Journal of Materials Science and Chemical Engineering, 2021, 9, 1-10
https://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

Fabrication and Characterization of Poly(Styrene-Butadiene-Styrene)/ Thermoplastic Polyurethane Blends

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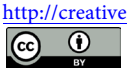
How to cite this paper: Tsai, Y., Kuo, M.-C. and Wu, J.-H. (2021) Fabrication and Characterization of Poly(Styrene-Butadiene-Styrene)/Thermoplastic Polyurethane Blends. *Journal of Materials Science and Chemical Engineering*, **9**, 1-10.
https://doi.org/10.4236/msce.2021.92001

Received: August 28, 2020
Accepted: February 7, 2021
Published: February 10, 2021



Abstract

This investigation presents thermoplastic elastomers (TPEs) based on poly (styrene-butadiene-styrene) (SBS) and thermoplastic polyurethane (TPU) materials were prepared with varying compositions. A series of works were conducted on the relationships between rheological, optical properties, morphology, mechanical properties, abrasion resistance and thermostability given. The results showed that the shear viscosity of SBS not obvious effect with TPU content. The optical properties of the SBS/TPU blend that its uniform transparency. The morphology characteristics indicating the phase diversion and the variation in the size of the SBS domains from large to small as the TPU contents increased, with heterogeneous domain dispersions. Additionally, the mechanical properties, abrasion resistance and thermal resistance are improved as the amount of added TPU is increased, suggesting that the blending of SBS with TPU is consistent with the compound rule.

Keywords

Thermoplastic Elastomers, Poly(Styrene-Butadiene-Styrene), Thermoplastic Polyurethane

1. Introduction

Blending is the process of mixing two or more polymers in different proportions to yield particular performance. One of the primary advantages of blending is its simplicity, as it requires common equipment and technology and its various components have predictable physical and chemical properties, facilitating the

predication of the properties of the mixture [1]-[6].

TPEs-based SBS has mechanical characteristics that resemble many respects to those of conventional vulcanized rubber, but with the advantages of low-temperature flexibility, chemical stability and electrical insulation [7]. This material is commonly adopted to produce plastic modifiers, footwear and other adhesive applications. However, the heat-resistance and abrasion resistance of existing SBS available on the market cannot meet our requirements. Moreover, the development of TPE formulations responds to market feedback. The developmental TPE must meet three major requirements—clarity, thermal resistance and softness [8]. Therefore, modifying for SBS is required.

In our earlier work, polypropylene was used as a modifier effectively to improve the heat-resistance of the SBS [6]. Nevertheless, the resulting light scattering and phase separation are known to affect the final optical transparency of the blends. Because thermoplastic polyurethane is transparent, heat-resistant and high abrasion resistance [7] [9] [10] [11] [12]. In this study, we investigated the SBS blend with TPU to improve the mechanical properties, abrasion resistance, and thermal resistance, while maintaining its transparency. The SBS/TPU blends are suitable for footwear, anti-vibration and shock-absorbing foam applications in the future.

2. Experimental

2.1. Materials

The polymers utilized were SBS radial copolymer (grade: TPE475) with a styrene content of 40%, manufactured by LCY Chemical Industry Inc., Taiwan. Ester-type (grade: EX-85A, abbreviated TPU-EX) and ether-type (grade: ER-85A, abbreviated TPU-ER) thermoplastic polyurethane were of commercial grade, manufactured by Coating Chemical Industry Inc., Taiwan.

2.2. Sample Preparation

SBS containing TPU-EX (abbreviated SEX) and TPU-ER (abbreviated SER) (as shown in **Table 1**) were prepared by melt blending pellets of both components in a twin-screw extruder (Werner and Pflederer, Model-ZSK 26 MEGA compounder). Extrusion was performed at a screw rotation rate of 500 rpm and temperature of 170˚C - 190˚C. The extruded thread was then pelletized. These blended pellets were then injected into 2 mm thick molds.

