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Assessment of Thermoplastic Elastomeric Composites Through Extruder: Effect of Styrene Block Copolymer

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A B S T R A C T

This paper examines the effects of styrene-(ethylene-co-butylene)-styrene triblock copolymer (SEBS) on the morphological, thermal, and mechanical properties of binary thermoplastic polyether-ester elastomer (TPE)/SEBS composite.These composites were manufactured by direct melt-compounding TPE with four levels of SEBS loading (20, 30, 40, and 50 wt %). Scanning electron microscopy (SEM) investigation shown that TPE/SEBS blends with 40 wt% or more SEBS concentration, SEBS displays a small amountincessant phase. DSC analysis displayed that the melting temperature (Tm) of the TPE/SEBS blends didn't alteration with SEBS concentration. Mechanical properties such as hardness, flexural modulus, and compression set were reduced linearly with increasing SEBS concentration.

Keywords: TPE/SEBS blends, Morphology, Thermal properties,Mechanical properties

1. INTRODUCTION

Polymer blends are currently very significant in outcome new high-recital organic materials without synthesizing new polymers. Melt blending is a multipurposetechnique to manufacture polymeric materials. Polymer blending is a convenientmethod to generate materials with particular enhanced properties, which is frequently a faster and more cost-effective means of attaining a preferred set of properties than synthesizing a new polymer (Chirawithayaboon and Kiatkamjornwong, 2004).The amalgamation of two or more polymers generallyoutcomes in a multiphase blend, instead of a homogeneous material (Huang et al., 2020). The morphology and interfaces among microphases are predominant effects in determining the eventual properties of these multiphase blends (Anbinder et al., 2020). Consequently, for efficient blending, these factors must be under control to achieve reproducibility in the properties of the blend.

Thermoplastic elastomers are increasing in significance as innovativematerials, which cover the boundary among rubbers and plastics. Thermoplastic elastomers are materials, whichdisplay alone combination of strength, flexibility, and processability owing to their phase-separated microstructure. The elastomers are copolymers composed of two unlike types of segments, specifically a hard crystalline phase and a soft rubbery phase. The strength of elastomers is delivered by the hard phase, whereas the elastomeric behaviorascends from the soft phase. The elastomers are processed at a high temperature as the hard phase melts and flows. In the molten state, the hard and soft segments form a homogenous compounded phase.The properties of thermoplastic elastomers rely on the nature and quantity of the hard phase in the copolymers.A thermoplastic elastomer is extensively used in many fields such as the automotive industry, electric equipment, sports, and so on due to its excellent processability and elasticity (Zhan et al., 2017).Thermoplastic polyester elastomer (TPE) is a type of thermoplastic that consists of block structure polybutylene terephthalate (PBT) as hard section and amorphous polytetramethylene glycol (PTMG) as a soft section.The chemical structure of the thermoplastic polyester elastomer (TPE) is revealed in Scheme 1.

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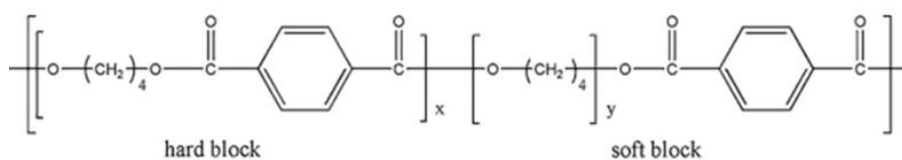
Scheme 1- Chemical structure of the thermoplastic polyester elastomer (TPE).

Due to tremendous processability and elasticity, superior oil and chemical resistance, superior lightweight, fatigue-resistance, recyclability, high heat resistance, alongsidefantastic low-temperature impact strength, TPE is extensively used in the areas of the automotive industry, electronics, and electronic parts, and even increasinglysubstitutes the cross-linked rubbers (Yao and Yang, 2010).The thermoplastic elastomer has an elastomeric performance at room temperature, which can be molded at high temperature identicalto common thermoplastic. The binary blend of polystyrene (PS) and poly(vinyl methyl ether, PVME) is miscible and severalrumors have been published on the mechanism for interactions. J.H. Ryou et al reported (Ryou et al., 1993) that there is the interaction among the ether group and aromatic ring of PS, based on the change in IR spectra of miscible and immiscible PS/PVME films.

