



Improvement of the physical and mechanical properties of HIPS by SEBS and PIB

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ABSTRACT

Objective: The aim of this study was to investigate the combined effects of styrene-ethylene-butylene-styrene (SEBS) and polyisobutylene (PIB) on the thermal, mechanical, and morphological properties of high-impact polystyrene (HIPS) and to evaluate their effectiveness in improving the performance of HIPS through binary and ternary blend formulations.

Methods: Binary and ternary HIPS/PIB/SEBS blends containing 1–2 wt% PIB and 1–5 wt% SEBS were prepared using twin-screw extrusion followed by injection molding. The blends were characterized by the melt flow rate (MFR) test, Vicat softening temperature (VST) test, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), Izod impact test, and environmental stress crack resistance (ESCR) test based on elongation-at-break measurements before and after immersion in oil.

Results: PIB acted primarily as a plasticizer, resulting in increased melt flowability, whereas SEBS significantly enhanced the thermal stability and toughness of HIPS. VST dropped from 95.3 to 94.5 and 93.1, then increased to 96.4 and 96.5 in blends No. 1-8 and No. 9-13 respectively. The thermogravimetric analysis demonstrated improved thermal degradation resistance with increasing SEBS content (the highest result achieved at 446.9 °C for HI-3), while DSC results indicated good compatibility among the blend components. SEM observations revealed finer elastomer dispersion and a fracture morphology with greater ductility. Furthermore, the simultaneous addition of PIB and SEBS markedly improved the impact strength up to 19.2 J/m and environmental stress crack resistance, with the best overall performance achieved for blends containing 1 wt.% PIB and 2 wt.% SEBS.

Conclusion: The incorporation of SEBS and PIB provides an effective strategy for simultaneously improving the flowability, toughness, thermal stability, and environmental stress crack resistance of HIPS. The proposed ternary blends offer enhanced performance and demonstrate promising potential for engineering applications to improve mechanical and environmental durability.

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1. Introduction

High-Impact Polystyrene (HIPS), also known as toughened polystyrene, is conventionally synthesized as a heterogeneous blend in which polybutadiene rubber (PBR) domains are finely dispersed within a polystyrene (PS) matrix [1,2]. Due to its favorable characteristics, including enhanced impact resistance, ease of pigmentation, and thermoplastic processability, HIPS has been widely used across various industrial sectors [3]. In addition, HIPS can be susceptible to environmental stress cracking when exposed to oils; edible oils, such as sunflower oil, have been reported to act as active media that initiate cracking and fracture in HIPS [4,5]. To overcome these limitations, various modification strategies, involving melt blending with thermoplastic elastomers (TPEs), have been explored and are gaining increasing prominence [6,7]. TPEs are block copolymers composed of alternating hard (glassy) and soft (rubbery) segments, which endow them with a unique balance of elasticity and thermal processability [8]. The mechanical performance of high-impact polystyrene (HIPS) is influenced by several factors, including rubber particle size [9–12], the bimodal distribution of rubber particle size (RPSD) [13–15], and the characteristics of the rubbery phase used [16–19]. Craze initiation is linked to all rubber domains, but only larger rubber particles are effective in arresting crazes, which contributes to improved toughness. [20]. Furthermore, the overlap of crazes initiated by smaller particles with those by neighboring larger ones has been proposed as a method to improve impact resistance [21]. Among the various TPEs, styrene–ethylene–butylene–styrene (SEBS) has attracted considerable attention, due to its saturated midblock structure, which provides excellent

thermal and oxidative stability [22]. SEBS features a distinct biphasic structure, comprising thermoplastic polystyrene blocks and rubbery ethylene–butylene segments, which enhance mechanical performance and processability [8,23–25]. Due to its chemical similarity to PS, SEBS demonstrates favorable miscibility with HIPS, making it a promising candidate for impact modification [26].

The compatibility between SEBS and HIPS was studied [27]. The presence of styrene blocks in both SEBS and HIPS facilitated the uniform dispersion of SEBS domains within the HIPS matrix [28]. This resulted in a significant improvement in impact resistance; specifically, with the addition of 13 wt% SEBS, the value increased more than fourfold compared to pure polystyrene (PS). [29]. Furthermore, the incorporation of SEBS into the PS matrix not only enhanced mechanical strength but also reduced shear viscosity and mixing torque, indicating better processability [29]. This finding was further supported by the observed fine and relatively uniform dispersion of SEBS domains within the PS matrix [30,31].

Research has shown that a bimodal RPSD contributes significantly to enhancing toughness in HIPS systems [15,32–34]. Typically, polymer blends exhibit a dispersed-droplet morphology, where the minor rubbery phase is finely distributed within a continuous thermoplastic matrix [35–38]. A novel HIPS formulation incorporating a styrene–butadiene diblock copolymer was developed to generate two populations of rubber particles with a bimodal size distribution, resulting in improvements in impact resistance[32].

In addition to mechanical integrity, environmental stress cracking resistance (ESCR) represents a critical design criterion, especially for polymer systems exposed to

chemically aggressive environments. Environmental stress cracking generally involves the combined effects of mechanical stress and an aggressive chemical environment, and its mechanisms involve the diffusion of environmental agents, localized plasticization, craze initiation, and the subsequent weakening and fracture of craze fibrils [39-41]. The incorporation of low-molecular-weight or soft polymeric components can reduce the intermolecular interactions and chain cohesion within the polymer matrix, resulting in reduced tensile strength and modulus and facilitating deformation and failure at lower applied stresses [40,42].

Various material engineering approaches have been explored to improve the Environmental Stress Crack Resistance (ESCR) of HIPS. For instance, larger rubber domains were identified as crucial for developing a morphology that is resistant to stress-induced cracking [43]. Polyisobutylene (PIB) is recognized for its excellent resistance to oxidizing and acidic environments owing to its highly saturated hydrocarbon backbone and low concentration of reactive functional groups [44-46]. The incorporation of polyisobutylene (PIB) has been reported as an effective approach for improving the environmental stress crack resistance (ESCR) of HIPS, particularly in applications involving exposure to oily or fatty substances. The improvement in ESCR has been attributed to the combined effects of PIB and mineral oils, with complementary behavior reported when the two additives are used together. In addition, the rubber particle size and morphology of HIPS remain important factors governing ESCR, indicating that the effectiveness of PIB is also dependent on the morphology of the underlying rubber phase

[47]. Enhancing ESCR requires both the retardation of crack propagation and the reduction of the penetration of environmental agents. The significance of elongation at break as a critical mechanical indicator related to ESCR was emphasized [48]. Studies on styrenic polymer systems have shown that PIB-based thermoplastic rubbers can enhance interfacial interactions [49]. However, in HIPS-containing ternary blends, morphology and mechanical performance depend strongly on blending design, phase distribution, and phase continuity [50]. Accordingly, in the present HIPS/SEBS/PIB system, PIB is proposed to have a possible dual effect: it may improve the interfacial adhesion between HIPS and SEBS, while inappropriate dispersion or excessive loading may disrupt phase continuity and weaken stress transfer. The flexible butylene segments of SEBS are identified as the main contributors to impact energy absorption, while the styrene blocks enhance compatibility with the polystyrene phase. Additionally, the inclusion of PIB, which has flexible methyl side groups and a saturated backbone, is expected to offer further stress dissipation and enhance chemical resistance, potentially leading to improved toughness and ESCR [28,51].

In the present study, the binary and ternary blends of HIPS, SEBS, and PIB were systematically formulated and investigated. Elucidating the combined effects of SEBS and PIB on mechanical behavior and environmental durability was emphasized. The novelty of this work is in exploring the concurrent reinforcement mechanisms arising from the combined addition of SEBS and PIB, which aim to enhance both the impact strength and ESCR in HIPS-based systems.

2. Materials and Methods

2.1. Materials

The High-impact polystyrene (HIPS-7240) (melt flow rate (MFR) = 5.4 g/10 min. Vicat softening temperature (VST) = 95.3°C, Izod impact strength (notched) = 11.3 J/m) was supplied by Tabriz Petrochemical Company 8(Tabriz, Iran). Polyisobutylene (PIB; INDOPOL H-100, viscosity@100C=200-235cSt. Mn=910) was supplied by BP Chemicals Limited (London, United Kingdom). Styrene-ethylene-butylene-styrene (SEBS; Globalprene 7550 U; styrene content = 30 %wt.; specific gravity = 0.91; MFR = 0.2 g/10 min) was purchased from LCY Grit Corp. (Zhenjiang, Taiwan).

