

# ***Stress-Strain Behavior of a Fractionated Cariflex\* SBS Rubber***

## **INTRODUCTION**

Fetters et al.<sup>1</sup> have reported the presence of three peaks in the gel permeation chromatograms of commercial samples (Cariflex 1101 and Cariflex 1102) of ABA poly(styrene-*b*-butadiene) block copolymer. These peaks were assigned to polystyrene homopolymer, AB poly(styrene-*b*-butadiene) diblock copolymer as well as the triblock copolymer. However, Inagaki et al.<sup>2</sup> using a thin-layer chromatography technique argued that the peak attributed to diblock was wrongly ascribed and was in fact caused by the presence of an ABA poly(styrene-*b*-butadiene) copolymer of lower molecular weight than the main triblock component.

The effects of these polymeric impurities on this type of ABA block copolymer have been investigated<sup>1,3,4</sup> and reviewed by Fetters.<sup>5</sup> For an SIS block copolymer it was found<sup>5</sup> that added low molecular weight polystyrene was located in the polystyrene domains with the result that the material simply behaved as an SIS copolymer of higher styrene content. If the molecular weight of the added polystyrene is significantly greater than the endblock molecular weight, it is not all situated in the domains.<sup>5</sup> Addition of extra midblock homopolymer leads to a decrease in tensile strength.<sup>5</sup> The blending of SB diblock copolymer into pure SBS rubber even at low levels has a very significant effect on tensile strength,<sup>5</sup> but for up to at least 5% of added diblock there is very little difference in the values of the stress at 400% strain and the percentage set at break.<sup>5</sup> This is what would be expected for the addition of a species which can only be trapped at one end.

In this note we report on the stress-strain behavior of a Cariflex 1102 sample which has been carefully fractionated to remove the polymeric impurities in an attempt to repeat the findings of the already mentioned blending experiments and check the conclusion of Inagaki et al.<sup>2</sup> concerning the nature of the major impurity.

## **EXPERIMENTAL**

The characterization data for both Cariflex 1101 and 1102 are given in Table I. The two low molecular weight components seen in the Cariflex 1102 chromatogram were removed by a simple fractional precipitation procedure using a 1% (w/v) solution in benzene at  $25 \pm 0.01^\circ\text{C}$ . *N*-Phenyl-2-naphthylamine was added (0.3% w/v) as antioxidant. Precipitation was achieved by adding freshly redistilled ( $\times 3$ ) methanol. The efficiency of the fractionation was monitored by GPC. Four fractionation stages were required to obtain a sample free from both contaminants.

All GPC experiments were performed with 0.25% (w/v) solutions in chloroform using a Waters Associates Model 502 apparatus at an elution rate of 0.2 ml/min. Faster elution rates often show only one peak for samples which are clearly heterogeneous at 0.2 ml/min.

Test pieces for tensile measurements were cut from sheet cast from carbon tetrachloride<sup>6</sup> and dried under high vacuum at  $50^\circ\text{C}$  for 14 days. Examination of the samples by infrared spectroscopy showed no evidence of residual solvent. The tensile test pieces were strained at a rate of 2.5 cm/min at  $20^\circ\text{C}$  using a Howden tensometer.

## **RESULTS AND DISCUSSION**

From the GPC traces, using a DuPont Curve Resolver Model 310, it was found that Cariflex 1101 contained 63% triblock while for Cariflex 1102 the triblock component accounted for 69% of this commercial sample. Cariflex 1101 contained 8% polystyrene and Cariflex 1102 contained only 2%, leaving in both cases the major impurity at a level of 29% which is appreciably higher than the value of 19% reported by Fetters<sup>5</sup> for a supposedly identical sample (Kraton 1101).

It was also found that the molecular weights of the major impurity for both Cariflex 1101 and 1102 were approximately half that of the triblock, which lends considerable credence to the idea that this component results as the consequence of an incomplete coupling reaction.<sup>5</sup>

As stated earlier, the effects of homopolymer and diblock copolymer impurities on the mechanical

\* Known as Kraton in the United States.

TABLE I  
Characterization Data

	Cariflex 1101	Cariflex 1102	FA2
Composition, wt-%			
Triblock	63	69	100
Major impurity	29	29	0
Polystyrene	8	2	0
$\bar{M}_n \times 10^{-3}$	100	64	84
$\bar{M}_w/\bar{M}_n$	1.48	1.44	1.08
Styrene, wt-%	27	25.5	25.5
Microstructure, %			
<i>trans</i> -1,4-	45	47	46
<i>cis</i> -1,4-	38	38	39
1,2-	17	15	15

TABLE II  
Stress-Strain Data

Property	Cariflex 1102	FA2
Stress at 10% strain, kg/cm <sup>2</sup>	7.1	7.2
Stress at 100% strain, kg/cm <sup>2</sup>	16.5	18.5
Stress at 300% strain, kg/cm <sup>2</sup>	21.6	23.8
10% Modulus, kg/cm <sup>2</sup>	71.0	72.0
100% Modulus, kg/cm <sup>2</sup>	16.5	18.5
300% Modulus, kg/cm <sup>2</sup>	7.2	7.9

properties of SBS and SIS block copolymers have been investigated<sup>1,3,5</sup> by adding these contaminants to pure triblock polymers. This work is believed to be the first report on the effect of removing the impurities from a commercially available material by fractional precipitation. The effect of this is shown in Figure 1 and Table II, where Cariflex 1102 and sample FA2, a fractionated sample of Cariflex 1102, are compared up to about 700% strain.

The removal of the impurities clearly results in enhanced tensile properties, but the change is not as dramatic as might have been expected following the removal of 31% by weight of nontriblock

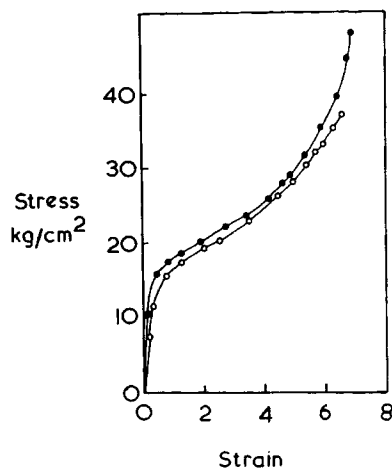


Fig. 1. Stress-strain diagram for Cariflex 1102 (O) and fractionated sample FA2 (●).

polymer. At 10% strain the gain in modulus is minimal, but at 100% and 300% strain, the gain is around 10%.

If the Inagaki suggestion<sup>2</sup> is correct, it would be reasonable to suppose that the removal of a lower molecular weight triblock fraction, which would have a significant proportion of its endblocks located in polystyrene domains, would result in an extension to higher strains of the linear part of the stress-strain curve beyond the yield point. In fact, both curves in Figure 1 cease to be linear at around 370% strain.

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