A thermoplastic elastomer is like one kind of polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene triblock copolymers (SEBS). It has fine softness, processability, colorability compression set, and good compatibility with other polymers. At blending conditions, the SEBS has still some elasticity owing to the existence of polystyrene domains that perform as a physical cross-link. This decreases phase break-up and stabilizes the shaped morphology. Depending on the SEBS sort used and the proceeding situations, the TPE/SEBS blends can display co-continuous structures over a wide range of elastomer content. SEBS is moreoverextensively used for multi-component molding owing to bonds easily to 'hard' polymer, soft-touch grip, and good colorability. Consequently, SEBSs are often used as compatibilizers in fragile polymers (D'orazio et al., 1993; Gupta and Purwar, 1984a; Gupta and Purwar, 1984b). Severalscientists have exposed that the modulus and stress decrease with increasing SEBS concentration(Jazani et al., 2011; Ma et al., 2010; Setz et al., 1996). Lately, Mayumi et al (Mayumi et al., 2008) reported that TPEE/hydrogenated midblock of styrene-b-ethylene-b-butylene-styrene (SEBS) alloy possesses high softness and good adhesion to polystyrene (PS), polycarbonate (PC), and acrylonitrile butadiene styrene. The morphology of the TPEE/SEBS alloy exhibitedsubstantial interaction with PTMG in the TPEE matrix. Takahashi et al (Takahashi H, 1997)likewise reported that the TPEE/SEBS alloy covers the region of higher softness and lower Cs than the softest TPEE. The softest alloy exhibited a Shore-A hardness score of 55 and a Cs score of 55 (70°C, 22h). Therefore, the formation of an elastomer with the gains of TPEE and SEBS is preferred to enlarge the effectiveness of TPEEtechnologically.

In this paper, we reportto developsoftness and decrease compression set of a TPE by combining with several quantities of SEBS concentration. Compositions of TPE and SEBS have been different and the properties of the blends were observed by the tensile test,thermal properties, and morphology of the blends.

2. EXPERIMENTAL

2.1. Materials

PBT-PTMG copolymer-based TPE granules were kindheartedlydelivered by Allod Werkstoff GmbH & Co. KG, Germany. The loadpercentage and molecular load of the PTMG segment in this PBT-PTMG copolymer are approximately 50% and 100 g/mole, respectively. Thermoplastic elastomer (SEBS) was provided by Kraton (FG1901) having an MFI of 22 and a density of 0.91 g/cm^3. SEBS comprises 30 wt% fractions of polystyrene (PS) block in its configuration. This grade of SEBS likewise comprises 1.4-2 wt% of maleic anhydride attached to the rubbery block.

2.2. Methods

Processing of TPE/SEBS blends

All the components were dried in a vacuum oven at 60°C for 48h and then cooled down to room temperature before use.The ingredients were stored in a desiccator earlier to processing.All the materials were instantaneously added into the extruder beforemixing. The extrusion of a TPE was performed by totaling 20-50 wt% of SEBS into a Berstorff twin-screw extruder (ZE-25A UTX, KraussMaffei Berstorff GmbH, Germany). The diameter of the screws was 25 mm and the length/diameter ratio (L/D) was 44. Processing temperatures ranged from 200°C in the neighboring hopper to 220°C in the die and the speed of the screw was 150 rpm.The result of the extruder was cooled and grinded into small pellets. The achieved pellets were used to make thin plates in an electrically heated hydraulic press. After 5 minutes of preheating, the pellets were hot-pressed for another 5 minutes at 210°C and then water-cooled to ambient temperature with a cooling rate of 10°C per minute.

