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Processing and Dynamic Mechanical Properties of PS-HI/SEBS Blends

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Summary: Thermoplastic elastomers have been successfully used as impact modifiers for thermoplastics. Dynamic mechanical properties and phase transitions are very important for their application. In this paper, the copolymers high-impact polystyrene, PS-HI, styrene-ethylene/butylene-styrene block copolymer, SEBS, and their blends PS-HI/SEBS were investigated. Rheological behaviour of those samples during processing was followed by measuring the torque vs. time in the extruder Haake Record 90. The investigations were done by DMA analysis. The primary viscoelastic functions, the storage modulus, E`, the loss modulus, Eˇ, and loss tangent, tgδ, were determined in the temperature range –150°C to 160°C. The correlation of the processing parameters and primary viscoelastic functions with content of the hard, PS, phase were discussed.

Keywords: dynamic mechanical properties; high-impact polystyrene; processing; PS-HI/SEBS blends; styrene-ethylene/butylene-styrene block copolymer

Introduction

Blending two or more polymers offer a great possibility to modify thermoplastic materials with aim to improve their properties. Thermoplastic elastomers, especially styrene-ethylene/butylene-styrene block copolymer, SEBS, styrene-butadiene-styrene block copolymer, SBS, and styrene-isoprene-styrene block copolymer, SIS, have been succesfully used as a impact modifiers for thermoplastics.[1-4] Those triblock copolymers are convenient for thermoplastic modification because of their unique combination of mechanical properties and processability. Thermodynamic incompatibility of the styrene and elastomeric midblock cause the microphase separation of the material. The polystyrene microdomains, PS act as physical crosslinks between the elastomer sequencies, which results with high tensile strenght of material, while rubber midblock gives its elasticity.

Styrene-ethylene/buthylene-styrene block copolymer also has a great application as a compatibilizer, what is more and more important in recycling of polymer materials.[5-9]

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Polymer scrap ussually contain two or more thermoplastics with poor impact strenght due to their immiscibility. Compatibilisation results with better morphology and properties of blends. In this paper, the processing behaviour and dynamic mechanical properties of copolymers PS-HI, SEBS and their blends are investigated.

Experimental

Materials

The investigations were done with high impact polystyrene, PS-HI 417, DIOKI, Zagreb, Croatia, with the content of polybutadiene, PB, 8 % weight, styrene-ethylene/buthylene-styrene block copolymer, SEBS, Kraton 1650, Kraton Polymers, Germany, with the content of polystyrene, PS, 29 % weight (with ethylene/buthylene, EB, as rubbery midblock) and with their blends. The compositions of the blends studied are shown in Table 1.

Table 1. Compositions of the investigated samples.

SAMPLE	PS-HI/ SEBS weight%	SOFT PHASE PB weight%	SOFT PHASE EB weight%	HARD PHASE PS weight%
1	100/0	8.0	/	92.0
2	75/25	6.0	17.7	76.3
3	30/70	2.4	49.7	47.9
4	0/100	/	71.0	29.0

Specimens Preparation

The blends were prepared by using Haake Record 90 twin extruder with the intensive mixing profile, Haake TW 100, with the following temperatures in zone 150/200/200/150°C and the frequency of rotation 60 min^{-1}. The specimens were obtained by compression molding at 220°C; the mold temperature was 40°C.

Measurements

Torque vs. time curves were recorded during the processing of the blends PS-HI/SEBS in whole range of compositions, in the extruder Haake Record 90. Output, Q, as well as pressures, in front die pressure, p_3, die pressure, p_4, and back pressure, p_5, were followed by computer.

The storage modulus, E`, loss modulus, E", and loss tangent, tanδ, of PS-HI, SEBS and PS-HI/SEBS blends were measured using a Dynamic Mechanical Analyser 983, TA Instruments, in resonant frequencies mode in temperature range from –150°C to 160°C, with amplitude 0.2 mm and heating rate 5 °C/min.

