Enhancement of the High-Temperature Properties of an SEBS Thermoplastic Elastomer by Chemical Modification

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ABSTRACT: A procedure was developed for benzoylating the polystyrene segments in polystyrene-*b*-poly(ethylene-*co*-butene)-*b*-polystyrene (SEBS) triblock copolymers. The products were characterized by NMR spectroscopy, gel permeation chromatography, dynamic mechanical thermal analysis, and membrane osmometry. The mechanical properties of the parent and benzoylated copolymers, measured from 25 to 150°C, indicated that benzoylation increases the utility of the polymers at elevated temperatures. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1203–1210, 2002

Key words: modification; block copolymer; elastomers; mechanical properties

INTRODUCTION

The relationships between the structure and mechanical properties of polystyrene-polybutadiene-polystyrene (SBS) block copolymers have been thoroughly investigated.[1,2] SBS block copolymers lose most of their strength above 60–70°C,[3,4] even though the T_g of the polystyrene segments is 100°C. The midsegments of SBS block copolymers were hydrogenated to produce polystyrene-*b*-poly(ethylene-*co*-butene)-*b*-polystyrene (SEBS) block copolymers.[5–7] SEBS block copolymers retain their mechanical properties somewhat better than do SBS block copolymers at elevated temperatures,[8] but the block copolymers are still limited by the T_g's of their end segments.

Efforts have been made to increase the T_g of the end segments of SEBS block copolymers to make them more useful at elevated temperatures. Weiss and coworkers,[9–11] for example, sulfonated SEBS block copolymers (Kraton G®) to obtain block copolymer ionomers that have significantly better tensile moduli, elongations, and ultimate strengths at 70–200°C than those of the parent copolymer. Polyionomers are, however, hygroscopic and sometimes difficult to process, and for some applications, it is worthwhile to pursue other methods of modifying the end segments of SEBS copolymers. Udding[12] treated Kraton G® with 3-azidosulfonylbenzoic acid to attach *m*-carboxybenzenesulfonamide groups to the styrene units and thereby obtain a polymer with improved tensile strength. Hayashi[13] alkylated the styrene units of Kraton G® using benzyl chloride or benzhydryl chloride as reagents in the presence of AlCl₃ and obtained products with higher moduli than those of the parent polymer but did not report T_g or tensile data. Similar work was reported by Matsumoto and Oshima.[14] Liu and Jiang acetylated the styrene units in specially modified SEBS and then converted the resulting acetyl groups to carboxylic acid and alcohol groups, the degrees of substitution being 2–36 percent.[15]

In this article, we describe the benzoylation of polystyrene segments in SEBS copolymers and report the mechanical properties of the resulting copolymers. We will subsequently report on napthoylation,[16,17] arylsulfonation,[18] nitration,[18] and acetylation/oximation[19] reactions of SEBS and the physical behavior of the resulting polymers.

EXPERIMENTAL

Kraton G®, a thermoplastic elastomer that is the result of hydrogenating a polystyrene–polybutadiene–polystyrene block copolymer, was obtained from the Shell Chemical Co., Houston, TX. The polymer is a triblock copolymer containing polystyrene end segments and a central ethylene/butene copolymer segment. Most of the work was done with type 1652 Kraton G®, which is reported by the manufacturer to have a molecular weight of 50,000 and to contain 30 wt % styrene units. Some experiments were done with type 1657 Kraton G®, which is reported to contain 13 wt % styrene units and about 30% of a polystyrene–poly(ethylene-*co*-butene) diblock.

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TABLE I
Effect of Reaction Times on Extent of Benzoylation, Molecular Weight, and Molecular Weight Distribution

Reaction time (h)	Solvent	M_n/M_n^0 Observed	M_n/M_n^0 Calculated[a]	M_w/M_n	% Benzoylation
0	—	1.0	—	—	—
1.0	CS_2	—	1.10	1.07	35
1.5	CS_2	—	1.12	—	42
2.0	CS_2	—	1.16	—	53
3.0	CS_2	1.24	1.21	1.13	70
3.0	CH_2Cl_2	1.00	1.09	1.12	30
5.5	CH_2Cl_2	1.07	1.10	1.13	35
24.5	CH_2Cl_2	1.09	1.18	1.15	60
48	CH_2Cl_2	1.15	1.14	1.17	70
72	CH_2Cl_2	1.20	1.21	1.21	71

[a] Calculated for extent of benzoylation.