2.2. Materials Preparation

To investigate the simultaneous effects of SEBS and PIB on the improvement of the flowability and the mechanical, thermal, morphological and ESCR properties of HIPS, thirteen different blends were prepared. These formulations were selected to separate the individual effects of PIB and SEBS from their combined influence on HIPS. Specifically, HI-1 was used as the neat HIPS reference sample. HI-2 and HI-3 were designed as single-additive controls to evaluate the effect of PIB and SEBS respectively. The remaining formulations were divided into two combinatorial series: HI-4 to HI-8, in which the weight of PIB was kept constant at 1 wt.% and that of SEBS was increased from 1 to 5 wt.%, and HI-9 to HI-13, in which PIB was kept constant at 2 wt.% and that of SEBS was also increased from 1 to 5 wt.%. This design allowed us to compare the effects of the individual additives with those of the combined formulations and to assess composition-dependent trends in thermal,

mechanical, and flow behavior. The compositions of high-impact polystyrene /polyisobutylene /styrene-ethylene-butylene-styrene (HIPS/PIB/SEBS) mixtures are provided in Table 1.

Table 1.

Percentage compositions of high-impact polystyrene /polyisobutylene /styrene-ethylene-butylene-styrene (HIPS/PIB/SEBS) mixtures (at 25 °C).

Sample	HIPS %	PIB %	SEBS %
HI-1	100	0	0
HI-2	99	1	0
HI-3	99	0	1
HI-4	98	1	1
HI-5	97	1	2
HI-6	96	1	3
HI-7	95	1	4
HI-8	94	1	5
HI-9	97	2	1
HI-10	96	2	2
HI-11	95	2	3
HI-12	94	2	4
HI-13	93	2	5

2.3. Blend preparation

All blends were prepared using various proportions of HIPS/PIB/SEBS according to Table 2. These blends were melt-compounded in a twin-screw extruder (TEK 30, Samsung Engineering Co., Ltd., 30 mm, 32 L/D) equipped with a K-50 pelletizer, ensuring the homogeneous dispersion of PIB and SEBS within the HIPS matrix. The extruded pellets were dried and stored for 24 hours at 25°C to relieve residual internal stresses and prevent premature deformation during processing [45]. The controlled melt processing was aimed to preserve the morphology of PBR and to introduce SEBS domains, facilitating optimal mechanical performance and processability.

Table 2.

Extrusion and pelletizing conditions of all polymer blends.

Zone	1	2	3	4	5	6	Die head
Temperature, °C	170	175	180	185	190	190	195
Screw speed: 153 rpm							

2.4. Sample Preparation

Samples for evaluating IZOD impact and for tensile testing were prepared using injection molding machines (Billion, France) based on ISO 180 and ASTM D 638 respectively [40,42, 43]. This procedure ensured reproducible dimensions and minimized variations in

mechanical testing, providing a reliable assessment of the combined effects of PIB and SEBS on the toughness and ductility of HIPS. The parameters for the injection molding of samples are shown in Table 3.

Table3.

Injection molding conditions for the preparation of all test specimens.

No.	Parameter	Unit	Set value
1	Zone 1-4, nozzle temperature	°C	185-190-190-190-195
2	Injection pressure,	bar	70
3	Holding 1-3 pressures,	bar	40-30-10
4	Mold temp.	°C	30
5	Feeding velocity	rpm	150

2.5. Characterization

The melt flow rate (MFR) of the samples was determined using a standard MFR tester [45]. The VICAT softening temperature was measured with a VICAT apparatus (Instron line CEAST, Italy) [45]. The thermogravimetric analysis (TGA) was conducted using a thermal analyzer (PerkinElmer, USA) at a heating rate of 10 °C/min (25 °C to 600 °C) in an air atmosphere [45]. The glass transition temperatures (T_g) of neat HIPS and its blends were determined by differential scanning calorimetry (DSC, Mettler–Toledo, Switzerland). The TGA analyses of the samples were performed using the same instrument under identical conditions. Impact strength and tensile tests were carried out at room temperature using universal testing machines (Lloyd tensile instrument, UK) following ISO 180 A and ASTM D 638 respectively. Each reported

value represents the average of 3 measurements. The morphological behavior of the blends was examined in accordance with ASTM D2240 using scanning electron microscopy (SEM; Mira 3, Tescan, Czech Republic). The ESCR study was utilized by measuring the elongation retention of blends as follows: Tensile sample bars were mounted on cylindrical fixtures, which could provide about 2% strain, and immersed in sunflower oil for 10 days. Then the sample bars were washed and dried for 2 hours before tensile test according to ASTM D 638 [48].

3. Results and discussion

3.1. Thermal properties

3.1.1. Melt Flow Rate (MFR) and VICAT Softening Temperature (VST)

The values of MFR for all HIPS/PIB/SEBS blends are summarized in Figure 1. The clear plasticizing effect of PIB was observed in

sample HI-2 [44], which exhibited a higher MFR compared to neat HIPS (HI-1).

As the SEBS content in blends HI-4 to HI-8 increased, the melt viscosity increased, resulting in a corresponding decrease in MFR.

Similarly, blends HI-9 to HI-13 exhibited a reduction in MFR as the SEBS content increased, indicating the reinforcing effect of SEBS on melt flow behavior [40].

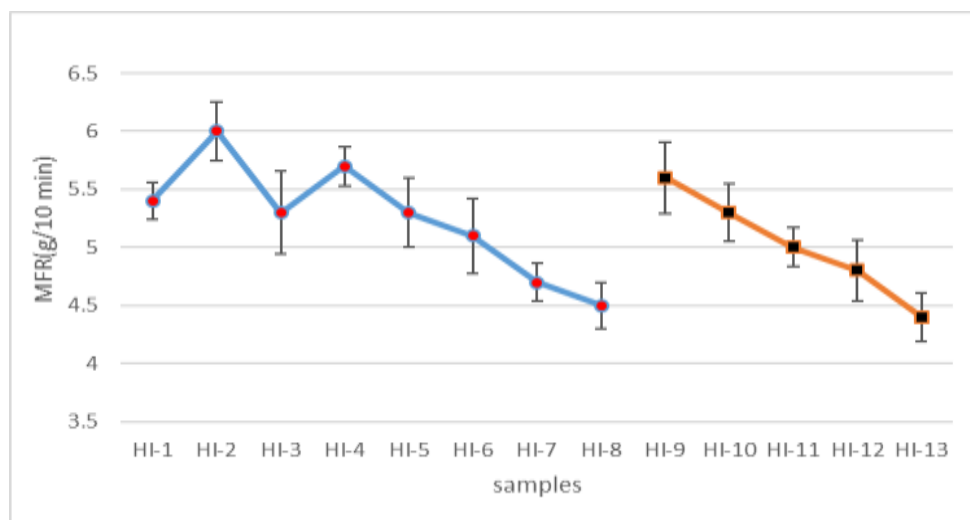


Figure 1. Values of the melt flow rates (MFR) of HIPS/PIB/SEBS blends.