2.3. Rheological Studies

Rheological studies were conducted using a capillary rheometer (Dynisco LCR7000) at 190˚C at shear rates of 3250 - 5000 s^{-1}. The capillary length (20 mm)-to-diameter (1 mm) ratio was 20 with a compound entrance angle of 120˚. The preheat time for each sample was 5 min.

2.4. Optical Properties

Haze (H) and the total light permeation coefficient (T) were measured by a

Table 1. Compositions of SBS/TPU blends, wt%.

Sample	Materials		
	SBS	TPU-EX	TPU-ER
SBS	100	–	–
SEX7525	75	25	–
SEX5050	50	50	–
SEX2575	25	75	–
TPU-EX	–	100	–
SER7525	–	75	25
SER5050	–	50	50
SER2575	–	25	75
TPU-ER	–	–	100

Haze/Turbidimeter (Nippon Denshoku Industries, Japan, model No. NDH 2000) according to the ISO 13468 and ISO 14782 methods (specimen thickness, 2mm). The refractive index (RI) was measured using an ABBE-refraktometer (KRUSS, Germany, model No. AR 2008) according to the ASTM D1218 method.

2.5. Morphological Analysis

Morphology was evaluated using a JEOL JSM6360 Scanning Electron Microscope (SEM). The SBS/TPU blends were immersed in gasoline to dissolve SBS at ambient temperature for 24 h and dried to remove the solvent. Before observation, the gold was sputtered onto the sample surface and an SEM was used to examine the sample.

2.6. Mechanical Properties Measurements

Mechanical properties were measured using a Universal Tensile Tester with a tension velocity of 500 mm·min^{-1} based on ASTM D412C specifications. The Shore hardness test was determined by a Shore A durometer from ASTM D2240.

2.7. Abrasion Resistance Testing Method

Abrasion resistance was measured using an abrasion tester (Cometech Testing Machines Co., Ltd., Taiwan, model No. QC-618D) in accordance with ASTM D5963. Under a load of 10 N, samples were rubbed with the roller abrasion cloth. The abrasion distance was 40 m. The sample weight was measured before and after the test. The weight loss was the abrasion loss (with an accuracy of 0.1 mg) and was used to measure the abrasion resistance. Each data point was obtained from the average value of five measurements.

2.8. Thermostability Measurements

The heat shrinkage of each 2 mm-thickness specimen (ASTM D412 Die C) was determined. The original length (L_o) of each was 115 mm. A specimen was placed into the thermal cabinet at 115˚C for 10 min without any stress and the

final length (L_f) was measured. Five measurements of each specimen were made and the results averaged to obtain a mean value. Heat shrinkage was calculated by the following equation:

$$\text{Heat shrinkage} = L_o - L_f \,/\, L_o \times 100\% .$$

3. Results and Discussion

3.1. Rheological Behavior

Rheological behavior of polymer composites in melt state is very critical to understand processability and structure-property of these materials. Figure 1 shows plots of apparent shear viscosity versus shear rate of SBS/TPU blends with various blend proportions. At all shear rates, SBS showed a lower viscosity than that of TPU-EX and TPU-ER. The viscosity curve of SBS/TPU blends to be closer to the curve of SBS. This is attributed to the SBS acting as a lubricant of the polymer chains, which can then easily move over each other. As a consequence, ease of processability and lower flow resistance of the materials were observed.

