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Effect of Styrene-Butadiene-Styrene Block Copolymer on Dynamic-Mechanical Properties of High-Impact Polystyrene

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EFFECT OF STYRENE-BUTADIENE-STYRENE BLOCK COPOLYMER ON DYNAMIC-MECHANICAL PROPERTIES OF HIGH-IMPACT POLYSTYRENE

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ABSTRACT

For the selection of the polymer materials and polymer blends for various fields of applications, dynamic-mechanical properties, the primary viscoelastic functions as well as the stability of materials on different loads are very important. Since polymer materials are viscoelastic, their mechanical properties are dependent on temperature and time. The dynamic-mechanical properties of high-impact polystyrene, (PS-HI) and blends of PS-HI and styrene-butadiene-styrene block copolymer, (SBS) were investigated. Under the conditions of dynamic-mechanical load, the investigated systems will have different behavior due to the various content of the hard phase, polystyrene and soft phase, polybutadiene. The investigations were done by DMA analysis. The primary viscoelastic functions were determined. The influence of the constant stress on the strain and moduls at various temperatures was examined. The effects of the time on moduls changes was obtained by generating the master curves. The viscoelastic functions and the stability on the constant load, the changes of the moduls with time and temperature depend on the amount of polystyrene in the examined copolymers and blends. This investigation presents the possibility of predicting a useful lifetime of materials.

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INTRODUCTION

For the selection of the polymer materials and polymer blends for various fields of applications, their dynamic mechanical properties, primary viscoelastic functions, as well as the stability of those materials on constant loads are very important. Since polymer materials are viscoelastic, their viscoelastic functions are dependent on temperature and time (1-3). It is especially evident in complex multiphase systems, copolymers and polymer blends (4). In styrene-butadiene copolymers and blends the content of the hard phase polystyrene (PS) and soft phase polybutadine (PB), as well as their proccessing conditions are the main factors which influence on viscoelastic behavior (5-7). High impact polystyrene, HI-PS, is described as a two phase material consisting of an added or graft copolymerized elastomeric component, which is dispersed in a continous matrix of polystyrene. Appropriately designed triblock copolymers of the styrene-butadiene-styrene (SBS) type phase separate to give materials that behave as thermoplastic elastomers. A great deal of research has been concerned with blending homo-polymer polystyrene with such block copolymers. In this paper, we invesigated the effect of SBS on dynamic mechanical properties for blends with PS-HI and SBS block copolymer, PS-HI/SBS blends. The viscoelastic functions, the stability on the constant load and changes of the modulus with time and temperatures are presented for PS-HI/SBS blends as well as for PS and SBS copolymers and are related to the amount of soft phase (PB) and hard phase (PS) in investigated copolymers and their blends.

EXPERIMENTAL

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 given in Table 1.

Specimens Preparation

Blends of PS-HI/SBS were prepared by using a twin extruder Haake Record 90 (laboratories system) with the intensive mixing profile, Haake TW 100 with the following temperatures in zone 150/200/200/150 and the frequence of rotation 60 min^{-1}. The specimens for investigation were obtained by compression

Table 1. Tg of the hard and soft phases, values of E′ and intensities of the tgδ of the hard and soft phases for PS-HI, SBS and PS-HI/SBS blends; intensity I

SAMPLE	PS-HI/ SBS	HARD PHASE,PS	T_g soft phase,PB (° C)		T_g hard phase,PS (° C)		E′ (GPa)		$I\alpha_s$ soft phase	$I\alpha_s$ hard phase
	% weight	% weight	tg δ	E″	tg δ	E″	-120 °C	25 °C	tg δ	tg δ
1	100	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	100	29.0	-76.39	-84.28	113.3	111.3	2.100	0.018	0.570	0.330

molded at 230°C; mold temperature 40°C and a rate 100 mm/s. The dimensions of investigated specimens were ca. 18.32mm x 12.94mm x 4.64mm.

Measurements of Dynamic Mechanical Properties

The Dynamic Mechanical Analyzer 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, (tgδ), 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 constant stress of 14.92 kPa, at temperatures 25, 30, 35, 40 and 45°C. The specimens were stressed for 15 minutes at constant stress, and then allowed to relax for 15 minutes. The temperature was then increased in increments of 5°C followed by an equilibration period of 15 minutes before initation of the next stress/relax cycle. The master curve at 20°C, as reference temperature, was obtained by using time/temperature superposition software.

RESULTS AND DISCUSION

Copolymers PS-HI and SBS as well as PS-HI/SBS blends consist of two phases, hard phase (PS) and soft phase (PB) which is evident from the DMA results (Table 1). Copolymers and PS-HI/SBS blends have a single glass transitions, Tg, of the hard phase, PS, at positive temperature value between Tg of the PS phase in SBS and PS phase in PS-HI (Table 1). The same is valid for Tg of PB phase at negative temperature. With the decrease of the hard phase PS in copolymers and blends examined, the intensity of the relaxation maximum tgδ of the soft phase increases, while the intensity of the relaxation maxima tgδ of the hard phase decreases. The storage modulus E' decreases (Table 1.). The glass transitions of PS and PB phases are decreased (Table 1). Those changes are connected with less rigidity and higher flexibility of soft segments in the samples with lower content of the hard phase (5, 6). Viscoelastic data creep (strain) and recovery (stress relaxation) collected by performing measurements under constant load are shown in Table 2. The example is given on Figure 1. As the content of the hard phase PS decreases in examined copolymers and blends (Table 2), their creep and recovery increase at constant temperature. The creep and recovery also increase with the temperature at constant content of the hard phase PS. The isothermal curves of the creep modulus 1/S vs. time obtained on the base of the creep data, are shown on Figures 1b-5b. The values of the creep modulus in function of temperature before

Table 2. The creep and recovery data at constant load at various temperatures for PS-HI, SBS and PS-HI/SBS blends

