

ICM11

Effects of HIPS on the mechanical, thermal and morphological properties of SEBS and SIS type elastomers

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Abstract

In this study, the effect of PS on the mechanical, thermal and morphological properties of SEBS and SIS type elastomers -based shoe sole material was investigated in flow direction 0° and flow direction 90°. The structure and properties of the composites are characterized using a scanning electron microscopy (SEM), Differential scanning calorimeter (DSC) and Energy dispersive X-ray spectroscopy (EDS). Furthermore, SEBS/PS and SIS/PS polymer blends were subjected to examinations to obtain their elasticity modulus, yield strengths, strength @ break, elongation @ break, hardness, izod impact strength, wear rate, melt flow index (MFI), vicat softening point and heat deflection temperature (HDT).

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Key words: High impact polystyrene, styrene ethylene butadiene styrene, styrene isoprene styrene, thermoplastic elastomer, polymer blends

1. Introduction

Styrene block copolymers are the most widely used TPEs, accounting for close to 45% of total TPE consumption worldwide at the close of the twentieth century [1]. Styrenic TPEs are usually styrene butadiene styrene (SBS), styrene ethylene/butylene styrene (SEBS), and styrene isoprene styrene (SIS). Styrenic TPEs usually have about 30 to 40% (wt) bound styrene; certain grades have a higher bound styrene content. The polystyrene endblocks create a network of reversible physical cross-links which allow thermoplasticity for melt processing or solvation. With cooling or solvent evaporation, the polystyrene domains reform and harden, and the rubber network is fixed in position [2]. Principal styrenic TPE markets are: molded shoe soles and other footwear; extruded film/sheet and wire/cable

covering; and pressure sensitive adhesives and hot-melt adhesives, viscosity index improver additives in lube oils, resin modifiers, and asphalt modifiers [3].

A vast amount of research, particularly in the area of thermoplastic elastomers, has been focused in studying the relation between the processing conditions in extrusion and the final polymer morphology. Savasci et al. pointed out that the ideal filler materials in elastomers exhibited an increase in bending strength, ultimate tensile stress, and toughness and a decrease in cost [4]. G. Matinez et al. reported that mechanical and processing properties of PS/SBR blend [5]. P. V. Sreenivasan et al. investigated the mechanical properties and morphology of nitrile rubber toughened polystyrene [6]. Blends of SEBS, SBR and SIS have been studied by many researchers such as Savadekar et al.[7], Botros et al [8], Tasdemir et al. [9] and Raghu et al [10].

In this study, the effect of PS on the mechanical, thermal and morphological properties of SEBS, SIS and SBR type elastomers based material was investigated in flow direction 0° and flow direction 90°. The structure and properties of the composites are characterized using a scanning electron microscopy (SEM), Differential scanning calorimetry (DSC) and Energy dispersive X-ray spectroscopy (EDS). Furthermore, SEBS/HIPS and SIS/HIPS polymer blends were subjected to examinations to obtain their elasticity modulus, yield strengths, strength @ break, elongation @ break, hardness, izod impact strength, wear rate, melt flow index (MFI), vicat softening point and heat deflection temperature (HDT).

2. Experimental

2.1. Compositions and Materials:

Ten different polymer composites were prepared. Compositions of SEBS/HIPS/CaCO₃ and SIS/HIPS/CaCO₃ polymer composites that were formed are given in Table 1.

