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# **Dynamic Mechanical Study of Sodium Sulfonated Random Ionomers based on Hydrogenated Styrene-Butadiene Copolymer**

**(Supplementary Material)**

by

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## Plots of Representative Dynamic Mechanical Data for the P(SEB-7.6-SSNa).

Figure A(a) shows the storage modulus as a function of temperature at 1 Hz;  $m_m$  and  $m_c$  indicate, respectively, the slopes of the plot in the region of the glass transition of the matrix and the cluster; in addition,  $E'_g$  and  $E'_i$  indicate, respectively, the storage modulus in the glassy region (at -40 °C), at the ionic plateau (at 50 °C). In the study performed by Kim et al.,<sup>1</sup>  $E'_g$  was defined as either the value of  $E'$  at 100 °C or at a temperature 40 °C below the lower  $T_g$ ; in addition  $E'_i$  was defined as the value of  $E'$  at the point of minimum slope. In the present study, because the lower  $T_g$ , which is obtained from the peak of the loss tangent curve, changes only from -8 to 10 °C with an increase in the ion content (see Figure 4),  $E'_g$  is defined as the value of  $E'$  at -40 °C; moreover, because the ionic plateau is well developed and the slope of the  $E'_i$  is nearly zero over a wide range of temperatures,  $E'_i$  is defined as the value of  $E'$  at 50 °C.

Figure A(b) shows the loss modulus ( $\log E''$ ) as a function of temperature at 1 Hz;  $T''_{g,m}$  and  $T''_{g,c}$  are obtained from the peak maxima of the glass transitions of the matrix and cluster regions, respectively. Figure A(c) shows the loss tangent ( $\tan \delta$ ) as a function of temperature at 1 Hz;  $A_m$  and  $A_c$  are, respectively, the peak areas of the glass transitions of the matrix and cluster regions. Also the peak maxima ( $T_{g,m}$  and  $T_{g,c}$ ), the peak heights ( $H_m$  and  $H_c$ ) and the peak widths at half-height ( $W_m$  and  $W_c$ ) of the two glass transitions are obtained from Figure A(c). It should be mentioned that these ionomers show a third  $\tan \delta$  peak in addition to the peaks of the glass transitions of the matrix and cluster regions. This peak appears at 240–300 °C in each ionomer. The presence of a high temperature peak above  $T_g$  was also seen in other polymer systems, including ionomers. In some cases, it was called “dynamic cross-linking” and ascribed to the decomposition and cross-linking of the polymer, in studies by Lee and Goldfarb<sup>2</sup> and by Gauthier and Eisenberg.<sup>3</sup> Figure A(c) shows the area  $A_d$  of the third peak, the subscript “d” indicating decomposition. The peak area was ca. 10 % of the sum of the values of  $A_m$  and  $A_c$ . The peak position and area were found to be independent of ion concentration. The values of  $A_c$  were obtained after the elimination of the value of  $A_d$  from the overlapping peaks.

