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Creep Relaxation and Stress Relaxation of PS-HI/SEBS Blends

Vesna Rek,[1] *Tamara Holjevac Grgurić,*[*1] *Želimir Jelčić*[2]

[1]Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg19, Zagreb, Croatia
[2]DIOKI d.o.o., Žitnjak bb., Zagreb, Croatia

Summary: For the selection of the polymer materials and polymer blends for various fields of applications the stability of material under constant deformation and constant load are very important. In this paper, the copolymers high-impact polystyrene, PS-HI, styrene-ethylene/buthylene-styrene block copolymer, SEBS, and their blends PS-HI/SEBS were investigated. The investigations were done by DMA analysis. The secondary viscoelastic functions, creep, creep modulus, stress and flexural relaxation modulus were investigated in creep and stress relaxation experiment at temperatures 25, 35, 45, 55 and 65 °C during 1 h. The master curves were created by time-temperature correspondence principle, TTC. The correlation of the secondary viscoelastic functions with time, temperature and content of the hard, PS, phase was discussed.

Keywords: creep; dynamic-mechanical behavior; high-impact polystyrene; master curve; PS-HI/SEBS blends; stress relaxation; styrene-ethylene/butylene-styrene block copolymer; time-temperature superposition

Introduction

Creep experiments have a great importance in the design of plastic products, because they reflect the load-bearing capacity of end-products. Chemical engineers have to care about creep failure in polymer structures, and they should be able to estimate the polymer material durability in order to prevent premature failures and to avoid large deformation.

Stress-relaxation experiments are also important for consideration of time-dependent performance of polymer materials. Today, metals are more and more replaced with plastics in structural components, so the study of the creep and stress relaxation behaviour in polymers and metals is important for further development of advanced long-life materials.

Time-temperature correspondence principle, TTC, gives the possibility to determine the rheological behaviour of polymer material from creep and stress relaxation data, over a much

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longer experiment range of time on the base of measurements at a higher temperatures.[1-4] It was found that the distribution of relaxation times of a polymer is shifted by a change in temperature through the induced change in free volume.[5] Time-temperature correspondence principle holds for thermorheologicaly simple polymeric materials. There are many reasons why the TTC principle doesn't valid for some polymer material, like the occurrence of more than one relaxation mechanisms with distinct temperature dependence.[6-10] For example, in inhomogeneous polymer blends each component has a different temperature-dependence rheology and TTC principle, usually fails. Although, many authors reports that the time-temperature correspondence principle holds for miscible[11-16] and also immiscible blends.[17-21]

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 mid block) and with their blends. The compositions of the blends studied are shown in Table 1.

Table 1. The compositions of 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.

