J Mater Sci (2011) 46:2281–2287
DOI 10.1007/s10853-010-5068-1

Thermal and mechanical properties of poly(ether ester)-based thermoplastic elastomer composites filled with TiO_2 nanoparticles

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Received: 26 August 2010 / Accepted: 9 November 2010 / Published online: 23 November 2010

Abstract Poly(butylene terephthalate)-*block*-poly(tetramethylene glycol) (PBT-PTMG)-based thermoplastic elastomer (TPE) was filled with nano TiO_2 particles by direct melt blending. The particle content in matrix was varied from 1.3 to 4.9 vol.%. The samples were characterized using SEM, μCT, DSC, TGA, DMTA and tensile test. SEM examination shows strong interfacial interactions between TPE matrix and TiO_2 particles due to formation of chemical bonds. The incorporation of TiO_2 particles increases overall the thermal properties of soft and hard segments such as the glass transition temperature, the melting temperature, and the thermal stability of material. The tensile properties of TPE are also significantly improved indicated by increased tensile strength and modulus. Increasing particle content leads to increased mechanical properties and thermal stability of composites.

Introduction

Thermoplastic elastomers (TPEs) are materials which exhibit a unique combination of strength, flexibility, and processability due to their phase-separated microstructure. The elastomers are copolymers composed of two different types of segments, namely a hard crystalline phase and a soft rubbery phase. Strength of elastomers is provided by the hard phase, while the elastomeric behaviour arises from the soft phase. The elastomers are processed at a high temperature when the hard phase melts and flows. In the molten state, the hard and soft segments form a homogenous mixed phase. Upon cooling, the hard segments crystallize and act as physical crosslinks. The crystallization process of hard phase is the driving force for the phase separation [1–3]. The properties of TPEs depend on the nature and amount of the hard phase in the copolymers. Different TPE systems have been discussed extensively in books by Holden et al. [4] and Bhowmick and Stephens [5]. One important class of TPEs are copoly(ether ester)s or TPE-Es. The first TPE-E copolymers obtained by modification of poly(ethylene terephthalate) with up to 20 wt% of poly(ethylene ether) were described by Coleman [6]. After that, the Dupont Co. developed poly(ether ester) elastomers which were commercially introduced in 1972 under the trade name Hytrel®. Nowadays, the polyester-based TPE-Es are widely produced and used in many applications. The commercial polyester elastomers are mostly based on poly(butylene terephthalate) (PBT) as rigid segment and poly(tetramethylene glycol) (PTMG) as flexible segment. The chemical structure of PBT-PTMG copolymer is shown in Scheme 1. Many researchers conclude that after crystallization the PBT-PTMG system can be described by a two-phase model: a crystalline PBT phase and a homogenous amorphous PTMG phase mixed with non-crystalline PBT segments [7–9]. In recent years, the crystallization process, the microstructure, and phase behaviour of PBT-PTMG systems have been studied in detail [10–12]. El Fray and co-workers investigated the influence of chemical composition on the phase structure and structure–property relationships of polyester-based TPE-Es [13]. Interesting results are reported on the basis of studies on the influence of chemical composition and molecular weight of PTMG segments on the mechanical properties of PBT-PTMG copolymers [14, 15]. For example, the hardness of PBT-PTMG copolymer is decreased in the temperature range of

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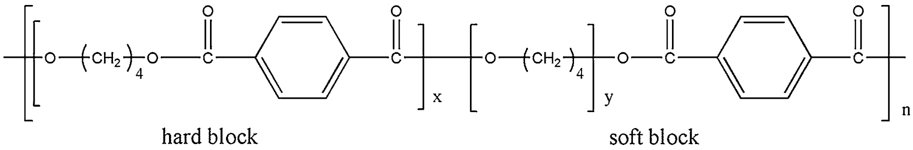
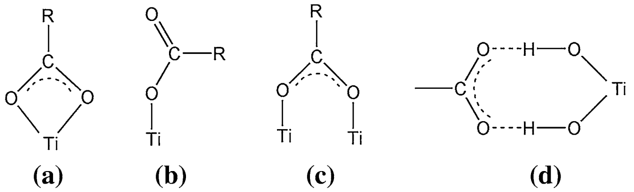
Scheme 1 Chemical structure of PBT-PTMG copolymer-based thermoplastic elastomer