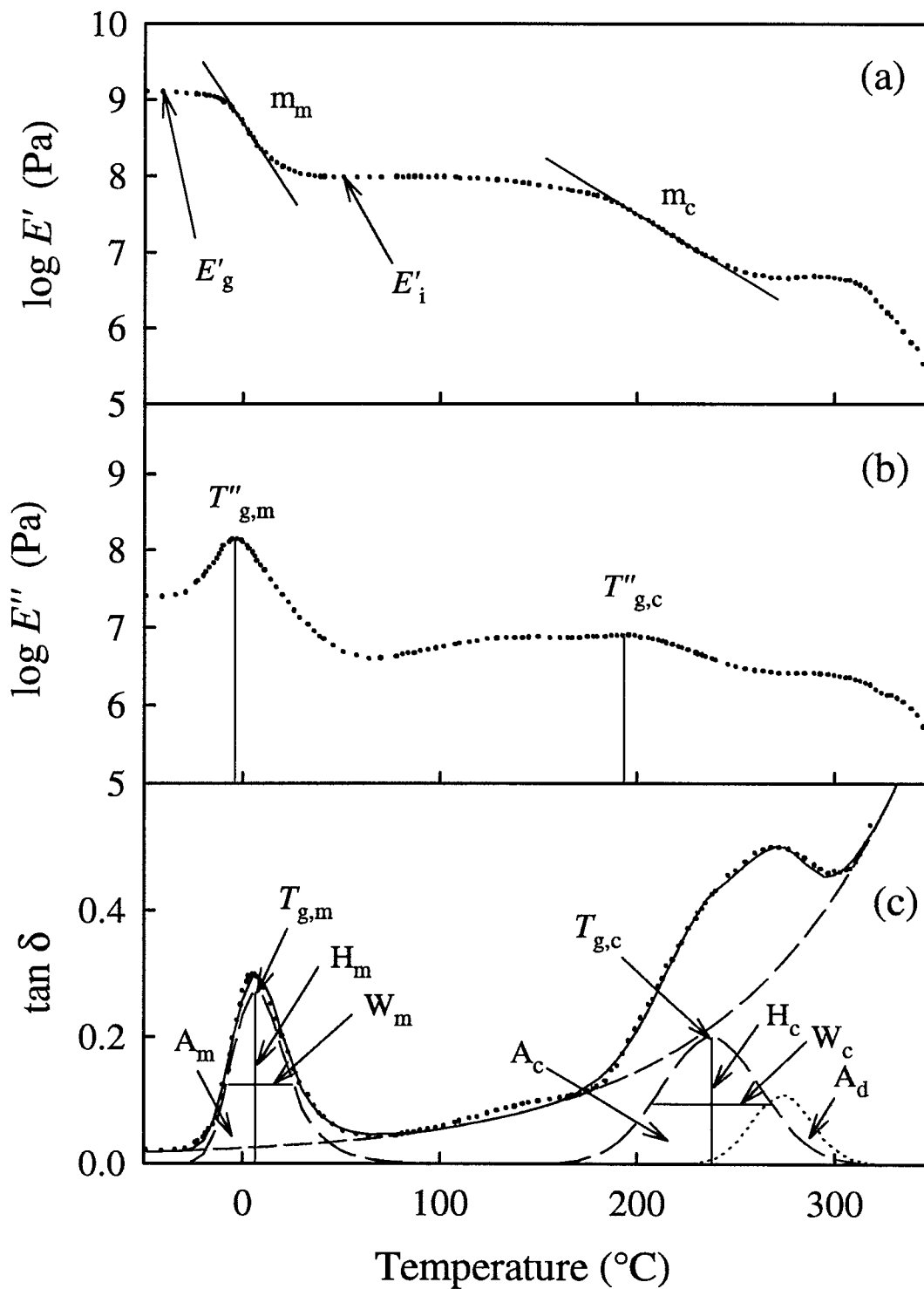


Figure A. Plots as a function of temperature for P(SEB-7.6-SSNa) at 1 Hz of (a) the logarithm of the storage modulus, (b) the logarithm of the loss modulus, and (c) the loss tangent.

**Table A. Density and Glassy Modulus at 1 Hz as a Function of Ion Content**

sample notation	ion content (meq/cm <sup>3</sup> )	density (g/cm <sup>3</sup> )	log $E'_g$ at -40°C (Pa)
PSEB	0.00	0.95	9.281
P(SEB-0.5-SSNa)	0.11	--	9.239
P(SEB-1.8-SSNa)	0.38	0.97	9.283
P(SEB-2.4-SSNa)	0.50	---	9.285
P(SEB-4.0-SSNa)	0.82	0.99	9.256
P(SEB-5.4-SSNa)	1.09	---	9.287
P(SEB-5.8-SSNa)	1.17	1.02	9.296
P(SEB-7.2-SSNa)	1.42	---	9.246
P(SEB-7.6-SSNa)	1.50	1.04	9.238
P(SEB-7.7-SSNa)	1.52	---	9.295
P(SEB-9.0-SSNa)	1.75	1.07	9.291
P(SEB-12-SSNa)	2.27	1.05	9.229
P(SEB-15-SSNa)	2.79	1.13	9.282
P(SEB-18-SSNa)	3.28	1.15	9.228
		mean:	9.27±0.05

## Changes in the Properties of the Matrix and Cluster Phases as a function of Ion Content.

Figures B(a)–(c) show, respectively, the slope  $m_m$  of the storage modulus, the width  $W_m$  at half-height of the  $\tan \delta$  peak, and the peak height  $H_m$  of the  $\tan \delta$  curve in the glass transition of the matrix phase, plotted against ion content.  $H_m$  decreases with increasing ion content, in parallel with the behavior of other ionomer systems.<sup>1,4-6</sup> The trend of  $H_m$  corresponds to that of  $A_m$ , but the trends of  $W_m$  and  $m_m$  are different. In the range of 0–3 mol % ion content,  $\log(m_m)$  and  $W_m$  are almost constant.  $\log(m_m)$  decreases with increasing ion contents over 3 mol %.  $W_m$  increases slightly with increasing ion content until 8–9 mol %, beyond which it levels off. The activation energies ( $E_{a,m}$ ) for the glass transition of the matrix phase are plotted against ion content in Figure D(a).  $E_{a,m}$  is almost constant until 8–9 mol %, beyond which it decreases with increasing ion content. These properties of the matrix phase are discussed in a later section.