Results and Discussion

Rheological behaviour of the blends PS-HI/SEBS during processing was followed by torque, TQ, output, Q, and viscosity, TQ/Q values. The change of the torque values with the SEBS content is presented in the curve on the Fig. 1.

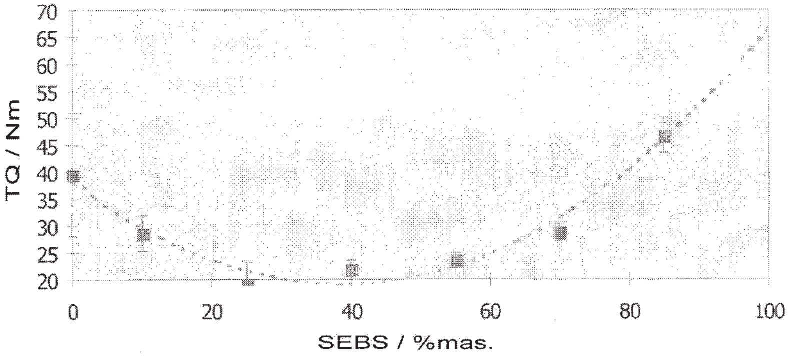


Fig. 1. The influence of the composition of blends on torque value.

It was found that the torque value decrease with increasing content of styrene-ethylene/buthylene-styrene block copolymer until 40 % mas. in PS-HI/SEBS blends. After that, the torque increasing is due to the higher viscosity of the rubbery component. Such behaviour indicate better processability of blends PS-HI/SEBS with lower content of styrene-ethylene/buthylene-styrene copolymer, what is also visible from curve output vs. SEBS content

(Fig. 2).

The viscosity obtained from the TQ/Q ratio increase with increasing content of thermoplastic elastomer, as well as the ratio of pressure differences in the extruder and Q (Fig. 2).

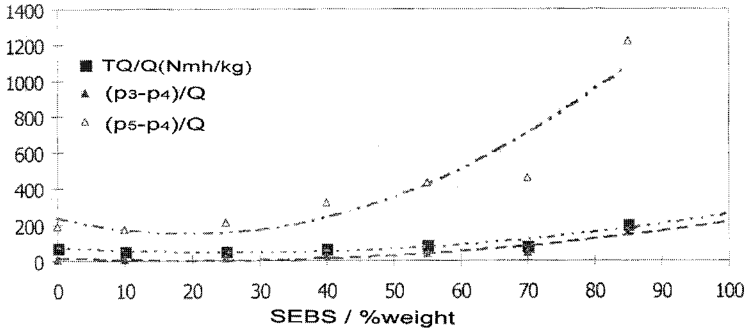


Fig. 2. The process parameters for PS-HI, SEBS and PS-HI/SEBS blends; torque, TQ, output, Q, pressures in the extruder, in front die pressure, p_3, die pressure, p_4, and back pressure, p_5.

The results of dynamic mechanical behaviour of copolymers PS-HI and SEBS and their blends PS-HI/SEBS are reported in Table 2. and Fig 3.

PS-HI and SEBS copolymer consist of two phases what is evident from DMA results. (Table 2) PS-HI has two glass transitions; Tg of the soft, polybutadiene phase at –67°C, and Tg of the hard, polystyrene phase at 111°C.

SEBS block copolymer has the glass transitions of the soft, ethylene/buthylene phase at –40°C, and Tg of the hard, polystyrene phase at 110°C. The same values for those glass transitions was found in previous reports.[10]

PS-HI/SEBS blends consist of hard, polystyrene phase and two soft phases, ethylene/buthylene and polybutadine phase (Table 2). It can be seen that PS-HI/SEBS blends have a single glass transitions of the hard, polystyrene phase at positive temperatures, which are above the glass transition of the PS block in the neat SEBS (110°C) and PS-HI copolymer (111°C). The glass transition, Tg of the polystyrene component is higher in the blend with lower content of PS-HI. Tg of the soft, ethylene/buthylene, EB phase decrease with increasing hard segments in the PS-HI/SEBS blends. Similar observatins for the glass transition of the soft phase in blends was reported in many papers.[11-13]

Table 2. Glass transitios, T_g, storage modulus, E`, and intensities of loss tangent, tgδ, for PS-HI, SEBS and PS-HI/SEBS blends.