Table 1. Composition of the different rubber formulations

<i>SEBS/HIPS/CaCO₃</i>					<i>SIS/HIPS/CaCO₃</i>				
Groups	SEBS (%)	HIPS (%)	CaCO ₃ (%)	Paraffinic Oil (%)	Groups	SIS (%)	HIPS (%)	CaCO ₃ (%)	Paraffinic Oil (%)
1	30	30	10	30	1	55	30	10	5
2	27.5	35	10	27.5	2	50	35	10	5
3	25	40	10	25	3	45	40	10	5
4	22.5	45	10	22.5	4	40	45	10	5
5	20	50	10	20	5	35	50	10	5

Styrene ethylene butylenes styrene block copolymer (calprene H6110) was supplied by Dynasol Elastomers (Houston, TX-USA). Total styrene ratio is 30 %. Melt flow rate (230°C /2.16 kg) is 1,5 g/10min. Styrene isoprene styrene block copolymer (Europrene Sol T 190) was supplied Polimeri Europa (Milan, Italy). Its specific gravity is 0.928 g/cm³, melt flow rate (190°C /5.0 kg) is 9.0 g/10min. Styrene ratio is 16 %. High impact polystyrene (porene PS HI650) was supplied by IRPC public company limited (Bangkok, Thailand). Melt flow rate (200°C /5.0 kg) is 8.0 g/10min. Tensile strength is 22.8 MPa. Calcium carbonate (CaCO₃) (Esen calcite A-3) was supplied by Esen mikronize (Istanbul, Turkey). CaCO₃ ratio is ≥98%. Its specific gravity is 2.7 g/cm³, particle size is 2.70–3.30 μ. Paraffinic oil was supplied Petroyag (Kocaeli, Turkey). Its density is 0,8576 g/cm³.

2.2. Composite Preparation:

CaCO₃ was dried in a Yamato Vacuum oven ADP-31(Yamato/VWR Scientific Products, Japan) at 110 °C for 24 hours before being blended with SEBS/HIPS and SIS/HIPS. Mechanical premixing of solid compositions was done using a LB-5601 liquid-solids blender (The Patterson-Kelley Co., Inc. east

Stroudsburg, PA - USA) brand batch blender at 10 min. Samples with various proportions of SEBS/HIPS and SIS/HIPS were produced between 150–190 °C at 5–6 bar pressure, and a production rate of 40 rpm, with a Microsan co-rotating twin-screw extruder (L/D ratio is 30, Ø:25 mm, Microsan Instrument Inc. Kocaeli-Turkey). Polymer composites were also dried in Vacuum oven at 110 °C for 6 hours after extrusion. Extrusion conditions are given in Table 2. Plate samples of the granulated polymeric blends were made in plate machine. Plate machine-extruder head construction stages are given in figure 1. Also test samples were removed from plate (flow direction 0° and flow direction 90°) as shown in Figure 1.

Table 2. Extrusion conditions of the SEBS/HIPS/CaCO₃ and SIS/HIPS/CaCO₃ polymer composites

Process	Extrusion	
	SEBS/HIPS/CaCO ₃	SIS/HIPS/CaCO ₃
Temperature (°C)	150–190	150–190
Pressure (bar)	5–6	5–6
Screw speed (rpm)	40	40



Fig. 1. Plate machine, extruder head and flow directions

2.3. Test Procedure:

Composite specimens were conditioned at 23°C and 50% humidity for 24 h before testing (ASTM D618). Tensile tests were performed according to ASTM D638 specification. They were carried out using a Zwick Z010 (Zwick GmbH, Ulm-Germany) testing machine with a load cell capacity of 10 kN at a cross-head speed of 50 mm/min. The elastic modulus, yield strength, strength at break and % elongation was determined from the stress–strain curves. Hardness test were done according to the ASTM D2240 method with Zwick hardness measurement equipment. To investigate fracture behavior, Izod impact test (notched) was done at room temperature according to the ASTM D256 method with Zwick B5113 impact test device (Zwick GmbH & Co. KG Ulm, Germany). The wear tests were done according to the DIN 53 516 method with Devotrans DA5 (Devotrans quality control test equipment Istanbul-Turkey) abrasion test equipment. Flow behavior testing of all the mixtures was done according to ISO 1133 standard with Zwick 4100 MFI equipment. The fractured surfaces of the composites were coated about 10 nm in thickness with gold (Au) (80%)/palladium (Pd) (20%) alloys to prevent electrical charging by Polaron SC 7620 (Gala Instrumente GmbH, Bad Schwalbach-Germany). The surfaces of the prepared samples were observed by the JEOL-JSM 5910 LV (JEOL Ltd., Tokyo, Japan) scanning electron microscopy (SEM) at an acceleration voltage of 20 kV. Elemental analysis was done using Energy dispersive X-ray spectroscopy (EDS) (Incax-sight- model: 7274- Oxford Instruments, England). Heat deflection temperature (HDT) and Vicat softening point tests were done according to ISO 75 and ISO 307 standard with determined by CEAST 6521 (Ceast SpA Pianezza, Italy) HDT-vicat test equipment. Five samples were tested in each set and the average value was reported.

