of $nTiO₂$ and TPE and the strong bonds generated between nTiO² and TPE. In contrast, when the SEBSMA coating was applied (Fig. 3, f), the dispersion of nZnO particles was lower than in Fig. 3 (e) but some nanoparticles were separated into lighter parts by the mixing process. Furthermore, the SA coating of nZnO particles provides better surface adhesion as well as fine dispersion with the SA coating of $nTiO₂$ particles.

SEM photomicrographs of fracture surfaces of nanocomposites are given in Fig 4. Uncoated nTiO₂ or nZnO with nanocomposites, as seen in Fig. 4 (a) and (d), randomly distributed in the TPE matrix, respectively, and some large agglomerates, larger than 1 µm in size were exposed above the fracture surface. Big particles are distributed in TPE to $TPE/3$ UnTiO₂ nanocomposite so that no functional polymer is present and the interfaces appear to be individually wet and/or weak to the adhesion of the components. This confirms the low tensile features and impact strength of the nanocomposites discussed above. Fig. 4 (b) and (e) show nanocomposites containing 3SAnTiO₂ and 3SAnZnO particles,

respectively. These nanoparticles were more uniformly distributed embedded in the TPE matrix and dispersed well without agglomerates. This indicates a strong interaction, adhesion, and direct contact between TPE and nTiO₂/nZnO by wetting the nanoparticles. Moreover, 3SAnTiO₂ particles had better distribution than 3SAnZnO particles in the TPE matrix. This also confirms the outcomes of superior mechanical features of the nanocomposites. Fig. 4 (c) and (f) showed morphological structures of nanocomposites containing 3SEnTiO₂ and 3SEnZnO particles. The TPE/3SEnTiO₂ or TPE/3SEnZnO system had some large parts and the average particle size was smaller than the TPE/3UnTiO₂ or TPE/3UnZnO system. This shows the compatibility of SEBSMA was better with 3SEnTiO2/3SEnZnO than 3UnTiO2/3UnZnO. However, nanoparticle agglomerates appeared in some regions of the TPE matrix reduced tensile features of the TPE/3SEnTiO₂ or 3SEnZnO nanocomposites. To compare the experimental results, 3SAnTiO₂ particles provide better surface adhesion and fine structure to TPE than 3SAnZnO particles, which confirms the outcomes of superior tensile features of TPE/3SAnTiO₂ nanocomposite.

Fig. 4: SEM images; a) TPE/3UnTiO₂, b) TPE/3SAnTiO₂, c) TPE/3SEnTiO₂, d) TPE/3UnZnO, e) TPE/3SAnZnO, and (f) TPE/3SEnZnO.

C O N C L U S I O N .

PBT-TEGT block copolymer-based TPE/nMO nanocomposites were manufactured using a melt mixing process tracked by a hot press machine. This work examined the influences of surface-modified nMO particles on the mechanical and morphological features of TPE/nMO nanocomposites. The obtained results indicated that the inclusion of nMO particles in TPE increased the tensile features of TPE/nMO nanocomposites compared to pure TPE matrix while the impact strength and elongation at break reduced. Furthermore, the addition of SA or SEBSMA coated-nMO particles to TPE significantly changes the tensile features like yield strength, tensile strength, and tensile modulus but impact strength and elongation decreased. SEBSMA coated nMO particles provided better surface bonds besides fine dispersion with SA-coated nMO. nTiO₂ has given higher yield strength, tensile strength, and tensile modulus due to its stiff structure, and its higher hardness compared to nZnO was effective in this outcome. In contrast, TPE/nTiO₂ nanocomposites were expected to have lower elongation when compared with nZnO-reinforced nanocomposites, but in particular, the opposite was found to be more than 1 wt%. This suggests that the compatibility of SA or SEBSMA was better with nTiO2 than nZnO. Moreover, nZnO agglomerates present in certain regions of TPE reduce the tensile features of TPE/nZnO nanocomposites.

D I S C L O S U R E S T A T E M E N T .

The author(s) did not report any potential conflict of interest.

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