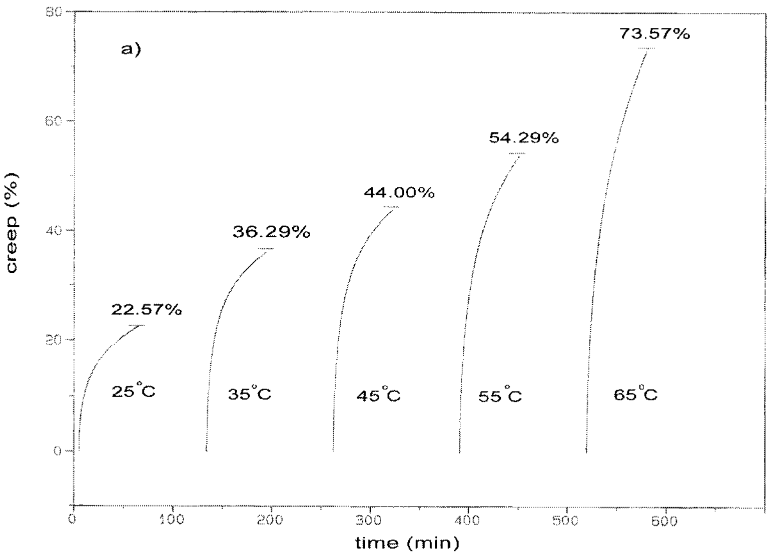
Measurements

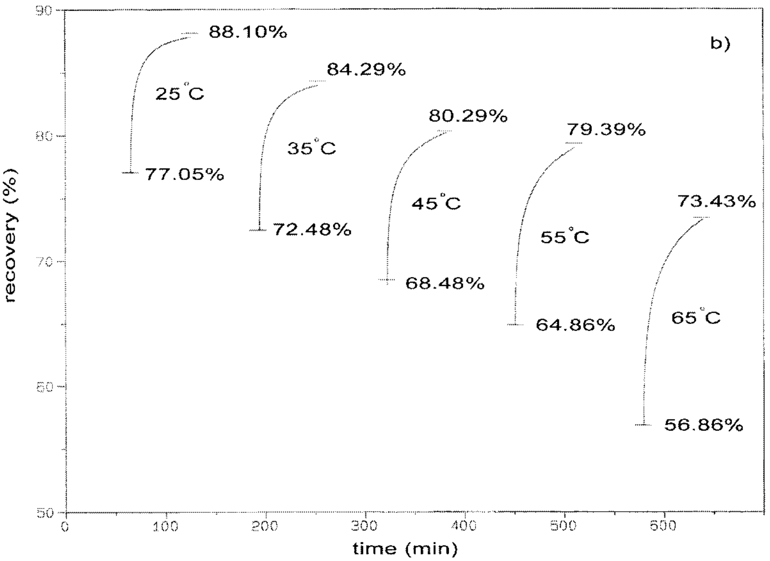
Creep relaxation and stress relaxation experiments were done by Dynamic Mechanical Analyser 983, TA Instruments in creep fatigue regime. In creep experiments, the specimens were stressed for 1 h at constant stress, and then allowed to relax for 1 h. The temperature was then increased in increments of 5°C followed by an equilibration period of 15 min before of the next displacement/recovery cycle. The creep experiments were done at 25, 35, 45, 55 and 65°C. Using the time-temperature superposition correspondence principle the master curves for reference temperature, $T_{ref.}$ = 25 °C were created, from short-therm experiments performed at 25,35,45,55 and 65 °C.

Stress relaxation experiments were performed under a constant strain in the temperature range from 25 °C – 65 °C, in 10 °C intervals during 1 h. The master curves for reference temperature, $T_{ref.}$ = 25 °C were constructed also from short-therm experiments performed at 25, 35, 45, 55 and 65 °C using the time-temperature correspondence principle, TTC.

Results and Discussion

The creep curves for all examined samples were determined under a constant load during 1 h at each temperature. Then, the load was removed and the recovery curves were determined. The example of obtained isothermal creep and recovery curves is shown in Fig.1. Viscoelastic data, creep and recovery are given in Table 2.


a)
creep (%)
time (min)
0
20
40
60
80
0
100
200
300
400
500
600
22.57%
36.29%
44.00%
54.29%
73.57%
25°C
35°C
45°C
55°C
65°C


b)
recovery (%)
time (min)
50
60
70
80
90
0
100
200
300
400
500
600
88.10%
77.05%
25°C
84.29%
72.48%
35°C
80.29%
68.48%
45°C
79.39%
64.86%
55°C
73.43%
56.86%
65°C

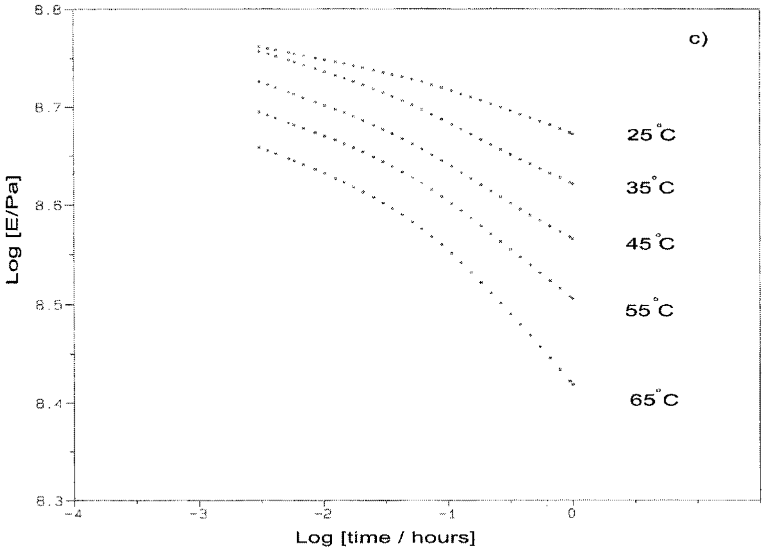


Fig. 1. The example of creep (a), recovery (b) and creep modulus vs. time (c) at different temperatures for PS-HI/SEBS 75:25 blend.

