Linear viscoelastic behavior of acrylonitrile-butadiene-styrene (ABS) polymers in the melt: Interpretation of data with a linear viscoelastic model of matrix/core-shell modifier polymer blends

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Abstract

The linear viscoelastic behavior of acrylonitrile-butadiene-styrene (ABS) polymers with different rubber content has been investigated in the frame of a linear viscoelastic model, which takes into account the interconnectivity of the dispersed rubber particles. The model developed in our previous work has been shown to properly predict the low frequency plateau for the storage modulus, which is generally observed in polymer blends containing core-shell-type impact modifiers. In the present study, further experiments have been carried out on ABS polymers with different rubber content to verify the validity of our linear viscoelastic model. It has been found that our model describes quite properly the rheological behavior of ABS polymers with different rubber content, especially at low frequencies. The experimental data confirm that our model describes the rheological properties of rubber-modified thermoplastic polymers with strong adhesion at the particle/matrix interface more accurately than the Palierne model.

Keywords : acrylonitrile-butadiene-styrene, constitutive equation, viscoelasticity, shear flow, impact modifier.

1. Introduction

A number of engineering thermoplastics can be modified to improve their impact strength by the addition of a small amount of rubbery material if the rubbery material is dispersed as particles on a microscopic scale and well bound to the matrix material (Collyer, 1994; Miles and Rostami, 1992). Acrylonitrile-butadiene-styrene (ABS) polymers have been widely used in various industrial fields because of their high impact resistance, good dimensional stability and processability. Most ABS polymers are made by grafting styrene and acrylonitrile monomers directly upon cross-linked polybutadiene (PB) latex particles in a batch or continuous emulsion polymerization process. ABS polymer thus obtained consists of a styrene-acrylonitrile copolymer (SAN) matrix in which SAN-grafted PB particles are dispersed.

Since Zosel (1972) studied the viscoelastic properties of ABS polymers in the molten state, some characteristic rheological behaviors of these polymers have been reported (Han, 1971; Kubota, 1975; Münstedt, 1981). In particular, at high rubber concentration, a pronounced increase in the

storage modulus G' was observed in the low frequency region. To explain this low frequency plateau, Münstedt (1981) suggested that the dispersed particles can be interconnected, thus building up a three-dimensional network within the material and that this network structure would be stabilized by agglomeration of the particles or by overlapping of chains grafted to neighboring particles. Aoki and coworkers (1982, 1987; Masuda, *et al.*, 1987) characterized, in detail, the rheological properties of ABS with respect to rubber content, rubber particle size, acrylonitrile content (AN %) in grafted SAN, and degree of grafting.

Palierne (1990) proposed a linear viscoelastic constitutive equation for viscoelastic emulsions with interfacial tension under a small-amplitude oscillatory flow. Palierne's emulsion model can predict a pronounced increase in elasticity at low frequencies and a very long mechanical relaxation time, both of which are related to the deformability of suspended particles and their recovery (Graebling, *et al.*, 1993). However, the model fails to predict a low frequency plateau for the storage modulus G', which is generally observed for ABS polymers and polymer blends containing core-shell impact modifiers (Bousmina

and Muller, 1993; Memon and Muller, 1998).

In our previous study (Choi, *et al.*, 2000), Palierne's emulsion model was utilized to develop a linear viscoelastic model for the rheological description of matrix/core-shell modifier blends with strong adhesion at the particle/matrix interface. In our model, it has been assumed that the total mean stress of the blends is the sum of a mean stress and an additional stress that can be formulated by the Palierne model and the standard three-parameter Maxwell model, respectively. Moreover, the damage factor ξ and its evolution equation have been introduced into the model in order to describe the relative contributions of the mean stress and the additional stress to the total stress. The experimental data obtained for the PMMA/core-shell PBA blends have shown that our modified model is able to more properly describe the rheological properties of incompatible polymer blends, especially in the low-frequency region, than the Palierne model.

In the present study, a major emphasis is placed on the interpretation of the experimental data obtained for ABS polymers with different rubber content in the frame of our linear viscoelastic model. Comparison of the experimental data to the theoretical predictions of our model and the Palierne model are made to verify the validity of our approach.

