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DYNAMIC MECHANICAL BEHAVIOUR OF STYRENE / BUTADIENE COPOLYMERS AND THEIR BLENDS

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ABSTRACT: The dynamic mechanical behaviour of high impact polystyrene (PS-HI), styrene/butadiene/styrene block copolymer (SBS) and PS-HI + SBS blends were investigated. Dynamic mechanical analysis (DMA) was performed in the temperature range -100°C to 100°C. The primary viscoelastic functions were determined. The copolymers PS-HI and SBS as well as PS-HI+SBS blends were investigated in creep-fatigue regime and relaxation at temperatures 25, 30, 35, 40 and 45°C. Dynamic mechanical behavior of PS-HI, SBS and PS-HI + SBS blends depends on the copolymer and blends composition, the hard phase content, time and temperature. With the decrement of the hard phase PS concentration, the loss tangent of the soft phase increases while the loss tangent of the hard phase and the storage modulus decrease. All samples have a single T_g of the hard phase and a single T_g of the soft phase. The glass transition temperatures decrease as the content of the PS phase decreases. At the constant load the creep values increase and those of creep modulus decrease over a period of time, for all examined samples. These effects are more pronounced in samples with lower content of hard phase and at higher temperatures. The time-temperature correspondence principle was applied to create master curves for the reference temperature 25°C for the creep modulus of PS-HI, SBS and PS-HI + SBS blends on a time scale far outside of the range measured by DMA experiments. These results enable us to predict the useful life of our copolymers and their blends in a wide range of time and temperature.

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1. INTRODUCTION

Multicomponent polymeric system have been intensive studied in order to develop new types of *materials having various functions and properties* $^{1-6)}$.

Styrene/butadiene copolymers have found use as elastomers when the copolymer is rich in butadiene. When styrene is the major component it is used as a high clarity impact thermoplastic $^{7-11)}$.

Dynamic mechanical properties (DMA) and behavior in creep fatigue regime of these copolymers systems and their blends depend on the content of soft polybutadiene phase (PB) and hard polystyrene phase (PS) and may be attributed to their morphology $^{12-14)}$.

With knowledge of DMA behaviour and behaviour under fatigue regime of styrene/butadiene copolymers and their blends it may be possible to adjust the content of soft PB phase and hard PS phase in the blends to obtain the materials with desired dynamic mechanical properties under service conditions.

In this paper the dynamic mechanical behaviour of high impact polystyrene (PS-HI), styrene/butadiene/styrene block copolymer (SBS) and their blends (PS-HI + SBS) is investigated. The key objective is to observe how the content of PB and PS phases in those systems influence their viscoelastic properties, primary viscoelastic function as well as the creep modulus in creep fatigue regime. These properties as a function of time and temperature must be taken into account in the selection of materials for structural or engineering applications.

2. EXPERIMENTAL

2.1. Materials

The investigations were done with high impact polystyrene (PS-HI) 457, OKI, Croatia, Zagreb, with the content of polybutadiene, PB, 8 % weight, styrene/ butadiene/styrene block copolymer (SBS) commercial grade, Kraton 1101, Shell. Co., Germany, with the content of polystyrene (PS) 29 % weight and PS-HI + SBS blends. The compositions of starting copolymers and blend compositions of the PS-HI + SBS systems are listed in Table 1.

2.2. 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 and the frequency of rotation 60 min^{-1}. The specimens were obtained by compression molding at 230°C; the mold temperature was 40°C and the rate 100 mm/s. The dimensions of investigated specimens were 18 x 13 x 5 mm.

2.3. Measurements of Dynamic Mechanical Properties

The Dynamic Mechanical Analyser 983, TA Instruments, was used to obtained temperature scans (from -100 to 100°C) of the storage modulus E', loss modulus E" and the loss tangent tan δ of PS-HI, SBS and PS-HI + SBS blends. The conditions were as follows: the rate of heating 5°C/min, resonant frequencies and amplitude 0.2 mm. The creep (strain) behavior, recovery and creep modulus as a function of time and temperature was measured using creep mode software at the constant stress of 14.9 kPa at temperatures 25, 30, 35, 40 and 45°C. The specimens were stressed for 15 min at constant stress, and then allowed to relax for 15 min. The temperature was then increased in increments of 5°C followed by an equilibration period of 15 min before initiation of the next stress/relax action cycle. Using the time-temperature correspondence principle the master curves for reference temperature, T_{ref} , 25°C were created, from short-terme experiments performed at 25, 30, 35, 40 and 45°C 15-17).