Table 2. The creep and recovery data for PS-HI, SEBS and PS-HI/SEBS blends.

SAMPLE	PS-HI/ SEBS weight%	HARD PHASE PS weight%	CREEP (%)					RECOVERY (%)				
			25°C	35°C	45°C	55°C	65°C	25°C	35°C	45°C	55°C	65°C
1	100	92.0	6.33	8.67	14.67	24.67	57.00	8.10	9.48	11.19	14.27	20.00
2	75:25	76.3	22.57	36.29	44.00	54.29	73.57	11.04	11.62	12.19	14.28	16.57
3	30:70	47.9	38.57	44.29	51.57	71.71	96.86	12.95	14.86	17.72	24.19	26.85
4	100	29.0	17.24	30.33	45.00	80.62	93.19	11.66	14.52	20.72	29.05	36.43

In all examined samples the creep and recovery values depend upon the time. On the basis of creep data the isothermal curves of the creep modulus E vs. time were obtained at 25, 35, 45, 55 and 65 °C an example is given in Fig.1. The creep values increase, while the creep modulus decrease with time under the constant temperature. Under the constant load polymers undergo molecular rearrangements in attempt to minimize local stress.[22-24] Those processes are faster at higher temperature. As a consequence of this the creep and recovery values increase as the temperature increases (Table 2., Fig. 1a-1b.), while creep modulus decreases with temperature (Fig. 1c.). This behaviour indicates the dependence of viscoelastic properties of copolymers and their blends on time and temperature.

High-impact polystyrene, PS-HI, has the lowest creep and recovery values at all examined temperatures (Table 2.). It was found that the styrene-ethylene/buthylene-styrene block copolymer, SEBS, shows higher creep and recovery than PS-HI. It is due to the higher content of the soft phase. Soft, ethylene/buthylene, EB, phase has negative glass transition temperature, so it is more flexible and liable to deformation than hard, polystyrene phase at examined creep temperatures.

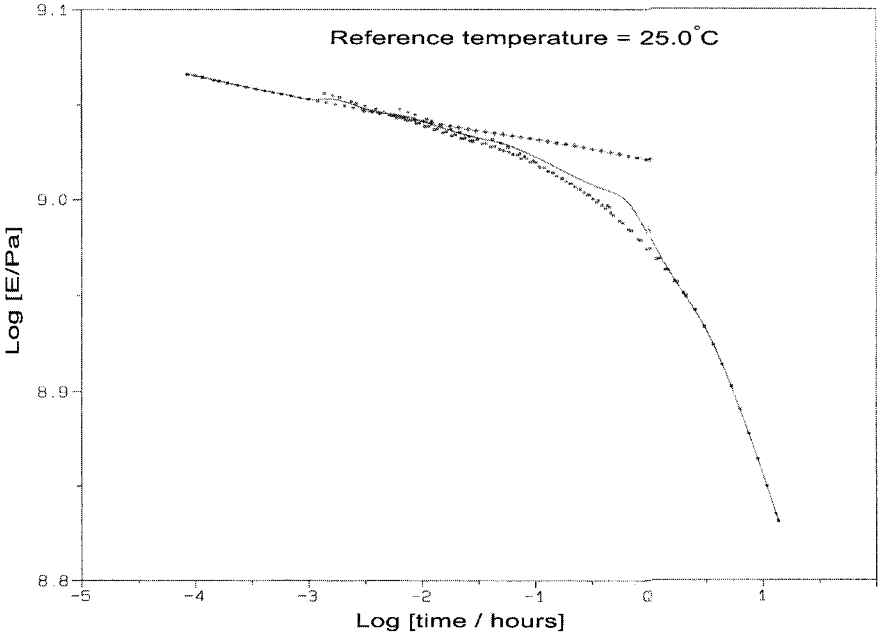


Fig. 2. Master curve at 25°C for PS-HI; creep relaxation measurement.