2. Linear Viscoelastic Model

The low-frequency plateau of the storage modulus G', generally observed for ABS polymers and polymer blends containing core-shell-type impact modifiers, can be attributed to a network structure formed by the interconnectivity of the dispersed rubber particles. In the model developed in our previous study (Choi, *et al.*, 2000), the total mean stress is assumed to be the sum of a mean stress and an additional mean stress, which can be formulated by the Palierne model and the three-parameter Maxwell model, respectively. The rheological behavior of the matrix chains trapped by the shell of the dispersed particles is described by introducing a frequency-dependent parameter ξ and its evolution equation:

$$\frac{d\xi}{dt} + \frac{\xi}{\theta} = |\dot{\gamma}|(1 - \xi), \tag{1}$$

where $\dot{\gamma}$ is the shear rate and the quantities ξ/θ and $|\dot{\gamma}|(1-\xi)$ are proportional to the rate of restoration and rupturing of the entrapment of matrix chains to the shell of the dispersed particles, respectively.

The steady-state solution of eq. (1) should be obtained numerically at a given frequency. Because the shear rate varies periodically with time under a small amplitude oscillatory shear flow, the matrix polymer chains at the particle/matrix interface experience different shear rates with time even at the steady state. Therefore, a part of

matrix chains initially attached to the shell of the dispersed particles repeat the process of attachment/detachment even at a constant frequency; therefore, the steady-state solution of eq. (1) changes periodically with time. It is thus quite reasonable to suppose that those matrix chains repeating the process of attachment/detachment contribute little to the additional mean stress, whereas the other matrix chains that consistently adhere to the shell of the rubber modifier contribute significantly to the additional mean stress. Therefore, we suppose that the ratio of the additional mean stress to the mean stress is directly related to the fraction of matrix chains that remain to adhere to the shell of the dispersed particles, which is expressed as $(1 - \xi_{max})$. From these considerations, the damage factor involving ξ_{max} is incorporated into eq. (1) to properly describe the relative contributions of the mean stress and the additional stress to the total mean stress. Thus, the total stress can be expressed as follows:

$$\sigma = \xi_{max}\sigma_m + (1 - \xi_{max})\sigma_p, \tag{2}$$

where σ_m is the mean stress arising in the blends due to microflows of polymer around the dispersed rubber particles, and σ_p is an additional mean stress due to the interconnectivity of the dispersed rubber particles.

In the small-amplitude oscillatory shear flow, the mean stress can be expressed by the Palierne model which considers only the hydrodynamic interaction between the dispersed particles:

$$\sigma_m(t) = \gamma_0(G_m' \sin \omega t + G_m'' \cos \omega t), \tag{3}$$

$$G_m^*(\omega) = G_m'(\omega) + G_m''(\omega) = G_M^*(\omega)\frac{1 + 3\phi H(\omega)}{1 - 2\phi H(\omega)}, \tag{4}$$

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

Here $G_M^*(\omega)$ and $G_I^*(\omega)$ are, respectively, the frequency-dependent complex moduli of the matrix and the inclusions, ϕ is the volume fraction of inclusions of radius R, and α is the interfacial tension. For the sake of simplicity, we assume that the rubber particles are monodisperse in size and that the interfacial tension is constant; that is, $\beta' = \beta'' = 0$.

Under small-amplitude oscillatory shear flow, the additional mean stress can be expressed as follows:

$$\sigma_p = \gamma_0(G_p' \sin \omega t + G_p'' \cos \omega t) \tag{6}$$

$$= \gamma_0\left[\left(G_1 + \frac{G_2(\tau\omega)^2}{1 + (\tau\omega)^2}\right)\sin \omega t + \frac{G_2\tau\omega}{1 + (\tau\omega)^2}\cos \omega t\right]$$