Scheme 2 Binding modes of carboxylate with titania surface: **a** chelating bidentate, **b** monodentate, **c** bridging dentate and **d** hydrogen bonding

0–50 °C with flexible PTMG contents more than 60 wt%. Besides, the tensile strength of PBT-PTMG system depends mainly on the rigid PBT content and temperature when the molecular weight of PTMG is within the range of 650–2000 g/mol.

In this study, we used commercial PBT-PTMG copolymer as matrix and prepared TPE-E/nano-TiO_2 composites by direct melt blending. It is known that metal oxide nanoparticles such as TiO_2 can interact with acidic functionalities of polymers, increasing the particle–matrix interaction. As described in Scheme 2, four possible structures of carboxylate coordinated to a titania surface are reported [16, 17]. In the first structure, carboxylate is bounded to one Ti(IV) centre in a chelating bidentate mode (a). The carboxylate could also be bounded to one Ti(IV) in a monodentate (ester-like linkage) mode (b), and next, the carboxylate group could bind with each of its oxygen atoms to two Ti(IV) atoms yielding the bridging bidentate mode (c). Besides these three direct binding modes, carboxylate could also build up hydrogen bonding with hydroxyl groups (OH) on the titania surface as shown in mode (d). All these binding modes can lead to increased interactions between TPE-E matrix and TiO_2 particles. As a result, the properties of TiO_2 nanoparticle-filled TPE-E composites should be significantly changed. Our goal is therefore to investigate the influence of incorporation of nano-TiO_2 particles and particle content on thermal and mechanical properties of selected TPE.

Experimental

Materials and sample preparation

PBT-PTMG copolymer-based TPE-E granules were kindly provided by Allod Werkstoff GmbH & Co. KG (Germany). The weight percent and molecular weight of PTMG segment in this PBT-PTMG copolymer are about 50% and 1000 g/mole, respectively. The nano-TiO_2 under the trade name of Aeroxide® P25 was provided by Evonik Industry (Germany). The nanoparticles were unmodified with a hydrophilic surface nature. Other important characteristics of these nanoparticles are as follows: specific surface area (BET) 50 m^2/g and average diameter of particles 21 nm. All materials were used as received.

The nanoparticles were blended with TPE-E in a Berstorff twin-screw extruder (ZE-25A UTX, KraussMaffei Berstorff GmbH, Germany). The diameter of the screws was 25 mm and the length/diameter ration (*L*/*D*) was 44. The process temperature was ranged from 200 °C near the hopper to 220 °C at the die. The screw speed was 150 rpm. Each TPE-E/TiO_2 composite was three times extruded to ensure a better dispersion quality of nanoparticles. The nanoparticle contents in composites are 1.3, 2.6 and 4.9 vol.% (volume fraction). The palletized composite extrudates were then injection moulded.

Characterization

Morphology and particle dispersion

The morphology of nanoparticles filled TPE-E composites was examined by using scanning electron microscopy (SEM, JEOL JSM-6300). The specimens were sputtered with a thin gold film prior to inspection. The dispersion of TiO_2 particles in matrix was also determined by means of micro-computerized tomography (μCT). Using this method, the three-dimensional dispersion of particles in TPE-E matrix was obtained.

Dynamic mechanical thermoanalysis

The dynamic mechanical thermoanalysis (DMTA) tests were carried out using a Gabo Qualimetrer Explexor 25N machine in tension mode. The tests were run in a temperature range of −100 to +150 °C. The frequency and heating rate were 10 Hz and 2 °C/min, respectively.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis was performed using a Mettler Toledo instrument under nitrogen atmosphere. The following procedure was used: each sample was heated from −100 to 250 °C at a heating rate of 10 °C/min and then held at 250 °C for 5 min to ensure an identical thermal history. The specimen was subsequently cooled down to room temperature at a cooling rate of 10 °C/min.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) test was performed using a DTG-60 instrument (SHIMADZU Corp.) under nitrogen atmosphere in a temperature range from 50 to 550 °C at a heating rate of 10 °C/min. In the selected temperature range, only organic substances could decompose. The inorganic TiO_2 particles would remain.