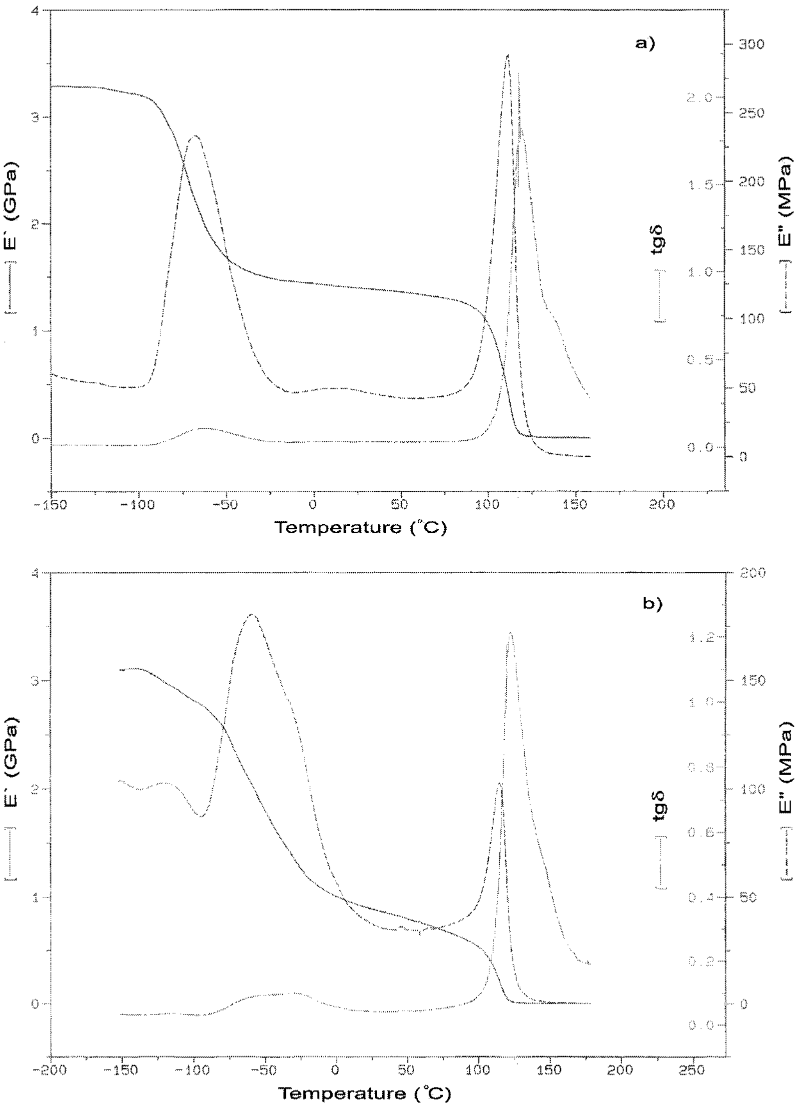
SAMPLE	PS-HI/ SEBS weight%	HARD PHASE PS weight%	T_g PB °C	T_g EB °C	T_g PS °C	E’ / GPa		$I\alpha_s$ PB	$I\alpha_s$ EB	$I\alpha_s$ PS
			E“	E“	E“	-150°C	25°C	tg δ	tg δ	tg δ
1	100	92.0	-67.6	/	111.0	3.287	1.395	0.109	/	1.794
2	75:25	76.3	-121.3	-59.8	114.0	3.108	0.889	0.034	0.098	1.211
3	30:70	47.9	-122.1	-34.4	120.0	5.288	0.076	0.059	0.359	0.373
4	100	29.0	/	-40.1	110.2	1.688	0.052	/	0.416	0.201