Benzoylation procedure

Benzoyl chloride (12 mL, 0.10 mol) was added, under a stream of nitrogen, to a solution of Kraton G® 1652 (15.0 g, 0.043 mol of styrene repeating units) in either methylene chloride or carbon disulfide (420 mL). Aluminum chloride (14.0 g, 0.10 mol) was then added and the solution was stirred at room temperature. After appropriate reaction times (Table I), the reaction mixture was treated with tetrahydrofuran (~100 mL) to terminate the reaction and to solubilize reaction mixtures that had become gels. The solution was filtered and added slowly to rapidly stirred methanol to obtain the benzoylated polymer. This was purified by reprecipitation from the tetrahydrofuran solution into methanol and dried under a vacuum at room temperature. Yields were, generally, in close agreement with those expected based on the extents of benzoylation, as estimated by NMR analysis. A similar procedure was used for the benzoylation of Kraton G® 1657. ^{1}H-NMR spectra of the parent and benzoylated copolymers in a $CDCl_3$ solution (20 mg/mL) were recorded using a Varian XL-400 NMR spectrometer. The spectra were recorded at 25°C using an 11° pulse angle, an acquisition time of 2 s, and a pulse delay of 10 s. Sixteen transients were collected in each case. The aromatic proton resonance of the partially benzoylated polymers occurred in three general areas (A, 6.3–6.8 ppm; B, 6.8–7.3 ppm; and C, 7.3–7.9 ppm). Studies on benzoylated polystyrenes led to the conclusion that area A was due to the protons *ortho* to the polymer backbone in both styrene and benzoylated styrene units, that area B was due to *m-* and *p* protons of styrene units, and that area C was due to the remaining seven aromatic protons of the benzoylated styrene units. Based on this information, the extent of benzoylation could be calculated from any combination of the relative areas of the *A*, *B*, and *C* signals. A convenient relationship is shown below, where A_A and A_C are the relative areas of the *A* and *C* resonances:

$$\% \text{ Benzoylation} = \frac{100 \times \dfrac{A_C}{7}}{\dfrac{2}{A_A}} = 28.6 \, A_C/A_A$$

Gel permeation chromatography

Gel permeation chromatographs were obtained using a Waters 150-C ALC/GPC instrument which was equipped with a set of six Styragel® columns having a continuous porosity range of 500–10^6 Å. Molecular weight averages and dispersities reported herein are based on a standard polystyrene calibration and are not adjusted for differences in characteristic ratios among polystyrene, Kraton G®, or its benzoylated derivatives.

Dynamic mechanical thermal analysis (DMTA)

Measurements of polymer glass transition temperatures were made with a Polymer Laboratories dynamic mechanical thermal analyzer equipped with a Hewlett–Packard data analyzer. The T_g's of the poly-(ethylene-*co*-butene) segments were measured using the single- or dual-cantilever mode at a heating rate of 2°C per min and a frequency of 1 Hz. Measurements of the T_g's of the end segments were made in the shear mode at a heating rate of 2°C per min and a frequency of 1 Hz.

Mechanical property measurements

All polymer samples were compression-molded. Microdumbbell specimens were then cut. The specimens were approximately 1 mm in thickness and 2.5 mm in width.