Morphology

The morphology of the TPE blends was examined with scanning electron microscopy (SEM, JSM-6360LV at an accelerating voltage of 8 kV; JEOL, Tokyo, Japan). The SEM specimens were held in liquid nitrogen for 30 min and then broken into two pieces. The fractured surfaces of the specimen were coated with a thin layer (10–20 nm) of gold-palladium.

Thermal properties of the TPE/SEBS blends

Thermal properties of the blends were measured by differential scanning calorimetry (DSC) Q2000 DSC (TA Instruments). 10 mg of each specimen was

heated from 30°C to 280°C at 10°C/min and held at 280°C for 5 min to eliminate the different thermal history, and then cooled to 30°C from 280°C at 10°C/min under an N_2 atmosphere using a technique provided by Dow.Universal Analysis Software v5.5.22 (TA Instruments, New Castle, DE) was used to find themelting temperature (T_m) and heat of fusion(ΔH_m) in the second scan.

Mechanical properties of the TPE/SEBS blends

The tensile propertiessuch as tensile strength, elongation at break, and tear strength were performedon a screw-driven universal testing machine (Instron 4466) equipped with a 10 kN electronic load cell and mechanical grips. The tests were carried out at a crosshead speed of 30 mm/min and acquired data. All tests were conducted according to the ASTM standards, and five replicates were tested for each sample to get an average value.Hardness characteristics of solid materials for scratching, cutting, wear, expansion, penetration, and expressing resistance to instruments.The hardness (Shore-A) was performed by using a durometer (TECLOCK, GS-719N). Hardness was immediately realized with pressure foot contact.The lower temperature range of the TPE/SEBS mixture was determined using the TW (temperature withdrawal) tester (145-L, Yasuda, Japan), which is standardized in ASTM D1329.

3. RESULTS AND DISCUSSION

3.1. Morphologyoftheblends

The microstructural characterization of TPE/SEBS composites was examined using scanning electron microscopy (SEM).The SEM investigation offers an insight interfacial activity of block copolymer blends. The cryo-fracture specimens were etched with tetrahydrofuran (THF) to extract the SEBS rubber particles from the blends. Figure1 exhibits the micrograph of cryo-fracture surfaces for different compositions of TPE/SEBS blends. From Figure, we see that the size of the voids left behind after etching by THF islarger for the blends with higher SEBS concentration. The TPE matrix ligaments among the SEBS particles are getting shorter with increasing SEBS concentration, which could facilitate the brittle-ductile transition or rigid-soft transition in the blends with increasing SEBS (Tanrattanakul et al., 1997). TPE/SEBS blends with 40 wt% or higher SEBS concentration, SEBS displays a fewincessant phases.
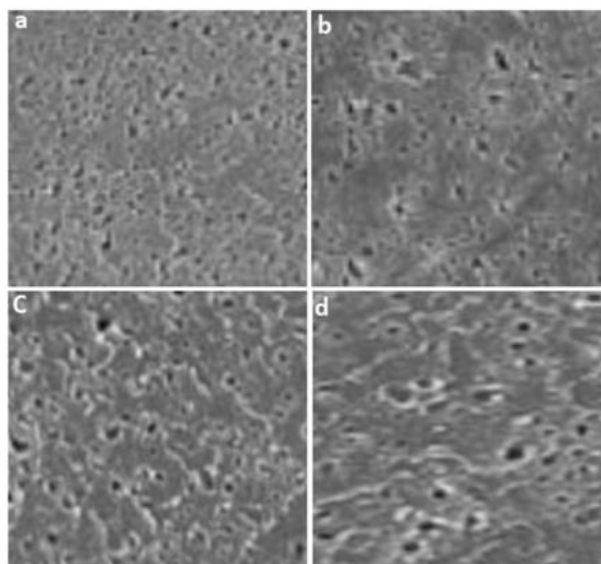
Fig. 1-Cryo-fractured surfaces for the different TPE/SEBS blends (w/w%) (a) 80/20, (b) 70/30, (c) 60/40, (d) 50/50, after extraction with tetrahydrofuran (THF).