Kim et al. found that in SEBS/PPE blends glass transition of ethylene/buthylene phase decrease as the amount of PPE was increased.[10] Paul and co-workers also found in SBS/PPE blends that Tg of the soft segment is shifted to lower temperature in blends with higher content of hard segments.[14] Some authors explained such behaviour by increased difference in the thermal expansion coefficient between soft and hard phase in the blends.[10,12,13] As a consequence of this increased thermal stress around the soft phase results, which cause the dilation of the soft domains. Therefore, the glass transition of the soft segments decrease with decreasing the amount of the soft phase in the blends.

It wasn`t observed significant difference between the glass transitions of polybutadiene phase in the investigated PS-HI/SEBS blends.

It can be seen that the storage modulus, E′, in platou region increase with increasing content of the hard, polystyrene phase (Fig. 3).

The intensity of the loss tangent in α_s maximum of polybutadiene phase decreases as the amount of styrene-ethylene/buthylene-styrene block copolymer increase, as well as the intensity of hard, polystyrene phase (Fig. 3.). At the same time, the intensity of α_s on tgδ/T curve of soft, ethylene/buthylene phase increase. It is obvious the influence of styrene-ethylene/buthylene-styrene block copolymer on the toughness and impact properties of high-impact polystyrene.


a)
E' (GPa)
tgδ
E" (MPa)
Temperature (°C)
-150
-100
-50
0
50
100
150
200
0
1
2
3
4
0.0
0.5
1.0
1.5
2.0
0
50
100
150
200
250
300
b)
E' (GPa)
tgδ
E" (MPa)
Temperature (°C)
-200
-150
-100
-50
0
50
100
150
200
250
0
1
2
3
4
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
50
100
150
200