SAMPLE	PSHI/ SBS	HARD PHASE	CREEP, (%)					RECOVERY, (%)				
	% weight	% weight	25 °C	30 °C	35 °C	40 °C	45 °C	25 °C	30 °C	35 °C	40 °C	45 °C
1	100	92.0	4.510	6.243	8.471	8.224	10.20	2.710	2.86	4.00	4.63	5.00
2	90/10	85.8	5.129	6.119	7.667	9.029	10.82	4.690	5.260	5.370	5.720	6.570
3	75/25	76.5	11.96	14.00	15.61	17.11	18.93	6.54	6.86	7.53	8.00	8.33
4	60/40	67.2	12.21	12.79	11.93	14.64	24.64	7.24	7.02	7.38	8.07	9.14
5	45/55	57.9	31.67	32.38	34.29	35.71	38.57	14.28	15.26	15.84	16.37	17.68
6	30/70	48.6	41.88	43.19	42.93	44.76	47.38	16.86	17.72	18.29	18.57	19.28
7	15/85	39.3	32.71	33.76	35.6	37.69	41.36	19.28	20.86	21.72	22.57	23.71
8	100	29.0	39.05	35.24	35.95	38.52	39.76	25.93	30.24	30.76	29.77	30.16

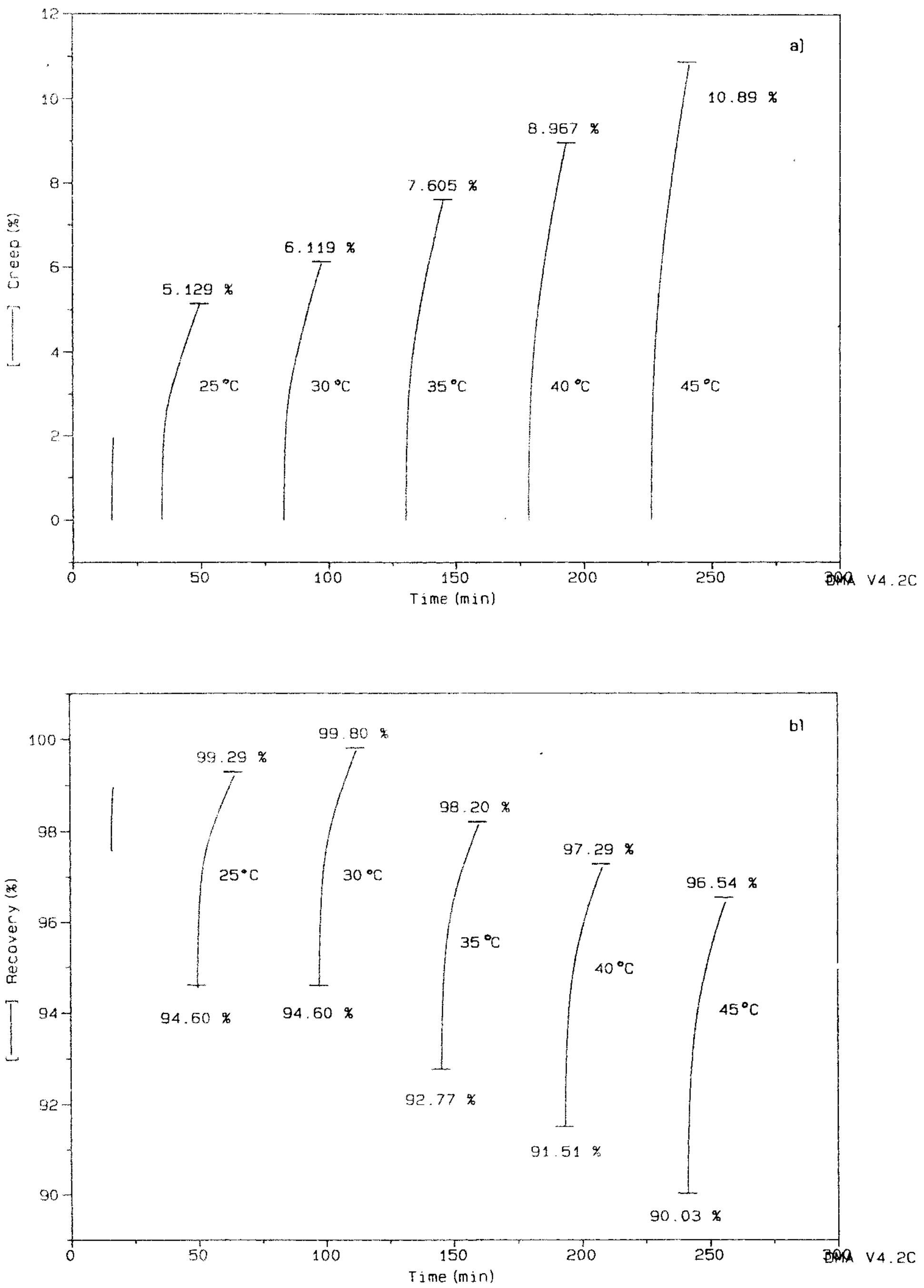

Figure 1. The example of creep at constant load as a function of temperature for PS-HI/SBS 90/10 blend; a) creep, b) recovery, c) creep modulus vs. time.