Substituting eqs. (3)(6) into eq. (2), it can be shown that

the total mean stress of polymer blends is given by

$$\sigma = \gamma_0(G' \sin \omega t + G'' \cos \omega t)$$

$$= \gamma_0[\xi_{max}G_m' + (1 - \xi_{max})G_p']\sin \omega t$$

$$+ \gamma_0[\xi_{max}G_m'' + (1 - \xi_{max})G_p'']\cos \omega t \qquad (7)$$

where

$$G' = \xi_{max}G_m' + (1 - \xi_{max})G_p' = \xi_{max}G_m' + (1 - \xi_{max})\left(G_1 + \frac{G_2(\tau\omega)^2}{1 + (\tau\omega)^2}\right), \qquad (8)$$

$$G'' = \xi_{max}G_m'' + (1 - \xi_{max})G_p'' = \xi_{max}G_m'' + (1 - \xi_{max})\frac{G_2\tau\omega}{1 + (\tau\omega)^2}. \qquad (9)$$

3. Experimental

3.1. Materials

The SAN matrix and ABS polymer, kindly supplied by Cheil Industry Inc., were synthesized separately. The SAN matrix used in this study is a homogeneous copolymer with $M_w = 90,000$ and $M_n = 45,000$. For all ABS polymers, the diameter of the PB core is 300 nm and the degree of grafting is 60%. The acrylonitrile (AN) contents of the matrix and the grafted SAN are, respectively, 28.5 and 25%. When the difference in AN content is small, the SAN-grafted PB particles are, in general, expected to be well-dispersed in the matrix (Kim, et al., 1990).

3.2. Blend preparation

The ABS polymer was blended with the SAN copolymer in order to change the PB content (or rubber content). All SAN/ABS blends used in this work contained 0.05, 0.3, 0.4, and 0.5 weight fraction of the original ABS, corresponding to 0.023, 0.135, 0.18, and 0.225 rubber contents, respectively. Blending was performed at 200°C and 60 rpm for 10 min by using a Brabender Plasticoder. The blends thus obtained were molded into 25-mm discs at 200°C under vacuum.

3.3. Rheological measurements

The dynamic and steady shear measurements of the ABS samples were carried out on a Rheometrics Mechanical Spectrometer (RMS 800) with a parallel plate geometry. The sample discs used were 25 mm in diameter and 2 mm in thickness. The frequency sweeps from 0.01 to 100 rad/s were carried out at various temperatures from 150 to 210 °C. Since the morphology of the blends was stable during the time of measurements for these experimental conditions, the complex moduli G' and G" measured at 150, 170, 190, and 210°C were superposed into a master curve at 170 °C according to the time-temperature superposition prin-

ciple (Ferry, 1980).

4. Results and Discussion

4.1. Time-temperature superposition

According to the time-temperature superposition principle, the WLF equation is expressed as follows:

$$\log a_T = -\frac{C_1(T - T_0)}{(C_2 + T - T_0)}, \qquad T_0 = 170°C, \qquad (10)$$

where a_T is a shift factor, T and T_0 are measured and reference temperatures, respectively. The shift factor a_T for SAN and all ABS Polymers with different rubber contents is plotted against the temperature difference $(T - T_0)$ in Fig. 1. The coefficients C_1 and C_2 determined by fitting the WLF equation to the experimental values of a_T are given in Table I. The solid and dotted lines in Fig. 1 represent the WLF equation of SAN and ABS polymers containing more than 13.5% rubber content, respectively. Table I and Fig. 1 show that the coefficients C_1 and C_2 of SAN are different from those of ABS polymers containing more than 13.5% rubber content. These results indicate that the rheological properties of SAN are quite different
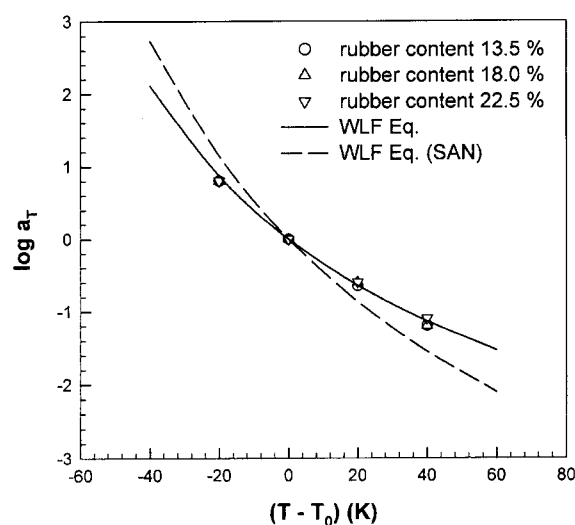

Fig. 1. Shift factors a_T for SAN and ABS polymers plotted against temperature difference $(T-T_0)$.