Stress–strain measurements were made at various temperatures using an Instron mechanical tester equipped with an environmental box. Microdumbbells were stretched at a rate of 0.5 cm per min after an
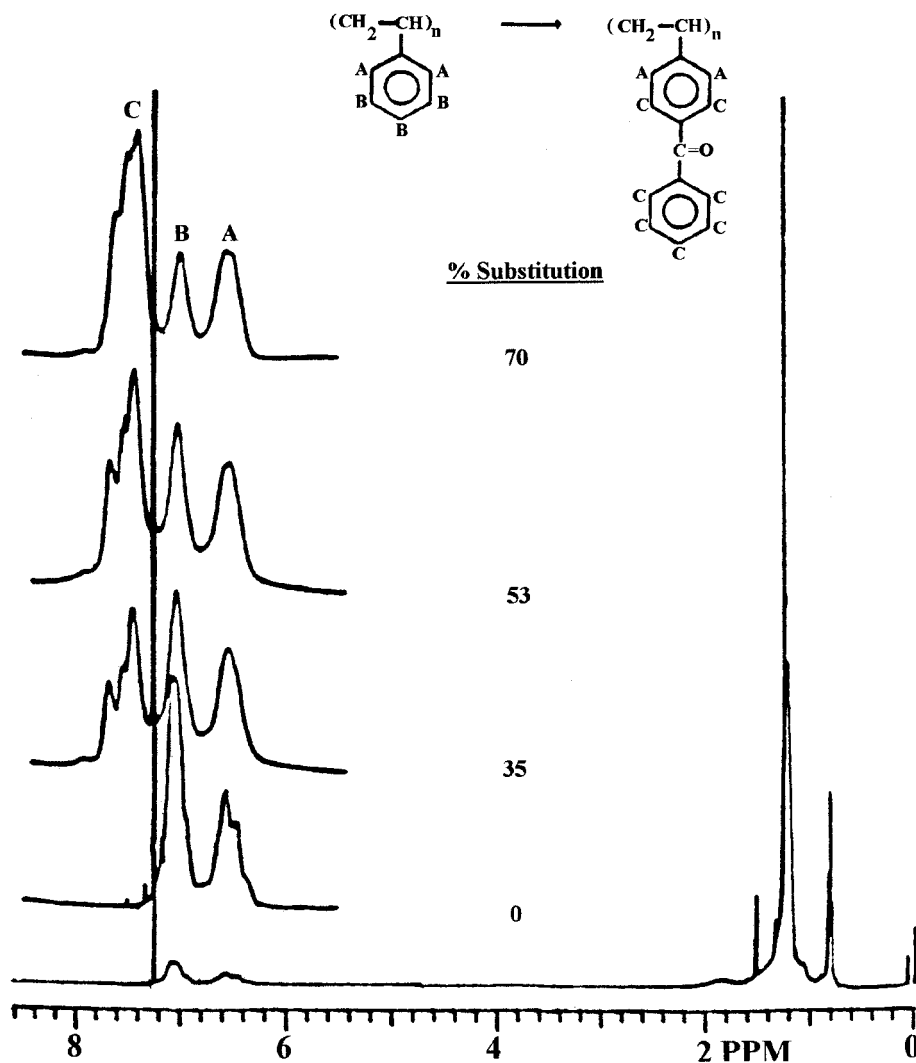
Figure 1 ^{1}H-NMR spectra, 400 MHz, of Kraton G® and benzoylated derivatives.

equilibration time of 30 min at the desired temperature. Young's moduli were calculated from the initial slopes of the stress–strain curves.

Permanent set after 100% elongation at various temperatures was measured using an Instron mechanical tester equipped with an environmental chamber. Hatch marks were placed on the microdumbbells. They were then stretched at a rate of 2 cm per min after an equilibration time of 30 min at the desired temperature. The samples were allowed to relax for 2 min between each hysteresis loop measurement. The permanent set was calculated by dividing the distance between the hatch marks after deformation of the polymer sample by the initial distance between them in the unstretched sample.

RESULTS AND DISCUSSION

Benzoylation studies

Many investigators have investigated the benzoylation of polystyrene using benzoyl chloride, aluminum chloride, and solvents such as carbon disulfide, methylene chloride, and nitrobenzene.[20–28] The reaction occurs cleanly and in high yield. It provides a convenient route to polyvinylbenzophenone and styrene–vinylbenzophenone copolymers. The compositions of the copolymers have been determined by a variety of analytical methods, including several NMR analyses, but detailed information about the NMR methods has not been provided.