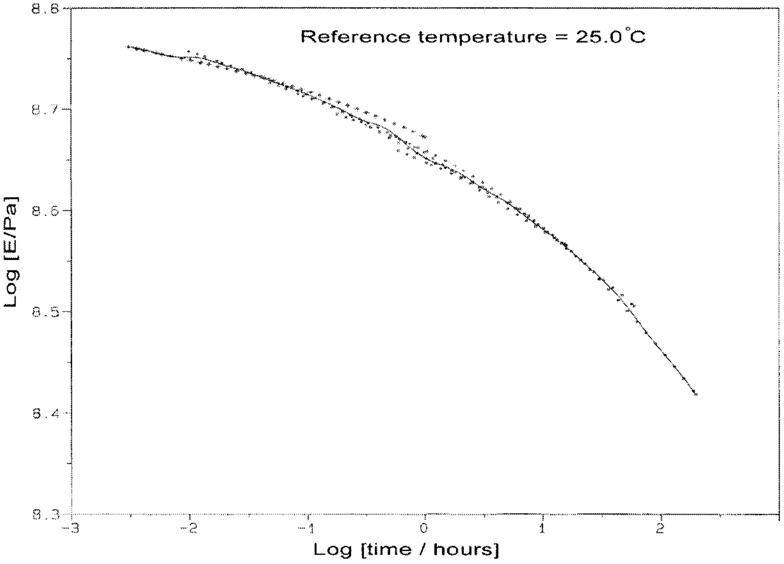


Fig. 3. Master curve at 25°C for PS-HI/SEBS 75:25 blend; creep relaxation measurement.

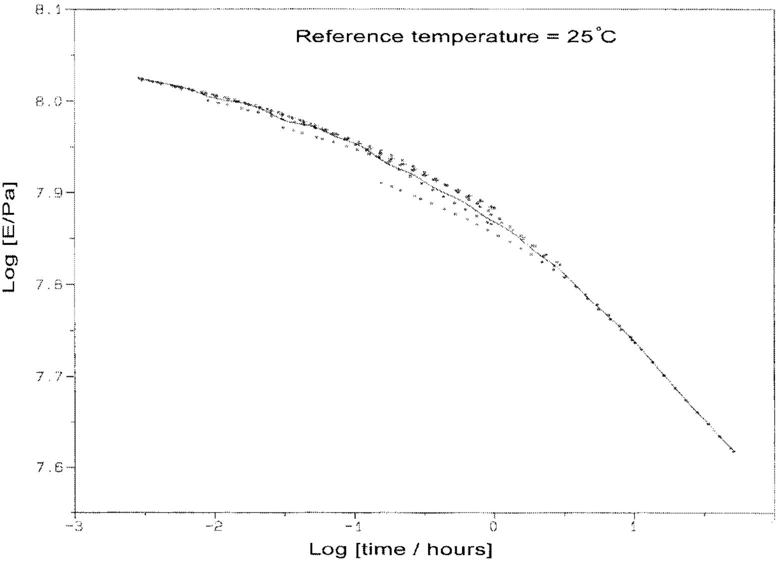


Fig. 4. Master curve at 25°C for PS-HI/SEBS 30:70 blend; creep relaxation measurement.

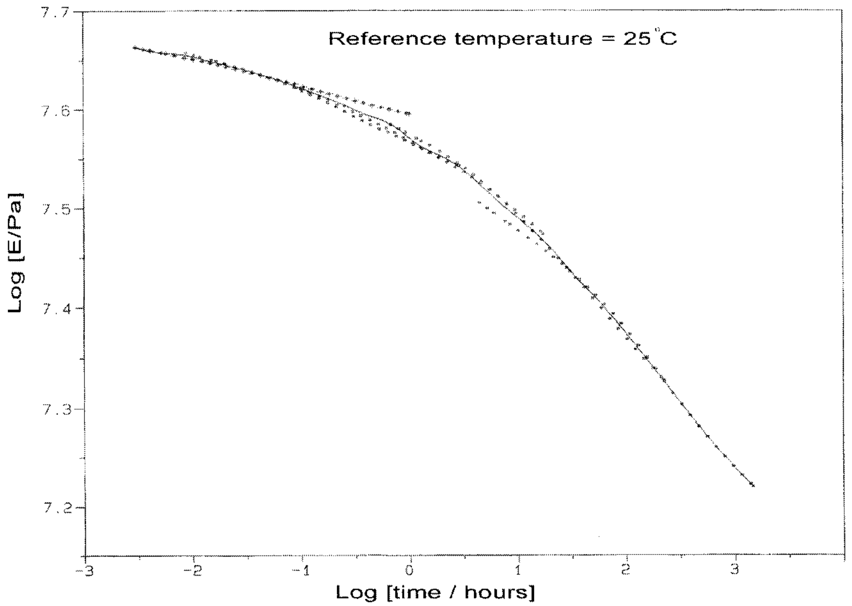


Fig. 5. Master curve at 25°C for SEBS; creep relaxation measurement.