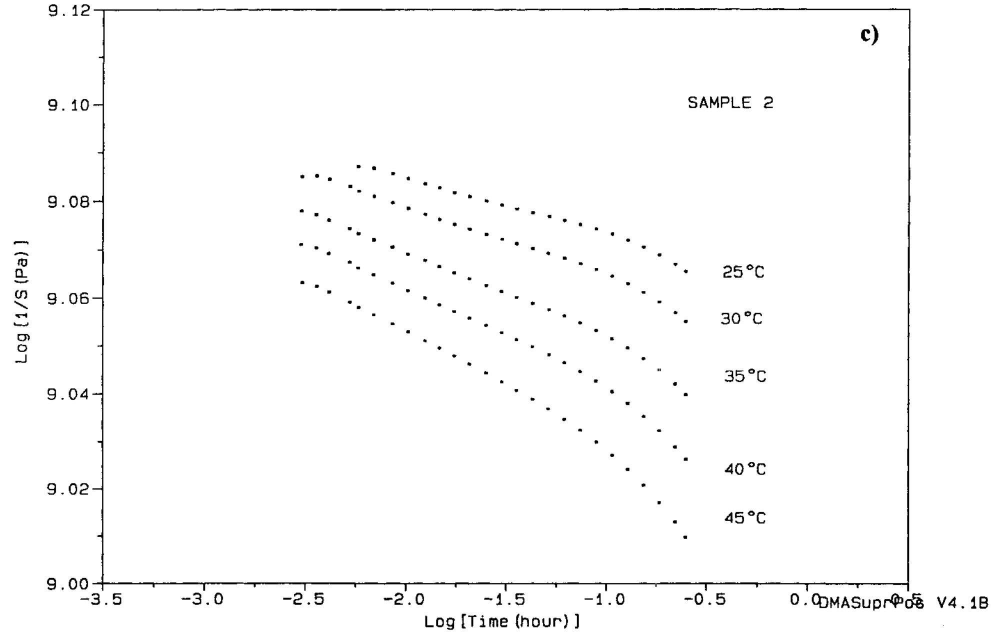

Figure 1. Continued

and after loading for PS-HI, SBS and PS-HI/SBS blends are given in Table 3. The modulus of all examined samples decrease as the time under loading increases at the constant temperature. The correlation between creep values and the creep modulus is evident (4-6). The curves 1/S vs. time are shifted to the lower values of the creep modulus with the increase of the temperature, under the same conditions of measurement. The influence of the hard phase PS on the creep modulus data is evident (Table 3). As the content of the hard phase PS decreases, the creep modulus also decreases. By selecting the reference curve 1/S vs. time, the curve at 25°C, and shifting all the other isothermal curves obtained at higher temperatures with respect to time, the master curves of creep modulus vs. time at references temperature were generated (Figure 2a - 5a). The curves show the effects of time on the creep modulus of PS-HI, SBS and PS-HI/SBS blends. At small time intervals, the examined materials exibite a relativly high creep modulus. At longer times viscous flow occurs and the materials exhibit a relativly low modulus (Figure 2a - 5a). This occurs because the polymer material under load undergoes molecular rearrangement in an attempt to minimize the localized stresses (1,3,4). The processes involved in

Table 3. Creep modulus, 1/S, before and after loading at various temperatures for PS-HI, SBS and PS-HI/SBS blends

SAMPLE	PS-HI/ SBS % weight	HARD PHASE % weight	CREEP MODULUS, 1/S (Pa) before loading					CREEP MODULUS, 1/S (Pa) after loading				
			25 °C	30 °C	35 °C	40 °C	45 °C	25 °C	30 °C	35 °C	40 °C	45 °C
1	100	92.0	2.120 10^9	2.097 10^9	2.097 10^9	2.097 10^9	2.087 10^9	2.028 10^9	1.960 10^9	1.914 10^9	1.914 10^9	1.865 10^9
2	90/10	85.8	1.238 10^9	1.220 10^9	1.199 10^9	1.180 10^9	1.160 10^9	1.166 10^9	1.138 10^9	1.099 10^9	1.065 10^9	1.025 10^9
3	75/25	76.5	7.750 10^8	7.313 10^8	7.123 10^8	6.962 10^8	6.782 10^8	6.850 10^8	6.311 10^8	6.061 10^8	5.852 10^8	5.601 10^8
4	60/40	67.2	7.548 10^8	7.750 10^8	7.674 10^8	7.548 10^8	7.352 10^8	6.652 10^8	6.850 10^8	6.750 10^8	6.542 10^8	5.831 10^8
5	45/55	57.9	1.071 10^8	1.045 10^8	1.017 10^8	9.810 10^7	9.363 10^7	8.097 10^7	7.900 10^7	7.540 10^7	7.177 10^7	6.702 10^7
6	30/70	48.6	4.455 10^7	4.362 10^7	4.270 10^7	4.119 10^7	3.925 10^7	3.084 10^7	3.084 10^7	2.983 10^7	2.842 10^7	2.660 10^7
7	15/85	39.3	3.615 10^7	3.582 10^7	3.476 10^7	3.342 10^7	3.185 10^7	2.772 10^7	2.698 10^7	2.571 10^7	2.428 10^7	2.252 10^7
8	100	29.0	1.901 10^7	1.862 10^7	1.774 10^7	1.680 10^7	1.591 10^7	1.373 10^7	1.373 10^7	1.304 10^7	1.213 10^7	1.142 10^7