Tensile test

The tensile test was performed using a Zwick 1474 universal testing machine (Roell, Germany) according to DIN EN ISO 527-2 at room temperature. The crosshead speed was 4 mm/min. The tensile modulus was determined by using a clip-on extensometer between 0.05 and 0.25% linear elongation.

At least five specimens for each characterization were tested, and the average values were finally taken.

Results and discussion

Morphology and particle dispersion

Figure 1 shows the SEM micrographs of TiO_2-filled TPE-E composites. It can be seen that the hydrophilic TiO_2 nanoparticles strongly agglomerate in the TPE-E matrix and the degree of agglomeration increases with increasing particle content. The reason is that the surface of hydrophilic TiO_2 nanoparticles contains a certain amount of hydroxyl groups formed during processing. These hydroxyl groups can build up hydrogen bonding among the nanoparticles resulting in a higher degree of agglomeration. Figure 2 gives a SEM micrograph with higher magnification showing particle–matrix interface. Interestingly, the particles/agglomerates are completely coated with a matrix layer with fibrillar structure indicating an excellent adhesion between TPE-E matrix and TiO_2 particles. According to Scheme 2, both Ti atoms and hydroxyl groups on particle surface can be bounded with carboxylate groups in PBT-PTMG copolymer. The good interfacial adhesion at interface is a proof of such chemical bonds. The μCT images in Fig. 3 show a three-dimensional dispersion of TiO_2 particles in matrix. Evidently, the particles and agglomerates are well dispersed in TPE-E although they result in high degree of agglomeration. It should be noted