As the content of the hard, polystyrene, PS, phase in PS-HI/SEBS blends decrease, the creep and recovery increase at the constant temperature. At all investigated temperatures the creep and recovery are more pronounced in the samples with lower content of the hard, PS, phase. The creep modulus decreases at all isothermal measurements as the content of hard, PS, phase decrease. The curves E` vs. time become more sheer with decreasing polystyrene content in samples. Such dependence of the creep modulus on the hard phase content is due to faster molecular rearrangements, changes of the conformations, in soft phase what is connected with negative Tg of soft phases, EB and PB.

The lower deformation at 25°C and 35°C of SEBS block copolymer in comparison with the blends may be assumed to the more influence of soft, polybutadiene phase in PS-HI/SEBS blends, which is more liable to deformation than EB phase due to its lower T_g.

By selecting as the reference the curve for 25 °C, and than shifting all other isothermal curves of the creep modulus vs. time obtained at 25,35,45,55 and 65 °C with respect to time, the master curves of creep modulus vs. time at references temperature are generated (Figs. 2-5).

The stress relaxation was determined under a constant strain at the same temperatures as the creep experiment during 1 h. The example of the stress relaxation results are shown on Fig. 6. The stress and recovery values are given in Table 3.

It was found that at the constant deformation the stress decreases with time in all investigated samples. The stress needs for holding the constant deformation decreases with increasing the temperatures for all samples (Table 3, Fig 6.). Such behaviours are connected with relaxation process in our samples which occur under the constant deformation and are more pronounced with time and at higher temperature.[25]

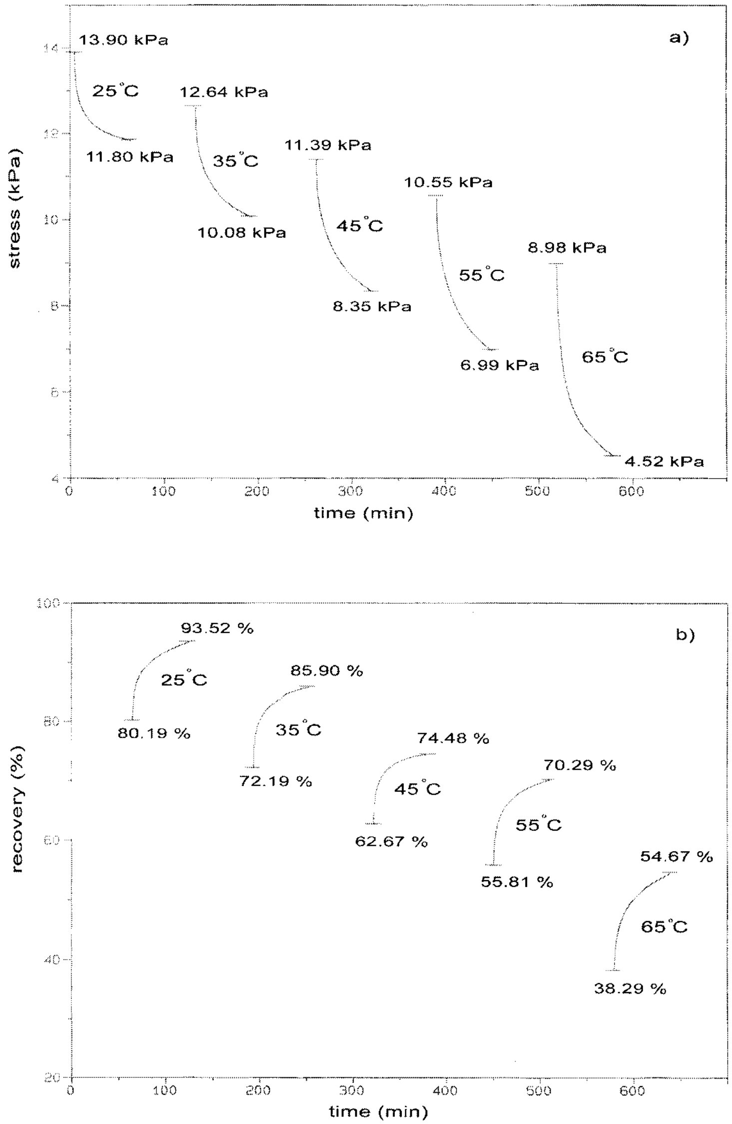
Table 3. The stress and recovery data for PS-HI, SEBS and PS-HI/SEBS blends.