Table 1. Effect of the rubber content of ABS polymers on parameters C_1 and C_2

Sample	C_1	C_2
SAN	7.2	146.1
ABS polymer (rubber content 2.3%)	7.2	146.1
ABS polymer (rubber content 13.5%)	5.0	134.5
ABS polymer (rubber content 18.0%)	5.0	134.5
ABS polymer (rubber content 22.5%)	5.0	134.5

from those of ABS polymers with relatively high rubber content.

4.2. Interfacial tension

Based on the following arguments, the interfacial tension between SAN and PB has been taken as 6.0 mN/m in this work. The surface tension values of SAN and PB have been published and the values at 170°C are 30.1 and 24.2 mN/m, respectively (Brandrup and Immergut, 1989). Since the polarity of SAN and PB are unknown, the following equation of Good and Girifalco has been employed to estimate their interfacial tension (Wu, 1982):

$$\alpha_{12} = \alpha_1 + \alpha_2 - 2\chi(\alpha_1\alpha_2)^{1/2}, \tag{11}$$

where the parameters α and χ are the surface tension and interaction parameter, respectively. Here the subscripts 1 and 2 represent SAN and PB, respectively. The interaction parameter χ involved in this equation is known to have the values between 0.8 to 1.0 for most polymers (Brandrup and Immergut, 1989; Wu, 1982). 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 ABS sample with 18% rubber content are plotted in Fig. 2 for various values of interfacial tension. As easily seen in Fig. 2, which shows that all three curves are completely overlapped, the effect of the interfacial tension on G' is negligibly small.

Graebling and coworkers (1993) have shown that the interfacial tension has a significant effect on the G' values at low frequencies, while the interfacial tension effect becomes negligibly small at intermediate and high fre-

quencies. However, for blend systems with high rubber content, the effect of the strong interaction at the particle/matrix interface on G' is much higher than that of the interfacial tension at low frequencies. Therefore, as shown in Fig. 2, the interfacial tension has little effect on the G' values of the ABS sample with 18% rubber content in the wide frequency region. The same trend has been observed for other ABS polymer samples. Therefore, it is supposed that the calculated G' data for all ABS polymers used in this study is reliable irrespective of the fact that the interfacial tension between SAN and PB has been taken as 6.0 mN/m.

Using the same procedure adopted in our previous study for PMMA/core-shell PBA blends (Choi, et al., 2000), the parameters G_1, G_2, and in the three-parameter Maxwell model have been determined for all ABS polymers from the stress relaxation and transient start-up shear flow tests; see Table II.

4.3. Small amplitude oscillatory shear flow

In Figs. 3 and 4, the complex shear modulus data for all

Table 2. Summary of the parameters used in our linear viscoelastic model

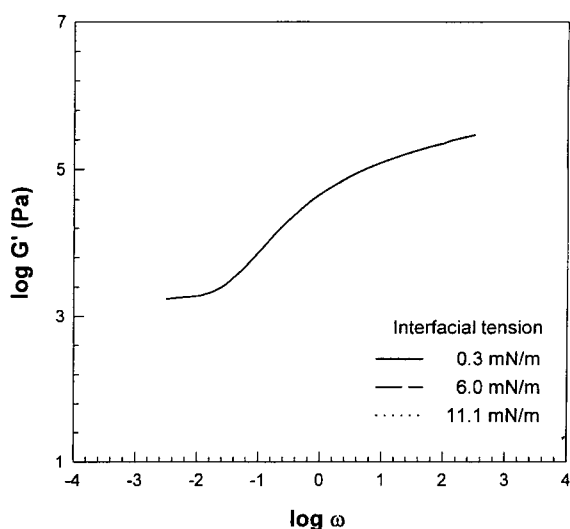|	ABS (2.3%)[a]	ABS (13.5%)	ABS (18.0%)	ABS (22.5%)
G_1 (Pa)	4464	1704	691	0[b]
G_2 (Pa)	60000	43000	36000	32000
τ (sec)	16	15	15	10
t* (sec)	69.25	59.25	59.25	39.25
θ (sec)	4000	10000	40000	200000

