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Surface-Modified Nanoparticles Reinforced Polymer Nanocomposites

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ABSTRACT

In this work, poly(butylene terephthalate)-block-poly(tetramethylene glycol) (PBT-PTMG)-based thermoplastic elastomer (TPE)/nano titan dioxide (nTiO2) nanocomposites were compounded by melt mixing process. Before compounding, the surface of the nanoparticles was modified with chloroacetic acid for better surface bond and good dispersion.The effect of unmodified and surface-modified nTiO2particleswith a varying concentration on the mechanical and thermal features of TPE/nTiO2 nanocomposites wasmade and evaluated.Samples of tensile and impact tests were obtained by a hot press machine. The outcomes showed that chloroacetic acid-containing nanocomposites gave a strong interfacial bond between nanoparticles and matrix due to chemical linkage while the absence of chloroacetic acid-induced agglomerates. The presence of chloroacetic acid increased tensile strength and impact strength but tensile modulus reduced due to its limited amount of usage in the coating of thenanoparticles. The inclusion of nTiO2in TPE significantly increases the overall thermal properties of the matrixsuch as the thermal degradation temperatureand thermal stability of nanocomposites.

Keywords: Thermoplastic elastomer, nano-TiO2, nanocomposites,mechanical properties,Thermal properties.

1. INTRODUCTION

Poly(butylene terephthalate)-*block*-poly(tetramethylene glycol) (PBT-PTMG)-based thermoplastic polyester elastomers (TPEs)are new ingredients that are gaining such importance across the boundaries between rubber and plastic. Thus, research on the viability of TPEs is important and required. Due to the phase-isolated microstructure, it has a unique combination of strength, flexibility, and processing. TheTPE consisting of poly(butylene terephthalate) (PBT), as a hard portion, and polytetramethylene glycol (PTMG) is a soft portion, have superior mechanical, thermal properties, and elasticity(Jiang et al., 2019). It has attracted interest due to its low specific gravity and great reprocessing, which has been considered as an environmentally friendly material that replaces vulcanized rubber and PVC.TPEs are also used forgears, tubing, electronics, electronic parts, and even increasingly substitute the cross-linked rubbers (Yao and Yang, 2010).The basic structure of the PBT-PTMGcopolymer-based TPE is revealed in Scheme 1(a). TPE shows outstanding mechanical properties (Nagai et al., 1997)at temperatures of 130°C combined with very good low-temperature flexibility. To improve the mechanical, thermal, and electrical properties of TPE, particulate fillers such as $CaCO_3$, SiO_2, ZnO, and TiO_2,etc. are added. Inorganic nano-metal oxide (nTiO_2) is one of them because, among all other semiconductor metal oxides families, nTiO_2 is inexpensive, electronic and optical stable, nontoxicity, and corrosion-resistant.The introduction of nano-TiO_2 into polymers can improve the mechanical and thermal properties of polymers due to the small size of organic polymers and inorganic nanoparticles and the strong interfacial interaction between large specific fields and quantum effects.As a result, these nanocomposites can be widely applied in coatings, rubbers, plastics,sealants, fibers, and other applications(Li et al., 2002; Takai et al., 1998; Wu et al., 2000).In this study, we used TPE as a matrix and made TPE/nTiO_2 nanocomposites by the melt mixing process. It is known that nTiO_2can react with acidic functionalities of polymers, increasing the particle-matrix interaction. The surface modification of nTiO_2 with chloroacetic acidand its hydrogen bonding are shown inSchemes1 (b) and (c), respectively.