SAMPLE	PS-HI/ SEBS weight%	HARD PHASE PS weight%	STRESS (%)					RECOVERY (%)				
			25°C	35°C	45°C	55°C	65°C	25°C	35°C	45°C	55°C	65°C
1	100	92.0	93.81	92.62	89.52	80.48	60.48	6.66	5.72	5.71	7.62	10.47
2	75:25	76.3	85.29	80.14	73.29	66.13	50.43	13.33	13.72	11.81	14.86	16.76
3	30:70	47.9	83.00	76.00	60.00	50.33	44.33	14.00	17.14	15.43	21.72	27.43
4	100	29.0	87.21	84.64	78.00	69.43	62.57	11.14	17.44	30.04	38.59	46.60

The stress of styrene-ethylene/buthylene-styrene block copolymer, SEBS is lower than the stress of high-impact polystyrene, PS-HI, but at the same time higher than stress of PS-HI/SEBS blends. It can be assumed that the flexibility of the soft PB phase (T_g –67°C) is higher than that of the soft, EB, phase (T_g –40°C). At the same time soft PB and EB phases have greater mobility, faster changes of the conformations, than hard PS phase.

Recovery of PS-HI and SEBS copolymers, as well as their blends, mainly increase with temperature at the same content of the hard, PS phase and also increases with decreasing of hard PS segments at the same temperature (Table 3).

The stiffness of the investigated systems decrease with time and temperature under a constant deformation, which is evident from isothermal curves flexural modulus, E` vs. time (Fig. 6d). With decreasing the hard, PS, phase content those curves are shifted to lower values. From the isothermal curves of the flexural modulus vs. time at temperatures at 25,35,45,55 and 65 °C the master curves were created by selecting as the reference the curve for 25 °C and than shifting all other isothermal curves of the creep modulus vs. time with respect to time.