In the present study, the Kraton G® samples were benzoylated using either carbon disulfide or methylene chloride as solvents. Reactions conducted in carbon disulfide proceeded much faster than did those conducted in methylene chloride. As indicated in Table I, 70% of the styrene units could be benzoylated in about 3 h when carbon disulfide was the solvent, but, using comparable reaction conditions, the reaction had to be conducted for 50 h to obtain an equivalent extent of substitution when methylene chloride was the solvent. The reaction mixtures tended to become gels at high conversions when carbon disulfide was used. This depended on the poly-

TABLE II
Influence of Polymer Concentration on $\overline{M_n}/\overline{M_n^0}$ and $\overline{M_w}/\overline{M_n}$ for Benzoylation of Kraton
G® 1652 in CS₂ After 3-h Reaction

Polymer concentration (g/L)	% Benzoylation	M_n/M_n^0		M_w/M_n
		Observed	Calculated	
—	0	—	—	1.07
5	65	1.17	1.19	1.14
35.8	70	1.23	1.21	1.13
71.4	70	1.12	1.21	2.57

mer concentration and did not occur when it was below 5 g/L. It appears, however, that benzoylation continues to occur even after the reaction mixtures gel. The gelation is a result of an interaction between aluminum compounds in the reaction mixture and benzoylated styrene units in the products and is not due to chemical crosslinking. Addition of tetrahydrofuran to the reaction mixtures breaks up the gels. The benzoylated polymers were soluble in carbon disulfide and methylene chloride after purification. The reaction mixtures did not become gels when methylene chloride was employed as the solvent.

Figure 1 shows 400-MHz ^{1}H-NMR spectra of Kraton G® and of benzoylated Kraton G® samples. The aromatic proton resonance region consists of three general areas, which are designated A, B, and C. An NMR study of benzoylated polystyrenes,[29] where the ratio of aromatic to aliphatic proton resonance could be used to establish the proportion of benzoylated styrene units, enabled the aromatic proton resonance assignments shown in Figure 1 to be developed. Based on these assignments, the extents of benzoylation obtained in the reactions were calculated. Approximately 70% of the styrene units in Kraton G® 1652 could be benzoylated using either carbon disulfide or methylene chloride as solvents for the reaction. In contrast, only approximately 50% of the styrene units in Kraton G® 1657 could be benzoylated under the same conditions. These results, coupled with the fact that polystyrene can be completely benzoylated, suggest that the poly(ethylene-*co*-butene) segments in Kraton G® may make it difficult for styrene units near them to become benzoylated. This could be due to an

ability of the poly(ethylene-*co*-butene) segments to render the local solvent environment of some styrene units to be less polar than that of others and thereby make them more difficult to benzoylate. This effect would be larger for Kraton G® 1657 than for Kraton G® 1652 because the polystyrene segments in the former are much shorter than are those of the latter. Thus, a larger proportion of the styrene units in the 1657 polymer could have their reactivity influenced by a neighboring poly(ethylene-*co*-butene) segment than would be the case for the 1652 polymer. Weiss and coworkers[10] also reported that polystyrene and Kraton G® 1652 differ in their reactivity toward acetyl sulfate. This phenomenon merits further study. It is interesting to note that acetylation of styrene–acrylonitrile copolymers has been reported to be influenced by the copolymer microstructure.[30]

Gel permeation chromatography was used to evaluate the possibility that polymer chain degradation or crosslinking might have accompanied the benzoylation process. Since multiblock materials were being considered and since the compositions of one of the blocks varied, only molecular weight distributions and relative molecular weights were studied. Table I lists M_n/M_n^0 and M_w/M_n values for benzoylated polymers produced using various reaction conditions. The M_n/M_n^0 values compare the number-average molecular weights of the benzoylated products to those of the original Kraton. Also included in Table I are M_n/M_n^0 values calculated for the benzoylated polymers, based on the extents of benzoylation. The agreement between the measured and calculated M_n/M_n^0 values is surprisingly good, in view of the large differences in the polymer–solvent interaction that might be expected to prevail between the original and the benzoylated copolymers. This suggests that little, if any, chain degradation accompanies the benzoylation reaction. M_w/M_n values increase slightly as benzoylation proceeds, suggesting that branching reactions may occur to a minor extent. This is especially evident when the polymer concentration is high, as shown by the data in Table II.

TABLE III
Glass Transitions Measured for Kraton G® 1652 and
Benzoylated Derivatives by DMTA

Mol % styrene units benzoylated	T_g (E-*co*-B)[a] (°C)	T_g (S)[a] (°C)
0	−34	98
35	−38	114
45	−34	116
53	—	118
70	−34	121

[a] E-*co*-B, poly(ethylene-*co*-butene); S, polystyrene.