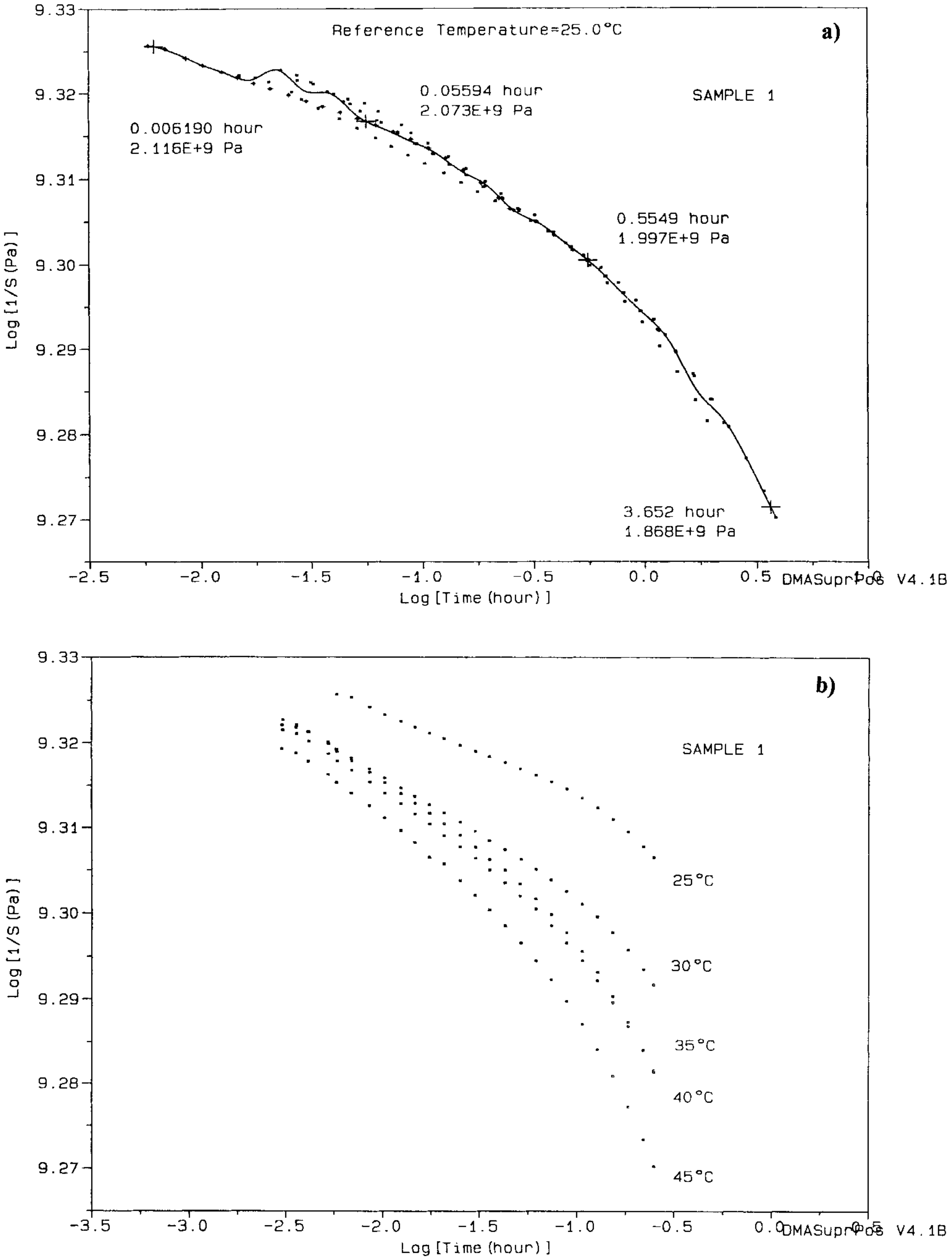

Figure 2. Master curves at 25°C and creep modulus, 1/S, vs. time at various temperature for PS-HI, sample 1 and Ps-HI/SBS 90/10 blend, sample 2; a) master curves, b) 1/S vs. time.

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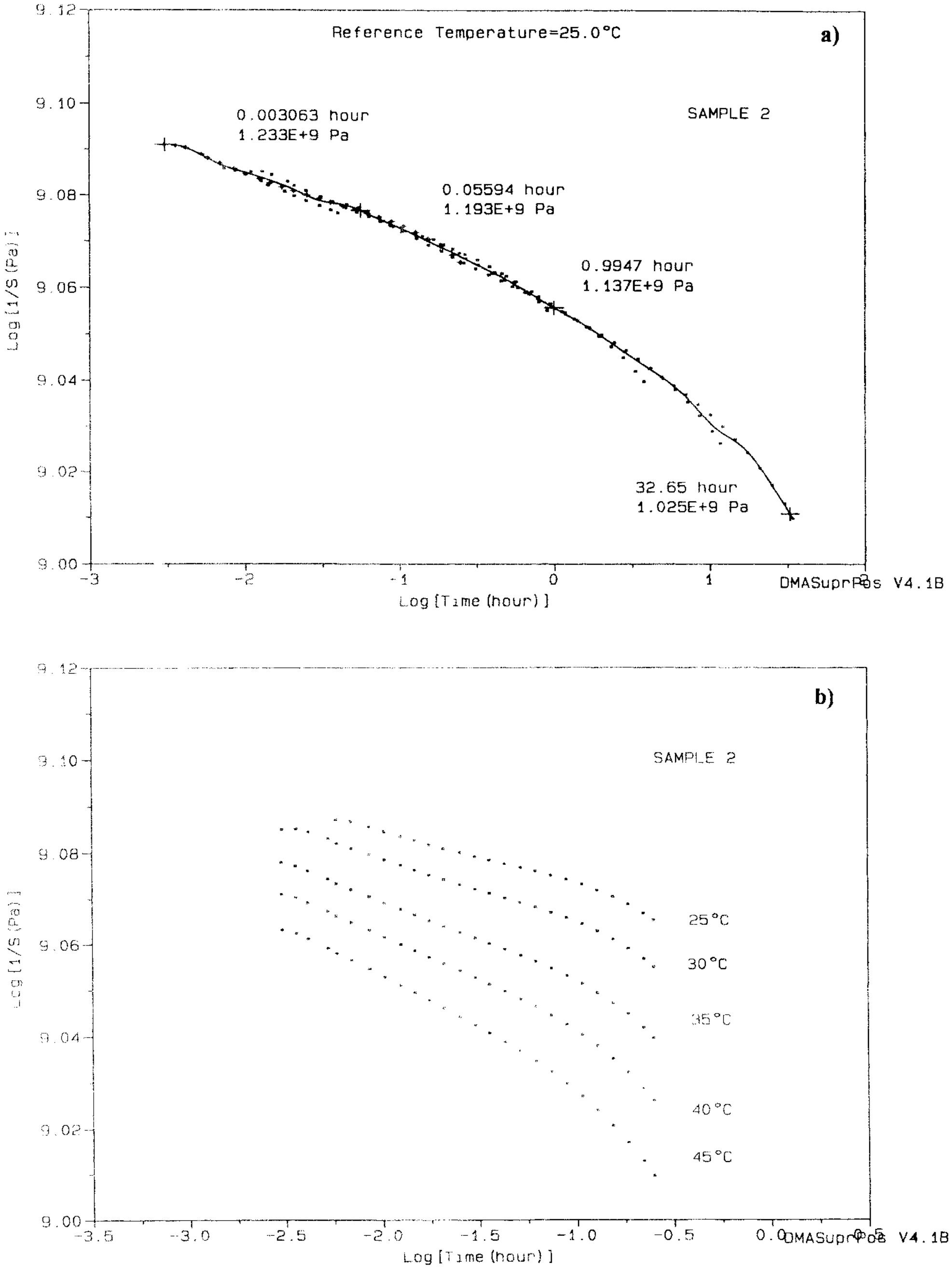