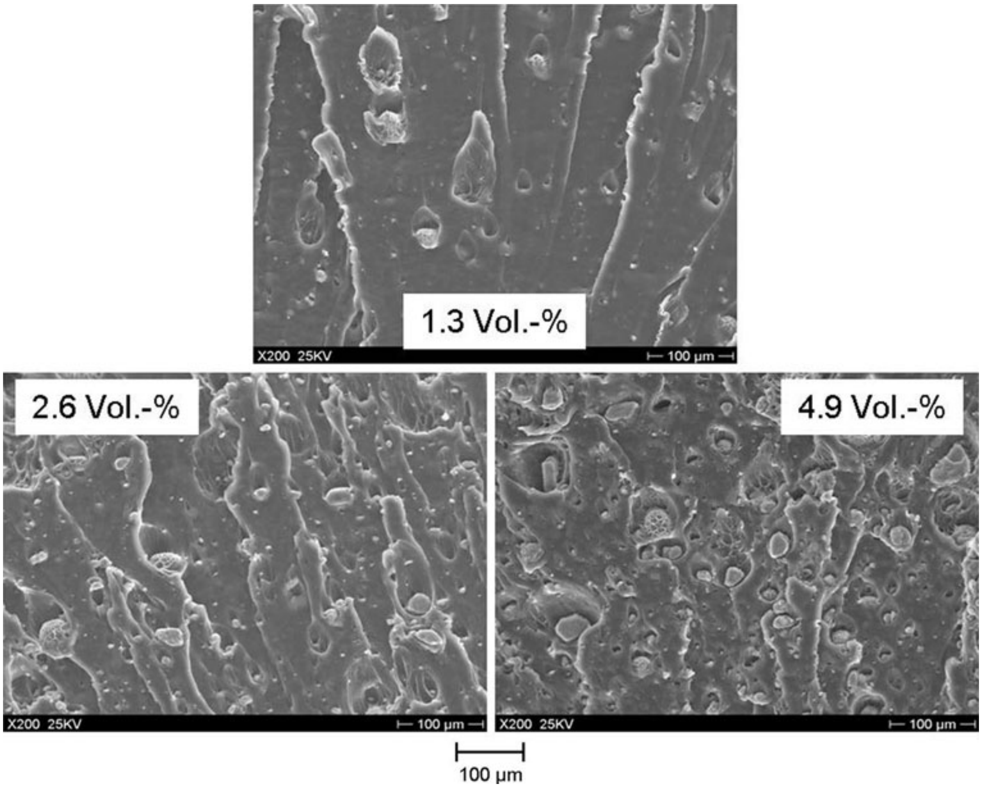


Fig. 1 SEM micrographs of TPE-E/TiO_2 composites

that only the particles/agglomerates larger than 0.5 μm can be detected by μCT examination. The particles smaller than 0.5 μm could not be observed in the μCT images. The presence of large agglomerates in TPE-E matrix indicates that the shear forces by extruding process were not effective enough to break down such agglomerates/aggregates of TiO_2 particles.

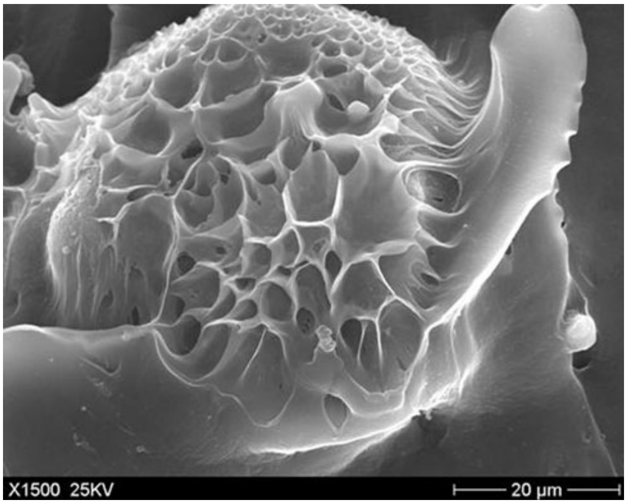


Fig. 2 SEM micrograph showing an interface between TPE-E matrix and TiO_2 particles

DMTA results

Dynamic mechanical measurements can provide a good impression of the phase behaviour of copolymers. Figure 4 shows the DMTA results of pure PBT-PTMG copolymer and its composites. Similar to [12], the tan δ curves of all materials in this study exhibit only one broad glass transition peak at about −45 °C (T_g^1) which is attributed to the soft PTMG segment. Compared to PTMG homopolymer with a T_g at about −50 °C [10, 12], the single intensive glass transition peak in pure PBT-PTMG block copolymer shifts clearly to higher temperature. This increase of T_g (PTMG) in the copolymer is caused by chemical linkage to the rigid PBT block and partial block mixing with amorphous PBT segment. However, the glass transition peak for amorphous PBT segment is not observed in the tan δ-temperature curve. This indicates that either a non-crystalline

Fig. 3 μCT Images of TPE-E/TiO_2 composite containing 2.6 vol.% of TiO_2 particles