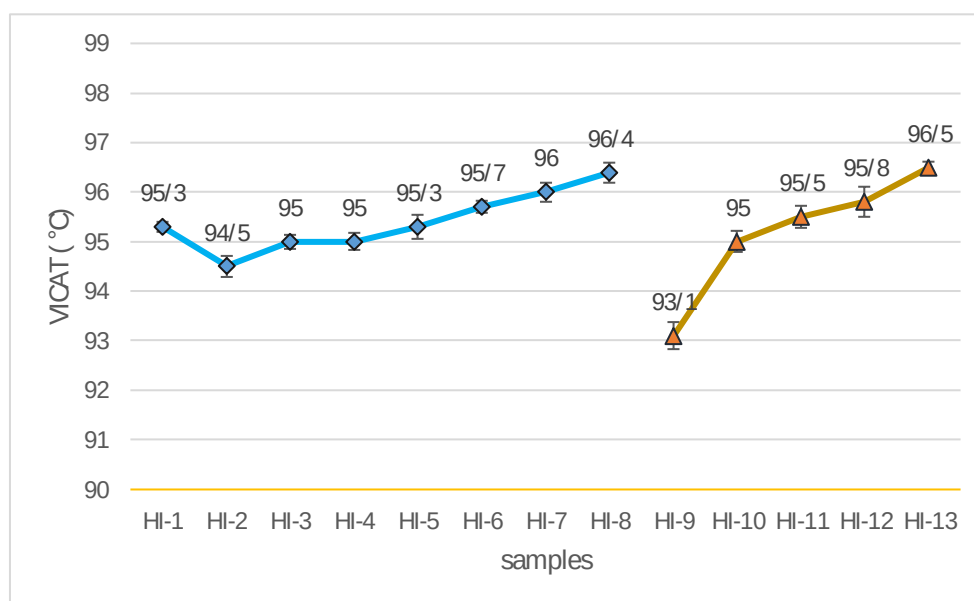


Figure 2. VICAT softening points of blends.

As shown in Figure 2, the VICAT softening temperature indicates an inverse trend compared to that of MFR. The incorporation of PIB led to a decrease in VICAT values, consistent with its plasticizing effect, while the addition of SEBS caused an increase in

VICAT values, reflecting the higher melt viscosity and enhanced thermal resistance imparted by the block copolymer. These trends collectively indicate that the flowability of HIPS can be effectively tuned by adjusting the

relative concentrations of PIB and SEBS, balancing melt fluidity with thermal stability.

3.1.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) curves (Figures 3,4) revealed a distinct two-step degradation mechanism for all HIPS/PIB/SEBS blends in an oxidizing atmosphere. The first degradation stage,

occurring between 300 and 450 °C, corresponds to the thermo-oxidative decomposition of the HIPS matrix. This process involves random chain scission, depolymerization, and partial char formation, accompanied by the evolution of volatile species such as styrene monomer, toluene, and other low-molecular-weight hydrocarbons above 450 °C [32, 45].

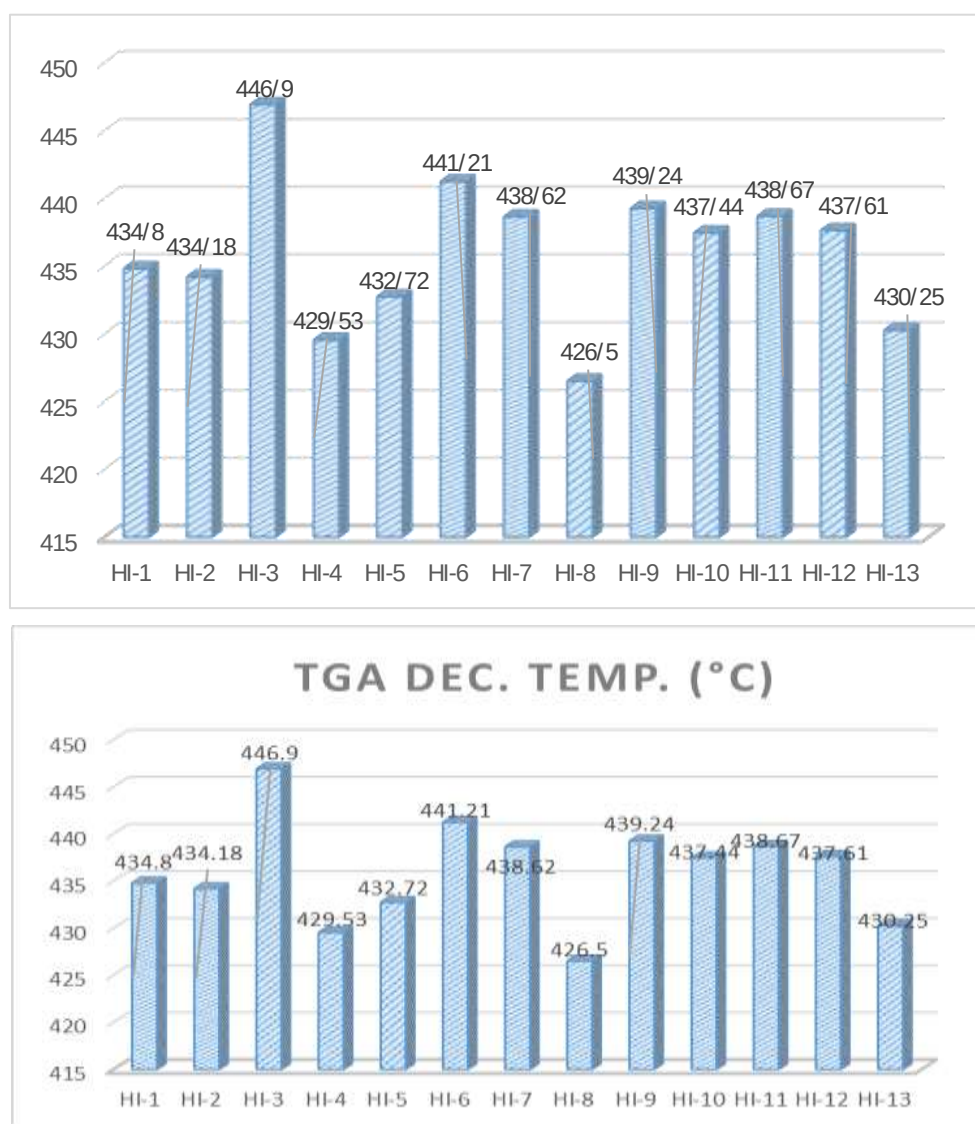


Figure 3. Results of the thermogravimetric analysis (TGA) of HIPS/PIB/SEBS blends.

The second degradation step, extending from 450 to 600 °C, is attributed to the gradual oxidation and decomposition of residual amorphous carbonaceous matter, indicating

complete thermal decomposition of the polymeric phases.

A comparative assessment across the series of blend blends demonstrated that the

incorporation of 1 %wt PIB (HI-2) led to a slight reduction in thermal stability, attributed to the lower molecular weight and greater chain flexibility of PIB, which facilitates earlier onset of degradation. In contrast, 1 %wt. SEBS (HI-3) significantly enhanced the degradation temperature, implying improved oxidative stability due to the reinforcing triblock structure of SEBS and the stabilization of interfacial domains between PS and rubbery phases [45,52]. For samples HI-4 to HI-8, in which the PIB content was maintained constant at 1 %wt and the concentration of SEBS increased from 1 to 5 %wt, the

degradation temperature initially rose and then plateaued. The maximum thermal stability was achieved in HI-6 (96% HIPS, 1% PIB, 3% SEBS), signifying the optimal interaction between PIB and SEBS, leading to improved energy dissipation and restricted segmental motion at elevated temperatures.

At higher concentrations of PIB (HI-9 to HI-13), a similar trend was observed, although the enhancement in thermal stability became less pronounced, likely due to competitive effects between PIB and SEBS in the interfacial zones, which limit the efficiency of radical stabilization at high SEBS loadings.