3.2. Thermal analysis

DSC heating curves of TPE/SEBSblends are shown in Figure2, and the transition temperature and heat of fusion are concise in Table 1. The melting temperature (T_m) and crystalline temperature (T_c) of TPE/SEBS blends was not affected by the presence of the SEBS concentration. The endothermic (ΔH_m) and exothermic (ΔH_c) heat of fusion of TPE/SEBS blends reduced with an increasing quantity of SEBS. We can further see that the melting temperature (T_m) of TPE has not changed and the endothermic (ΔH_m) of TPE has decreased slightly according to the amount of SEBS added.According to studies (Sreekanth et al., 2009), the melting point of TPE is reported at 202.6°C attributed to the α phase, a thermodynamically unstable phase. DSC thermogram of TPE, displayed a fusion peak at 211.9°C, indicative of a more stable thermodynamically phase. Recognize the crystalline phase in blends TPE/SEBS is very significantowing is related to blends performance.The melting temperature and the ΔH_m fusion peak are shown in Table 1.It can be perceived that there is a substantialreductionin ΔH_m values from TPE structure in blends, which is indicative of a reduction in crystalline phase; this is because the SEBS trend to averting access TPE chains to an ordered structure to extend the TPE matrix. Reduction on fusion peak is an outcome of lamellar thinning of TPE crystals in blends with SEBS, linear structure have more pretention on this property than radial, according to ΔH_m values.On the contrary, it can perceive that SEBS existencereasons a slight reduction in melting temperature when SEBS amount increase in blends, being more substantial for linear than radial SEBS, indicative that TPE crystalline phase is varyingowingto the presence of processing oil added.
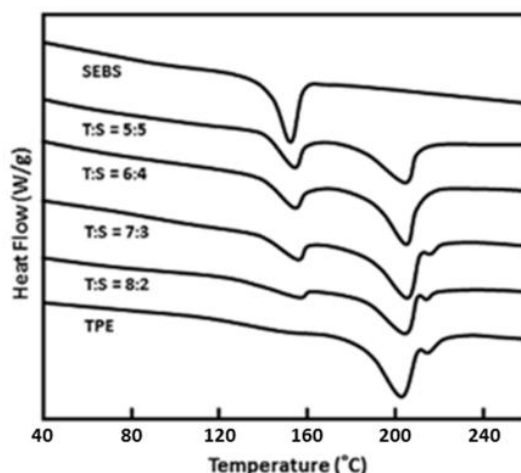
Fig. 2-DSC heating curves of TPE/SEBS blends with various blending ratios.

Table-1:Thermal properties of TPE/SEBS blends.

TPE/SEBS (w/w %)	T_m (^{o}C)	ΔH_m (J/g)	T_c (^{o}C)	ΔH_c (J/g)
100/0	202.6	28.6	164.3	27.4
80/20	206.3	18.2	169.6	24.6
70/30	206.4	11.2	168.5	15.8
60/40	206.4	11.3	167.3	15.6
50/50	206.5	11.4	166.6	15.3

3.3. Mechanical properties of the TPE/SEBS blends

The hardness of a particular composite material refers to its stiffness or resistance to permanent correction of its shape as well as the application of force on it.It is an indication of the composite to resist crack propagation when subjected to a sudden impact on it. The hardness (Shore-A) of several compositions of TPE/SEBS blends is illustrated in Figure3. It can be seen that the hardness of the TPE/SEBS blends linearly reduced with the increase of SEBS content. The reduction in hardness outcomes from a rubbery nature of the SEBS. It is generally observed that as the ratio of rubbery material to hard material (such as plastic) increases, the layer of hard material between the rubbery phases becomes progressively thinner. Consequently, the blends will become more soft(Fung and Li, 2005). To substitute the thermoset rubbers, TPE has to convert a product having a lower hardness. It is revealed that a combination ratio of TPE/SEBS may be adopted to control the hardness of TPE.