3. Result and Discussion

Mechanical properties of the SEBS/HIPS/CaCO₃ and SIS/HIPS/CaCO₃ polymer composites are given in Table 3.

Table 3. Mechanical properties of the SEBS/HIPS/CaCO₃ and SIS/HIPS/CaCO₃ polymer composites
SEBS/HIPS/CaCO₃

Mechanical Properties	Flow direction (0°)					Flow direction (90°)				
	Group 1	Group 2	Group 3	Group 4	Group 5	Group 1	Group 2	Group 3	Group 4	Group 5
Elasticity Modulus (MPa)	28.3±5	31.5±8	48.9±15	57.7±18	106.0±27	22.4±3	29.1±5	44.4±13	54.6±7	99.5±21
Yield Strength (MPa)	1.5±0	1.6±0	3.9±1	5.2±1	5.5±1	1.3±0	1.6±0	2.6±0	4.1±1	5.2±1
Strength @ Break (MPa)	7.6±1	7.7±1	8.0±1	8.6±1	9.8±2	5.7±0	6.1±1	6.7±1	8.5±1	8.9±1
Elongation @ Break (%)	649.4 ±57	625.9 ±50	389.0 ±43	324.0 ±10	251.7 ±14	633.6 ±36	589.9 ±41	373.4 ±18	297.3 ±22	184.7 ±13
Hardness (Shore A)	77.6±2	81.2±2	87.8±2	90.0±1	90.6±1	75.6±1	81.0±2	84.8±2	88.8±1	89.8±1
Izod Impact Strength (kJ/m ²) (notc.)	14.1±2	16.5±1	21.9±1	22.0±2	37.9±3	13.4±1	14.0±1	19.5±0	25.3±2	32.1±1
Wear rate (cm ³ /Nm)	0.0180	0.0218	0.0214	0.0349	0.0379	0.0227	0.0270	0.0283	0.0376	0.0389

SIS/HIPS/CaCO₃

Elasticity Modulus(MPa)	2.5±1	2.8±1	3.4±1	3.9±0	3.9±1	1.6±0	1.8±0	3.0±1	3.2±1	3.7±0
Yield Strength (MPa)	0.1±0	0.2±0	0.2±0	0.2±0	0.3±0	0.1±0	0.1±0	0.2±0	0.2±0	0.3±0
Strength @ Break (MPa)	2.6±0	2.9±0	3.0±0	3.1±0	3.2±0	2.5±0	2.8±0	3.0±0	3.0±0	3.1±0
Elongation @ Break (%)	979.7 ±77	975.4 ±68	616.0 ±70	484.8 ±23	276.1 ±31	669.4 ±65	636.9 ±73	483.5 ±28	407.8 ±17	246.2 ±15
Hardness (Shore A)	40.4±1	41.6±0	46.0±1	49.8±1	54.4±2	39.8±1	40.2±0	44.2±0	48.8±1	53.6±1
Izod Impact Strength (kJ/m ²) (notc.)	Fracture behavior was not observed in (+24 °C) and (-25 °C)									
Wear rate (cm ³ /Nm)	0.0431	0.0551	0.0574	0.0608	0.0676	0.0531	0.0628	0.0641	0.0694	0.0760