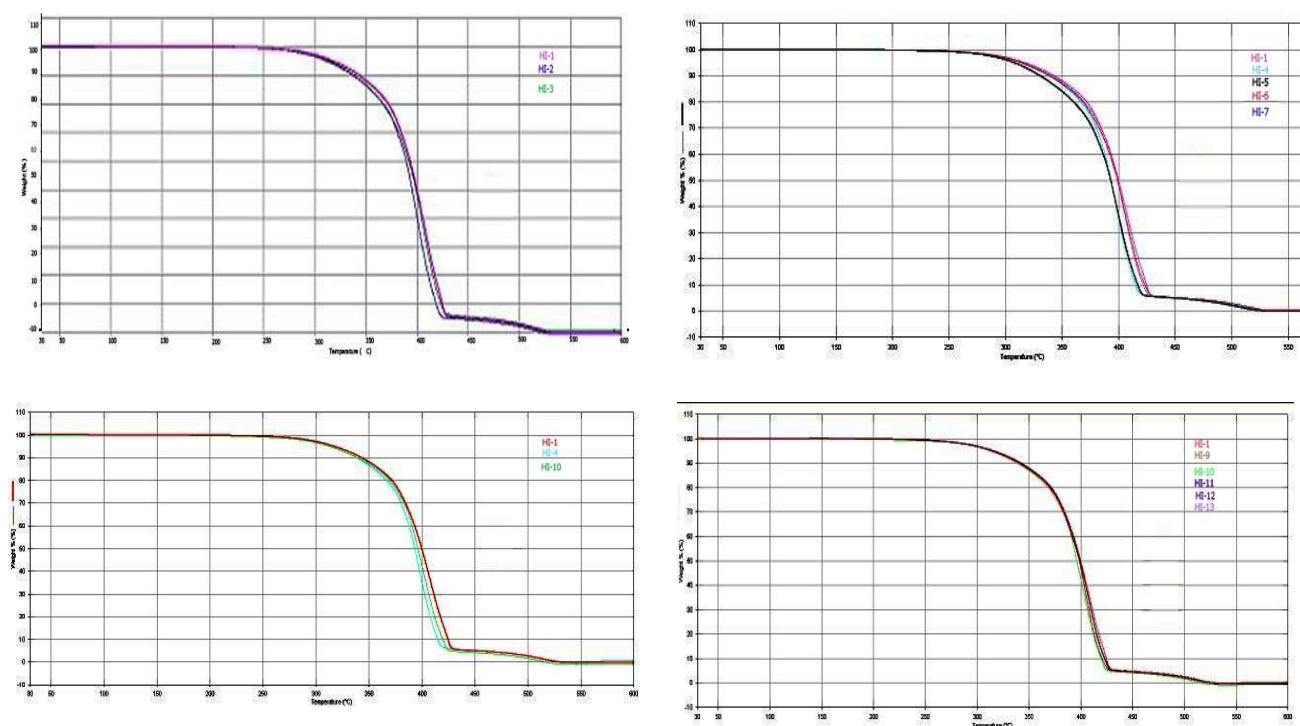


Figure 4. Comparison curves of the thermogravimetric analysis (TGA) of HIPS/PIB/SEBS blends.

3.1.3 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry (DSC) results for the HIPS/PIB/SEBS blend series are shown in Figure 4 and Table I2. Neat HIPS (HI-1) exhibited a glass transition temperature (T_g) of 92.09 °C, which is consistent with the values in the range of 90–105 °C reported in

literature for commercial high-impact polystyrene [53].

Upon the incorporation of PIB and/or SEBS, a gradual increase in T_g was observed, with values ranging from 97.68 °C to 99.35 °C, indicating restricted chain mobility within the polystyrene matrix. This enhancement in the thermal transition behavior is attributed to the reinforcing effect of SEBS domains and the

improved interfacial interactions between the rubbery phases and the HIPS continuous phase [42].

The maximum Tg of 99.35 °C was recorded for sample HI-8 (94 %wt HIPS, 1 %wt PIB, 5 %wt SEBS), suggesting an optimal cooperative interaction between the flexible PIB segments and the reinforcing SEBS copolymer. The SEBS phase likely enhances interfacial adhesion and network rigidity, whereas PIB imparts limited chain flexibility, resulting in an overall balanced morphology [23,28,42].

All blend compositions displayed a single, well-defined glass transition, without any evidence of multiple transitions or melting endotherms, confirming the absence of phase separation or crystallization. This behavior indicates the formation of a homogeneous amorphous phase, in which PIB and SEBS are molecularly compatible with the HIPS matrix at the studied concentrations. These findings are consistent with prior studies on polystyrene-based elastomeric blends, where similar miscibility and thermal homogeneity were reported [28,42].

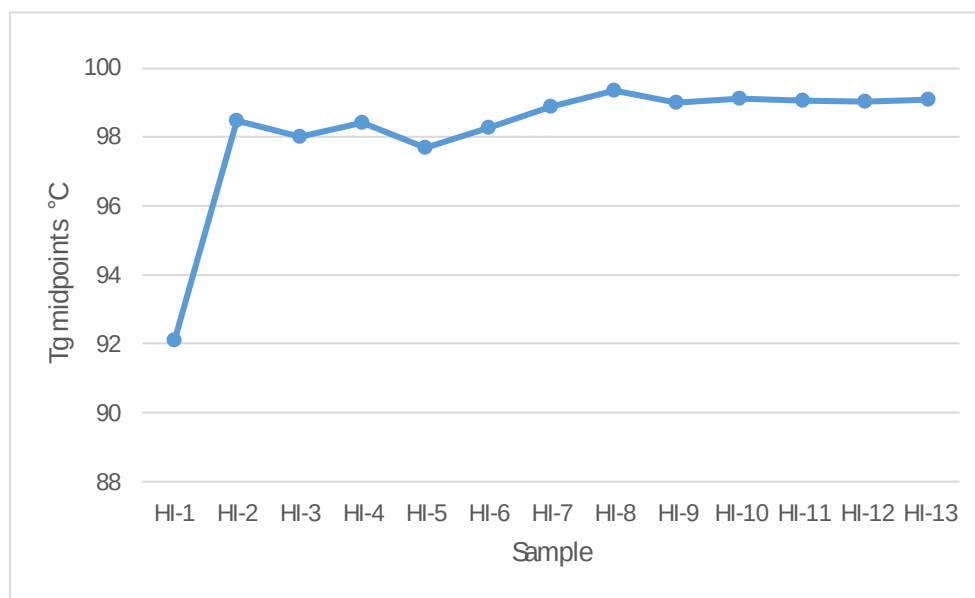


Figure 5. Midpoint glass transition temperatures (Tg) of HIPS/PIB/SEBS blends.

3.2. Morphology

The surface morphologies of the HIPS/PIB/SEBS blends are illustrated in Figure 6, displaying representative SEM micrographs for all thirteen samples. The images reveal the characteristic multiphase structure of HIPS-based systems, consisting of polybutadiene rubber (PBR), polyisobutylene (PIB), and styrene-ethylene-butylene-styrene (SEBS) phases dispersed within the polystyrene (PS) matrix [23, 30].

In the neat HIPS sample (HI-1), containing approximately 8 %wt low-cis PBR, the

microstructure shows spherical rubber domains ranging from 2 to 8 μm in diameter. These domains encapsulate small PS inclusions, forming the typical “salami” morphology characteristic of commercial HIPS. This structure contributes to the inherent toughness of the base polymer by promoting localized shear deformation and limited craze formation [54, 55]. Upon introducing 1 %wt PIB in HI-2, the micrograph displays slight surface whitening and edge stretching at the fracture surface, indicative of the formation microvoids and crazes. This morphological

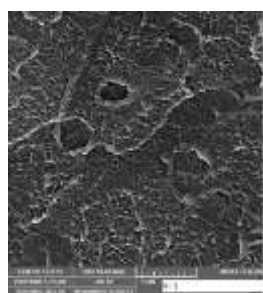
change reflects enhanced stress distribution and ductile deformation, consistent with the moderate improvement in the Izod impact strength observed for this composition [31, 57].

For HI-3, which includes 1 %wt SEBS without PIB, a greater number of finely dispersed particles is evident, which is attributed to the SEBS domains distributed within the PS matrix. These SEBS particles are smaller and more uniformly dispersed than the larger PBR domains, as the SEBS copolymer does not swell significantly in the PS phase. The presence of SEBS promotes improved stress transfer and interfacial compatibility, leading to enhanced energy absorption during the impact.

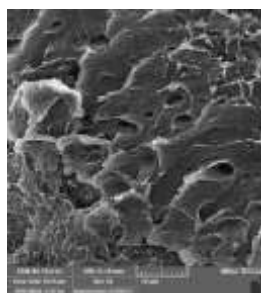
Samples HI-4 to HI-8 (1 %wt PIB with the content of SEBS increasing from 1 to 5 %wt) exhibit progressively finer and more homogeneously dispersed rubber domains. The fracture surfaces display uniform plastic deformation and a dense network of crazes, demonstrating improved ductility and energy dissipation capacity. The morphology evolves from discrete spherical domains to a more interconnected elastomeric network at higher

concentrations of SEBS, correlating directly with the notable rise in the Izod impact strength for these samples [54,56]. Comparatively, increasing the content of PIB from 1 to 2 %wt (sample HI-9 versus HI-4) results in smoother fracture surfaces with fewer sharp edges, reflecting the plasticizing effect of PIB and the improved interfacial relaxation during deformation. At this higher PIB level, further addition of SEBS (HI-10–HI-13) produces a visible increase in the density of crazes and fibrillar structures, consistent with the ductile fracture behavior and enhanced energy dissipation mechanisms such as shear yielding and void coalescence [23,35,57].