3. RESULTS AND DISCUSSION

Copolymers PS-HI and SBS as well as PS-HI + SBS blends consist of two phases, hard phase (PS) and soft phase (PB) what is evident from the DMA results (Table 1). Copolymers and PS-HI + SBS blends have a single glass transition T_g of the hard phase, PS, at a temperature between T_g of the pure PS phase in SBS and PS phase in PS-HI (Table 1). The same is valid for T_g of the PB phase at a lower temperature. With the decrease of the hard phase (PS) contents in copolymers and blends examined, the intensity of the tan δ relaxation maximum of the soft phase increases. The intensity of the tan δ relaxation maxima of the hard phase decreases at the same time. The storage modulus E′ decreases too (Table 1) with the decrease of the hard phase contents in the samples. The glass transitions of PS and PB phases decrease (Table 1). Those changes are connected with decreased rigidity in the samples with lower content of the hard phase [12,13].

Such behaviour of T_g and primary viscoelastic functions suggest that, within the limits of detection, there is a single composition dependent glass transition between the T_g values of the pure components while the storage modulus depends on composition. This is one of the widely use criteria for miscibility of polymer blends [12-14,18].

Table 1. Glass transition temperatures T_g of the hard and soft phases, values of E′ and tan δ of the hard and soft phases for PS-HI, SBS and PS-HI + SBS blends

SAMPLE	PS-HI+ SBS	HARD PHASE	T_g soft phase,PB °C		T_g hard phase,PS °C		E′ /GPa		Iα, soft phase	Iα, hard phase
	% weight	PS % weight	tg δ	E″	tg δ	E″	-120 °C	25 °C	tg δ	tg δ
1	100:0	92.0	-68.00	-74.20	/	124.1	4.300	2.070	0.080	3.300
2	90:10	85.8	-70.26	-76.43	126.2	121.3	2.880	1.300	0.130	2.260
3	75:25	76.5	-72.18	-78.33	125.0	120.5	2.540	0.930	0.155	2.100
4	60:40	67.2	-73.36	-78.55	122.1	120.3	2.500	0.510	0.210	1.220
5	45:55	57.9	-74.00	-80.04	120.3	119.1	4.800	0.680	0.265	0.615
6	30:70	48.6	-74.64	-80.77	119.3	118.2	2.110	0.100	0.466	0.508
7	15:85	39.3	-75.34	-82.56	114.3	112.2	2.110	0.018	0.512	0.390
8	0:100	29.0	-76.39	-84.28	113.3	111.3	2.100	0.018	0.570	0.330

For all samples examined, the viscoelastic creep and recovery data were obtained under the constant load. On the basis of the creep data, the isothermal curves of the creep modulus E vs. time were obtained. An example is given in Fig. 1. The creep and recovery increase with temperature at a constant content of the hard PS phase (Fig. 1a - 1b). The E vs. time curves are shifted to lower values with an increase of the temperature at the same conditions as shown in Fig. 1c.