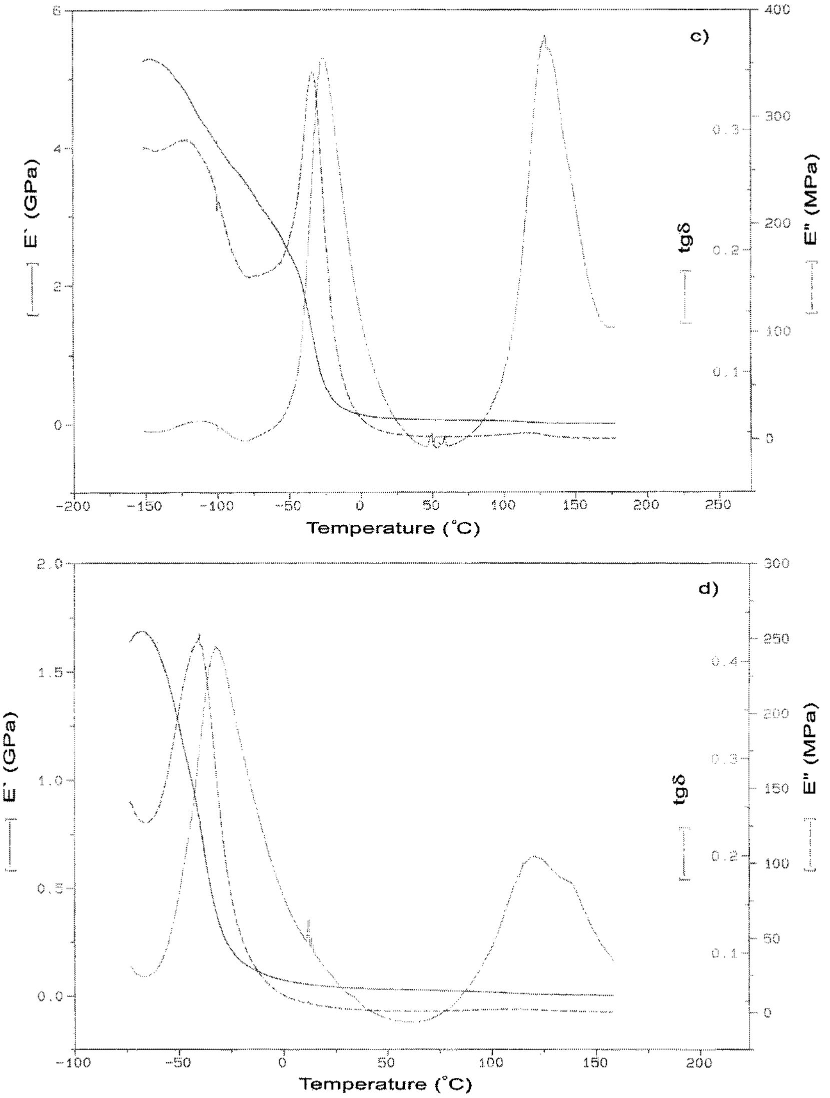


Fig. 3. DMA spectras for PS-HI (a), PS-HI/SEBS 75:25 blend (b), PS-HI/SEBS 30/70 (c) and SEBS (d).

Conclusion

The process parameters torque, TQ, output, Q, viscosity, TQ/Q and pressures in the extruder, in front die pressure, die pressure and back pressure, of copolymers PS-HI, SEBS and blends PS-HI/SEBS were obtained.

The process parameters, particularly torque vs. SEBS content changes against the curve with minimum at 40 % weight SEBS content.

PS-HI and SEBS are two phases systems with T_g of the hard, PS, phase at ~110°C and T_g of the soft phase, PB, at –67°C and T_g of EB at –40°C.

Blends PS-HI/SEBS have a single T_g for hard, PS, phase and for soft phases, EB and PB. The intensity of the soft, PB, phase and hard, PS, phase in α_s maximum on tgδ curve decrease as the SEBS content in the investigated systems increases.

The storage modulus, E′, in platou region increase with increasing content of the hard, polystyrene phase.

[1] S.Ghosh, D. Khastgir, A. K. Bhowmick, *J. Appl. Polym. Sci.,* **1998**, 67, 2015.
[2] K. R. Srinivasan, A. K. Gupta, *J. Appl. Polym. Sci.*, **1994**, 53, 1.
[3] V. Rek, T. H. Grgurić, Ž. Jelčić, *Macromol. Symp.*, **1999**, 148, 425.
[4] C. D. Han, D. M. Baek, J. Kim, K.Kimishima, T. Hashimoto, *Macromolecules*, **1992**, 25, 3052.
[5] M. Heino, J. Kirjva, P. Hietaoja, J. Seppälä, *J. Appl. Polym. Sci.*, **1997**, 65, 241.
[6] B. Ohlsson, H. Hassander, B. Törnell, *Polymer,* **1998**, 26, 6705.
[7] K. K. Shull, E. J. Kramer, *Macromolecules,* **1990**, 23, 4769.
[8] T. A. Vilgis, J. Noolandi, *Macromolecules,* **1990**, 23, 2341.
[9] L. Leibler, *Macromol. Chem. Macromol. Symp.*, **1988**, 16, 1.
[10] J. K. Kim, D. S. Jung, J. Kim, *Polymer,* **1993**, 34, 22, 4613.
[11] L. Moribitzer, G. H. Kranz, K. H. Ott, *J. Appl. Polym. Sci.*, **1976**, 20, 2691.
[12] L. Bohn, Angew. *Makromol. Chem.,* **1971**., 20, 129.
[13] L. Bohn, *Adv. Chem. Ser.*, **1975**, 142, 66.
[14] P. S. Tucker, J. W. Barlow, D. R. Paul, *Macromolecules*, **1988**, 21, 1678.