Figure C(a)–(c) show, respectively, the slope  $m_c$  of storage modulus, the width  $W_c$  at half-height of the  $\tan \delta$  peak and the peak height  $H_c$  of  $\tan \delta$  for the glass transition of the cluster phase, plotted against the ion content. Similar to the result for the matrix phase, the trend of the  $H_c$  against ion content parallels that of  $A_c$ , while those for the  $W_c$  and  $m_c$  are different.  $W_c$  does not change much over the range of ion contents studied here. Below ca. 7 mol %,  $m_c$  increases slightly with ion content, between 7 and 9 mol %, it increases up to a value of ca. 0.025, and beyond 9 mol %, it remains constant. The activation energies ( $E_{a,c}$ ) for the glass transition of the cluster phase are plotted against ion content in Figure D(b) in the supplementary material. Because of scatter in the data points, a detailed analysis for  $E_{a,c}$  is difficult. However it seems to increase with increasing ion content. The activation energies for ion hopping, which were calculated from the frequency dependence of the intersection of linear segments of the  $\log E'$  plot,<sup>7</sup> show almost the same tendency as was seen for  $E_{a,c}$ . These properties of the cluster phase are discussed along with those of the matrix phase in a later section.

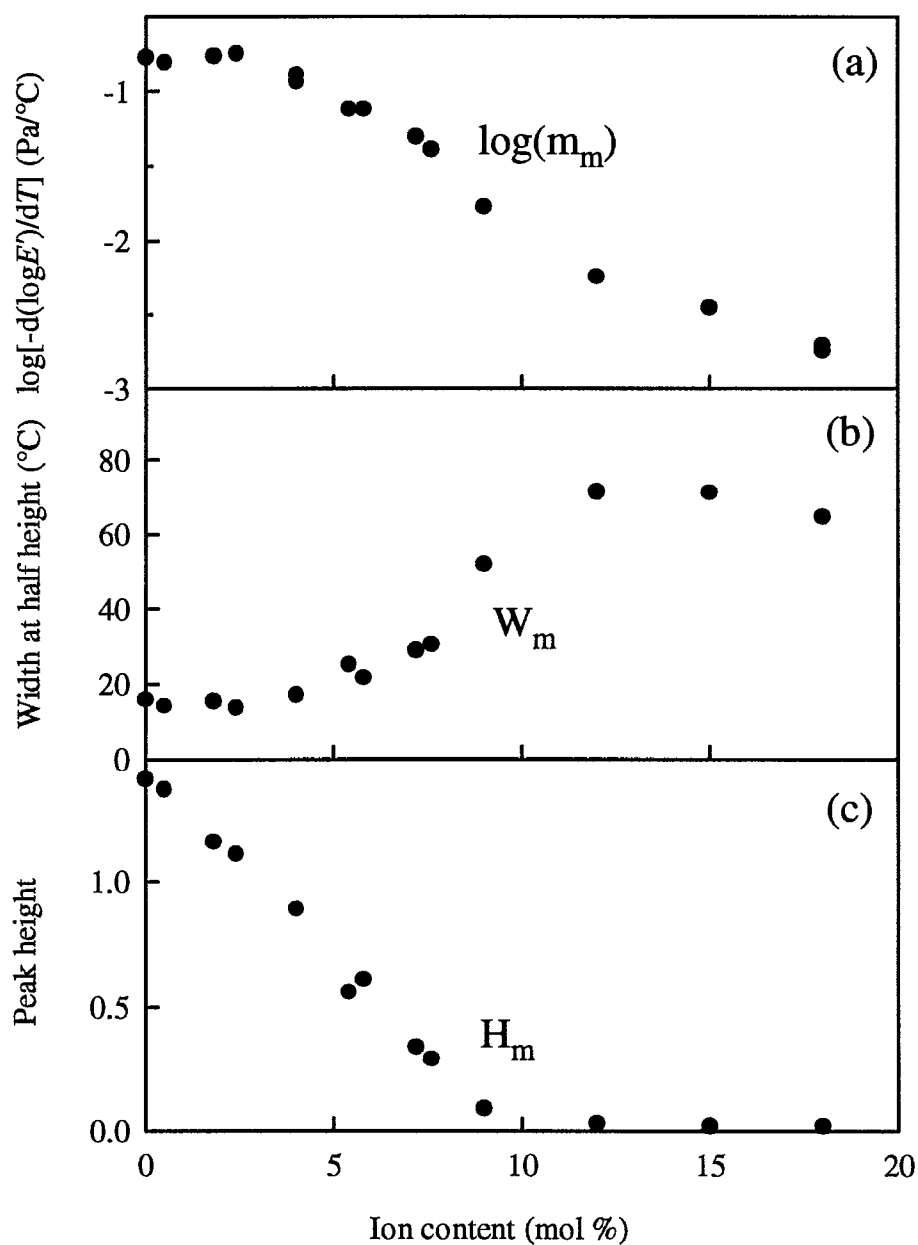


Figure B. (a) Plots of the logarithm of the slope of  $\log E'$ , (b) the width at half height of  $\tan \delta$  peak, and (c) the peak height of  $\tan \delta$  curve for the glass transition of the matrix, versus ion content (mol %).

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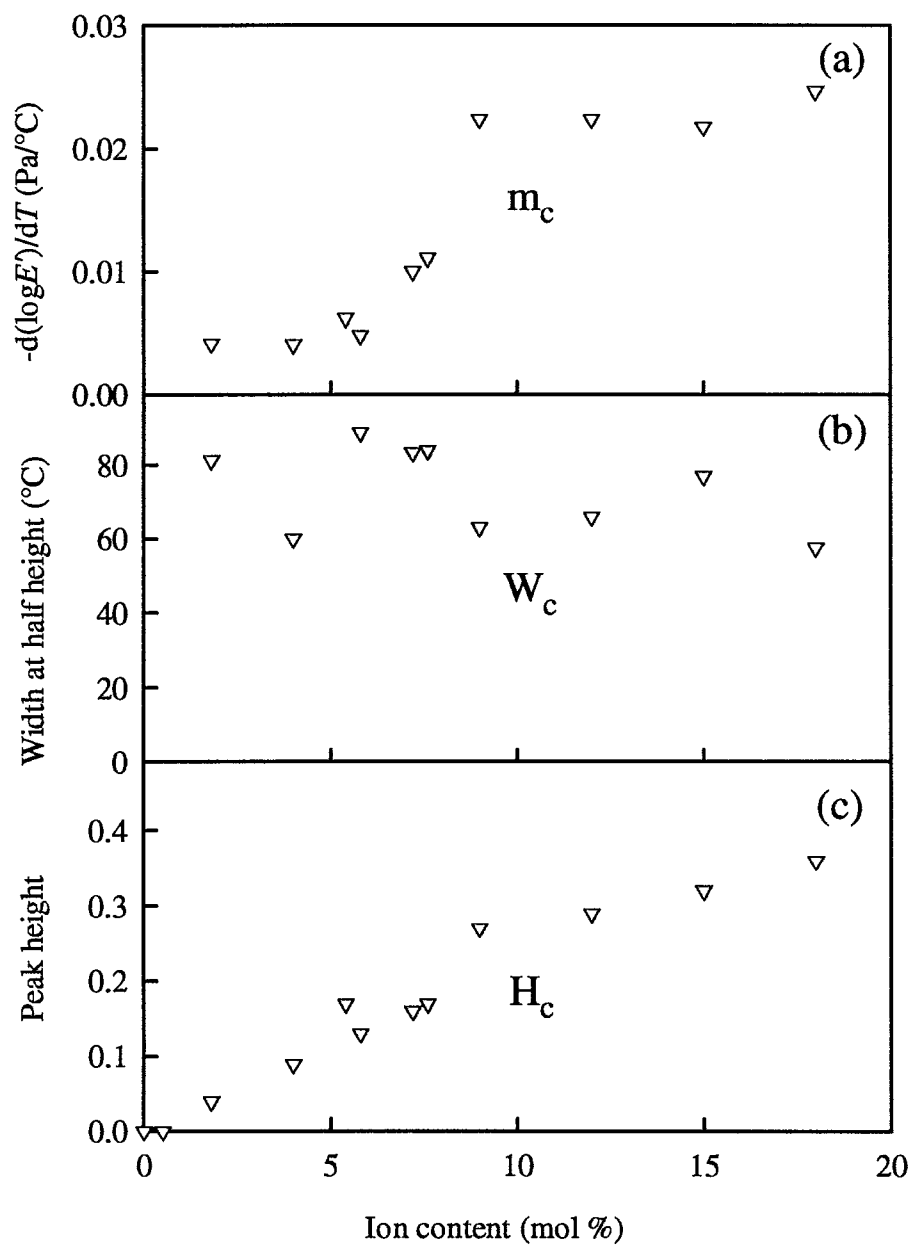