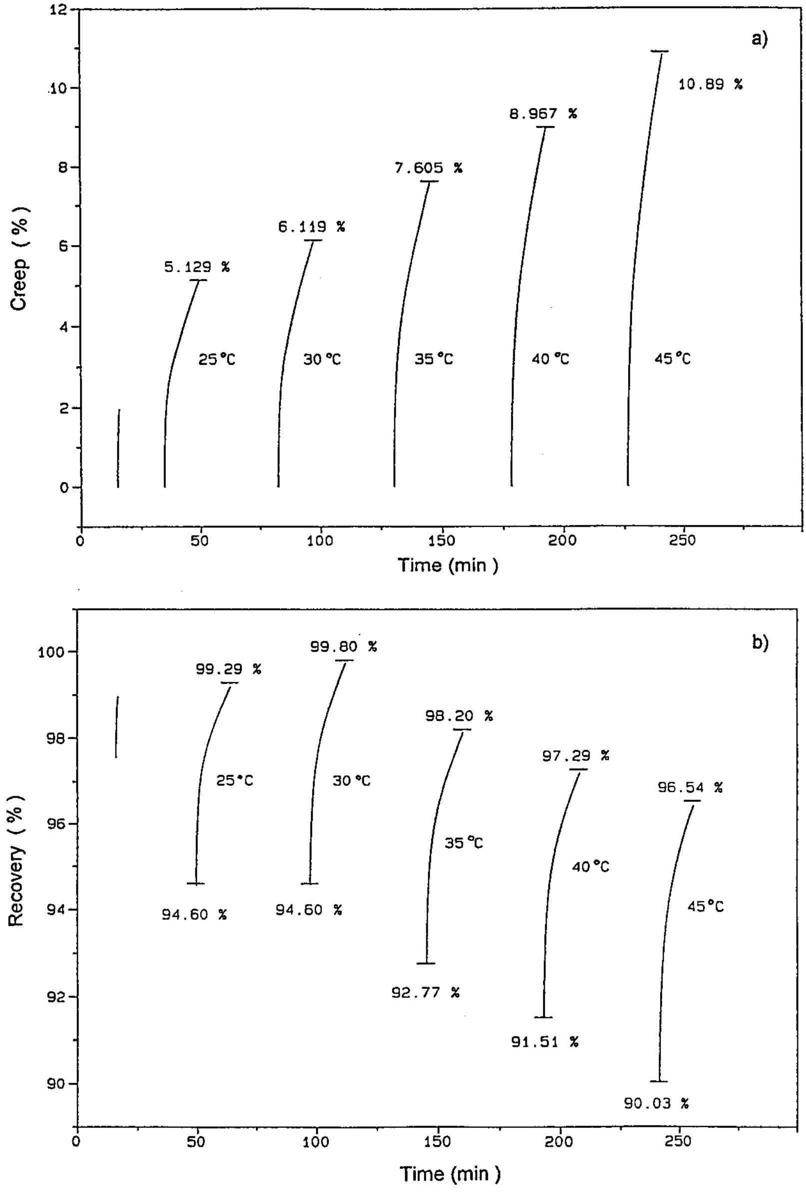

Figure 1. The example of creep at constant load as a function of temperature for PS-HI + SBS, 90:10 blend; a)creep, b) recovery

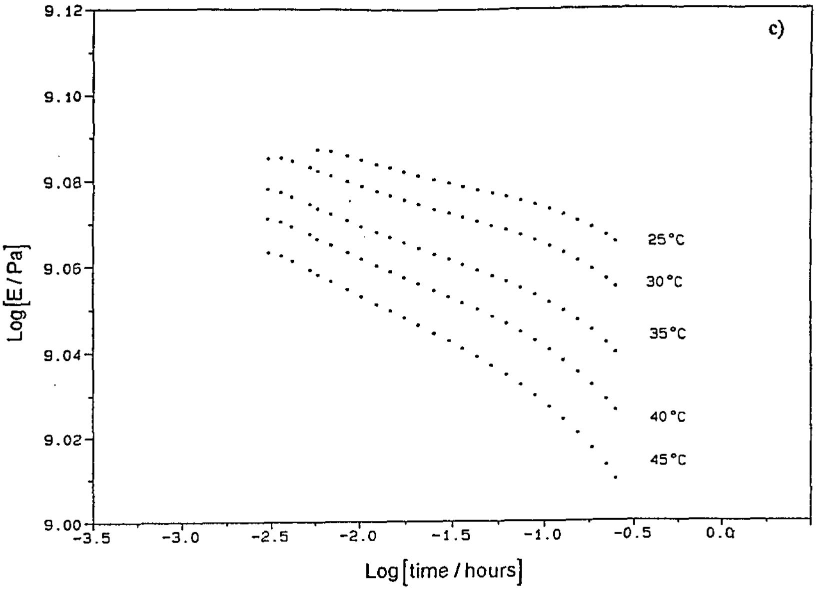

Figure 1. The examples of creep at a constant load as a function of temperature for PS-HI + SBS, 90:10 blend; c) creep modulus vs. time

The creep modulus E of all samples examined decreases with time under a constant temperature.