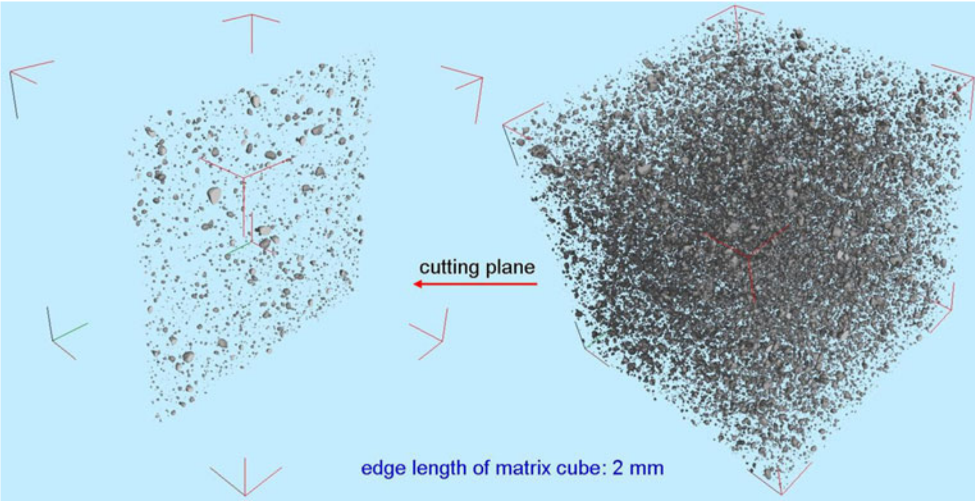
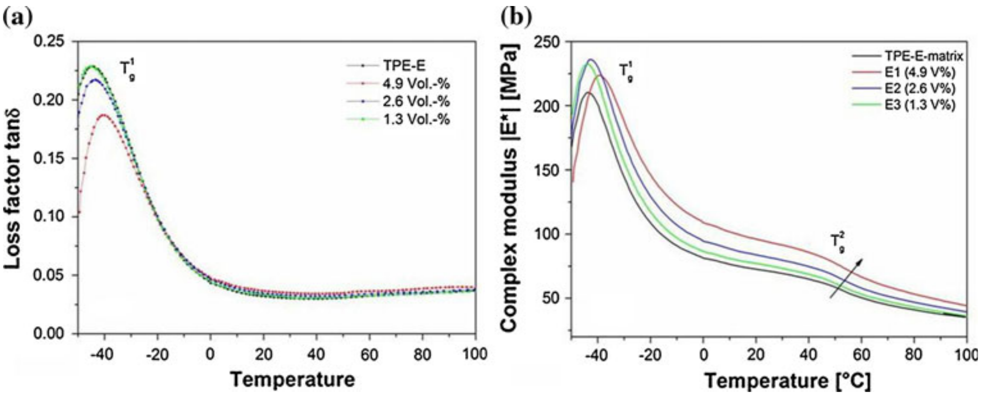


Fig. 4 Dynamical mechanical properties of TPE-E and its composites: **a** loss factor tan δ as a function of temperature and **b** complex modulus as a function of temperature



PBT phase does not exist or the weight fraction of amorphous PBT is very low in the PBT-PTMG composition. The reason is that in polymeric materials containing semicrystalline components during glass transition only the amorphous part undergoes the segmental motion, whereas the crystalline region remains as solid until its melting temperature is reached [18]. Generally, it is accepted that the amorphous PBT phase is mixed with PTMG phase forming a homogenous amorphous phase [12]. In the diagram of complex modulus |E*| versus temperature, two fast drop steps in complex modulus are observed. The first sharp drop in |E*| modulus occurs after the glass transition of PTMG segment. The second fast drop in |E*| occurs at about 50 °C at which the glass transition of amorphous PBT segment should take place [1].

By incorporation of TiO_2 particles, the glass transition peaks of PTMG segment in composites are clearly shifted to higher temperatures compared to neat matrix. This implies that the TiO_2 particles in TPE-E composites restrict the mobility of macromolecular chains of matrix due to chemical and physical interactions. In addition, increasing particle content leads to increased glass transition temperature of PTMG segment, the storage modulus and the complex modulus of TPE-E/TiO_2 composites. At 4.9 vol.% of TiO_2 particles, the improvements in glass transition temperature (PTMG) and storage modulus are 3.0 °C and 32.7%, respectively. The data obtained are listed in Table 1.

