

# Storage Modulus of Polybutadiene Core in Acrylonitrile–Butadiene–Styrene Polymers with Different Degrees of Grafting

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**ABSTRACT:** The linear viscoelastic behavior of acrylonitrile-butadiene-styrene (ABS) polymers in the molten state, with different degrees of grafting, was investigated within the framework of Palierne's emulsion model. The main aim of the present study is to quantitatively analyze the effect of grafting degree on the storage modulus  $G'$  of the polybutadiene (PB) rubber core dispersed in ABS polymers. According to our model calculations, the degree of grafting significantly affects the  $G'$  values of the PB core and, hence, the viscoelastic properties of ABS polymers. Our calculations showed that the Palierne model is very useful to calculate the storage modulus of the rubber particles dispersed in rubber-modified polymeric materials, at least in the high-frequency region. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 924–930, 2001

**Key words:** ABS polymers; degree of grafting; linear viscoelasticity; Palierne model

## INTRODUCTION

Acrylonitrile-butadiene-styrene (ABS) terpolymers have been widely used in various industrial fields because of their high impact resistance, good dimensional stability, and good processability. Most ABS polymers are made by grafting styrene and acrylonitrile monomers directly onto crosslinked polybutadiene (PB) latex particles in a batch or continuous emulsion polymerization process. ABS polymer thus obtained consists of a styrene–acrylonitrile (SAN) copolymer matrix in which SAN-grafted PB particles are dispersed. The viscoelastic properties of ABS polymers should depend on the amount of SAN grafted onto

the PB particles. In particular, the modulus of the PB particles dispersed in the SAN matrix is greatly affected by the degree of grafting.<sup>1,2</sup> Many studies of the viscoelastic behavior of ABS polymers in the molten state can be found in the literature,<sup>3–8</sup> but there seems no direct way of determining the storage modulus of the dispersed PB particles in ABS polymers.

Recently, Palierne<sup>9,10</sup> proposed an excellent linear viscoelastic model for incompressible viscoelastic emulsions. Comparison of the Palierne model with many experimental results<sup>11–13</sup> proved that it is very useful for predicting the rheological behavior of incompatible polymer blends under small amplitude oscillatory flow. In the Palierne model, the complex shear modulus of the emulsion is expressed as a function of the complex shear moduli of matrix and inclusions. Therefore, the complex modulus of inclusions can

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**Table I Structural Characteristics of ABS Materials Used in This Study**

Materials	Average Particle Diameter (nm)	Gel Ratio (%)	Rubber Content (%)	Degree of Grafting (%)
ABS1	300	82	21.6	39
ABS2	300	82	21.6	55
ABS3	300	82	21.6	63
ABS4	300	82	21.6	76
ABS5	300	82	21.6	86

be inversely calculated from the complex moduli of the emulsion and matrix.

In the present study we elucidate the effect of grafting degree on the viscoelastic behavior of ABS polymers within the framework of Paliarne's emulsion model. Our aim is to provide a quantitative method of determining the storage shear modulus  $G'$  of the dispersed PB particles in ABS polymers. We also discuss the influence of grafting degree on the  $G'$  values of the PB core and the overall viscoelastic behavior of ABS polymers.

## EXPERIMENTAL

### Materials

Five kinds of ABS polymers, kindly supplied by Cheil Industry Inc. (Korea), were investigated in this study and their structural characteristics are summarized in Table I. For all ABS samples, the polybutadiene (PB) spheres were crosslinked and well defined in size, and their mean particle sizes were determined by transmission electron microscopy (Fig. 1). The acrylonitrile (AN) contents of the matrix and grafted SAN were, respectively, 28.5 and 25% for all ABS materials used in this investigation. When the difference in AN contents is small, the SAN-grafted PB particles are generally expected to be well dispersed in the matrix.<sup>14</sup> This was verified by the transmission electron micrographs for the ABS samples, as shown in Figure 1.

The degree of crosslinking of the PB particles was determined by measuring the gel ratio of ungrafted PB rubber, prior to the grafting of PB latex particles with styrene and acrylonitrile monomers. As seen in Table I, because all structural characteristics except the degree of grafting are the same, any differences between the moduli

of the SAN-grafted PB particles in all ABS materials can be mainly attributed to their different degrees of grafting. The degree of grafting (DG), defined by

$$DG = \frac{\text{weight of grafted SAN}}{\text{weight of PB}}$$

was found to vary from 39% (ABS1) to 86% (ABS5). All ABS pellets were dried at 85°C under vacuum for 2 h and then compression-molded at 200°C into 2-mm-thick plates.