[a: rubber content; b: assumed value]

Fig. 2. Effect of interfacial tension on the storage modulus of ABS polymer with 18.0% rubber content.
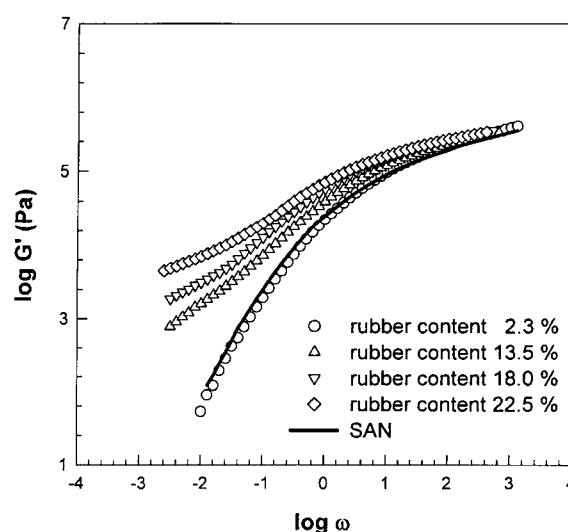

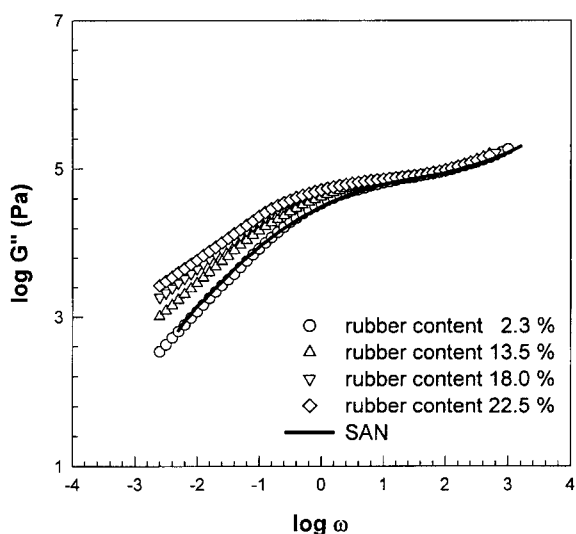Fig. 3. Master curves of G' for SAN homopolymer and ABS polymers at 170°C.

Fig. 4. Comparison between the experimental data for G' (symbol) and the Palierne model predictions (line) for SAN and ABS polymers.

ABS samples are provided as a function of frequency. As in the earlier studies for ABS polymers (Zosel, 1972; Kubota, 1975; Münstedt, 1981; Aoki and Nakayama, 1982; Aoki, 1987), the storage modulus increases significantly at low frequencies and the rubbery plateau region in the loss modulus shifts to the lower frequency region, as the rubber content increases.

The experimental data on G' are compared with the predictions of the Palierne model in Fig. 5. As in the PMMA/core-shell PBA blend system (Choi, *et al.*, 2000), a significant deviation of the theoretical predictions of the Palierne model from the experimental data is observed in
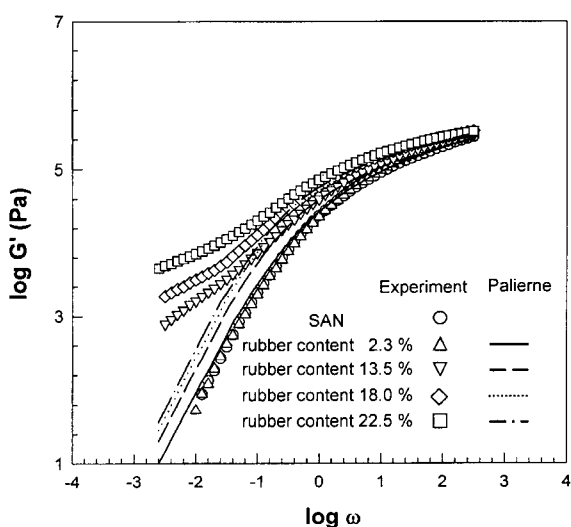