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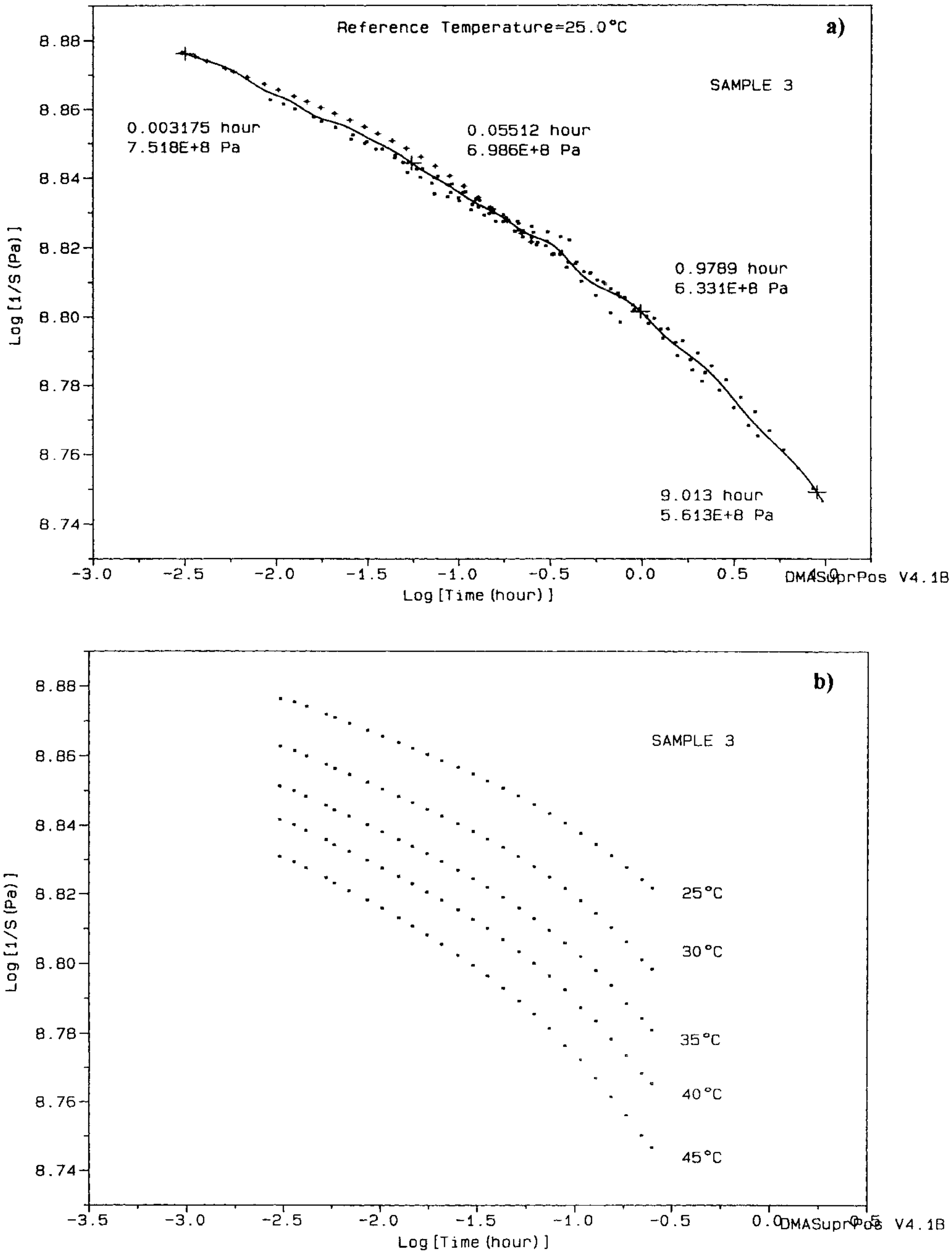

Figure 3. Master curves at 25°C and creep modulus, 1/S, vs. time at various temperature for PS-HI/SBS 75/25 blend, sample 3 and PS-HI/SBS 60/40 blend, sample 4; a) master curves, b) 1/S vs. time.

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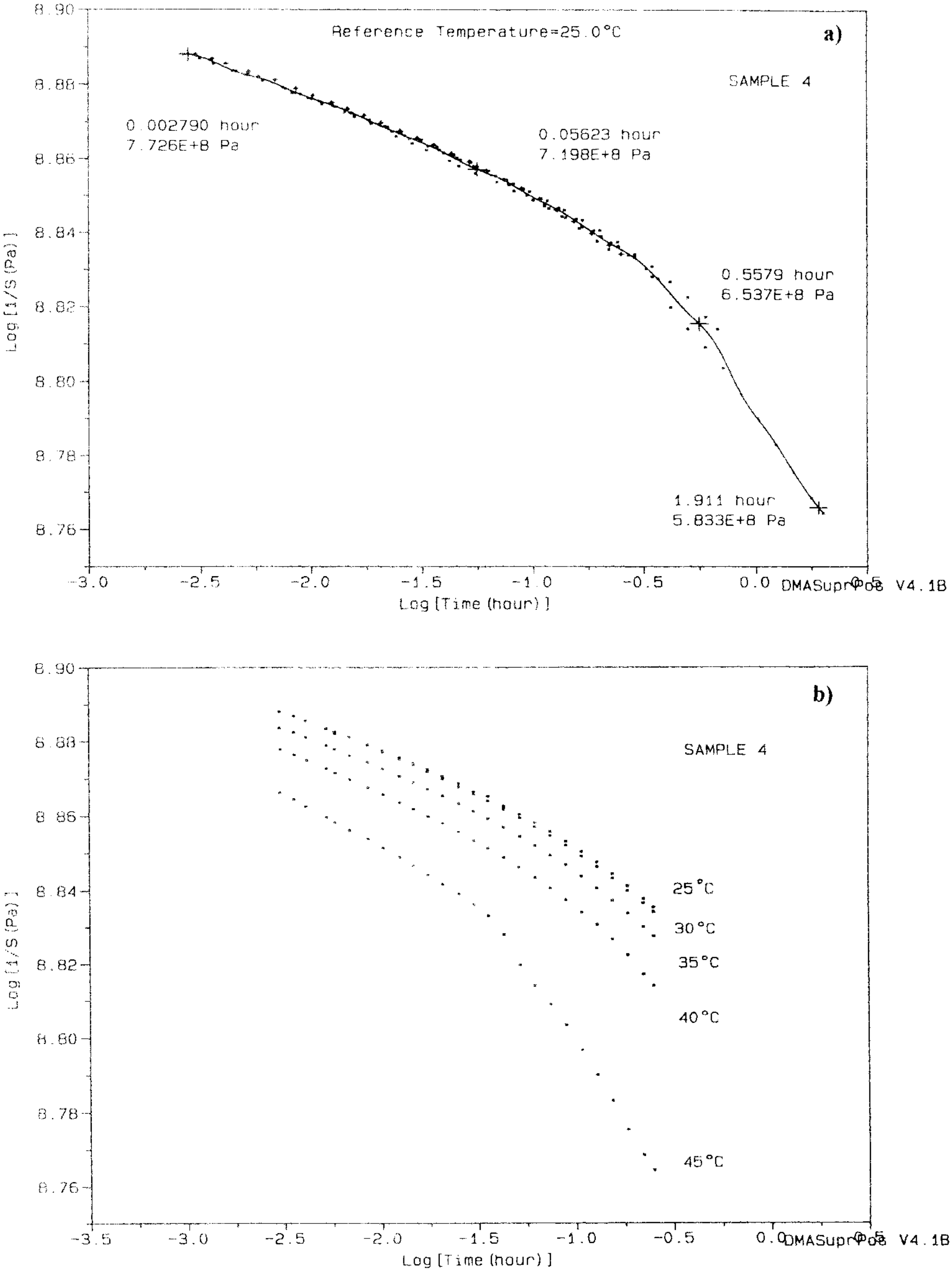