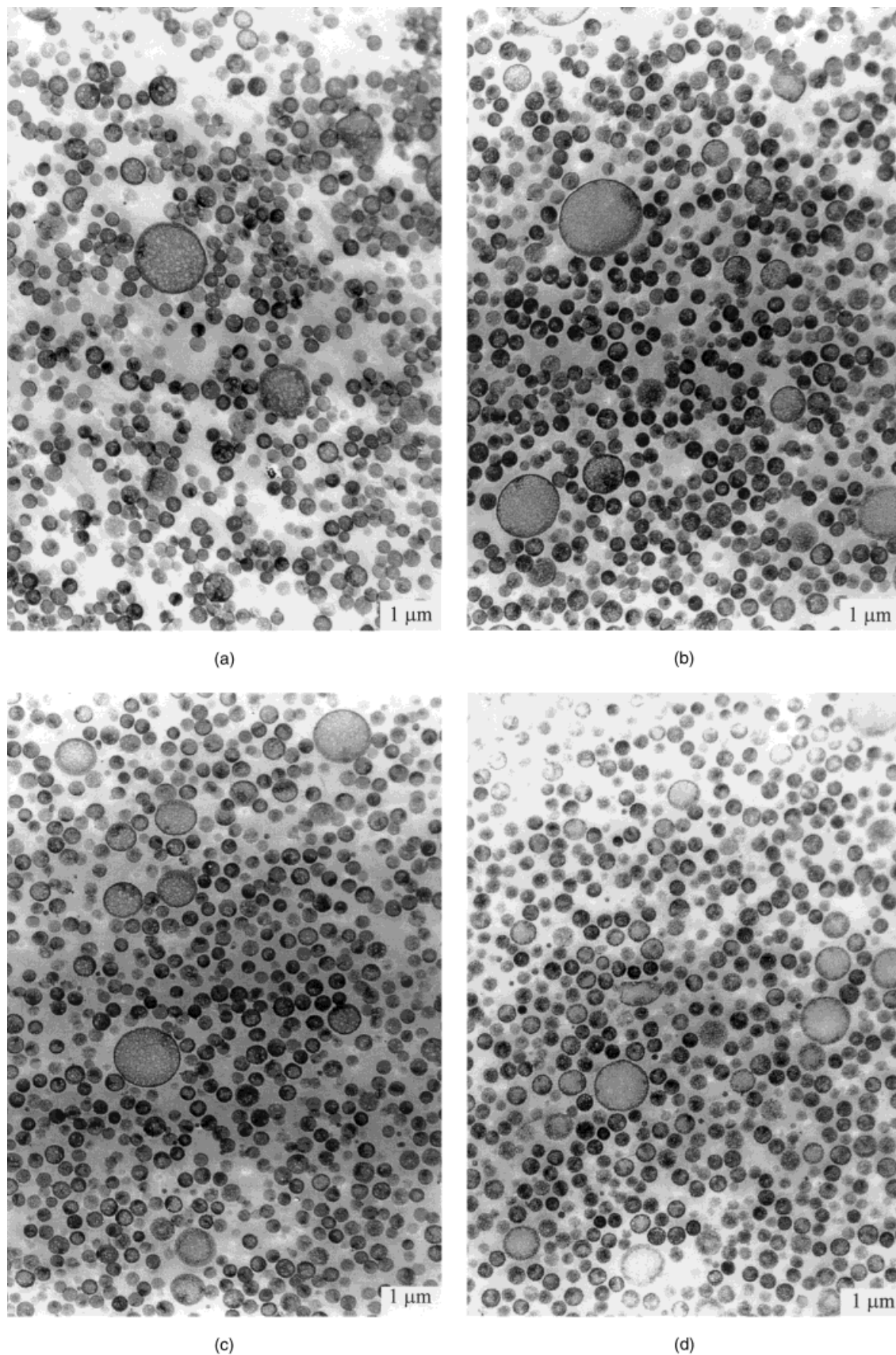
### Rheological Measurements

The dynamic shear measurements of the ABS samples were carried out on a Rheometrics mechanical spectrometer (RMS 800, Rheometric Scientific, USA) with parallel-plate geometry. The sample discs used in this work were 25 mm in diameter and 2 mm in thickness. The frequency sweeps from 0.01 to 100 rad/s were carried out at 190°C. All measurements were performed under nitrogen so as to minimize oxidative degradation at high temperature. The strain amplitude was kept to be at 2% to investigate the linear viscoelastic properties.