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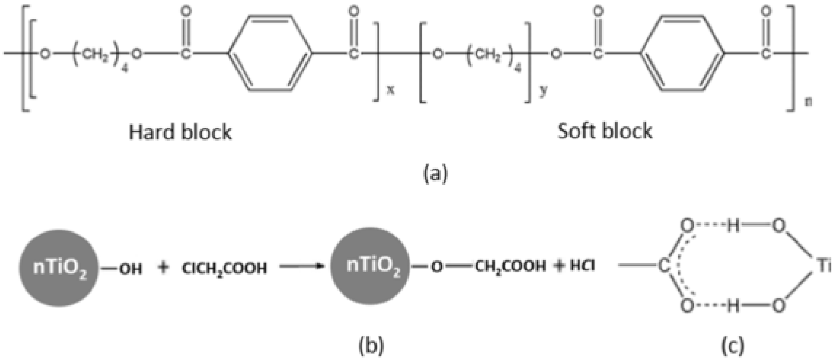

Scheme 1- (a) Basic structure of thermoplastic polyester elastomer (TPE); (b)surface modification of TiO_2 with chloroacetic acid (c) binding mode of carboxylate with titania surface: hydrogen bonding.

TPE/$nTiO_2$ nanocomposites continue to arouse great interest in scientists due to their flexibility in design in addition to advanced mechanical strength, good chemical, electrical and thermal properties(Rong et al., 2001).Despite a significant increase in mechanical properties, nanoparticles may agglomerate and thus reduce the properties of nanocomposites.To overcome this problem,dispersant and coupling agents are being used(Kruenate et al., 2004). In addition, the loss of impact strength due to the stiffness of inorganic ingredients is usually another problem.Researchers use ingredients of elastomeric nature to increase the toughness of composites(Bao and Tjong, 2007; Ishak et al., 2008).In this article, a simple technique for preparing novel TPE/$nTiO_2$ nanocomposites are reported. A highly homogeneous dispersed $CnTiO_2$/TPE composite was formed by interacting between nanofiller and matrix through covalent bonds and interacting with the acidic functionality of the polymer with -COOH moieties on the surface of carboxylated $nTiO_2$ particles.In this study reported herein, the effect of the inclusion of uncoated and coated $nTiO_2$ particles and particle content on the mechanical and thermal properties of the particular TPE.

2. EXPERIMENTAL

2.1. Materials and sample preparation

The polymer matrix TPE granules were kindheartedly delivered by M/S Rupal PlasticsLtd, Mumbai, Indiawith a grade was Hytrel 6356. The $nTiO_2$ under the trade name of Aeroxide® P25 was supplied by Evonik Industry (Germany). Chloroacetic acid (AR)from Shanghai ChemicalsCo., was used without further purification.

The $nTiO_2$ suspension (90-ml water, 5 g of $nTiO_2$) was stirred for 1 h and ultrasonicated for 20 min, then mixed with an ascertained amount of chloroacetic acid dissolved in 10 ml of deionized water.The mixture was heated to 80°C, and the reaction was performed for 2 h under air with continuous stirring.The pH value of the upper liquid layer was neutralized until the carboxylated $nTIO_2$ was purified by centrifugation and then washed with distilled water and no AgCl was detected when the $AgNO_3$ aqueous solution was added to the liquid. The quantity of carboxylated $nTIO_2$ was measured by acid-base titration.The $nTiO_2$ suspension (50 ml) was titrated with 0.005 M standard alkaline solution using phenolphthalein as an acid-base indicator.

Uncoated and coated $nTiO_2$ particles were added separately to the TPE in different ratios as 1, 3, and 5 wt%, and then extruded in a Berstorff twin-screw extruder (ZE-25A UTX, KraussMaffei Berstorff GmbH, Germany). The coding of the nanocomposites was done as follows:TPE/$1UnTiO_2$, TPE/$3UnTiO_2$, and TPE/$5UnTiO_2$ for uncoated and TPE/$1CnTiO_2$, TPE/$3CnTiO_2$, and TPE/$5CnTiO_2$ for coated. The diameter of the screws was 25 mm and the length/diameter ratio (L/D) was 44. The processing temperature was ranged from 200°C neighboring the hopper to 220°C at the die and the speed of the screw was 100 rpm.Each TPE/$nTiO_2$ composite was extruded three times to ensure better dispersion quality of the nanoparticles.The extrudate strands weregranulated and dried at 80°C under vacuum for 3 h.