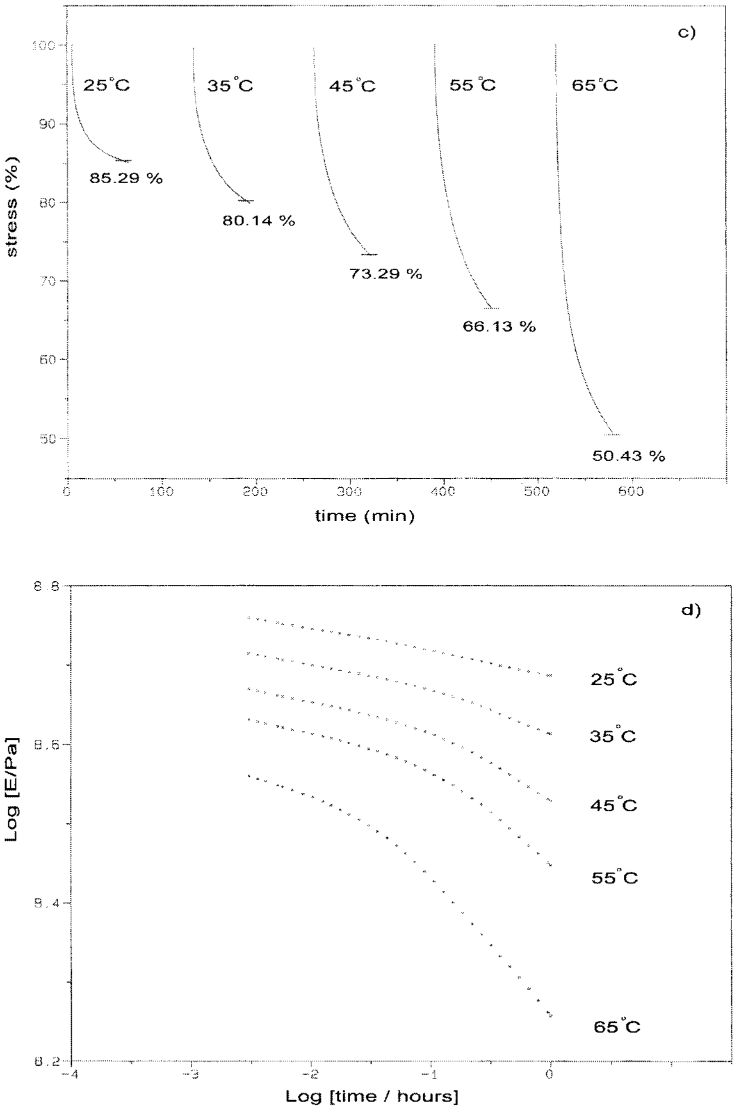


Fig. 6. The isothermal curves of stress (a), recovery (b), relative stress (c) and modulus (d) for sample PS-HI/SEBS 75:25.

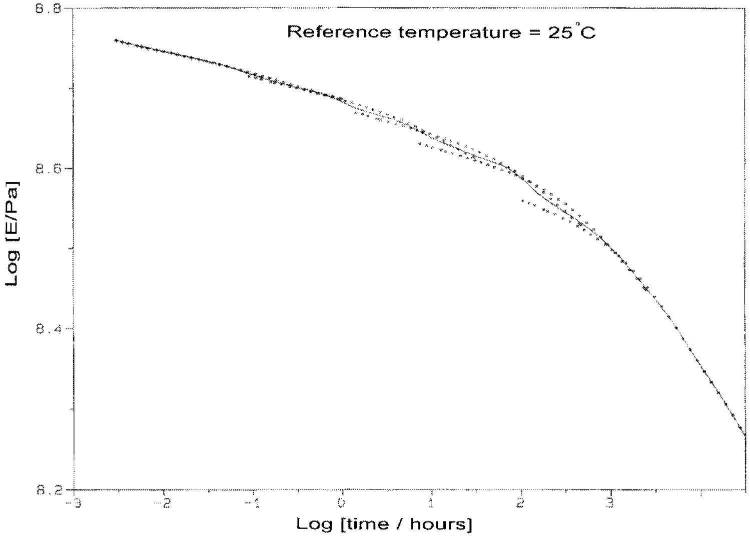


Fig. 7. Master curve at 25 °C for sample PS-HI; stress relaxation measurement.

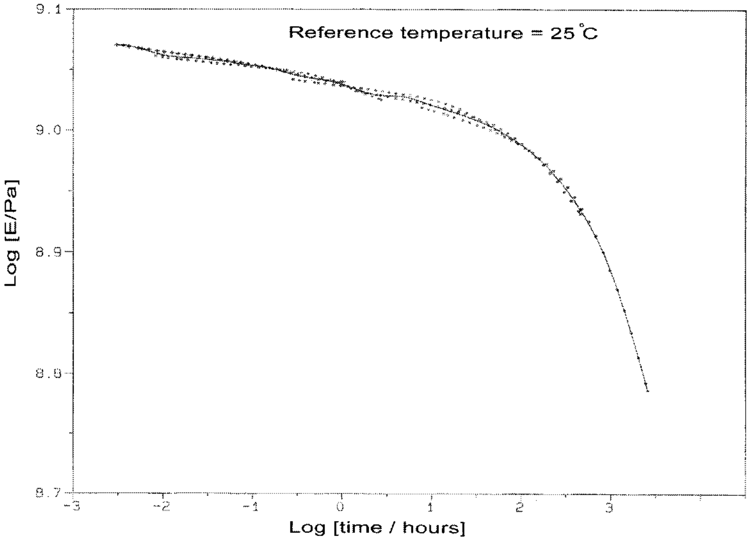


Fig. 8. Master curve at 25 °C for PS-HI/SEBS 75:25 blend; stress relaxation measurement.