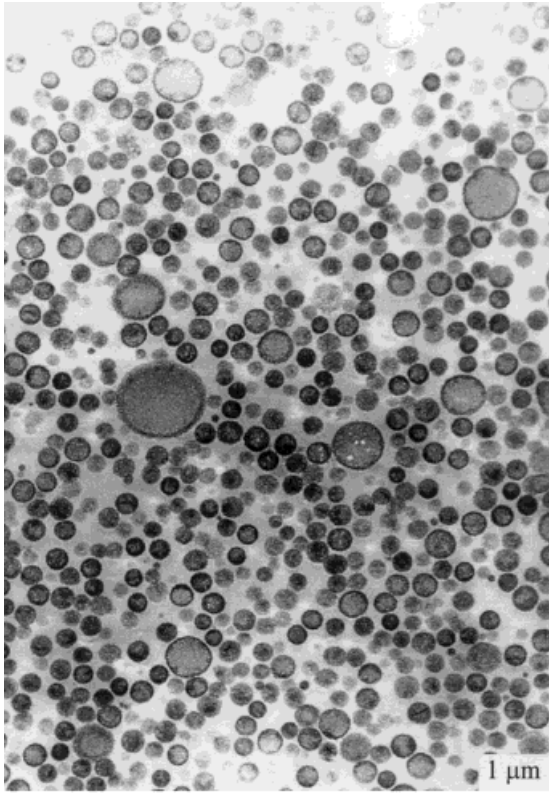
## RESULTS AND DISCUSSION

The complex shear moduli of all ABS samples are provided as a function of frequency, as shown in Figures 2 and 3. Figure 2 shows that the values of the storage modulus  $G'$  of all ABS polymers are much higher, especially at low frequencies, than that of the matrix SAN and that they depend strongly on the DG of the PB particles. The same trend is observed for the experimental values of loss modulus  $G''$ , although the influence of the DG appears to be weak. The data shown in Figures 2 and 3 are in good agreement with earlier experimental results obtained for ABS polymers<sup>3-8</sup> and polymer blends containing core-shell impact modifiers.<sup>15-17</sup>

The complex moduli measured at 0.01 rad/s are plotted as a function of DG in Figure 4. These figures show that the values of  $G'$  and  $G''$  first decrease, then increase as the DG increases. The ABS2 with 55% DG was found to have the lowest values of  $G'$  and  $G''$  among all the ABS samples. The value of DG that gives the lowest  $G'$  and  $G''$  values is sometimes called the critical degree of grafting.<sup>6</sup> A molecular interpretation of this phe-



**Figure 1** Morphology of ABS polymers determined by TEM: (a) ABS1; (b) ABS2; (c) ABS3; (d) ABS4; (e) ABS5.

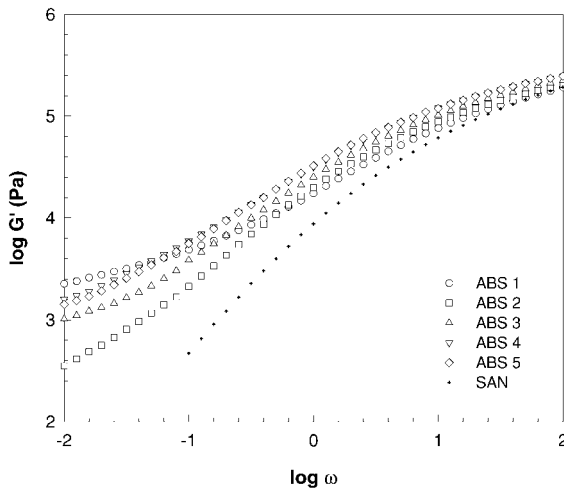
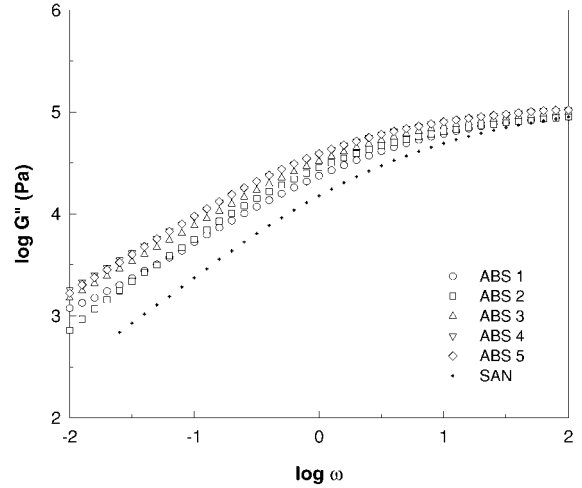