The master curves provide the possibility of predicting the creep modulus and useful life of our copolymers and blends materials in a wide range of time and temperature [15,19-21)]. 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 30, 35, 40 and 45°C with respect to time, the master curves of creep modulus vs. time at references temperature are generated (Figs. 2 - 9). The curves show effects of time on the creep modulus of PS-HI, SBS and PS-HI + SBS blends. At short time intervals the materials examined exhibit a relatively high creep modulus.

At longer times viscous flow occurs and the materials exhibits a relatively low modulus (Figs. 2 - 9).

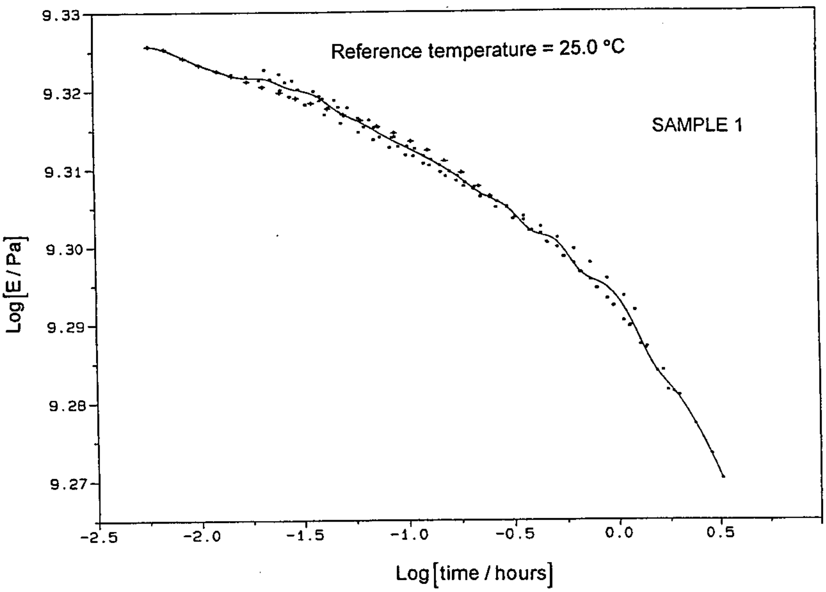

Figure 2. Master curve at 25°C for PS-HI (sample 1)

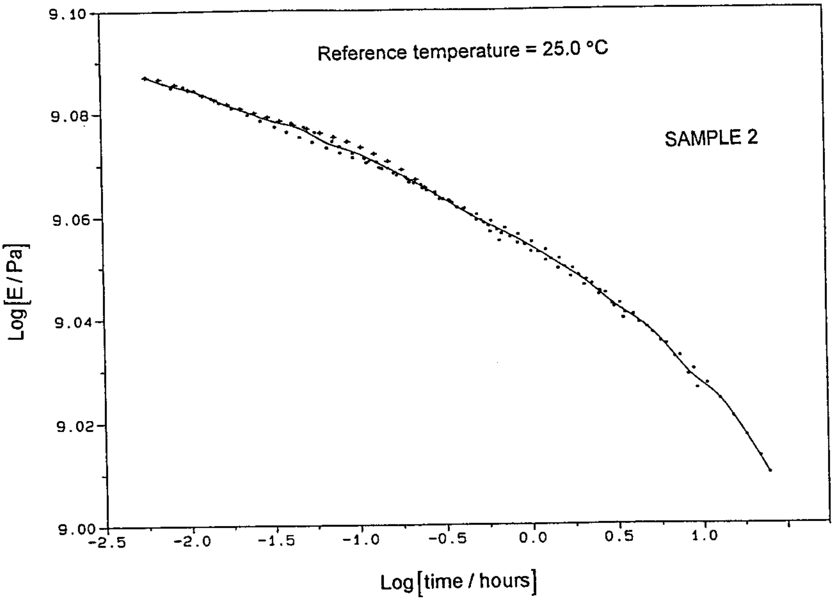

Figure 3. Master curve at 25°C for PS-HI + SBS, 90:10 (sample 2)