DSC results

The thermal properties of neat TPE-E and its composites are displayed in Fig. 5. From Fig. 5a, two glass transition peaks and two melting peaks in the DSC curves of all materials are observed, in which the glass transition peak at about −50 °C (T_g^1) and the melting peak close to 90 °C (T_m^1) are related to PTMG segment, while the glass transition peak around 50 °C (T_g^2) and the melting peak at about 175 °C (T_m^2) are attributed to PBT segment. The occurrence of two glass transition peaks proves the presence of two different amorphous phases, i.e. amorphous PBT and PTMG, which differ in chemical composition. Compared to pure TPE-E matrix, the TPE-E/TiO_2 composites reveal slightly increased glass transition temperatures of PTMG and PBT segments as given in Table 1. From the results, the incorporation of TiO_2 particles in TPE-E shows a strong effect on the melting temperature of PTMG segment. At 1.3 vol.% of particles, the melting temperature T_m (PTMG) increases from 86.5 °C of matrix to 97.2 °C of composite. The improvement is about 11 °C. Increasing particle content leads to decreased melting temperature of PTMG segment. At 4.9 vol.% of TiO_2 particles, the melting temperature of PTMG segment in composite is 3.1 °C lower than that of pure matrix. Unlike strongly affected T_m (PTMG) in composites, the melting temperature of PBT segment in TPE-E/TiO_2 composites only slightly increases compared to pure TPE-E matrix, but it shows similar

Table 1 Thermal properties of neat TPE-E and TPE-E/TiO_2 composites

Sample	Composition	T_g^1 (DMTA) [°C]	E′ (23°C) [MPa]	T_g^1 (DSC) [°C]	T_g^2 (DSC) [°C]	T_m^1 (DSC) [°C]	T_m^2 (DSC) [°C]	T_c^b (DSC) [°C]	ΔH^2 [J/g]	T_{onset} (TGA) [°C]
TPE-E	PBT^b-$PTMG^a$	−45.5	72.7	−57.2	52.0	86.5	174.6	132.0	23.2	395.8
E3	PBT-PTMG/TiO_2 (1.3 vol.%)	−44.7	75.9	−56.4	52.9	97.2	178.0	134.3	20.5	397.9
E2	PBT-PTMG/TiO_2 (2.6 vol.%)	−44.5	83.5	−55.5	52.6	95.6	177.2	135.4	19.7	398.7
E1	PBT-PTMG/TiO_2 (4.9 vol.%)	−42.5	96.5	−56.9	52.4	83.4	175.9	135.0	20.2	401.1

[a] For PTMG block, [b] for PBT block

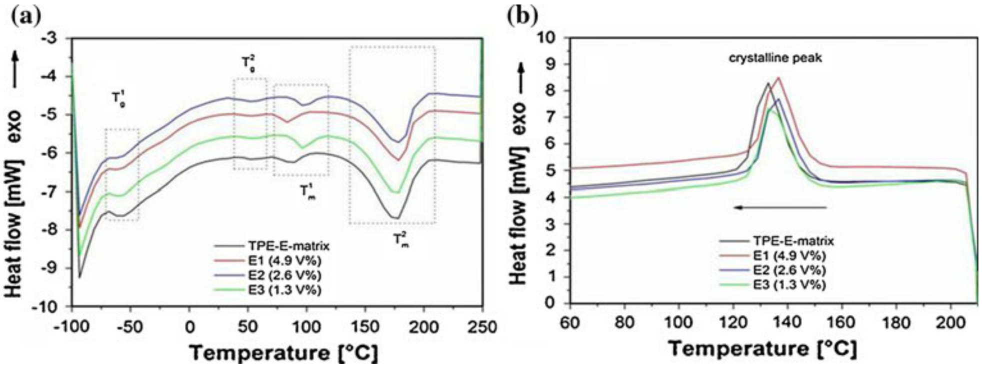


Fig. 5 DSC curves of TPE-E matrix and its composites: **a** melting process and **b** crystalline process