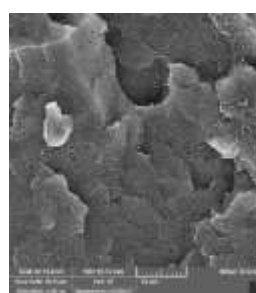
Overall, SEM observations confirm that the combined addition of PIB and SEBS generates a mutual toughening mechanism. PIB contributes to the flexibility and mobility of the matrix, while SEBS introduces elastic energy-absorbing domains with strong interfacial adhesion to the PS matrix. This microstructural cooperation explains the substantial improvements in impact resistance and the shift from brittle to ductile fracture observed in the mechanical testing results.



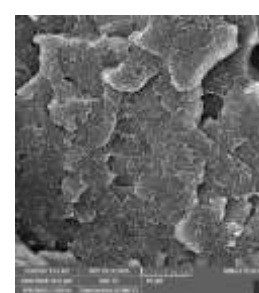
HI-1



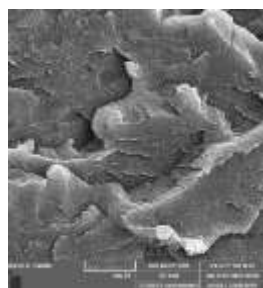
HI-2



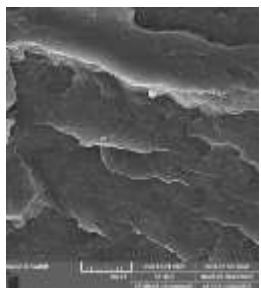
HI-3



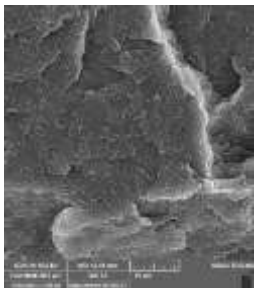
HI-4



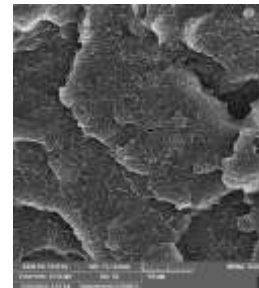
HI-5



HI-6



HI-7



HI-8

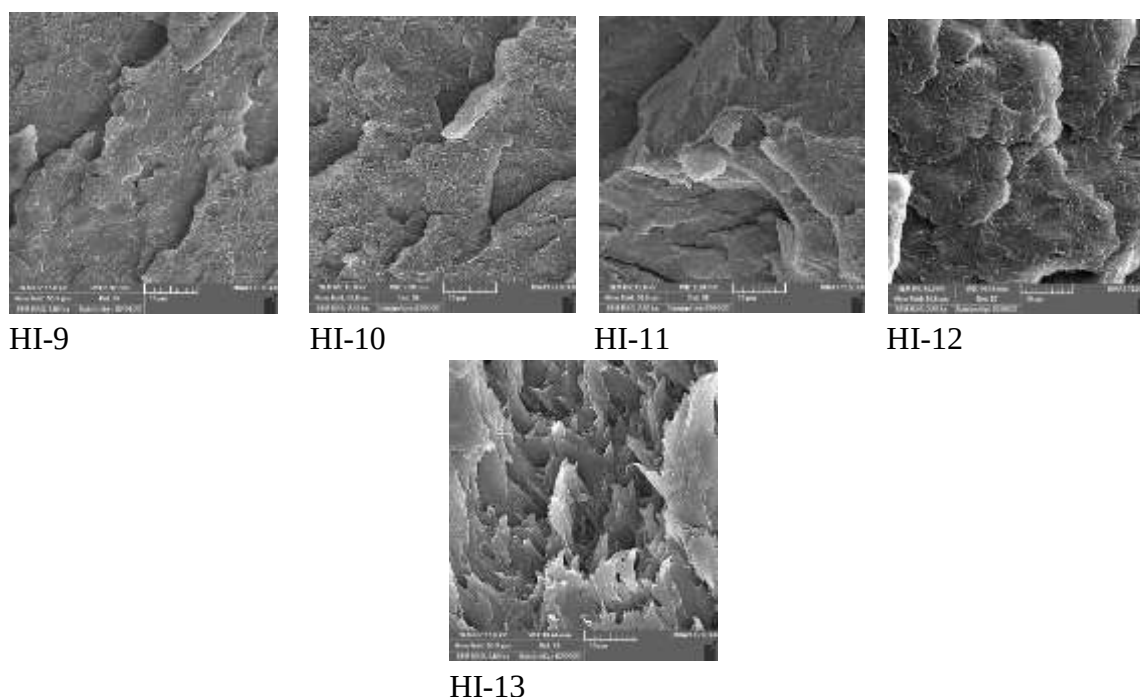


Figure 6. SEM micrographs of HIPS/PIB/SEBS blend samples (HI-1 to HI-13).

3.3. Mechanical Properties

3.3.1. Impact Strength (Izod Test)

Figure 6 presents the Izod impact strength values for HIPS/PIB/SEBS blends at ambient and 0 °C testing conditions. Neat HIPS (HI-1) exhibited the Izod impact strength of $11.3 \text{ J}\cdot\text{m}^{-1}$ at room temperature and of $10.5 \text{ J}\cdot\text{m}^{-1}$ at 0 °C, reflecting its inherently brittle nature and limited energy absorption capacity.

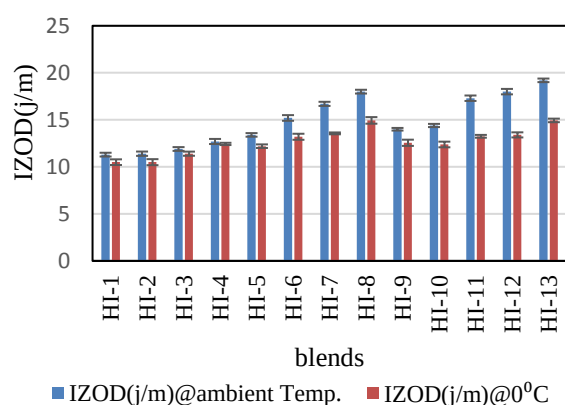


Figure 6. Comparison of the Izod impact strength of HIPS/PIB/SEBS blends at ambient and 0 °C. The addition of small amounts of PIB and SEBS significantly improved toughness. In

particular, sample HI-3, which comprised 99% HIPS, 1% PIB, and 1% SEBS, showed a notable increase in impact strength, highlighting a combined toughening effect of PIB and SEBS.

This result arises from the rubbery elasticity of SEBS combined with the flexible molecular segments of PIB, which together promote localized plastic deformation and effective energy dissipation under impact loading [32, 51]. As the SEBS content increased progressively from 1 %wt to 5 %wt (samples HI-4 to HI-8, with 1 %wt PIB held constant), the impact strength showed a pronounced rise—from $12.7 \text{ J}\cdot\text{m}^{-1}$ to $18.0 \text{ J}\cdot\text{m}^{-1}$ at ambient temperature—corresponding to a ~60% improvement compared to neat HIPS. This trend confirms that SEBS acts as a highly efficient energy-absorbing elastomeric phase dispersed within the rigid HIPS matrix. The enhanced interfacial adhesion between SEBS microdomains and the HIPS matrix likely facilitates efficient stress transfer and suppresses crack propagation [28,51,52].