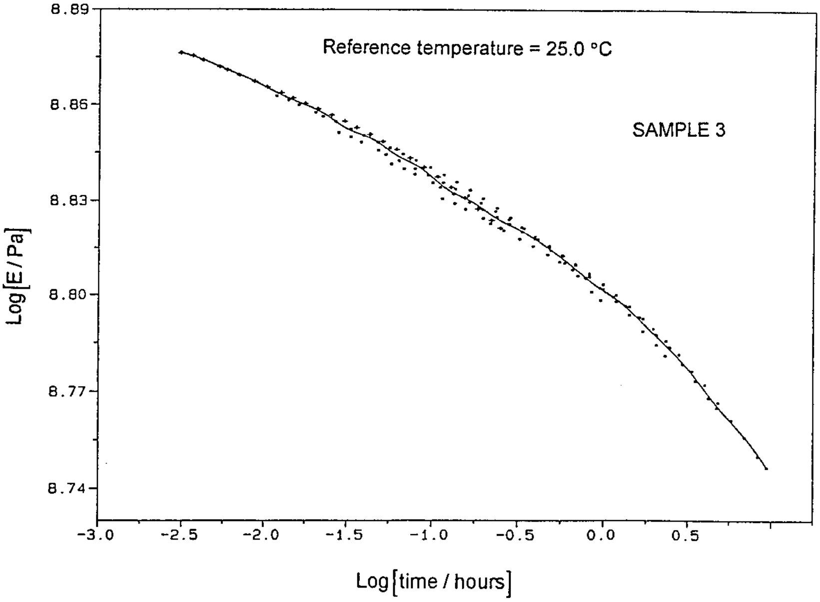

Figure 4. Master curve at 25°C for PS-HI + SBS, 75:25 (sample 3)

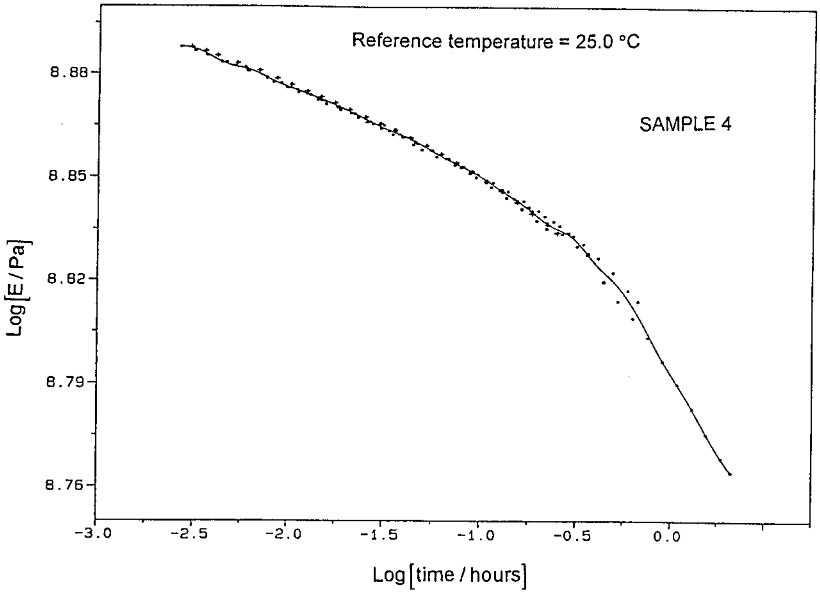

Figure 5. Master curve at 25°C for PS-HI + SBS, 60:40 (sample 4)