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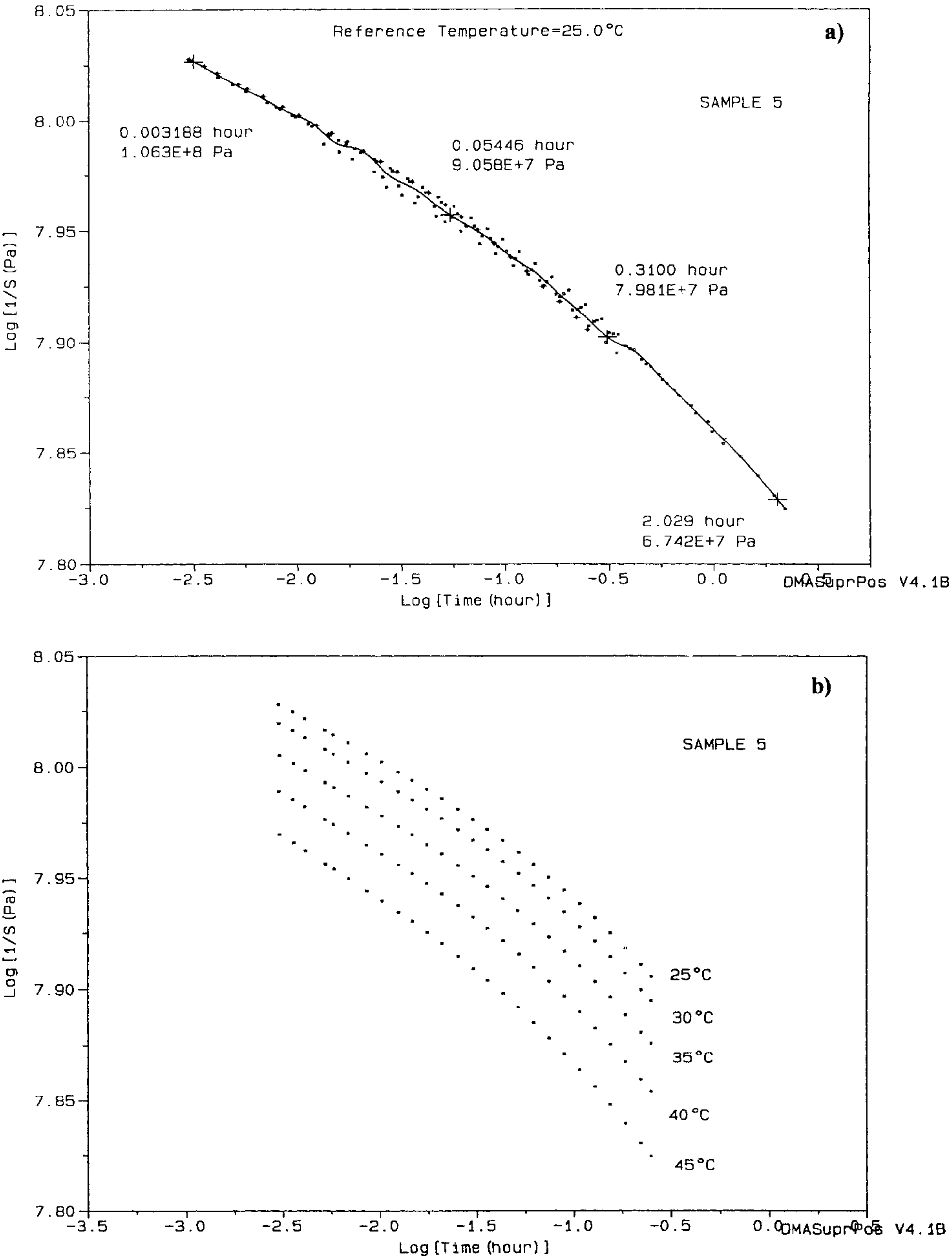

Figure 4. Master curves at 25°C and creep modulus, 1/S, vs. time at various temperature for PS-HI/SBS 45/55 blend, sample 5 and PS-HI/SBS 30/70 blend, sample 6; a) master curves, b) 1/S vs. time.