2.2 Characterizations

The tensile testwas measured using Shimadzu Universal Testing Machine (model AG-1, Japan). Samples were ~ 10 mm wide,1 mm thick, with a gauge length of 50 mm. A crosshead speed of 10 mm/min was used to measurethe tensile strengthand tensile modulus. The Izod impact test was determined on notched specimens using a 5.4 J pendulum hammer on a Zwick impact test machine.Five replicates of tensile measurement were performedfor each formulation. Transmission electron microscopy (TEM, JEM-2100F, JEOL) was used to examine the dispersion of TPE and $nTiO_2$. Scanning electron microscopy (SEM) examination wasperformed with a JSM-6360LV scanning electronmicroscope, and the specimens were coated with a thinlayer of gold before SEM examination. The crystallization and melting behaviors of nanocomposites were investigated by differential scanning calorimetry (DSC, Perkin Elmer DSC-7) in the N_2 atmosphere.Each sample (5-8 mg) was heated from 30 to 240°C at a heating rate of 10°C/min and then held at 240°C to confirmaduplicate thermal history. The sample was cooled down to 30°C at a cooling rate of 10°C/min.The thermal stability of the nanocomposites was determined using a thermogravimetric analyzer (TGA, TA Instruments Q500) with a heating rate of 20ºC/min in an N_2 atmosphere.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties of the nanocomposites

Metal oxide nanoparticles progress the mechanicalfeatures of the polymer matrix(Rahman et al., 2019). Typically, the tensile strength and elastic modulus increase while the impact strength decreases.Variation of tensile strength according to TPE/uncoated $nTiO_2$ ($TPE/UnTiO_2$) and TPE/coated $nTiO_2$ ($TPE/CnTiO_2$) nanocomposites and $nTiO_2$content is illustrated in Figure 1 (a). It was informed that the tensile features ofnanocomposites depend on the interaction and characteristics between the composition content (Zaman et al., 2014).It can be observed that the tensile strength (TS) increased with increasing $nTiO_2$ content up to 3 wt% $nTiO_2$loading (23% increment in tensile strength for 3% loading)and then decreased by increasing $nTiO_2$ loading to 5 wt% (5% decrement in tensile strength than 3% loading).The inclusion of $nTiO_2$ particles to the TPE improves the tensile strength of the matrix at 3 wt% $nTiO_2$due to strong stress transferfrom TPE to $nTiO_2$. At 5 wt% of $nTiO_2$particles, an improvement in tensile strength was reduced due to the relative low-stress transfer effect of nanoparticles. These outcomes were compatible with the results of the research study performed by Zaman et al(Zaman et al., 2013).To progress the filler dispersion progression in the TPE matrix and to stretch the interfacial bonding between $nTiO_2$ and TPE, chloroacetic acid is led to modify the $TPE/nTiO_2$ nanocomposites. The inclusion of $TPE/CnTiO_2$nanocomposite has created significantly noticeable interfacial bonding between filler and matrixthan those of$TPE/UnTiO_2$nanocomposite. The maximum tensile strength of the $TPE/CnTiO_2$ nanocomposite was24.9 MPa at 3 wt% of $nTiO_2$ contentand about 23% higher than that of the TPE matrix. A highly homogeneous dispersed $CnTiO_2$/TPE nanocomposite was formed by interacting between nanofiller and matrix through covalent bonds and interacting with the acidic functionality of the polymer with -COOH moieties on the surface of carboxylated $nTiO_2$ particles.