The variant of the flexural modulus of the TPE/SEBS blends in relation to their SEBS content is presented in Figure4. We can likewise see that the flexural modulus of TPE/SEBS blends linearly reduced as concentrations of SEBS increased. Consequently, there appears to be a direct relationshipbetween the increase in the ratio of SEBS to the TPE/SEBS systems and the modulus of the TPE/SEBS systems. This is a covenant with the hardness outcomes.

Typical tensile stress-strain curves for the blends are displayed in Figure 5. The outcome of incorporating the rubbery particles on the tensile strength, elongation at break and tear strength is summarized in Table 2. The effect of the SEBS contents in the tensile strength can be perceived. Overall,the tensile strength at break and tear strength is reduced as SEBS content. It seems that as the ratio SEBS to TPE increases, the layer of TPE among the SEBS phases becomes increasingly thinner. Therefore, the blends will become more soft and ductile. Elongation at break reducesincreasingly with the inclusion of up to 30 wt% of SEBS into the TPE/SEBS blend. With more increase of the SEBS content, the elongation at break increase from 425% (with 30 wt% SEBS) to 825% (with 50 wt% SEBS). It appears that the TPE matrix ligaments among the SEBS particles are getting shorter with increasing SEBS content, and TPE/SEBS blends with 40wt% or higher SEBS content, SEBS displays a fewincessant phases(Figure 1), which could facilitate the brittle-ductile transition or rigid-soft transition in the blends with increasing SEBS (Wu, 1985).

The compression set property of a polymer is its elastic recovery behavior under a precise loading or a precise deflection at several times and temperatures. The compression set property is directly linked tothe sealing ability of elastomers (Nagdi, 1993). The compression set properties of elastomers are normally measured by ASTM D395 method B, which defines the test specimen under a constant (usually 25 percent) deflection.The compression set of a thermoplastic elastomer (TPE) is higher than that of conventional cross-linked rubbers which cross-linked chemically(Walker and Rader, 1979). TPE likewisedisplays a higher compression set value. Nevertheless, one of the most fascinating points of SEBS is its brilliant compression set. Consequently, we expected that the compression set of TPE blending with SEBS could be developed.

The compression set of TPE/SEBS blends was revealed in Figure 6.As displayed in Figure6, the compression set of TPE was enhanced with an increasing amount of SEBS.However, when the test temperature is increased, the developmental effect decreases, and the compression set is not increased to 100°C because the test temperature is outside the glass temperature of the styrene hard block of SEBS, which acts as a physical cross-link.
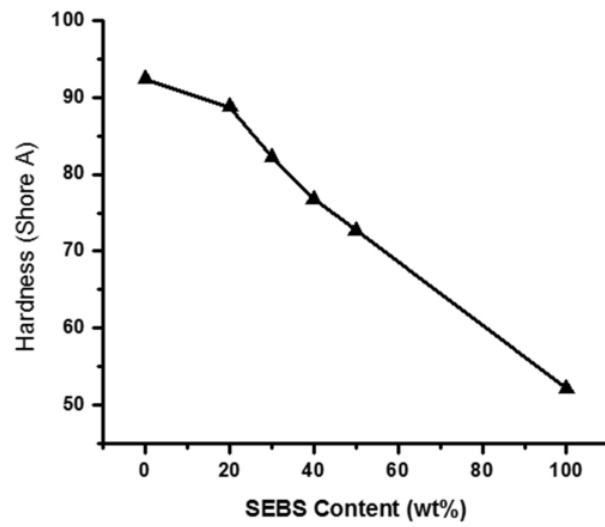
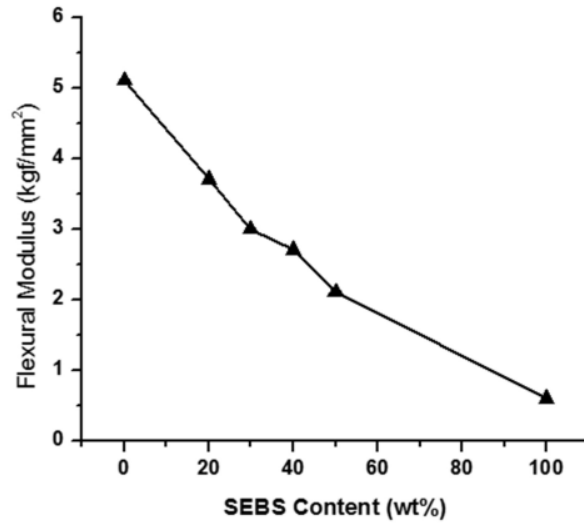**Fig. 3- Hardness of TPE/SEBS blends with different amounts of SEBS content.**