3.2. Transparency and Optical Properties

Figure 2 presents the optical transparency of the sheet samples (2 mm-thick) of

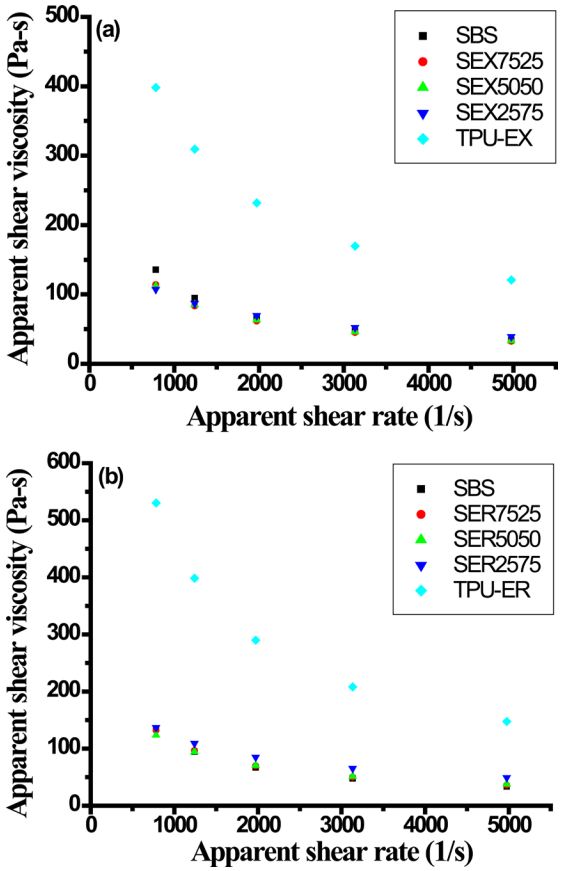


Figure 1. Plots of apparent viscosity vs. shear rate of (a) SBS/TPU-EX and (b) SBS/TPU-ER blends.

SBS blended with TPU-EX and TPU-ER and the optical properties are summarized in Table 2. Figure 2 shows all compositions are transparent. This resulted could be attributable to the RI contrast between SBS (RI = 1.595), TPU-EX (RI = 1.587) and TPU-ER (RI = 1.590) was small (reducing the amount of light

Table 2. Optical properties of SBS/TPU blends.

Sample	Refractive index	*T (%)	Haze (%)
SBS	1.595	80.6	25.7
SEX7525	1.582	64.2	26.9
SEX5050	1.581	63.2	27.4
SEX2575	1.583	61.8	29.3
TPU-EX	1.587	83.0	8.5
SER7525	1.587	77.3	24.9
SER5050	1.583	72.7	27.1
SER2575	1.583	69.1	28.2
TPU-ER	1.590	89.1	2.5

*T = total light permeation coefficient.