Fig. 5. Comparison between the experimental data for G'' (symbol) and the Palierne model predictions (line) for SAN and ABS polymers.

the low frequency region, especially for ABS polymers containing more than 13.5% rubber content. This discrepancy should be attributed to the presence of strong adhesion at the particle/matrix interface. The interactions between the SAN matrix and the grafted SAN are strong enough that a number of SAN matrix chains are trapped by the grafted SAN chains at low frequencies. The strong particle-matrix interfacial adhesion results in the increase of the effective radius of the SAN-grafted PB particles, thereby disturbing the flow of the matrix SAN chains around the particles, and the interconnectivity of the dispersed rubber particles is eventually formed at low frequencies.

The predictions of our model, in which the contribution of the interactions at the particle/matrix interface to the total stress of the blends is properly considered, are compared with the experimental complex modulus data in Fig. 6. It is easily seen that our model gives a better description of the rheological behavior of the SAN/ABS polymer blend system, especially in the low frequency region.

4.4. Consideration on the parameter θ

The values of θ used to fit our model to the experimental data are shown in Table II. The value of θ decreases with the increase of the rubber content since the number of SAN-grafted PB particles by which the SAN matrix chains can be re-trapped increases. The frequency-dependence of ξ_{max} for various values of θ is illustrated in Fig. 7. As the rubber content decreases, the transition region where ξ_{max} changes abruptly from zero to unity shifts to the lower frequencies. For the ABS polymers with low PB contents, the additional mean stress contributes very little to the total stress even at low frequencies and thus our model becomes essentially identical to the Palierne model. On the contrary, for the ABS polymers with high PB contents, the SAN matrix chains detached from the dispersed PB particles are easily re-trapped by another SAN-grafted PB particles, thus resulting in smaller θ. More precisely, the effect of the interactions at the particle/matrix interface becomes more significant at high rubber levels, especially in the low frequency region where the contribution of the additional stress predominates. To recapitulate, the mean stress contributes overwhelmingly to the total stress at low rubber contents, whereas the contribution of the additional stress becomes dominant, especially at low frequencies, as the rubber content increases.