In two directions (flow direction 0° and flow direction 90°) with the increased amount of HIPS in SEBS/HIPS/CaCO₃ and SIS/HIPS/CaCO₃ polymer blends, the elasticity modulus, yield strengths, strength @ break, hardness, izod impact strength and wear rate of the resultant material increased, whereas the elongation @ break decreased. Because of rigid structure of the HIPS, these values were increased. For example the elasticity modulus value of the SEBS/HIPS/CaCO₃ (Group 1) polymer composite was 28.3 MPa. However, the increasing of HIPS contents to the polymer composite resulted in higher elasticity modulus values. Also hardness value of the SEBS/HIPS/CaCO₃ (Group 1) polymer composite was 77.6 Shore A. However, the increasing of HIPS contents to the polymer composite resulted in higher hardness values. Similar result was obtained in SIS/HIPS/CaCO₃ polymer composites. The thermal properties of the polymer composites are given in Table 4.

Table 4. Thermal properties of the SEBS/HIPS/CaCO₃ and SIS/HIPS/CaCO₃ polymer compositesSEBS/HIPS/CaCO₃

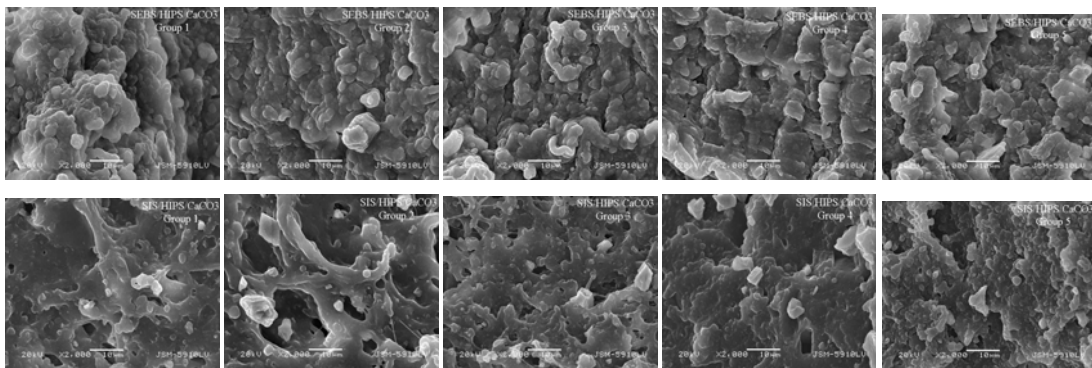
Thermal Properties	Group 1	Group 2	Group 3	Group 4	Group 5
MFI (g/10min) (230 °C – 3.8 kg)	2.6±0	9.2±2	20.1±2	24.2±4	25.2±2
Vicat Softening Point (°C- 1 kg)	57.8	59.8	64.2	67.6	73.2
HDT (°C-1.80 MPa)	-	-	-	-	52.6

SIS/HIPS/CaCO₃

MFI (g/10min) (230 °C – 3.8 kg)	39.7±3	46.9±5	48.5±1	50.1±2	51.1±1
Vicat Softening Point (°C- 1 kg)	-	-	-	-	-
HDT (°C-1.80 MPa)	-	-	-	-	-

As shown in Table 4, the melt flow index value of the SEBS/HIPS/CaCO₃ (Gr. 1) polymer composite was 2.6 g/10 min (230 °C–3.8 kg). However, the increasing of HIPS contents to the polymer composite resulted in higher MFI values. Similar result was obtained in SIS/HIPS/CaCO₃ polymer composites. The melt flow index value of the SIS/HIPS/CaCO₃ (Group 1) polymer composite was 39.7 g/10 min (230 °C–3.8 kg). However, the addition of HIPS to the polymer composite resulted in higher MFI values. The HDT and vicat softening temperature measurements showed that the addition of HIPS to the SEBS/HIPS/CaCO₃ increased the heat deflection temperature and vicat softening point values, as shown in Table 4. The HDT and vicat values of SIS/HIPS/CaCO₃ polymer composite were not measured. The HDT test was started at room temperature with a heating rate of 120°C/h and under a load of 1.8 MPa.