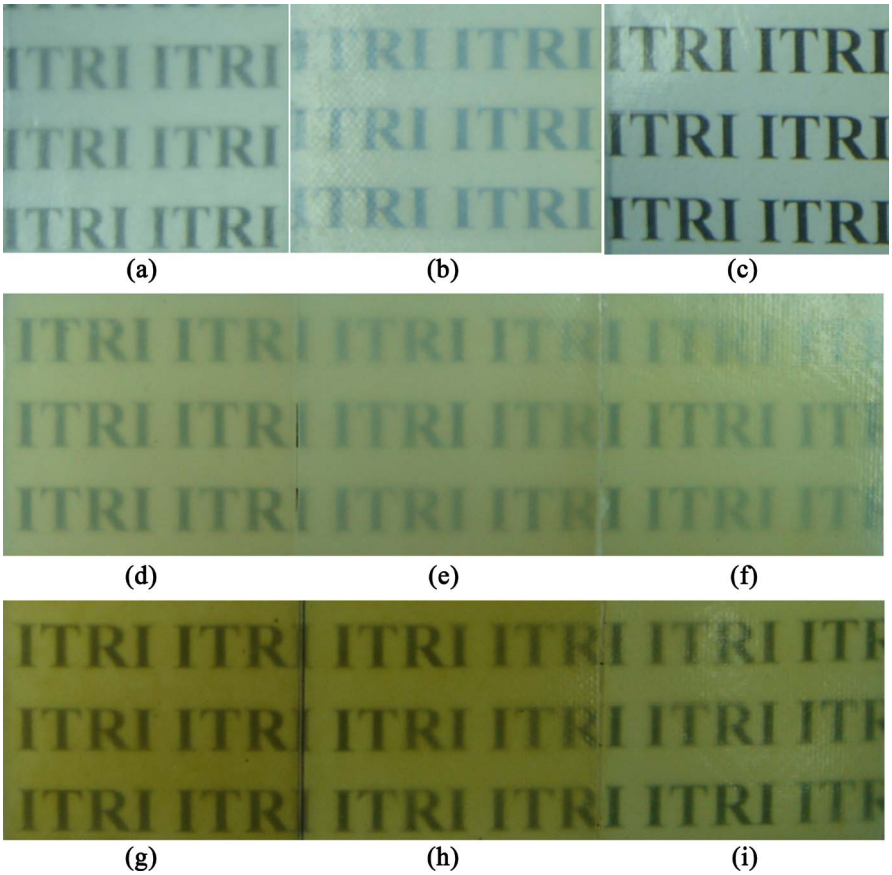


Figure 2. Transparency effects on SBS/TPU-EX and SBS/TPU-ER blends. (a) SBS; (b) TPU-EX; (c) TPU-ER; (d) SEX7525; (e) SEX5050; (f) SEX2575; (g) SER7527; (h) SER5050; (i) SER2575.

scattered). This observation is in agreement with previous observation by Khanarian [13]. In exploring the relationship between H and T of SBS/TPU blends, shows the SBS had lower T and higher H than the TPU. When SBS blending with TPU, the T was decreased and H was increased, indicating that light passing through the blends caused reflection and diffusion [13] [14].

3.3. Morphology

Figure 3 shows the morphology of SBS/TPU blends with various blend proportions. Due to the SBS was dissolved in gasoline and TPU was swelled in gasoline. The SBS/TPU at 75/25 (w/w) was dissolved in gasoline, and the morphological characteristics associated with the second phase (TPU domains) are those of dispersions in the SBS/TPU blends. When SBS blended with TPU content in 50 wt% - 75 wt%, clear shows the SBS was dissolved in gasoline to appearing as black holes in the SEM micrographs. The results indicating the phase diversion and the variation in the size of the second phase (SBS domains) from large to small as the TPU contents increased, with heterogeneous domain dispersions, as Scheme 1.

3.4. Mechanical Properties and Abrasion Resistance

Figure 4 displays the stress-strain behavior of SBS/TPU blends with various blend proportions, and the variations of hardness, tensile stress, elongation and tensile modulus are summarized in Table 3. Shows the hardness, tensile stress and tensile modulus of the SBS/TPU blends increased with the TPU content, and

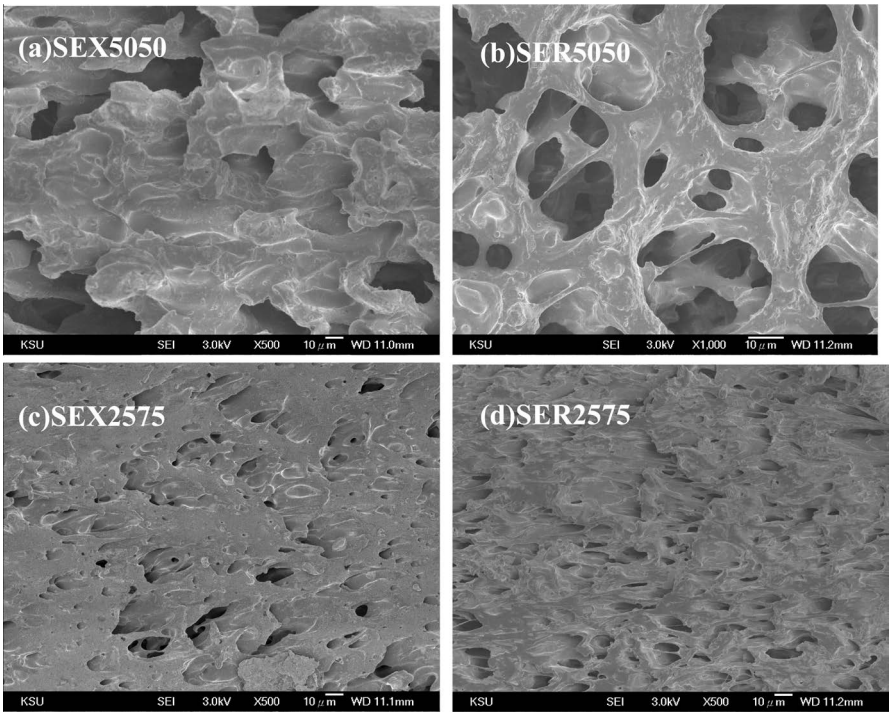
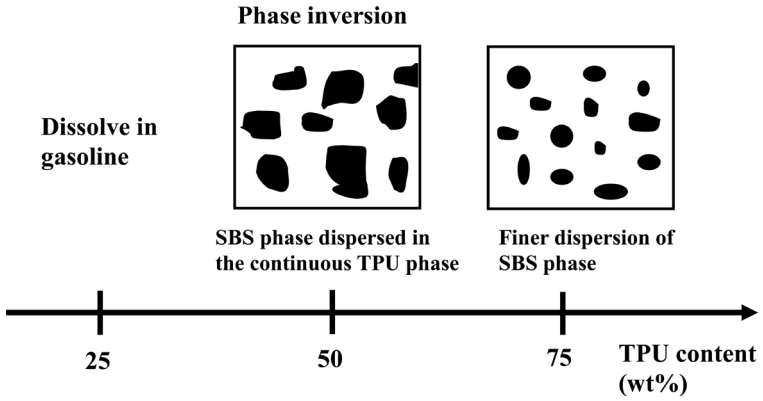