Fig. 4- Flexural modulus of TPE/SEBS blends with different amounts of SEBS content.
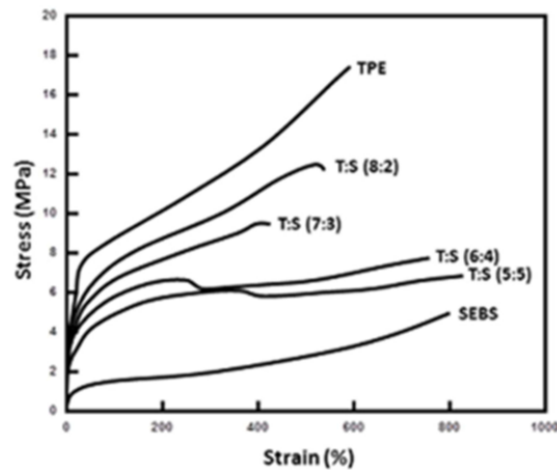

Fig. 5- Strain-stress curves of TPE/SEBS blends with various blending ratios.
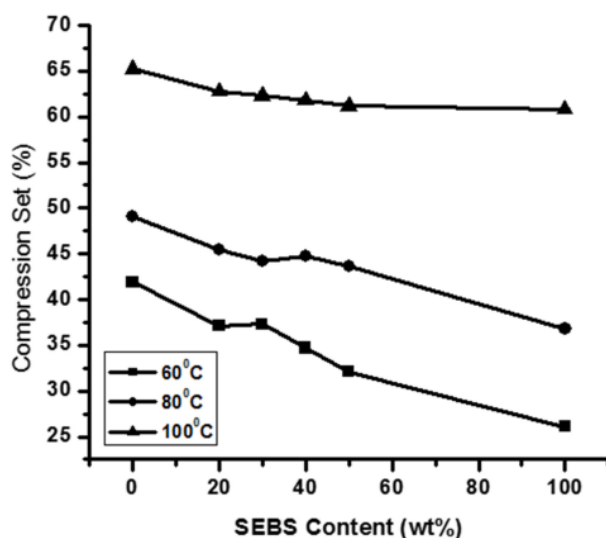
Fig. 6- Effects of SEBS content on compression set of TPE/SEBS blends as a function of test temperature.

Table-2:Tensile properties of TPE/SEBS blends.

TPE/SEBS (w/w %)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kgf/cm)
100/0	17.8 ± 1.1	598 ± 50	115
80/20	12.2 ± 0.9	565 ± 60	107
70/30	9.8 ± 0.7	425 ± 40	98
60/40	7.9 ± 0.5	780 ± 70	73
50/50	6.9 ± 0.5	825 ± 80	57
0/100	4.9 ± 0.3	797 ± 70	22.3

4. CONCLUSIONS

The particle sizes of SEBS are larger and the matrix ligaments of TPE in SEBS particles are getting shorter with the increasing content of SEBS, which makes the mixture more flexible.By mixing TPE/SEBS with 40 wt% or higher SEBS content, SEBS displays several continuous stages, which can facilitate brittle-ductile transition or rigid-soft transition in the blends with increasing SEBS.The hardness, flexible modulus, and compression set have decreased linearly with increasing SEBS content.The melting temperature (T_m) of TPE/SEBS blends didn't change with SEBS content. Therefore, we could increase smoothness and decreasethe compression set of TPE with blending with SEBS and the mechanical properties of the blend could be controlled by the amount of SEBS.

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