Physical and mechanical properties

DMTA measurements were used to evaluate glass transition temperatures for Kraton G® 1652 and its
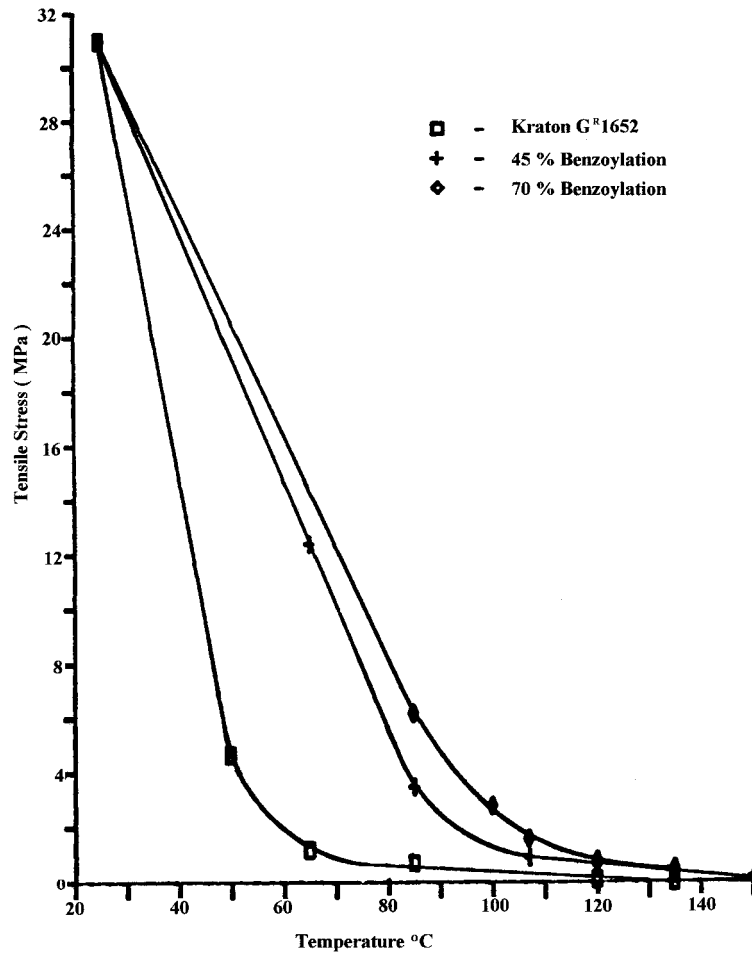
Figure 2 Tensile strength at various temperatures for Kraton G® 1652 and benzoylated derivatives.

benzoylated derivatives. Differential scanning calorimetry was not suitable for these measurements because the proportion of polystyrene segments in the samples was so low that transitions occurring within such segments could not be detected well. Table III provides the results of the DMTA measurements. The glass transition temperature of the poly(ethylene-*co*-butene) midblocks of the copolymers are unchanged by benzoylation of the polystyrene end blocks. The glass transition temperatures of the end blocks
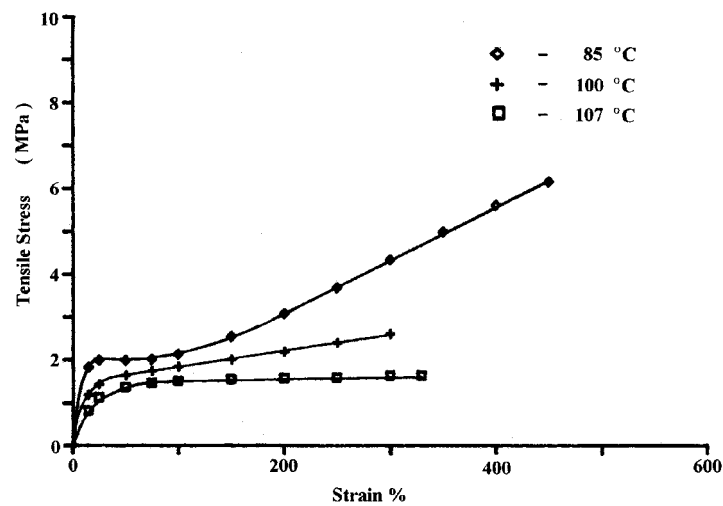