Figure C. (a) Plots of the slope of  $\log E'$ , (b) the width at half height of  $\tan \delta$  peak, and (c) the peak height of  $\tan \delta$  curve for the glass transition of the cluster, versus ion content (mol %).



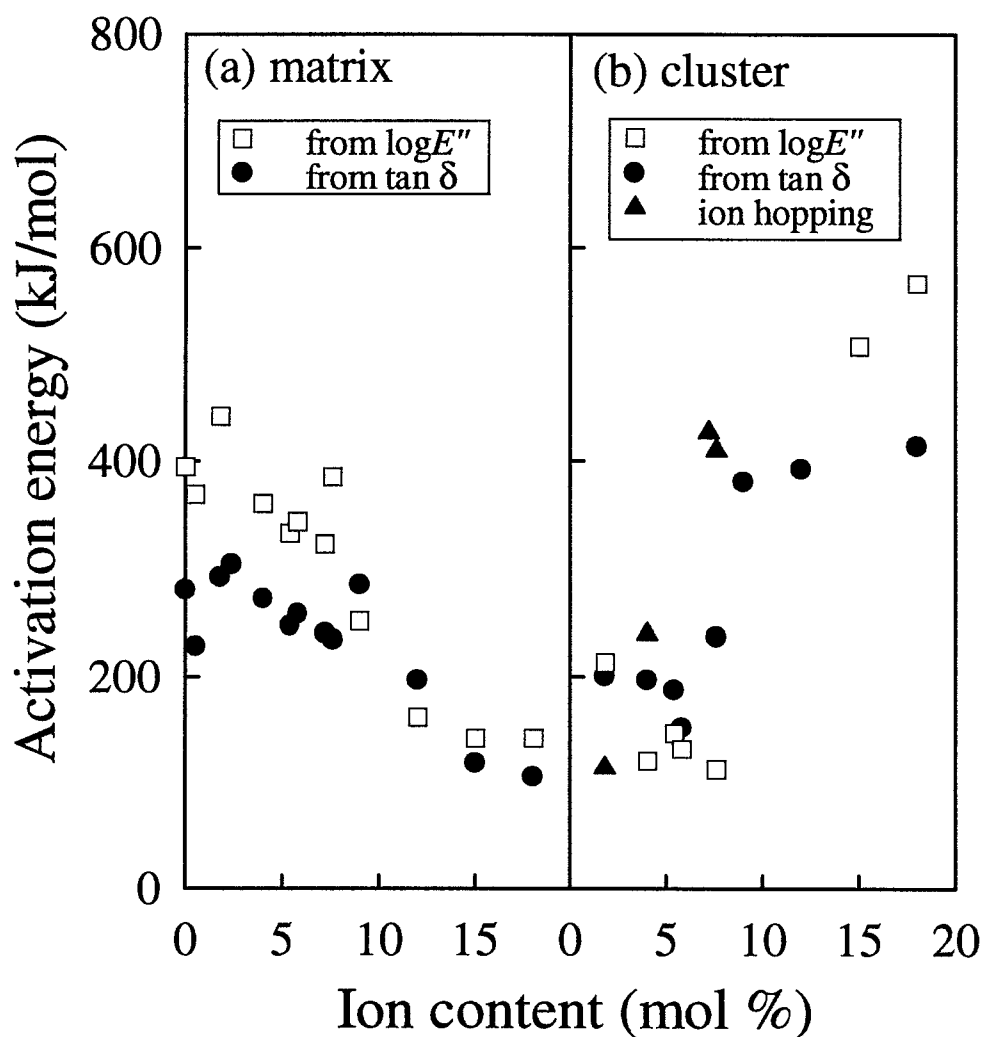


Figure D. (a) The activation energies of the glass transition of the matrix from  $\log E''$  ( $\square$ ) and  $\tan \delta$  ( $\bullet$ ) for versus ion content (mol %), (b) the activation energies of the glass transition of the cluster from  $\log E''$  ( $\square$ ),  $\tan \delta$  ( $\bullet$ ), and ion hopping ( $\blacktriangle$ ) for ion content (mol %).