(e)

**Figure 1** (Continued from the previous page)

nomenon has been attempted by the use of a correlation with the theory of de Gennes about conformation of polymers attached to a surface.<sup>8</sup>

In the Palierne model, the complex shear modulus  $G^*(\omega)$  of the blend at a given frequency  $\omega$  can


**Figure 2** Storage modulus versus frequency at 190°C for all ABS samples and SAN.

**Figure 3** Loss modulus versus frequency at 190°C for all ABS samples and SAN.

be expressed as a function of interfacial tension  $\alpha$ , volume fraction  $\phi$ , inclusion radius  $R$ , and the complex moduli of matrix  $G_M^*$  and inclusions  $G_I^*$  at the same frequency:

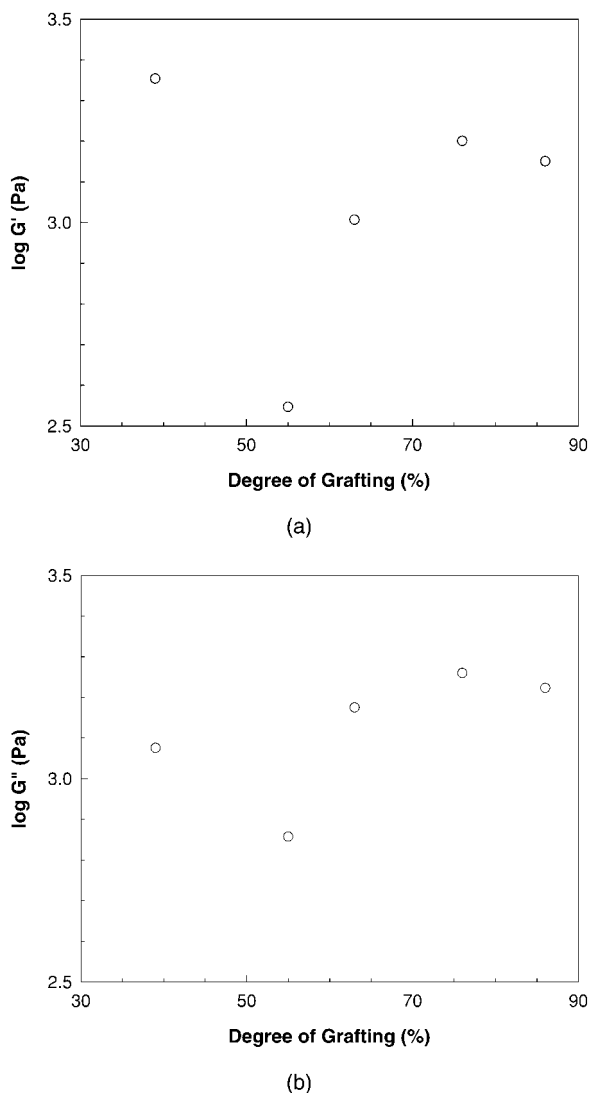
$$G^*(\omega) = G_M^*(\omega) \frac{1 + 3\phi H(\omega)}{1 - 2\phi H(\omega)} \quad (1)$$

where

$H(\omega)$

$$= \frac{[G_I^*(\omega) - G_M^*(\omega)][19G_I^*(\omega) + 16G_M^*(\omega) + 4(\alpha/R)[5G_I^*(\omega) + 2G_M^*(\omega)]}{[2G_I^*(\omega) + 3G_M^*(\omega)][19G_I^*(\omega) + 16G_M^*(\omega)] + 40(\alpha/R)[G_I^*(\omega) + G_M^*(\omega)]} \quad (2)$$