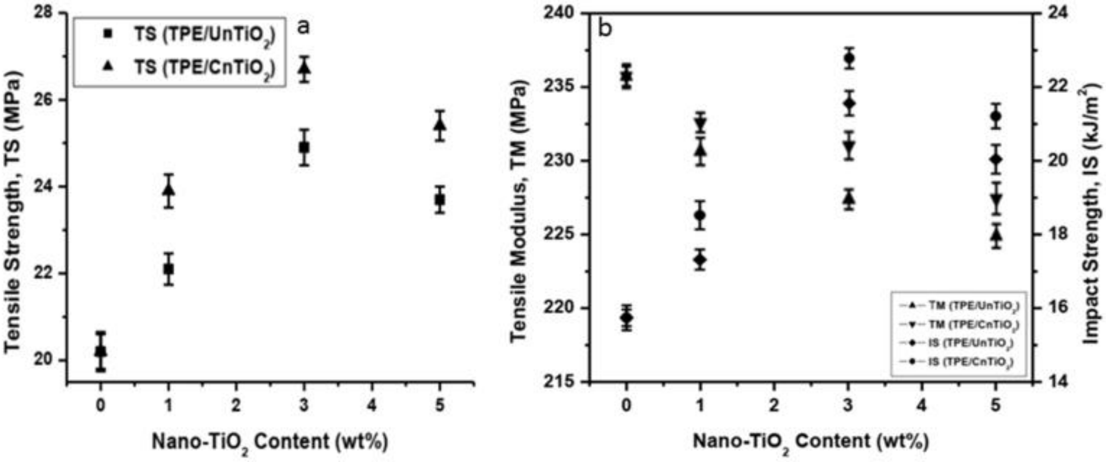

Fig. 1- (a) Tensilestrength and (b) tensile modulus and impact strength of $TPE/nTiO_2$ nanocomposite.

Figure 1 (b) displays the variation of tensile modulus and impact strength of the nanocomposites against $nTiO_2$ content.It can be observed that impact strength (IS) increased with increasing $nTiO_2$ content up to 3 wt% $nTiO_2$ loadingfor uncoated and coated nanocomposites and then decreased, but tensile modulus (TM) steadily declined with increasing $nTiO_2$ content.Maximum IS(22.9kJ/m^2) was obtainedat 3 wt% of $CnTiO_2$ content.At this stage, the IS value of the $TPE/CnTiO_2$ nanocomposite was about 18% higher than that ofthe $TPE/3UnTiO_2$and even 46% higher than that of the TPE matrix. The presence of chloroacetic acid provided the toughness of the composites through the molecular flexibility of the polymer matrix and induced this higher IS but lower TM as seen in Figure 1 (b). The reason for lower TM than that of TPE was the plasticizing effect of the chloroacetic acid.

3.2. 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(Ghazy et al., 2020). Figure 2 (a)-(b) represents the TEM microphotographs of $TPE/3UnTiO_2$ and $TPE/3CnTiO_2$nanocomposites, respectively. Figure 2 (a) shows considerably bigger $nTiO_2$ particles,which are not intercalated and probably form a ‘micro composite’ structure, possibly due to the absence of surface carboxylated $nTiO_2$.The black shape exhibits the $nTiO_2$ tactoids and the rest of the region represents an uninterrupted TPE. Nevertheless, some black shapes may indicate some weakly dispersed $nTiO_2$ aggregates.Figure 2 (b) on the other hand revealsrelatively small $nTiO_2$ particles compared to Figure 2 (a) and the $nTiO_2$ particles were separated into lighter parts by the blending manner. Therefore, surface carboxylated $nTiO_2$ should be mixed with TPE to better disperse $nTiO_2$ in the matrix and to increase the tensile features.

Figure 2 (c)-(d) illustrates the SEM microphotographs of $TPE/3UnTiO_2$ and $TPE/3CnTiO_2$ nanocomposites, respectively.The particles of $nTiO_2$ in Figure 2(c) were randomly distributed in the TPE matrix and some large portions were exposed above the fracture surface. Big elements are distributed in TPE to

TPE/3UnTiO$_2$ 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.As shown in Figure 2 (d), the TPE/3CnTiO$_2$system was more uniformly dispersed in the TPE matrix than the TPE/3UnTiO$_2$system.Changes in both particle size and interface indicate that TPE/3CnTiO$_2$system help break down particles and modify interfacial interactions. This result agrees with the outcomes of the tensile features in Figure 1.