decreasing tendency with increasing particle content. The maximum improvement in T_m (PBT) is 3.4 °C occurring at 1.3 vol.% of TiO_2 particles. The increase of melting temperatures of PTMG and PBT segments in composites should be attributed to the chemical linkage between matrix and TiO_2 particles as introduced in Scheme 2, which actually increases the chain length and the molecular weight of PBT-PTMG block. On the other hand, the addition of TiO_2 particles in TPE-E leads to decreased weight fractions of PTMG and PBT segments in the composition. This should be the reason for decreasing T_m (PTMG) and T_m (PBT) in composites with increasing particle content [1]. Furthermore, it is thought that the chemical interactions between matrix and TiO_2 particles mainly exist in the PBT/PTMG amorphous phase which is rich in PTMG segment [19]. Therefore, the increasing effect on melting temperature is more pronounced for PTMG segment than for PBT segment. As another result of chemical bonds between matrix and TiO_2 particles, the crystallinity of hard PBT segment in composites is clearly decreased due to decreased chemical regularity of macromolecular chains, indicated by decreased crystalline enthalpy (ΔH^2) as shown in Table 1. From Fig. 5b, the crystalline peaks of PBT segment in composites clearly shift to higher temperatures. This increase in crystalline temperature (T_c) of PBT segment in composites should be attributed to the nuclear effect of TiO_2 particles. All data obtained by DSC tests are listed in Table 1.

TGA results

The TGA curves are shown in Fig. 6. It can be seen that all materials exhibit a one-step degradation process in the temperature range of 330–460 °C. The weight loss of pure TPE-E and its composites below 330 °C is lower than 0.05% corresponding to loss of remaining humidity in matrix. The main decomposition corresponding to matrix back-bone degradation in pure TPE-E starts from about 330 °C with an accelerated rate. The average thermal degradation temperature (T_{onset}) of TPE-E which characterizes the thermal stability of a material is 395.8 °C. The incorporation of TiO_2 particles obviously reinforces the thermal stability of matrix, indicated by increased thermal degradation temperatures of composites as given in Table 1. The T_{onset} value of composites increases with increasing particle content. The maximum improvement in thermal stability is 5.3 °C at 4.9 vol.% of particles.

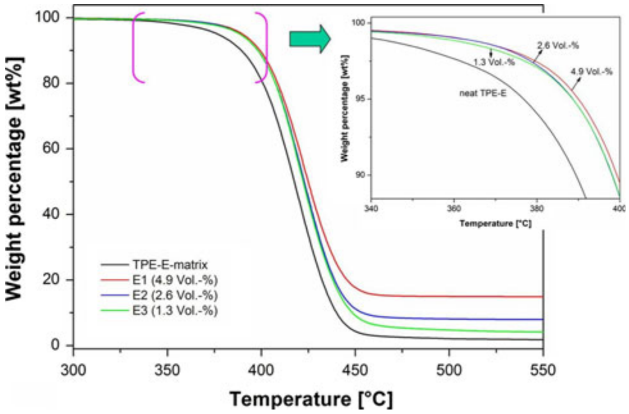


Fig. 6 TGA curves of TPE-E and its composites

Tensile properties

Figure 7 shows the typical stress–strain curves (S–S curves) of pure TPE-E and TPE-E/TiO_2 composites. It can be seen that the tensile stress increases continuously with increasing tensile strain in S–S curves. No yield point is observed. Obviously, the incorporation of TiO_2 particles reinforces the TPE-E matrix, and the composites still remain ductile. Figure 8 shows the tensile results in detail. From Fig. 8a, the tensile modulus significantly increases with increasing particle content. At 1.3 vol.% of TiO_2 particles, the tensile modulus of composite is comparable with pure matrix. At 2.6 and 4.9 vol.% of particles, the improvements in tensile modulus are 11 and 25%, respectively. Figure 8b shows the tensile strength of all materials as a function of tensile strain. Evidently, the tensile strength of all materials increases with increasing tensile strain in the studied strain range. The incorporation of TiO_2 particles into TPE-E improves the tensile strength of matrix at higher particle contents due to strong stress transfer from matrix to particles. At 1.3 vol.% of TiO_2 particles, an improvement in tensile strength does not occur due to relative low stress transfer effect of particles. Furthermore, increasing tensile strain leads to decreased