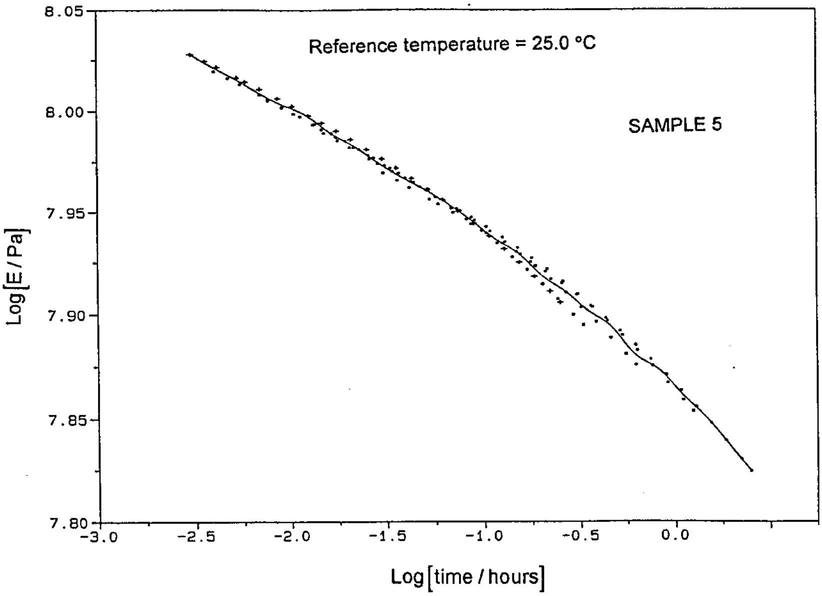

Figure 6. Master curve at 25°C for PS-HI + SBS, 45:55 (sample 5)

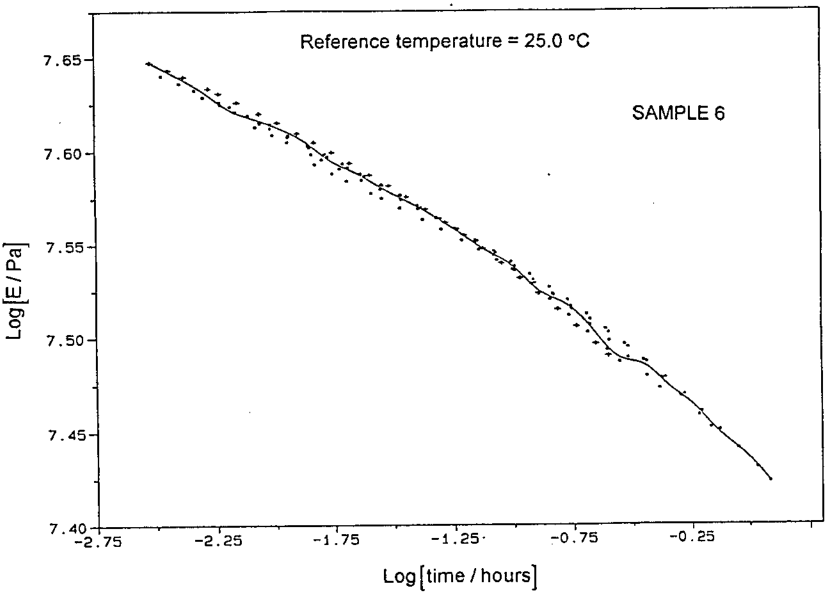

Figure 7. Master curve at 25°C for PS-HI + SBS, 30:70 (sample 6)