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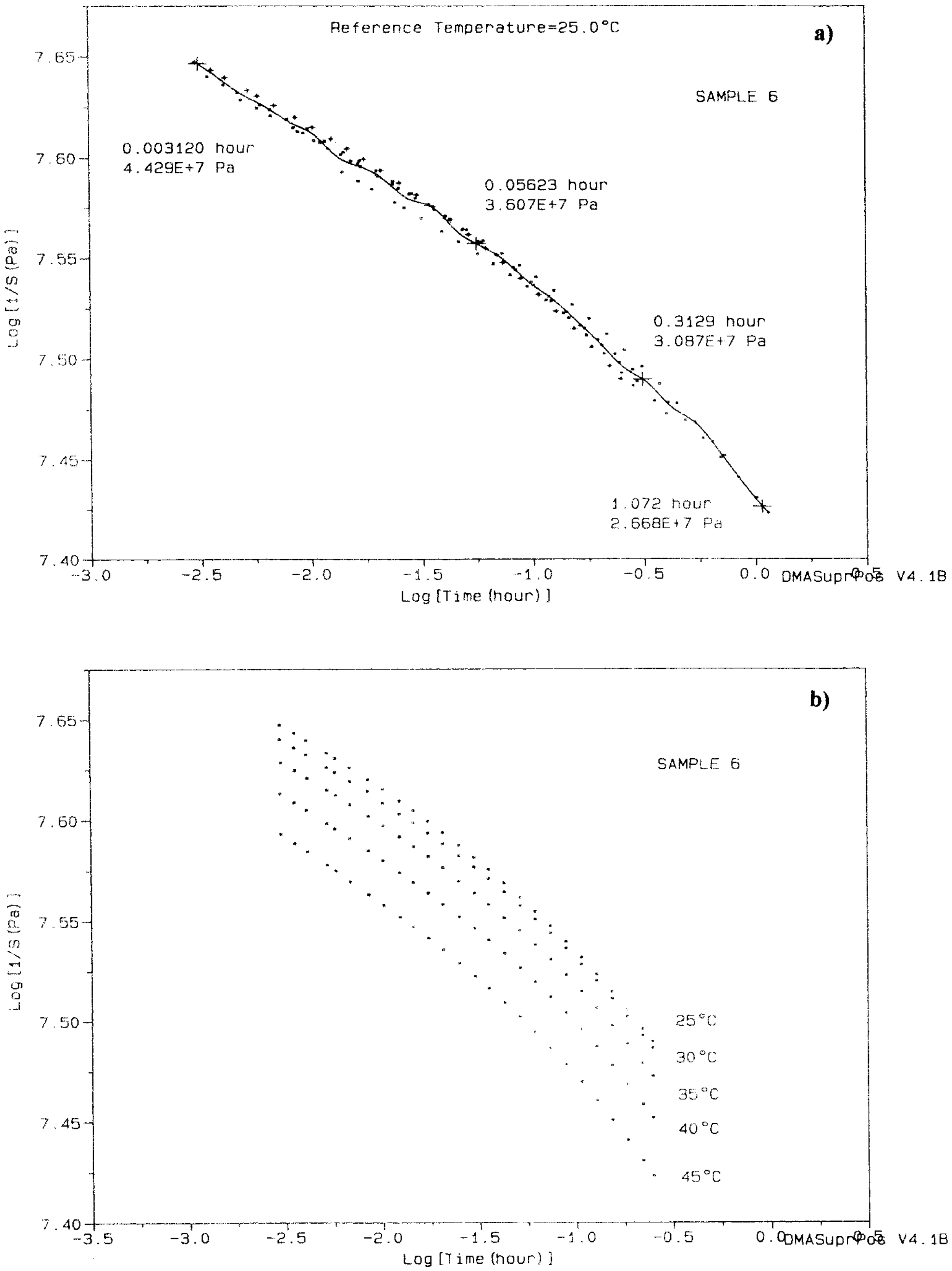

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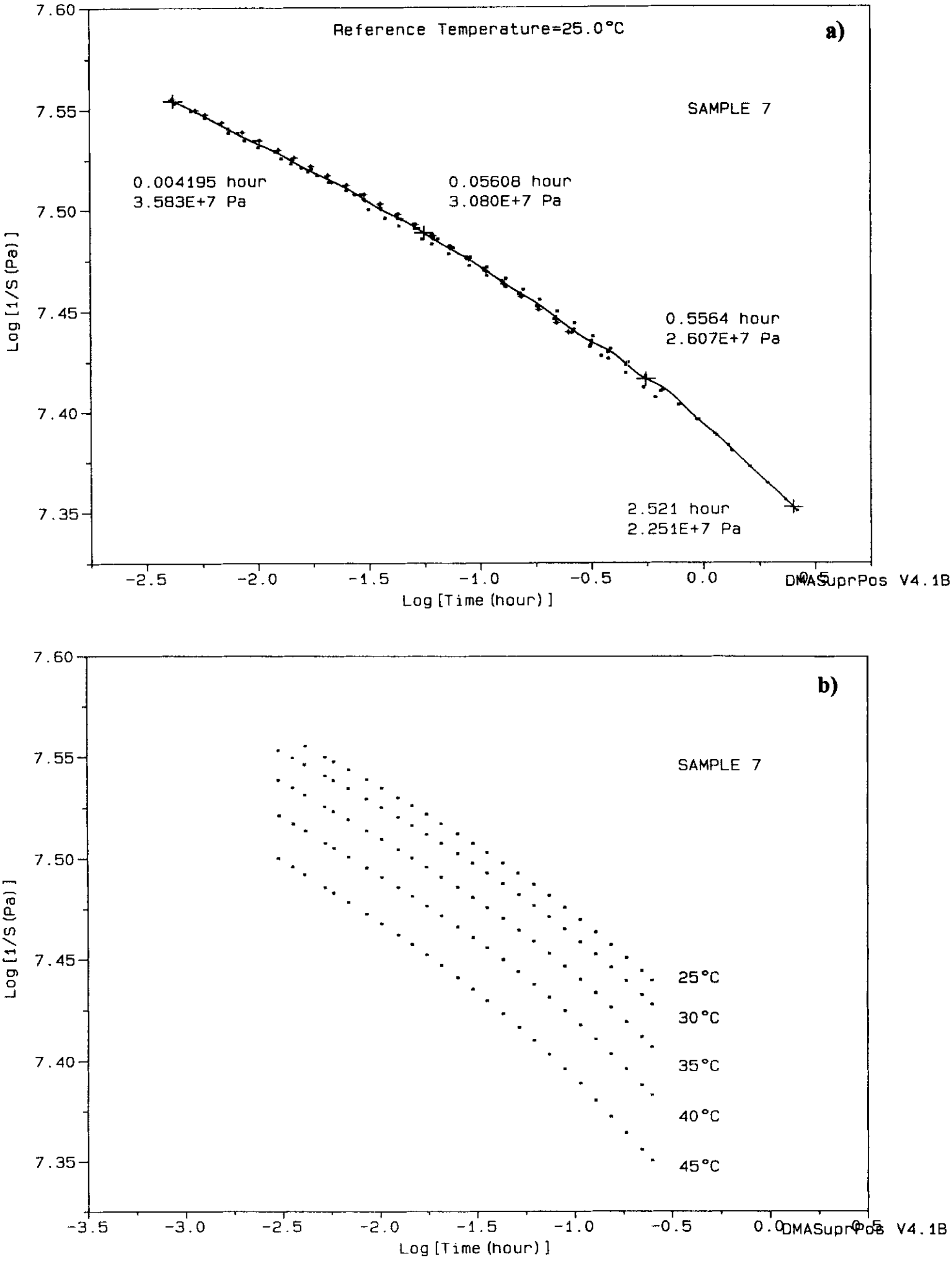

Figure 5. Master curves at 25°C and creep modulus, 1/S, vs. time at various temperature for PS-HI/SBS 15/85 blend, sample 7 and SBS, sample 8; a) master curves, b) 1/S vs. time.