Figure 3. SEM micrographs on SBS/TPU-EX and SBS/TPU-ER blends (×500). (a) SEX5050; (b) SER5050; (c) SEX2575 and (d) SER2575 were etched with gasoline for 24 h.



Scheme 1. Schematic illustration of the morphological change in SBS/TPU blends with increasing TPU content.

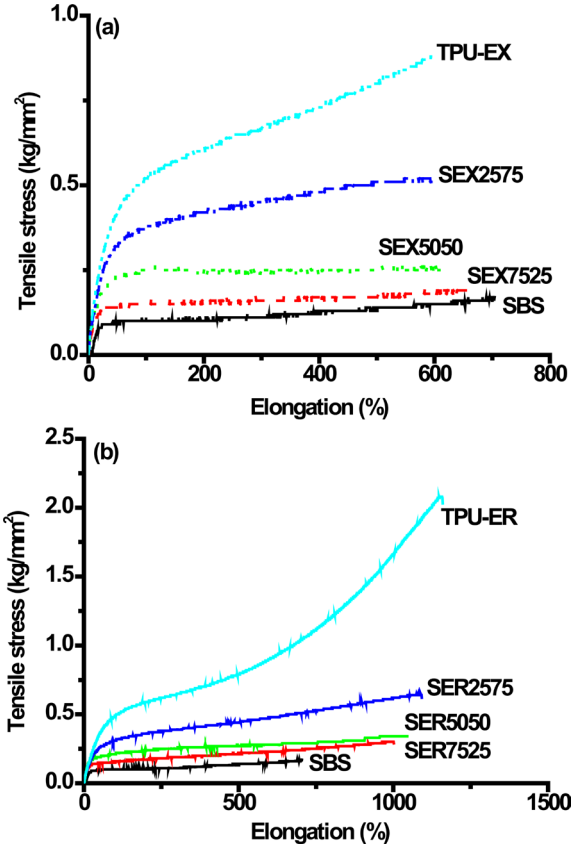


Figure 4. Plots of tensile stress vs. elongation of (a) SBS/TPU-EX and (b) SBS/TPU-ER blends.

the elongation decreases and increased with increasing TPU-EX and TPU-ER contents, respectively, because the hardness, tensile stress and tensile modulus of the SBS was lower than that of TPU, and its elongation was between those of TPU-EX and TPU-ER. These results indicate that SBS/TPU composite systems have the properties of each of its components, offsetting the mechanical weaknesses of the other.

Figure 5 plots the abrasion properties of SBS/TPU blends with various blend

Table 3. Mechanical properties of SBS/TPU blends.