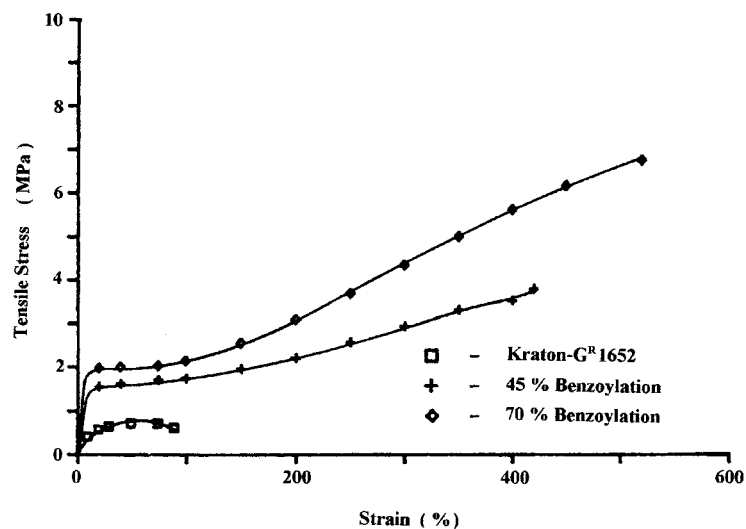**Figure 3** Stress–strain plots for 70% benzoylated Kraton G® at 85–107°C.

Figure 4 Stress–strain plots for Kraton G® 1652 and benzoylated derivatives at 85°C.

steadily increase from 98° for the unmodified polymer to 121° for the polymer that was 70% benzoylated. A Fox plot[31] was constructed from these values to estimate the glass temperature that would be expected for completely benzoylated polystyrene segments. The value obtained by extrapolation of the plot was 128°C.

Moldings prepared from the parent and benzoylated samples were tested from 25–150°C. As should be expected, tensile strengths and tensile moduli decreased dramatically with increasing temperature and the permanent set increased as the test temperature increased. Figure 2 shows the tensile strengths measured for Kraton G® 1652 and several of its benzoylated derivatives at various temperatures. The parent polymer has no strength above 65°C, whereas the 45 and 70% benzoylated materials have tensile strengths of 4–6 MPa (580–870 psi) at 85°C. Kraton G® 1652 must be at or below 50°C to have a tensile strength of 4 MPa.

Figure 3 shows stress–strain curves observed for the 70 % benzoylated polymer at various temperatures. The polymer shows elastomeric behavior at 85°C but undergoes viscous flow at 107°C. Since viscous flow occurs with Kraton G® 1652 at about 65°C, one may conclude that the upper temperature utility of this polymer can be increased approximately 40° by benzoylation. Figure 4 shows stress–strain data obtained at 85°C for Kraton G® 1652 and the 45 and 70% ben-

zoylated materials. It can be seen that benzoylation increases the modulus, ultimate strength, and ultimate elongation. Figures 3 and 4 indicate that the benzoylated materials have high initial moduli and that they undergo strain softening when initially stretched. The samples had to be stretched several times to 100% elongation before they exhibited reproducible hysteresis loops. This behavior is attributed to the existence of connectivity between the benzoylated polystyrene domains in the polymers, a result of the high volume fraction of benzoylated polystyrene segments.

It is known from studies on polystyrene–polybutadiene–polystyrene triblock copolymers that the Young's modulus increases when the polystyrene content of the copolymers is increased.[32] Table IV contains values of the initial (Young's) moduli measured for Kraton G® 1652 and the 45 and 70% benzoylated polymers at several temperatures. The values increase with an increasing extent of benzoylation and decrease with increasing temperature, as should be expected.