Similarly, in blends containing 2 %wt PIB (HI-9 to HI-13), the same compositional trend was observed. The impact strength improved from $14.0 \text{ J}\cdot\text{m}^{-1}$ for HI-9 (2 %wt PIB, 1 %wt SEBS) to $19.2 \text{ J}\cdot\text{m}^{-1}$ for HI-13 (2 %wt PIB, 5 %wt SEBS), representing the highest toughness among all blends. The presence of both PIB and SEBS in appropriate ratios creates a multiphase morphology in which rubbery domains effectively blunt crack tips and absorb impact energy through cavitation and shear yielding mechanisms [31, 56-58].

Testing at 0°C revealed a comparable but slightly reduced impact performance for all samples, consistent with the reduced ductility

of polymer chains at lower temperatures. Nevertheless, SEBS-rich blends retained superior toughness even under these conditions, confirming the temperature-resilient energy dissipation capability of the elastomeric components.

3.3.2. Environmental Stress Crack Resistance (ESCR) evaluation

The environmental stress crack resistance (ESCR) of the prepared blends was evaluated through measuring elongation-at-break before and after exposure to oil [48,57]. The results are shown in Table 3 and figure 7.

Table 4.

Compositions, elongation at break (before and after oil exposure), and percentage changes in elongation for HIPS/PIB/SEBS blends.

Sample	Elongation at break (%) before	Elongation at break (%) after	Change(%)	Elongation retention (%)
HI-1	42.7	38.1	-10.8	89.2
HI-2	43.6	41.3	-5.3	94.7
HI-3	41.7	41.6	-0.2	99.8
HI-4	41.7	41.3	-1	99
HI-5	44	45.8	4.1	104.1
HI-6	45.8	45.3	-1.1	98.9
HI-7	46.5	44.3	-4.7	95.3
HI-8	46.9	43.5	-7.3	92.7
HI-9	45.4	40.2	-11.5	88.5
HI-10	46.6	43.5	-6.7	93.3
HI-11	44.9	42.9	-4.5	95.5
HI-12	44	42	-4.5	95.5
HI-13	43.8	40	-8.7	91.3

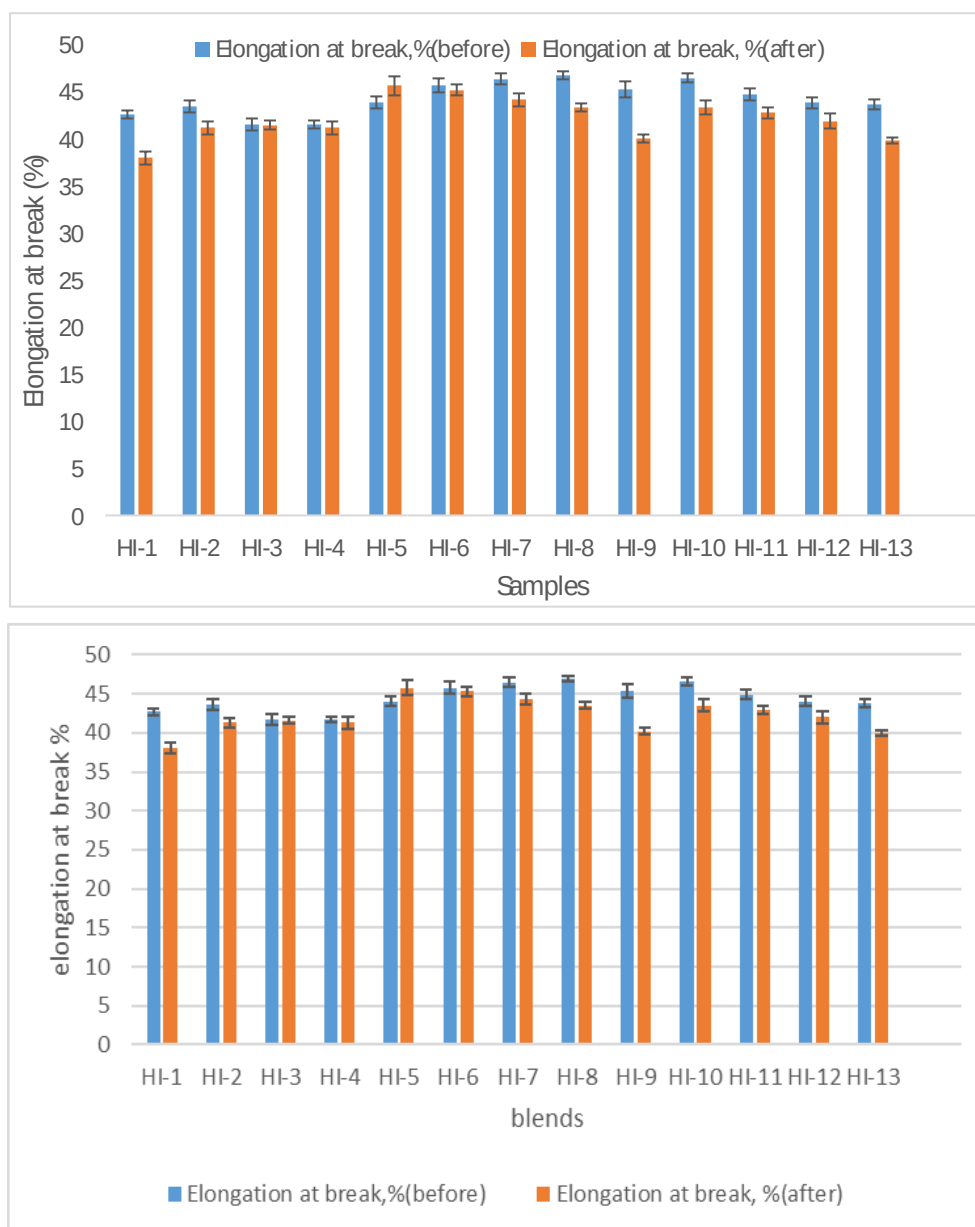


Figure 7. Elongation at break (before and after oil exposure) for blends.

Neat HIPS (HI-1) exhibited a significant decrease in elongation at break (-10.8%) after being exposed to oil, indicating its susceptibility to environmental stress cracking and poor resistance to hydrocarbon-induced degradation [56,57]. The reduction in elongation is primarily attributed to the swelling and partial extraction of the rubber phase in the oil medium, which weakens the interfacial adhesion between the rubbery

polybutadiene domains and the polystyrene matrix.

In contrast, the incorporation of SEBS substantially improved the oil resistance of the blends. Sample HI-3 (99 %wt HIPS, 1 %wt SEBS, without PIB) exhibited a negligible change in elongation (-0.24%), demonstrating the strong positive contribution of SEBS toward enhancing ESCR. This improvement can be ascribed to the saturated midblock (ethylene–butylene) structure of SEBS, which

is chemically inert to oil absorption and contributes to stress dissipation through its flexible elastomeric domains [23,27,29,57].

Furthermore, the addition of PIB along with SEBS produced a clear concurrent effect on oil resistance. Notably, sample HI-5 (97 %wt HIPS, 1 %wt PIB, 2 %wt SEBS) displayed an increase in elongation after being exposed to oil (+4.1%), indicating enhanced toughness and environmental stability. The flexible PIB segments likely acted as internal lubricants, reducing interfacial stress concentration, while SEBS provided physical reinforcement and elastic recovery under tensile deformation. Together, these mechanisms suppress crack initiation and propagation under environmental stress [57].

At higher loadings of SEBS or PIB (samples HI-6, HI-13), a gradual decline in post-exposure elongation was observed. This reduction may be associated with the phase crowding and reduced interfacial compatibility at elevated contents of the modifier, leading to the localized stress accumulation during oil penetration.

Overall, the combined incorporation of SEBS and PIB into HIPS produced thermally stable, mechanically robust, and oil-resistant materials with optimized toughness and processability, suitable for advanced applications such as manufacturing automotive components, impact-resistant housings, and chemically exposed polymeric structures.

4. Conclusion

A comprehensive evaluation of the HIPS/PIB/SEBS ternary blend system was performed to investigate the combined influence of SEBS and PIB on the thermal, mechanical, and morphological properties of high-impact polystyrene (HIPS).

The results of the melt flow rate (MFR) test demonstrated that the incorporation of PIB produced a distinct plasticizing effect, while increasing SEBS content progressively enhanced melt viscosity, leading to a reduction in MFR. This dual behavior provides an effective means of tuning processability for specific applications that require either improved flow or dimensional stability.