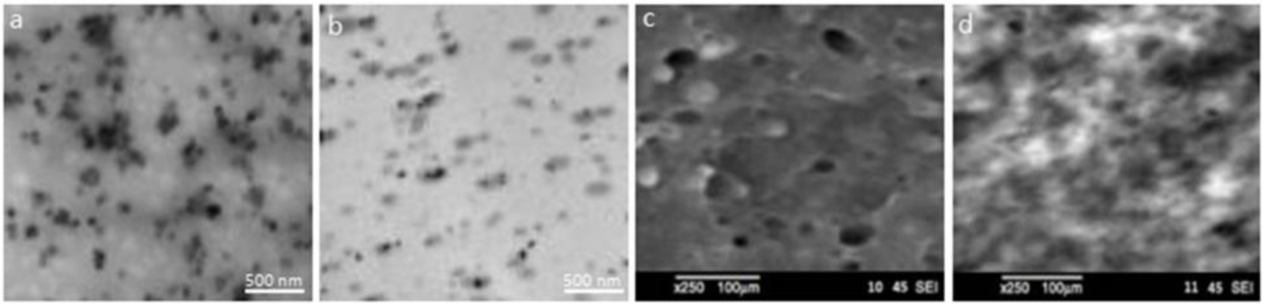

Fig. 2- TEM images of (a) TPE/3UnTiO$_2$ and (b)TPE/3CnTiO$_2$nanocompositesand SEM images of (c) TPE/3UnTiO$_2$ and (d) TPE/3CnTiO$_2$ nanocomposites.

3.3. Thermal properties of the nanocomposites

The results of the DSC of the TPE matrix and its nanocomposites are given in Table 1.As it can be noted from Table 1, the crystallization temperature(T_c) has improved from 136.5ºCof TPE to 138.3ºC of TPE/3UnTiO$_2$ nanocompositedue to the heterogeneous nucleation of nTiO$_2$.Significantly, TPE/3CnTiO$_2$ increased the T_c to 141.2ºC, much higher than TPE and even higher TPE/3UnTiO$_2$ due to the presence of surface carboxylated nTiO$_2$ favored the crystallization and provided better distribution of the nanoparticles.The interaction between TPE and surface carboxylated nTiO$_2$ was better than that of UnTiO$_2$ because during the melting, the acidic functionality of the polymer with -COOH moieties on the surface of the carboxylated nTiO$_2$ particles interacted with the TPE mode and the nTiO$_2$ through the covalent bonds.The TPE/3UnTiO$_2$ nanocomposite with 3CnTiO$_2$ has an obvious decrease of ΔH_c and ΔH_m. This is due to the formation of the chemical bonds between TPE and nTiO$_2$, which prevent the movement of the PBT molecules, thus decrease the crystallinity of the nanocomposites. Moreover, the inclusion of TiO$_2$ nanoparticles in TPE displays a slight effect on the melting temperature (T_m). At 3-wt% of TiO$_2$ nanoparticles, the $T_m$increases from 183.7ºC of the matrix to 188.9ºC of TPE/3UnTiO$_2$nanocomposites.The improvement is about 5.2ºC. The increase in T_m in nanocomposite should be attributed to the chemical linkage between the matrix introduced in Scheme 1 and the nTiO$_2$ particle, which increases the chain length and the molecular weight of the TPE.Moreover, the T_m of the TPE matrix was improved by the inclusion of CnTiO$_2$ seemingly. Take into account the nucleation effect of CnTiO$_2$ in TPE; one can consider that the crystallization of TPEin TPE/3CnTiO$_2$ is mostly measured by CnTiO$_2$ somewhat than by UnTiO$_2$.

Table 1:Thermal properties of pure TPE and TPE/nTiO$_2$ nanocomposites.