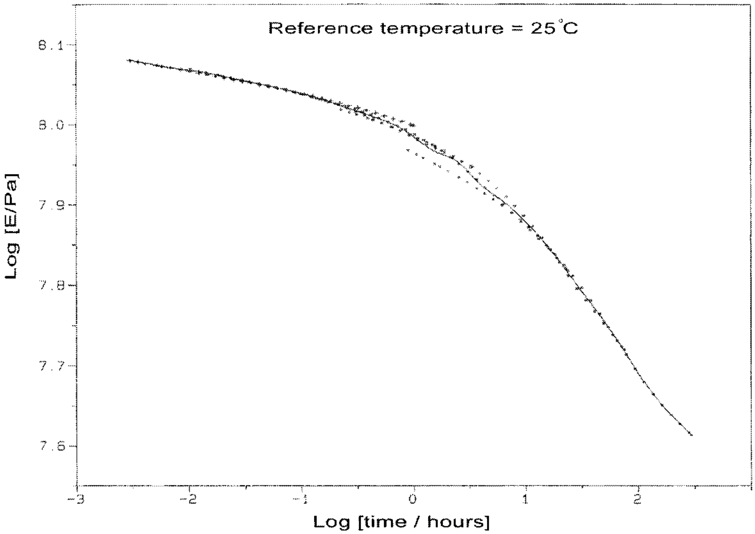


Fig. 9. Master curve at 25 °C for PS-HI/SEBS 30:70 blend; stress relaxation measurement.

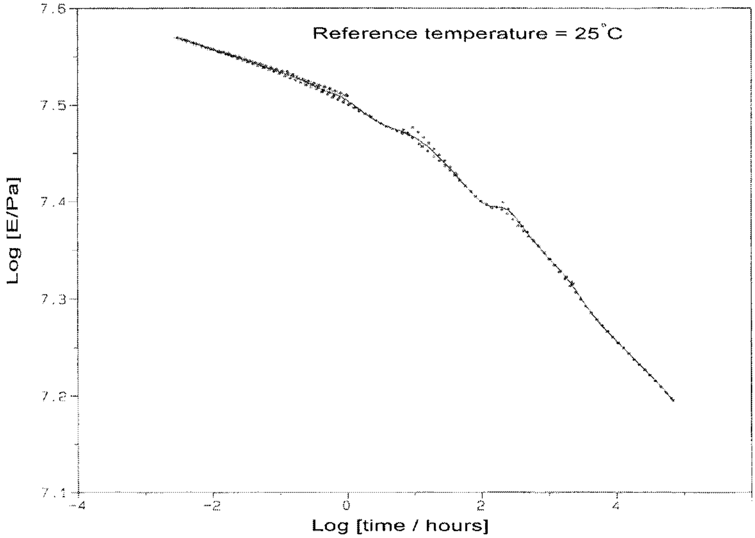


Fig. 10. Master curve at 25 °C for sample SEBS; stress relaxation measurement.

The master curves are shown on Fig. 7– 10. The master curves give us the possibility to examine the creep and flexural modulus of our samples and the possibility to predict useful life of examined samples in a wide range of time and temperature. At the short time interval the materials examined exhibit a relatively high creep modulus (Fig. 2-5.) as well as flexural modulus (Fig. 7-10.). At longer time period the viscous flow occurs, the modulus become lower what is in agreement with faster relaxation process which are more pronounced with time and are faster at higher temperatures.

With the lower content of hard, PS, phase in examined samples the master curves are in the lower region of creep and flexural modulus values, what is due to the faster relaxation process in those samples.

Conclusion

The correlation of the creep and stress relaxation and time, temperature as well as the content of the hard and soft phases in copolymers PS-HI, SEBS and their blends was obtained.

The secondary viscoelastic functions obtained from creep relaxation experiments (creep, recovery and creep modulus) and stress relaxation experiments (stress, recovery and flexural relaxation modulus) show dependence on time and temperature.

The creep increase with time and temperature, while the creep modulus decreases. The stress and flexural relaxation modulus decrease with time and temperature. Such behaviour is due to the relaxation process, which are more pronounced with time and are faster at higher temperature.

The creep and stress relaxation are more pronounced in samples with lower content of the hard, PS, phase. As a consequence of this creep and recovery values increase and stress value decrease in samples with lower content of hard phase, PS, while creep modulus and flexural relaxation modulus decrease. The lower creep and higher stress of SEBS in comparison with the PS-HI/SEBS blends may be assumed to the higher flexibility of soft, PB, phase.

The master curves were created using a TTC principle from creep and stress relaxation measurements.

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