Here, for the sake of simplicity, we assume that the rubber particles are monodisperse in size and that the interfacial tension is constant. For rubber-toughened PMMA blends containing more than 15% impact modifier, Bousmina and Muller<sup>15</sup> found that there is a large deviation of the Palierne model from experimental data in the low-frequency region, whereas the deviation becomes smaller as the frequency increases. They considered that the deviation of the model at low frequencies is the result of a network structure, formed by associating particles, which was not treated in the model. To properly describe the low-frequency behavior of rubber-toughened blends, they also attempted to empirically modify the Palierne model by simply adding a constant  $G$ , which would correspond to the modulus of the



**Figure 4** Storage (a) and loss (b) modulus at  $\omega = 0.01$  rad/s plotted against degree of grafting.

network structure, to the storage modulus of the blend.

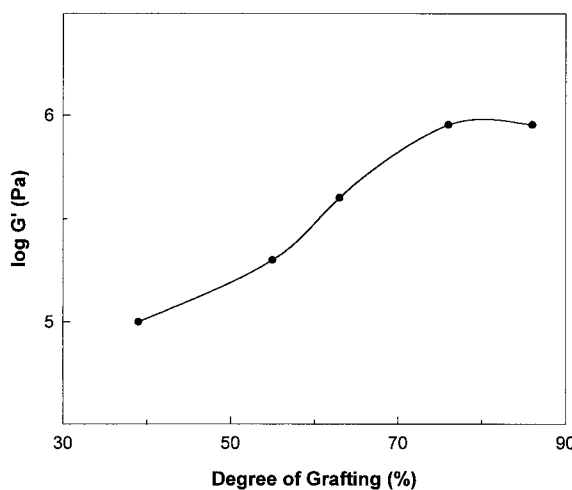
It was also previously reported by various authors<sup>15–17</sup> that the deviation of the Palierne model in the low-frequency region from experimental data increases as the impact modifier level increases. Because the rubber content of all ABS samples used in this work is more than 20%, the Palierne model may not properly describe their low-frequency behavior. However, as verified by other investigators,<sup>15–17</sup> the viscoelastic behavior of rubber-toughened blends can be properly described by the Palierne model in the high-frequency region, where the effect of the network structure on their viscoelastic behavior becomes negligibly small. In other words, in the high-fre-

quency region, the Palierne model can be safely used to calculate the complex storage modulus of the PB core in ABS samples. Therefore, in this work the frequency range was taken to be from 10 to 100 rad/s, where the Palierne model is considered to be able to properly predict the viscoelastic behavior of all ABS samples.

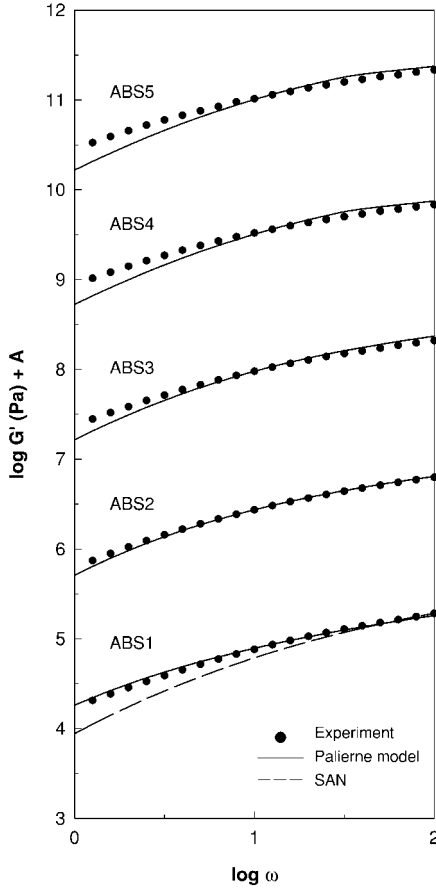
At  $\omega = 10$  rad/s, the complex modulus of the PB core at a given frequency can be calculated by inserting values of the complex moduli of the SAN matrix and ABS resins into eqs. (1) and (2). The calculated  $G'$  data of the PB core are plotted as a function of DG in Figure 5, which shows that the  $G'$  of the PB core increases as the DG increases, whereas the  $G'$  data of ABS4 and ABS5 are equal to each other. It is supposed that this can be attributed to different quantities of SAN polymers within the PB core of each ABS sample. That is, the PB core of the ABS sample with higher DG contains more SAN polymers, which causes the PB core to be more rigid. The fact that the  $G'$  values of the PB cores in ABS4 and ABS5 are equal to each other indicates that the amount of SAN polymers within the PB core of ABS4 is similar to that of ABS5.