Nanocomposites (w/w %)	T_m (°C)		T_c (°C)	ΔH_c (J/g)	T_{onset} (°C) (TGA)
	A	B	B		
Pure TPE	90.2	178.3	136.5	28.3	385.6
TPE/3UnTiO$_2$	97.6	183.7	138.3	27.2	391.4
TPE/1CnTiO$_2$	99.4	186.2	139.6	25.4	394.7
TPE/3CnTiO$_2$	104.3	188.9	141.2	24.9	398.5
TPE/5CnTiO$_2$	101.2	187.2	140.3	25.1	397.3

A: PTMG block; B: PBT block

The TGA probe provides important evidence in determining the thermal stability of nanocomposites.Thermal stability is a significant property, for which nanocomposite morphology plays an important role (Kilburn et al., 2006). The TGA curves are shown in Figure 3.It realizes that all samples exhibit a one-step decay process in the 330–470ºC temperature range.The weight reduction of TPE and its nanocomposite is less than 0.04% with a residual moisture loss of the matrix below 330ºC.The key decomposition related to matrix backbone ruin in TPE starts at about 330ºC with a hastened rate. The onset decay temperature (T_{onset}) of TPE, which indicates the thermal stability of aningredient, is 385.4ºC. The inclusion of TiO$_2$ nanoparticles reinforces the thermal stability of the matrix, specifying that the thermal decay temperature of the nanocomposite increase with the nanoparticle's concentration.The maximumincrease in thermal stability of TPE/3CnTiO$_2$ nanocomposite is 12.9ºCcompared to pure TPE.

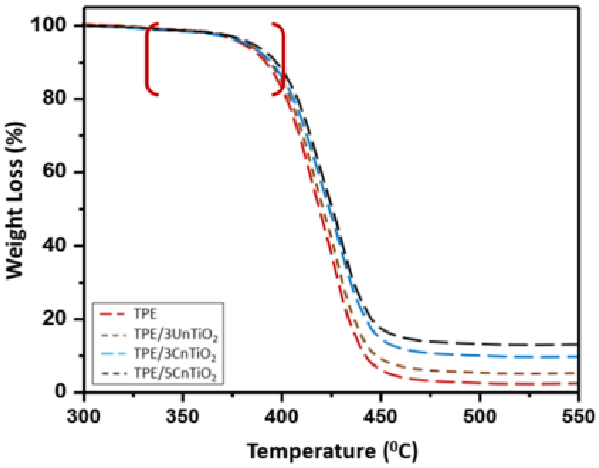

Fig. 3- TGA curves of pure TPE and TPE/nTiO$_2$ nanocomposites.

4. CONCLUSIONS

The PBT-PTMG block copolymer-based TPE/nTiO$_2$ nanocomposites were manufactured by a melt mixing process tracked by compression molding.This workexamined the influences of unmodified and surface carboxylatednTiO$_2$ particles on the mechanical, morphological, and thermal properties of TPE/nTiO$_2$nanocomposites. The inclusion of nTiO$_2$ particles in the TPE matrixenhancedthe tensile properties of TPE/nTiO$_2$ nanocomposite compared to TPE. Furthermore, the addition of chloroacetic acid-coated-nTiO$_2$ particles to TPE significantly improved tensile features such as tensile strength, and impact strength but decreased tensile modulus. When the chloroacetic acid-coated-nTiO$_2$ particles(CnTiO$_2$) were at 3 wt%, the tensile strength and impact strength of these nanocomposites reached their maximum valuesdue to better interfacial bond between TPEand nTiO$_2$particles. SEM tests showed that 3CnTiO$_2$ was incorporated into TPE, 3CnTiO$_2$ particles were evenly distributed in TPE, and their interface bond with TPE was higher than that of TPE/UnTiO$_2$ in the absence of 3CnTiO$_2$.DSC measurements showed that the inclusion of 3CnTiO$_2$ resulted in higher crystallization and melting temperatures enriched simultaneously.The crystallization or melting temperature of TPE/3CnTiO$_2$ is muchgreater than that of TPE/UnTiO$_2$ and that of TPE. The thermal stability of TPE/3CnTiO$_2$ was higher than that of TPE/UnTiO$_2$ because there is a compatibility between TPE and CnTiO$_2$.As a total result of this study, it was sound to confirm that improved morphology, tensile properties and, thermal degradation stability of TPE/nTiO$_2$ or TPE/CnTiO$_2$ were due to the existence of compatibility between TPE and nTiO$_2$ due to a coupling agent.

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