The fracture surfaces of the polymer composites were examined via SEM in an attempt to correlate the mechanical properties to the microstructural characteristics. Scanning electron micrographs of fractured surfaces of the SEBS/HIPS/CaCO₃ and SIS/HIPS/CaCO₃ polymer composites taken after Izod impact tests are shown in Figure 2 and energy dispersive X-ray spectroscopy (EDS) spectrums of the polymer composite are given in Figure 3.

Fig. 2. SEM micrographs of the SEBS/HIPS/CaCO₃ and SIS/HIPS/CaCO₃ polymer composites

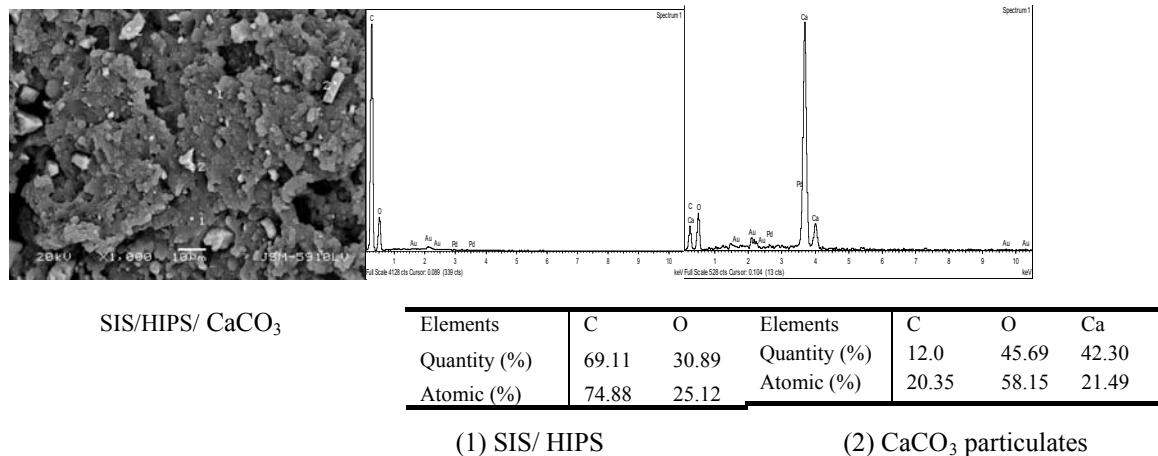


Fig. 3. Energy dispersive X-ray spectroscopy (EDS) spectra of SIS/HIPS/CaCO₃ polymer composites

The micrographs indicate that the CaCO₃ particulates are homogeneously dispersed on the fractured surfaces of polymer matrix. With addition of SEBS and SIS rubber to the HIPS, the adhesion and distribution of the present phases were considerably enhanced as well.

For example the SEM images of SEBS/HIPS/CaCO₃ composites (groups 1–5) given in Figure 2. In this system the SEBS particles exist as irregularly shaped domains in the HIPS matrix.

4. Conclusions

In two directions (flow direction 0° and flow direction 90°) with the increased amount of HIPS in SEBS/HIPS/CaCO₃ and SIS/HIPS/CaCO₃ polymer blends, the elasticity modulus, yield strengths, strength @ break, hardness, izod impact strength, MFI, HDT, vicat value and wear rate of the resultant material increased, whereas the elongation at break decreased. The micrographs indicate that the CaCO₃ particulates are homogeneously dispersed on the fractured surfaces of polymer matrix. With addition of SEBS and SIS rubber to the HIPS, the adhesion and distribution of the present phases were considerably enhanced as well.

Acknowledgements

This work has been supported by the Scientific Research Project Program of Marmara University (Project no: FEN-C- YLP-060510-0144). The authors are grateful to Marmara University for their financial support and the provision of laboratory facilities.

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