The thermogravimetric analysis (TGA) confirmed a two-step thermal degradation mechanism, in which the oxidative decomposition of HIPS predominated, followed by the degradation of residual carbonaceous species. The inclusion of SEBS significantly enhanced thermal stability, with the highest onset degradation temperature observed for HI-6, suggesting a favorable combined effect of SEBS and PIB. Differential Scanning Calorimetry (DSC) revealed a single, well-defined glass transition temperature (T_g) for all compositions, confirming full miscibility and an amorphous blend structure. The T_g values increased with the addition of SEBS and PIB, reaching a maximum of 99.35 °C for HI-8 (94 %wt HIPS, 1 %wt PIB, 5 %wt SEBS), which indicated the restricted chain mobility and enhanced interfacial interaction within the matrix.

Izod impact testing demonstrated a pronounced improvement in toughness upon the combined addition of SEBS and PIB, confirming their combined reinforcement effect. The most notable enhancement was observed for HI-8 and HI-13, with the Izod values increasing by nearly 70% compared to the same in neat HIPS, even at subzero temperatures (0 °C). This improvement can be attributed to the energy dissipation through the formation of microvoids and crazes, as verified by SEM micrographs.

The SEM analysis provided the direct evidence of the morphological evolution induced by SEBS and PIB. The characteristic “salami” structure of HIPS became more refined and uniformly dispersed upon the addition of SEBS, while PIB further improved interfacial adhesion and reduced interfacial stress concentration, resulting in smoother fracture surfaces and enhanced ductile deformation.

Finally, the results of the Environmental Stress Crack Resistance (ESCR) test confirmed that SEBS markedly enhances the oil resistance.

Abbreviations

SEBS	Styrene–ethylene–butylene–styrene
PIB	Polyisobutylene
HIPS	High-impact polystyrene
TGA	Thermogravimetric analysis
DSC	differential scanning calorimetry
SEM	scanning electron microscopy

ESCR environmental stress crack resistance

MFR melt flow rate

VST Vicat softening point temperature

Author Contributions

All authors contributed equally to the conceptualization of the article and writing the original and subsequent drafts.

Data Availability Statement

The authors confirm that the data supporting the findings of this study are available upon request.

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Conflict of interest

The authors declare no conflict of interest.

References

- [1] Grassi VG, Forte MMC, Dal Pizzol MF (2001) Morphologic aspects and structure-properties relations of high impact polystyrene. *Polímeros* 11(3):158–168. <https://doi.org/10.1590/S0104-14282001000300016>
- [2] Wang F, Chang L, Hu Y, Wu G, Liu H (2019) Synthesis and properties of in-situ bulk high impact polystyrene toughened by high cis-1,4 polybutadiene. *Polymers* 11(5):791. <https://doi.org/10.3390/polym11050791>
- [3] Capricho JC, Prasad K, Hameed N, Nikzad M, Salim N (2022) Upcycling polystyrene. *Polymers* 14(22):5010. <https://doi.org/10.3390/polym14225010>
- [4] Vilaplana F, Karlsson S, Ribes-Greus A (2007) Changes in the microstructure and morphology of high-impact polystyrene subjected to multiple processing and thermo-oxidative degradation. *Eur Polym J* 43(10):4371–4381. <https://doi.org/10.1016/j.eurpolymj.2007.07.017>
- [5] Hace D, Kovacevic V, Pajc-Liplin D (1996) Thermally stimulated oxidative degradation of high impact polystyrene with nitric acid. *Polym Eng Sci* 36:1140–1151. <https://doi.org/10.1002/pen.10508>
- [6] Zhao J, Wei D, Wang Z (2015) Thermoplastic elastomers based on high-impact polystyrene/waste styrene butadiene rubber powder blends enhanced by styrene–butadiene–styrene block copolymer and aromatic oil. *J Macromol Sci B* 54(3):262–

274.
<https://doi.org/10.1080/00222348.2014.1000739>
- [7] Jelčić Z, Holjevac-Grgurić T, Rek V (2005) Mechanical properties and fractal morphology of high-impact polystyrene/poly(styrene-b-butadiene-b-styrene) blends. *Polym Degrad Stab* 90(2):295–302.
<https://doi.org/10.1016/j.polymdegradstab.2005.02.021>
- [8] Holden G, Kricheldorf HR, Quirk RP (eds) (2004) *Thermoplastic elastomers*, 3rd ed. Hanser Publishers, Munich.
- [9] Bucknall CB, Davies P, Partridge IK (1987) Rubber toughening of plastics. Part 11: Effects of rubber particle size and structure on yield behaviour of HIPS. *J Mater Sci* 22:1341–1346.
<https://doi.org/10.1007/BF01233131>
- [10] Bucknall CB (2000) *Toughened plastics I: science and engineering*. Springer, Dordrecht.
- [11] Paul DR, Bucknall CB (1983) *Polymer blends: formulation and performance*. Wiley, New York.
- [12] Michler GH, Balta Calleja FJ (2005) Mechanical properties of polymers based on nanostructure and morphology. CRC Press, Boca Raton.
- [13] Song X, Zhang X, Yang D (1998) Morphology and mechanical properties of polystyrene/SBS blends. *Polymer* 39(2):371–382.
- [14] Chu KH, Hsieh TH (1976) The effect of bimodal rubber particle size on toughening of polystyrene. *Polym Eng Sci* 16(5):313–319.
- [15] Okamoto Y, Miyagi H, Kakugo M, Takahashi K (1991) Impact improvement mechanism of HIPS with bimodal distribution of rubber particle size. *Macromolecules* 24(20):5639–5644.
<https://doi.org/10.1021/ma00020a024>
- [16] Pearson RA, Yee AF (1991) Influence of particle size and particle/matrix interactions on toughening mechanisms in rubber-modified epoxies. *J Mater Sci* 26(14):3828–3844. <https://doi.org/10.1007/BF01184979>
- [17] Hunston DL (1984) Rubber-modified thermoplastics. *Polym Eng Sci* 24(4):267–273.
- [18] Kausch HH (1987) *Polymer fracture*, 2nd ed. Springer, Berlin.
- [19] Giakoumakis NS, Vos C, Janssens K, Vekeman J, Denayer M, De Proft F, et al (2024) Total revalorization of high impact polystyrene (HIPS): enhancing styrene recovery and upcycling of the rubber phase. *Green Chem* 26(1):340–352.
<https://doi.org/10.1039/D3GC02407E>
- [20] Dagli G, Argon AS, Cohen RE (1995) Particle-size effect in craze plasticity of high-impact polystyrene. *Polymer* 36:2173–2180.
[https://doi.org/10.1016/0032-3861\(95\)95293-A](https://doi.org/10.1016/0032-3861(95)95293-A)
- [21] Zhu LD, Yang HY, Cai GD, Zhou C, Wu GF, Zhang MY, et al (2013) Submicrometer-sized rubber particles as “craze-bridge” for toughening polystyrene/high-impact polystyrene. *J Appl Polym Sci* 129(1):224–229.
<https://doi.org/10.1002/app.38716>
- [22] Holden G (1990) *Thermoplastic elastomers: properties and applications*. Hanser Publishers, Munich.
- [23] Banerjee R, Ray SS, Ghosh AK (2018) Microstructure development and its influence on the properties of styrene-ethylene-butylene-styrene/polystyrene blends. *Polymers* 10(4):400.
<https://doi.org/10.3390/polym10040400>
- [24] Raha S, Kao N, Bhattacharya SN (2012)