### Modification of the Halpin-Tsai equations for the present system.

The Halpin-Tsai equation<sup>8</sup> used for the interpretation of the regular system is

$$\frac{M}{M_1} = \frac{1 + A_{\text{reg}} B_{\text{reg}} \phi_2}{1 - B_{\text{reg}} \psi \phi_2}$$

$M$  is the modulus of the system. The subscripts 1 and 2 refer, respectively, to the continuous phase and the dispersed phase. In the regular filled system, i.e. at low ion contents, the dispersed phase is the cluster, and the continuous phase is the matrix. In that case, the equation becomes

$$\frac{E'_c}{E'_m} = \frac{1 + A_{\text{reg}} B_{\text{reg}} \phi_c}{1 - B_{\text{reg}} \psi \phi_c}$$

where

$$B_{\text{reg}} = \frac{E'_c/E'_m - 1}{E'_c/E'_m + A_{\text{reg}}}$$

$$A_{\text{reg}} = k_E - 1$$

$$\psi = 1 + \frac{1 - \phi_{c,\text{max}}}{\phi_{c,\text{max}}^2} \phi_c$$

$E'_c$  and  $E'_m$  are the storage moduli of the clusters and the matrix phase in the ionic plateau region, respectively.  $A_{\text{reg}}$  is a constant dependent on geometry of the dispersed phase and Poisson's ratio of the continuous phase, and  $k_E$  is the Einstein coefficient.  $B$  is a constant dependent on the relative moduli of the dispersed and continuous phases,  $\phi_c$  is the volume fraction of the cluster phase, and  $\psi$  is a factor dependent on the maximum packing fraction  $\phi_{c,\text{max}}$  of the clusters in the regular system. The maximum packing fraction is the point beyond which the dispersed phase becomes continuous and the system can no longer be regarded as a filler system. The value of  $A_{\text{reg}}$  is generally given by

$$A_{\text{reg}} = \frac{7 - 5\nu_m}{8 - 10\nu_m}$$

where  $\nu_m$  is Poisson's ratio for the continuous phase (the matrix). In the range of regular systems in this study, the matrix phase is the rubbery PSEB, and therefore  $\nu_m$  is 0.50,<sup>9</sup> and  $A$  is 1.50.

In the inverted system, the Halpin-Tsai equation is

$$\frac{M_1}{M} = \frac{1 + A_{\text{inv}} B_{\text{inv}} \phi_2}{1 - B_{\text{inv}} \psi \phi_2}$$

The subscripts 1 and 2 in the inverted system retain the same meanings as those in the regular system. In the inverted system, the dispersed phase is the matrix, and the continuous phase is the cluster. The equations is

$$\frac{E'_i}{E'_c} = \frac{1 - B_{\text{inv}} \psi \phi_m}{1 + A_{\text{inv}} B_{\text{inv}} \phi_m}$$

where

$$B_{\text{inv}} = \frac{E'_c/E'_m - 1}{E'_c/E'_m + A_{\text{inv}}}$$

$$\psi = 1 + \frac{1 - \phi_{m,\text{max}}}{\phi_{m,\text{max}}^2} \phi_m$$

$$A_{\text{inv}} = \frac{8 - 10\nu_c}{7 - 5\nu_c}$$

$\nu_c$  is Poisson's ratio for the continuous phase (the clusters). The matrix acts not as filler particles but as the continuous phase when the volume fraction  $\phi_m$  of the matrix is above the value of the maximum packing fraction  $\phi_{m,\text{max}}$  in the inverted system. Because the cluster phase is thought to be similar to the glassy PSEB, the  $\nu_c$  of the glassy PSEB was calculated as the volume average of those of polyethylene, polybutylene and polystyrene. Therefore  $\nu_c$  is 0.44,<sup>9</sup> and  $A_{\text{inv}}$  is 0.75.

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