Because the magnitude of  $G''$  of the PB core for all ABS samples was found to be much smaller than that of  $G'$ , the effect of the DG on the  $G''$  of the PB core could not be detected. Thus, the value of  $G''$  of the PB core was taken as 4000 Pa for all ABS samples used in this study.

To confirm the validity of our calculations, we inserted the calculated values of  $G'$  and  $G''$  of the PB core into eqs. (1) and (2) and then calculated



**Figure 5** Storage modulus of PB core plotted against degree of grafting.



**Figure 6** Comparison between experimental data and Palierne model predictions for all ABS samples. ABS1:  $A = 0.0$ ; ABS2:  $A = 1.5$ ; ABS3:  $A = 3.0$ ; ABS4:  $A = 4.5$ ; ABS5:  $A = 6.0$ .

the storage modulus of each ABS sample. The calculated  $G'$  data of each ABS sample are compared with the experimental results in Figure 6, from which it is evident that the Palierne model predictions are in good agreement with the experimental data obtained for all ABS samples, especially at high frequencies. These results also show that the Palierne model is very useful to calculate the storage modulus of the PB core in ABS polymers, at least in the high-frequency region.

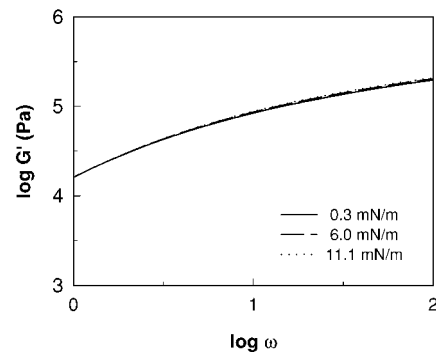
Based on the following arguments, the interfacial tension between SAN and PB was taken to be 6.0 mN/m in this work. The surface tension values of SAN and PB were previously published<sup>18</sup> and the values at 190°C are 30.1 and 24.2 mN/m, respectively. Because the polarity of SAN and PB are unknown, the following equation of Good and Girifalco<sup>18,19</sup> was used to estimate their interfacial tension:

$$\alpha_{12} = \alpha_1 + \alpha_2 - 2\chi(\alpha_1\alpha_2)^{1/2} \quad (3)$$

where the parameters  $\alpha$  and  $\chi$  are the surface tension and interaction parameter, respectively. Here, the subscripts 1 and 2 represent SAN and PB, respectively. The interaction parameter  $\chi$  involved in this equation is known to have values between 0.8 to 1.0 for most polymers.<sup>18,19</sup> Assuming the interaction parameter to be between these two extreme values, the interfacial tension between SAN and PB is calculated to be between 0.3 to 11.1 mN/m. To examine the effect of this range of interfacial tension values on the  $G'$  of the ABS samples, the  $G'$  data of the ABS2 are plotted in Figure 7 for various values of interfacial tension. As easily seen in Figure 7, the effect of the interfacial tension on  $G'$  is negligibly small. The same trend has been observed for the other ABS samples. For incompatible blend melts, it was observed that the interfacial tension does not significantly affect the calculated  $G'$  data at high frequencies, whereas its effect becomes more significant as frequency decreases.<sup>11</sup>

## CONCLUSIONS

The Palierne model was employed to determine the  $G'$  of the PB core in ABS polymers with different degrees of grafting. From our calculations, it was shown that the degree of grafting significantly affects the  $G'$  values of the PB core and, hence, the viscoelastic properties of ABS polymers because the quantity of SAN chains within the PB core varies, depending on the degree of grafting. In this work, it was found that the  $G'$  of the PB core increases up to 76% degree of grafting. Our calculations showed that the Palierne model is very useful to calculate the storage mod-



**Figure 7** Effect of interfacial tension on the storage modulus of ABS2 at high frequencies.

ulus of the PB core in ABS polymers, at least in the high-frequency region.

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