Sample	Hardness (shore A)	Tensile stress (kg/mm^2)	Elongation at break (%)	Tensile modulus (kg/mm^2)
SBS	45	0.17	703	0.59
SEX7525	50	0.19	657	0.76
SEX5050	62	0.26	607	0.81
SEX2575	72	0.52	593	0.87
TPU-EX	80	0.88	598	0.94
SER7525	55	0.31	999	0.43
SER5050	65	0.35	1044	0.52
SER2575	75	0.65	1092	0.63
TPU-ER	82	2.08	1155	0.73

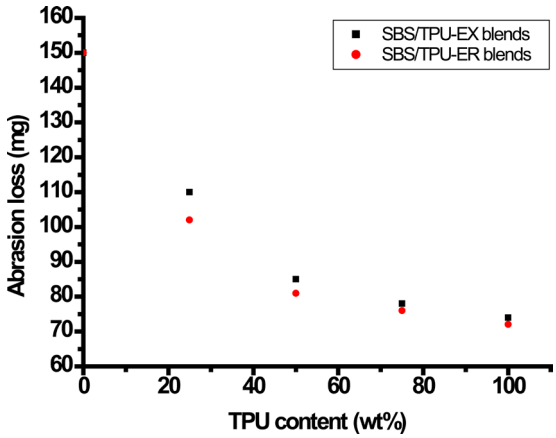


Figure 5. Abrasion loss of SBS with various amounts of TPU-EX and TPU-ER thermoplastic elastomers.

proportions. Shows the pure SBS has a relatively high abrasion loss, reaching 150 mg. The addition of TPU has a significant impact on the abrasion performance of the blends. With an increase in the TPU content, the abrasion resistance of the SBS/TPU blends is greatly enhanced compared with that of the pure SBS. When the TPU content reaching 75 wt%, the abrasion resistance of SBS decreased by a half.

3.5. Thermostability

Figure 6 plots the heat-shrinkage of the SBS blended with TPU-EX and TPU-ER. Experimental data indicate that SBS exhibits even higher heat shrinkage (around 7.6%) than the TPU-EX (around 0.3%) and TPU-ER (around 0.35%), and its heat shrinkage value decreased as the TPU-EX and TPU-ER content increased, because the heat shrinkage of TPU-EX and TPU-ER exceeded that of SBS. Moreover, the improvement in the heat shrinkage of SBS upon blending with TPU-ER was slightly better than that with TPU-EX. Experimental results indicate that the thermostability of SBS depends on TPU content. Heat

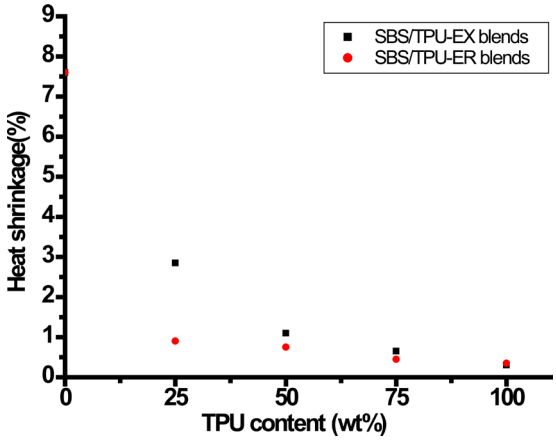


Figure 6. Thermal stability of SBS with various amounts of TPU-EX and TPU-ER thermoplastic elastomers.

shrinkage decreased from 7.6 % to a mere 0.5%, upon the addition of TPU, because of the excellent thermal resistance of the latter. Thus, combining TPU with SBS effectively dissipates heat and improves the thermal stability by a factor of 15.

4. Conclusion

Development of thermoplastic elastomers based on SBS blended with TPU. Shows the blending of TPU has a great impact on the performance of SBS. With increasing TPU content, the mechanical properties, abrasion resistance and thermal resistance of SBS/TPU blends are effectively improved. Furthermore, the SBS blending with TPU shows all compositions are transparent. On the processability, the processing performance of SBS/TPU blends is close to SBS, indicated blends not effect in the process of injection, extraction and blow molding.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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