- Modification of styrene-ethylene/butylene-styrene copolymer microstructure by polystyrene homopolymer and evolution of a cocontinuous blend morphology. *Polym Eng Sci* 52(12):2559–2572. <https://doi.org/10.1002/pen.23217>
- [25] Chanda M, Roy SK (2006) *Plastics technology handbook*, 4th ed. CRC Press, Boca Raton.
- [26] Paul DR, Newman S (eds) (1978) *Polymer blends*, vol 1. Academic Press, New York.
- [27] Agari Y, Yamamoto T, Nomura R (2006) Preparation and properties of polystyrene/SEBS blends with compositional gradients in their sheet direction. *Macromol Symp* 242:1–4. <https://doi.org/10.1002/masy.200651001>
- [28] Sang XM, Zhang L, Wang RZ, Chen XG, An M, Shen Y (2011) Study on mechanical properties of styrene-ethylene/butylene-styrene/polystyrene blends. *Adv Mater Res* 396–398:1422–1425. <https://doi.org/10.4028/www.scientific.net/AMR.396-398.1422>
- [29] Ballesteros A, Laguna-Gutiérrez E, Rodríguez-Pérez MA (2021) SEBS as an effective nucleating agent for polystyrene foams. *Polymers* 13(21):3836. <https://doi.org/10.3390/polym13213836>
- [30] Peydró MA, Parres F, Crespo JE, Juárez D (2011) Study of rheological behavior during the recovery process of high impact polystyrene using Cross-WLF model. *J Appl Polym Sci* 120:2400–2410. <https://doi.org/10.1002/app.33444>
- [31] Taşdemir M, Uluğ E (2012) Mechanical, morphological and thermal properties of SEBS, SIS and SBR-type thermoplastic elastomers toughened high impact polystyrene. *Polym Plast Technol Eng* 51(2):164–169. <https://doi.org/10.1080/03602559.2011.618169>
- [32] Alfarraj A, Nauman EB (2004) Super HIPS: improved high impact polystyrene with two sources of rubber particles. *Polymer* 45(25):8435–8442. <https://doi.org/10.1016/j.polymer.2004.10.005>
- [33] Li D, Peng J, Zhai M, Qiao J, Zhang X, Wei G (2008) Novel methods for synthesis of high-impact polystyrene with bimodal distribution of rubber particle size. *J Appl Polym Sci* 109(4):2071–2075. <https://doi.org/10.1002/app.24624>
- [34] Takahashi J, Watanabe H, Nakamoto J, Arakawa K, Todo M (2006) In situ polymerization and properties of methyl methacrylate-butadiene-styrene resin with bimodal rubber particle size distribution. *Polym J* 38:835–843. <https://doi.org/10.1295/polymj.PJ2005203>
- [35] Utracki LA, Wilkie CA (eds) (2002) *Polymer blends handbook*. Springer, Dordrecht.
- [36] Montoya M, Tomba JP, Carella JM, Gobernado-Mitre MI (2004) Physical characterization of commercial polyolefinic thermoplastic elastomers. *Eur Polym J* 40:2757–2766.
- [37] Kohári A, Halász IZ, Bárány T (2019) Thermoplastic dynamic vulcanizates with in situ synthesized segmented polyurethane matrix. *Polymers* 11(10):1663. <https://doi.org/10.3390/polym11101663>
- [38] Wang J, Zhang X, Jiang L, Qiao J (2019) Advances in toughened polymer materials by structured rubber particles. *Prog Polym Sci* 98:101160. <https://doi.org/10.1016/j.progpolymsci.2019.101160>
- [39] Brown RP (1981) *Failure of plastics and*

- rubber products due to environmental stress cracking. Rapra Technology Ltd, Shrewsbury.
- [40] Robeson LM (2013) Environmental stress cracking: a review. *Polym Eng Sci* 53(3):453–467.
<https://doi.org/10.1002/pen.23284>
- [41] Bubeck RA, Bales SE, Vander Sande JB (1981) Environmental stress cracking in impact polystyrene. *Polym Eng Sci* 21(10):632–637.
<https://doi.org/10.1002/pen.760211009>
- [42] Passaglia E, Aglietto M, Picchioni F, Ciardelli F (2002) Blends of syndiotactic polystyrene with SEBS triblock copolymers. *Polymer* 43(11):3323–3329.
[https://doi.org/10.1016/S0032-3861\(02\)00103-9](https://doi.org/10.1016/S0032-3861(02)00103-9)
- [43] Grassi VG, Dal Pizzol MF, Forte MMC, Amico SC (2011) Influence of small rubber particles on the environmental stress cracking of high impact polystyrene. *J Appl Polym Sci* 121(3):1697–1706.
<https://doi.org/10.1002/app.33794>
- [44] Puskas JE, Chen Y (2004) Polyisobutylene-based biomaterials. *J Polym Sci A Polym Chem* 42:5291–5301.
<https://doi.org/10.1002/pola.20114>
- [45] Mark JE (ed) (2005) Physical properties of polymers handbook, 2nd ed. Springer, New York.
- [46] Cochran T, Viola JP (2010) Impact modified styrenic polymers with improved stress crack properties. International patent WO 2010/107557 A1.
- [47] Reddy BR, Blackmon KP (2003) Monovinylaromatic polymer with improved stress crack resistance. US patent 6,613,837 B2, 2 September 2003.
- [48] Qin C, Ding YS, Dhyani H, Kivlehan T, Hong KZ, Monaghan M, et al (2001) ESCR behavior of plastic materials in medical environments. *J Reinf Plast Compos* 20(1):22–36.
<https://doi.org/10.1177/073168401772678364>
- [49] Puskas JE, Kwon Y, Altstädt V, Kontopoulou M (2007) Blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with polystyrene-based thermoplastic rubbers: a comparative study. *Polymer* 48(2):590–597.
<https://doi.org/10.1016/j.polymer.2006.11.045>
- [50] Corleto CR, Sosa J, Bradley WL, Hurtado J, Daumerie M (1996) Fracture behavior of high-impact polystyrene under an aggressive environment. *Polym Eng Sci* 36(1):146–150.
<https://doi.org/10.1002/pen.10395>
- [51] Samsudin SA, Hassan A, Mokhtar M, Jamaluddin SMS (2005) Effect of SEBS on the mechanical properties and miscibility of polystyrene rich polystyrene/polypropylene blends. *Prog Rubber Plast Recycl Technol* 21(4):261–276.
<https://doi.org/10.1177/147776060502100402>
- [52] Feldman D, Rusu M (2000) Degradation and stabilisation of styrene–ethylene–butadiene–styrene (SEBS) block copolymer. *Polym Degrad Stab* 71(1):113–122.
[https://doi.org/10.1016/S0141-3910\(00\)00162-2](https://doi.org/10.1016/S0141-3910(00)00162-2)
- [53] Vilaplana F, Ribes-Greus A, Karlsson S (2007) Analytical strategies for the quality assessment of recycled high-impact polystyrene: a combination of thermal analysis, vibrational spectroscopy, and chromatography. *Anal Chim Acta* 604(1):18–28.
<https://doi.org/10.1016/j.aca.2007.04.046>
- [54] Sharma R, Socrate S (2009)

- Micromechanics of uniaxial tensile deformation and failure in high-impact polystyrene (HIPS). *Polymer* 50(14):3386–3395.
<https://doi.org/10.1016/j.polymer.2009.04.073>
- [55] Rios-Guerrero L, Keskkula H, Paul DR (2000) Deformation processes in high-impact polystyrene as revealed by analysis of arrested cracks. *Polymer* 41(14):5415–5421. [https://doi.org/10.1016/S0032-3861\(99\)00725-9](https://doi.org/10.1016/S0032-3861(99)00725-9)
- [56] Keskkula H, Schwarz M, Paul DR (1986) Examination of failure in rubber toughened polystyrene. *Polymer* 27(2):211–216. [https://doi.org/10.1016/0032-3861\(86\)90328-9](https://doi.org/10.1016/0032-3861(86)90328-9)
- [57] Ossig A, Grassi VG, Dal Pizzol MF, Costa JM, Perez ACC, Jacobi MM (2014) The influence of rubber particle size distribution on ESCR of HIPS. In: Proceedings of XIV SLAP/XII CIP, 12–16 October 2014, Porto de Galinhas, Brazil. <https://doi.org/10.13140/2.1.4300.0965>
- [58] Park JY, Park OO (1996) Secondary phase inversion induced by addition of polystyrene during prepolymerization of high-impact polystyrene in a batch reactor. *Adv Polym Technol* 15(2):145–150. [https://doi.org/10.1002/\(SICI\)1098-2329\(199622\)15:2<145::AID-ADV4>3.0.CO;2-V](https://doi.org/10.1002/(SICI)1098-2329(199622)15:2<145::AID-ADV4>3.0.CO;2-V)