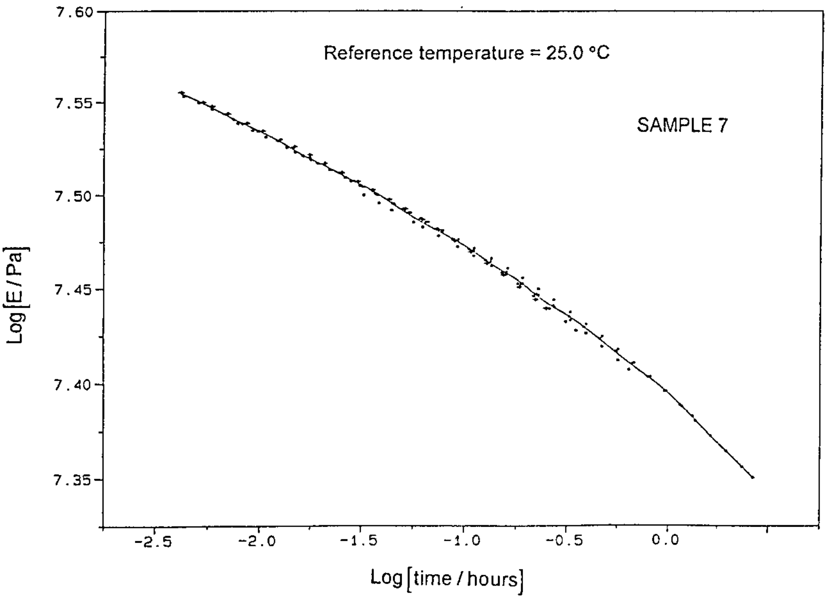

Figure 8. Master curve at 25°C for PS-HI + SBS, 15:85 (sample 7)

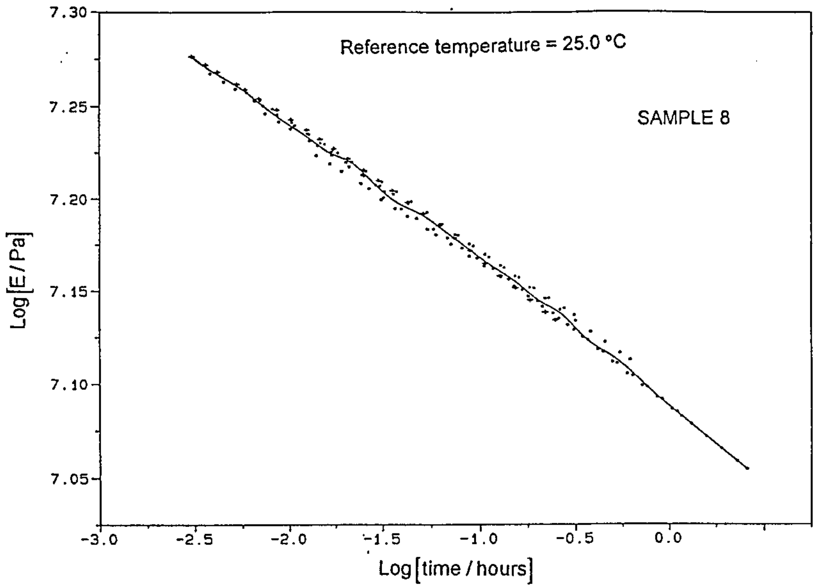

Figure 9. Master curve at 25°C for SBS (sample 8)

The results displayed above may be explained as follows. Under a constant load polymers undergo molecular relaxation or rearrangement in a attempt to minimise the localized stresses [15,19-21]. The processes involved in molecular rearrangement become more pronounced with time and are faster at higher temperatures. They are time and temperature dependent [15-17,19,22-24]. For blends it is possible that the dependence of relaxation time on temperature is different for each phase [21]. Faster rearrangement of the soft PB phase at the same conditions of creep experiments is due to its flexibility higher from that of the PS phase; the aromatic bulky groups of the latter retard relaxation processes. The creep measurements have been performed at temperatures above T_g of the soft PB phase what also enhances the flexibility and relaxation of the PB phase. As the content of the hard PS phase decreases, in all examined samples (Table 1), creep and recovery at 25, 30, 35, 40 and 45°C increase at a constant load. The modulus vs. time curve, in individual curves as well as in the master curves, are shifted to lower values with an decrease of the hard phase content, at the same conditions. (Figs. 1 - 9).

The master curves obtained allow us to examine the creep modulus of PS-HI, SBS and PS-HI + SBS blends on a time scale which is outside of the range measured by DMA experiments.

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