Permanent set information was obtained by elongating tensile specimens 100 % and then measuring the unrecovered elongation 3 min after removal of the stress. The values were similar for the parent and benzoylated polymers. Values obtained at various temperatures are listed in Table V. The benzoylated polymers had slightly higher permanent sets than those of the parent polymer

TABLE IV
Initial (Young's) Moduli of Kraton G® 1652 and of Benzoylated Derivatives at Several Temperatures

% Benzoylation	Young's modulus (MPa)				
	50°C	65°C	85°C	100°C	107°C
0	6	3	1.5	—	—
45	—	—	4.0	—	—
70	—	—	16.0	9	5.5

TABLE V
Permanent Set Data for Kraton G® 1652 and Benzoylated Derivatives at Various Temperatures

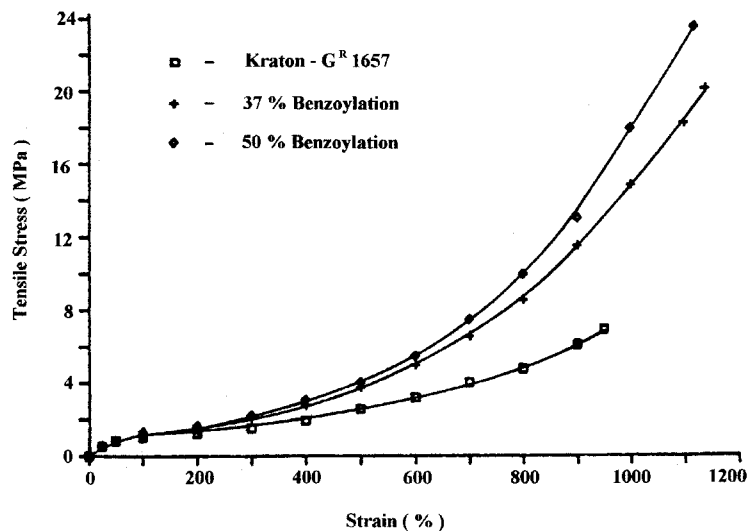| Sample	Permanent set			
	25°C	60°C	85°C	100°C
Kraton G® 1652	7	14	—	—
45% Benzoylated product	10	—	17	40
70% Benzoylated product	13	—	25	37

Figure 5 Stress–strain plots for Kraton G® 1657 and several benzoylated derivatives at 25°C.

at room temperature. This is attributed to the loss of connectivity between hard phases in the benzoylated copolymers which have a higher volume fraction of the hard phase than has the parent copolymer.

Studies on benzoylated Kraton G® 1657

The high initial modulus yield stress and permanent set values observed for the benzoylated Kraton G® 1652 samples compared to those of the parent copolymer are attributed to the fact that the volume fraction of benzoylated polystyrene segments in the benzoylated copolymers is higher than is the volume fraction of polystyrene segments in Kraton G® 1652. To obtain benzoylated Kraton G® samples with a lower volume fraction of benzoylated polystyrene segments, Kraton G® 1657 was benzoylated. This copolymer contains only 13 wt % polystyrene segments, whereas Kraton G® 1652 contains 30 wt % polystyrene segments. Benzoylation of Kraton G® 1657 thus enabled polymers to be prepared that had high proportions of the polystyrene segments benzoylated and in which the volume fraction of the benzoylated polystyrene segments was low enough that little connectivity between the benzoylated polystyrene phases could occur. Although Kraton G® 1657 contains about 30 wt % of diblock material and exhibits poor tensile properties at ambient temperature, benzoylation of this polymer improves the tensile properties dramatically. This is illustrated in Figure 5, which shows stress–strain curves for Kraton G® 1657 and its 37 and 50% benzoylated derivatives at 25°C. Furthermore, the benzoylated derivatives have low initial moduli and do not exhibit strain softening. Unfortunately, the tensile strengths of the benzoylated Kraton G® 1657's are not above 3 MPa at 65°C.[29]

CONCLUSIONS

The softening points and therefore the utility of SEBS triblock thermoplastic elastomers at high temperatures can be increased by benzoylating the styrene units in the copolymers. This increases the glass transition temperature of the hard segments in the polymers without influencing that of the central poly(ethylene-*co*-butene) segments. Benzoylation apparently increases the volume fraction of the hard phase in these polymers sufficiently that the hard phase becomes interconnected. This causes the polymers to have high initial moduli and to exhibit strain softening.

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