5. Conclusions

The rheological behavior of ABS polymers with different rubber content has been analyzed in the frame of a linear viscoelastic model, which considers properly the interconnectivity of the dispersed rubber particles. The
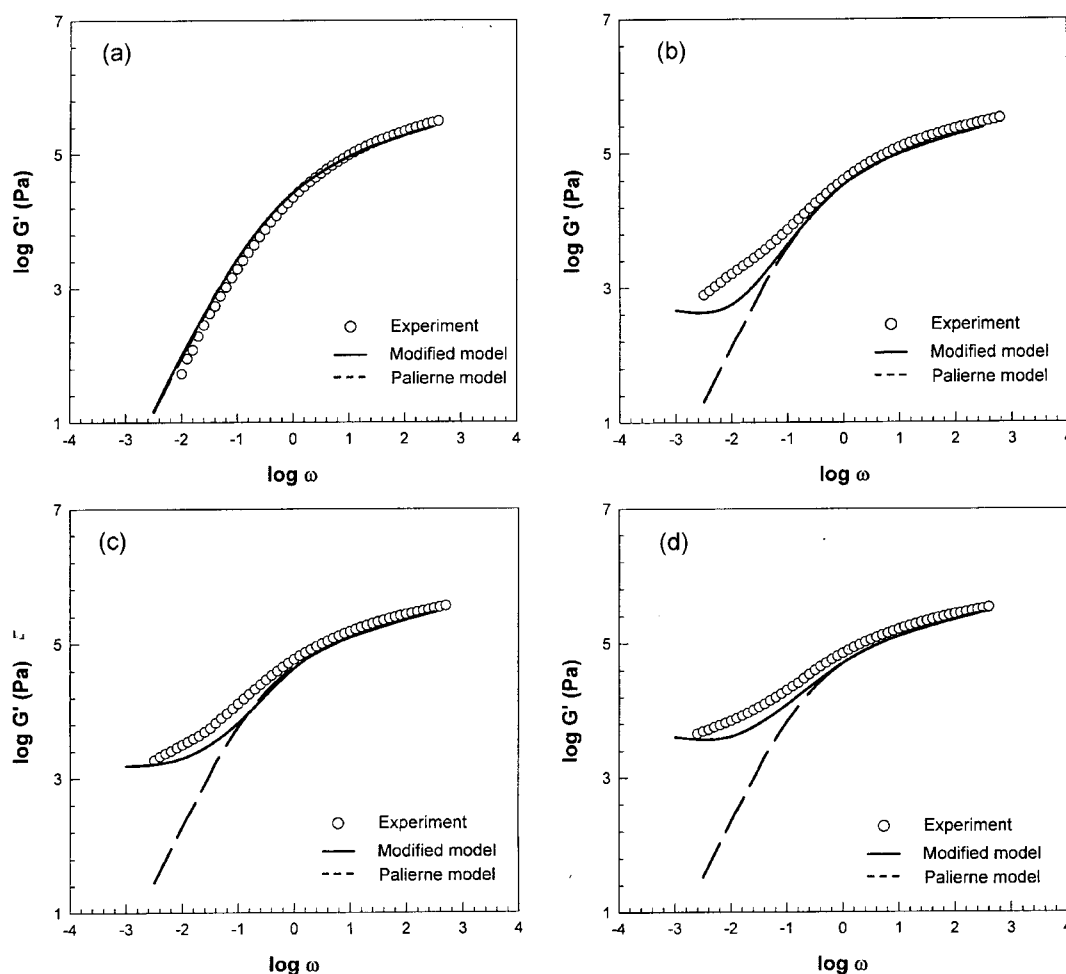
Fig. 6. Comparison of the experimental data for G' with our modified model predictions for ABS polymers: (a) 2.3% (rubber contents); (b) 13.5%; (c) 18.0%; (d) 22.5%.
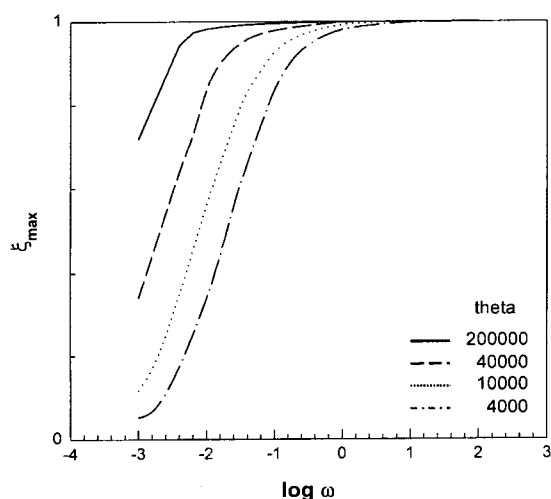

Fig. 7. The frequency-dependence of ξ_{max} for various values of θ for ABS polymers.

experimental data obtained for the ABS systems confirm that the model discussed in this study is able to describe the linear viscoelastic properties of rubber-modified polymer blends, especially in the low frequency region, more properly than the Palierne model. This indicates that for ABS systems the contribution of the additional mean stress due to the strong interaction at the particle/matrix interface cannot be neglected, at least in the low frequency region.

Comparison of the experimental data to the model description reveals that as the frequency decreases, the contribution of the additional stress becomes more important because the interaction at the particle/matrix interface becomes more significant compared to the stress experienced by the matrix chains. As the rubber content increases, the effect of the interaction between the SAN matrix and the SAN-grafted PB particles becomes more significant, especially in the low frequency region where the contribution of the additional stress predominates. Comparison of our model calculations to the experimental data is quite satisfactory and, in the near future, more blend systems will be studied to verify its validity further.

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