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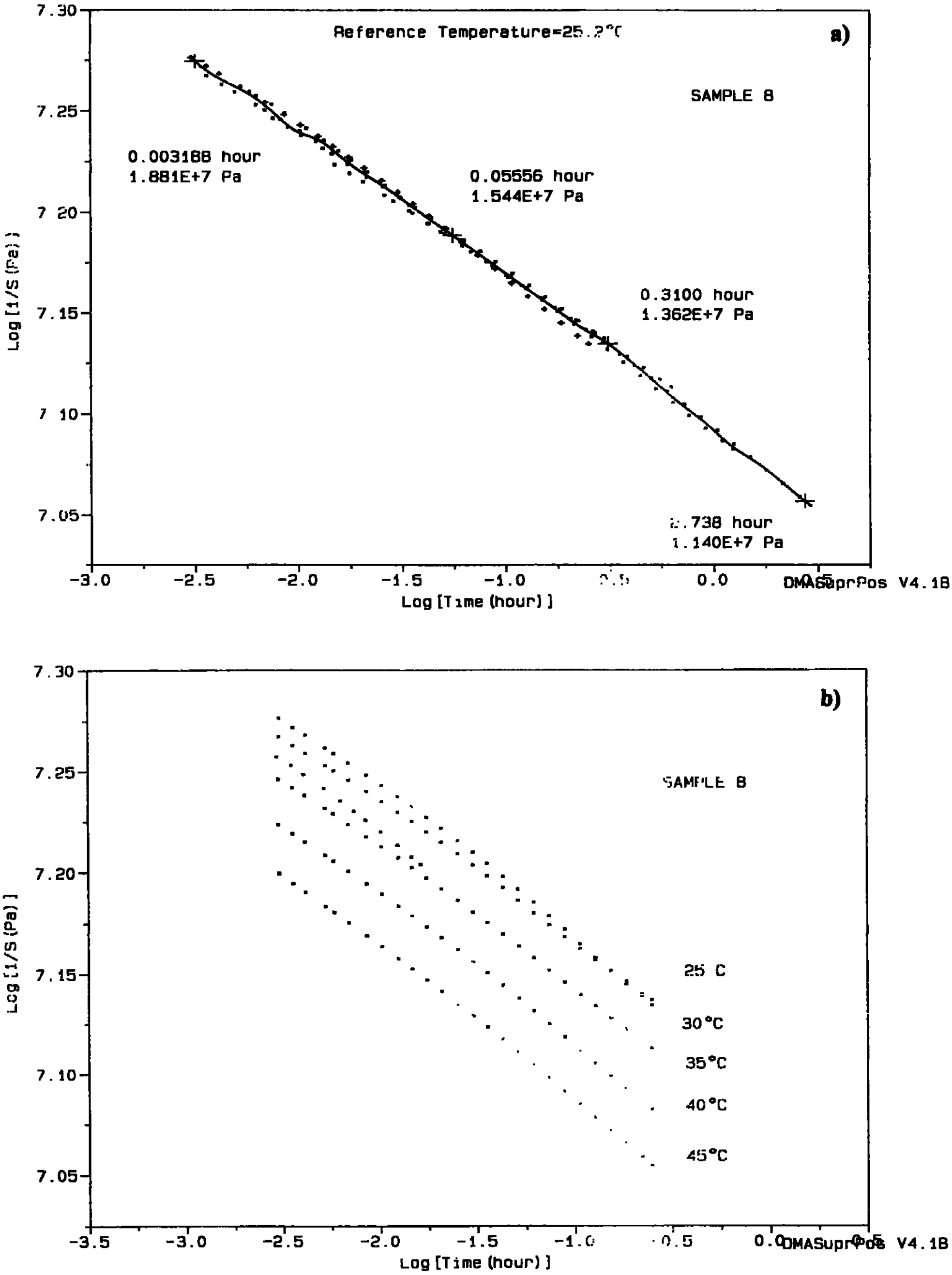

Figure 5. Continued

molecular relaxation or rearrangement occur faster at high temperatures (Figure 2b - 5b) (1, 3, 4). The obtained master curves allow us to examine the creep modulus of PS-HI, SBS and PS-HI/SBS blends on a time scale which is outside the range measured by DMA experiments. The master curve gives the possibility of predicting the creep modulus and useful life of examined copolymers and blends materials in a wide range of time and temperature (1-3, 4, 7).

CONCLUSION

The results of the investigation show that styrene-butadiene-styrene block copolymer SBS influences the viscoelastic properties of high impact polystyrene, PS-HI. The addition of the SBS copolymer into a PS-HI, copolymer resulted in a decrease of Tg of the soft phase (PB) and hard phase (PS) in PS-HI/SBS blends and decrease in the storage modulus. It is due to the lower content of the hard phase in PS-HI/SBS blends. With the decrement of the hard phase PS in examined copolymers and blends, the intensity of the loss tangent of the soft phase increases with the decrement of the intensity of the loss tangent of the hard phase at the same time. All samples of starting copolymers and PS-HI/SBS blends have the single Tg of the hard phase and single Tg of the soft phase. At the constant load, the creep increases and creep modulus decreases over a period of time. These effects are greater with a lower content of hard phase and higher temperatures. DMA combined with time/temperature software produce the master curves on the base of which the prediction of the effects of time and temperatures on PS-HI, SBS and PS-HI/SBS blends may be done, as well as the possibility of predicting their useful lifetime over a longer period of time which is outside the range measured by DMA.

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