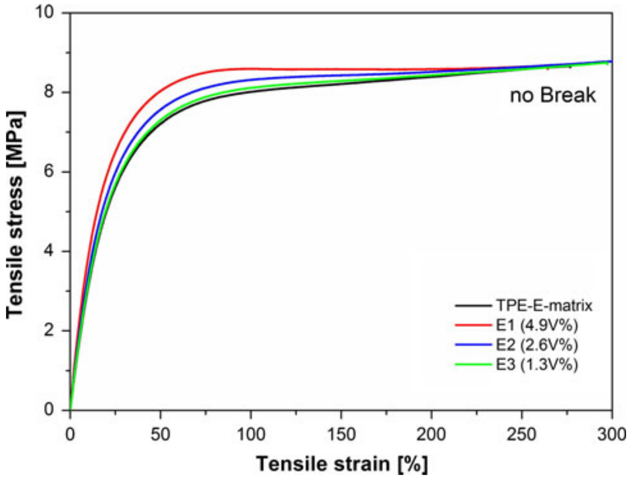


Fig. 7 Stress–strain curves of TPE-E matrix and TPE-E/TiO_2 composites

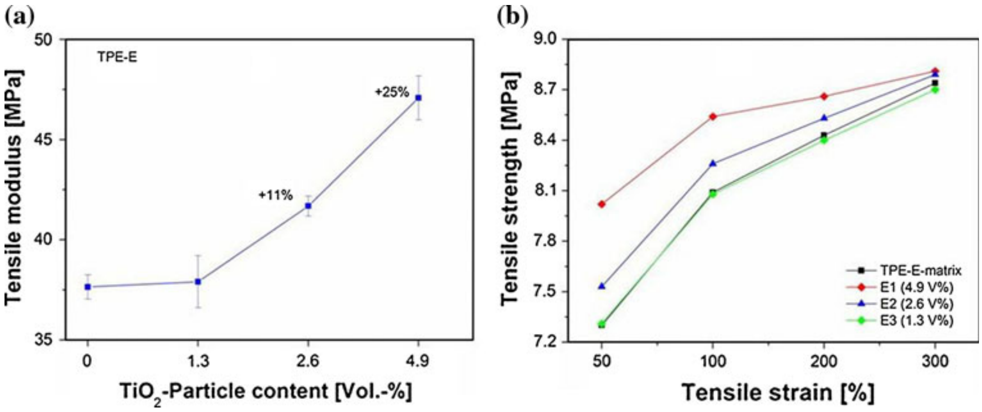


Fig. 8 Results of tensile tests: **a** tensile modulus as a function of particle content and **b** tensile strength of all samples as a function of tensile strain

improvements in tensile strength of composites. At 50% tensile strain, the composites E1 and E2 exhibit 10 and 3% improvements, respectively. At 100% tensile strain, the improvements are 6% for E1 and 2% for E2. At 300% tensile strain, the tensile strengths of all composites and pure matrix are comparable high. All samples kept undamaged up to 300% tensile strain after tensile tests.

Conclusions

PBT-PTMG block copolymer-based TPE-E/TiO_2 composites were prepared by direct melt blending and injection moulding. SEM and μCT analysis show that the TiO_2 particles are well dispersed in TPE-E matrix although they form large agglomerates due to strong interaction among particles. Besides, the SEM images show strong interfacial adhesion between TiO_2 particles and matrix due to chemical linkage. The incorporation of TiO_2 particles in TPE-E significantly increases overall thermal properties of matrix such as thermal degradation temperature and glass transition temperatures of PBT and PTMG segments. The melting temperatures of both segments are also improved, whereas the crystallinity of PBT segment is decreased. The tensile properties of TPE-E composites are clearly improved compared to neat matrix. Furthermore, the most obtained properties show increasing tendency with increasing particle content, such as thermal stability, storage modulus, glass transition temperatures, and tensile properties. In contrast, the melting temperatures of PBT and PTMG segments decrease with increasing particle content.

Acknowledgements The authors gratefully acknowledge German Research Foundation (DFG) for the fellowship in the framework of the graduate school GRK 814. They also thank Mr. Dieter Krüger from Allod Werkstoff GmbH (Germany) for kindly providing the TPE-E materials.

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