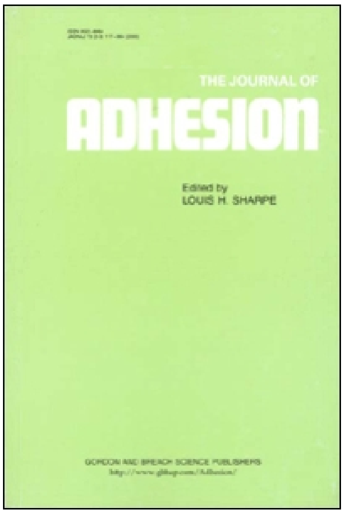

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Rheological properties of hot melt pressure-sensitive adhesives based on styrene--isoprene copolymers. Part 1: A rheological model for [sis-si] formulations

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RHEOLOGICAL PROPERTIES OF HOT MELT PRESSURE-SENSITIVE ADHESIVES BASED ON STYRENE—ISOPRENE COPOLYMERS. PART 1: A RHEOLOGICAL MODEL FOR [SIS-SI] FORMULATIONS

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The viscoelastic properties of hot melt pressure-sensitive adhesives (HMPSA) based on formulations of block copolymers and tackifying resins have been studied in detail, through the variation of the complex shear modulus, G^*, as a function of frequency, ω. In this first article, we analyze the individual behavior of the components of HMPSA blends: (1) the two copolymers, styrene-isoprene (SI) diblock copolymer and styrene-isoprene-styrene (SIS) triblock copolymer and (2) two tackifying resins. The viscoelastic behavior of the overall formulation is also presented. We have mainly studied the effects of (1) the molecular characteristics of the SI and SIS copolymers and (2) the composition of the blends (mainly the effect of SI content, S content in SIS and SI, resin content) on the viscoelastic properties. A theoretical approach based on concepts of molecular dynamics leads to a model which describes reasonably well the linear viscoelastic properties of individual components and their formulations. Our systematic study can be used to design new copolymer molecules which can mimic the rheological behavior and end-user properties of regular formulations at room temperature.

Keywords: Adhesion; Rheological properties; Hot-melt adhesives; Pressure-sensitive adhesives; Rheological model; Mechanical spectroscopy; Copolymers; Blends of block copolymers; Tackifying resin; Master curve

INTRODUCTION

A hot melt pressure sensitive adhesive (HMPSA) is a hot melt adhesive (HMA) formulated with a specific elastomer giving tack properties at room temperature and low pressure. Typical industrial applications for HMPSAs are labels and tapes.

The thermorheological properties of these families of adhesives govern to a large extent (1) their process behavior (blending, flow properties, pelletizing, die-cutting for label applications, open time and setting time in the case of HMAs) and (2) their end user properties (tack, adherence, shear resistance). In most cases, rheological (*i.e.*, viscoelastic) parameters may be associated with typical industrial characterization of processing ability and application properties.

Hot-melt formulations are basically made of two components: a polymer which brings the mechanical properties and a tackifying resin which gives the tack properties and governs the thermorheological properties through the control of the glass transition temperature.

In previous articles we have already described the rheological behavior of hot melt adhesives based on ethylene vinyl acetate random copolymers and model formulations based on linear polymers [1–4]. The present series of articles deals with the rheological properties at room temperature of HMPSA with a polymer base made of blends of block copolymers. In this case, formulations have to cope with a balance of low elasticity and viscous losses in order to obtain optimal tack, adherence, and shear resistance at room temperature.

In this first article, the blends studied are basically made up of four components: two pure polymers (one styrene-isoprene-styrene [SIS] triblock copolymer and one styrene-isoprene [SI] diblock copolymer) plus two tackifying resins. This article presents the rheological data (storage and loss shear modulus as a function of frequency) as a function of (1) the structural properties of the copolymers (molecular weights of the isoprene and styrene sequences) and (2) the composition of the blends (mainly diblock and resin contents). The rheological data have been analyzed through a rheological model based on concepts of molecular dynamics, which describes reasonably well the effect of the blend composition on the viscoelastic properties of the formulations.

EXPERIMENTAL

Samples

The formulations presented in this article are made of blends of [SIS] triblock and [SI] diblock copolymers with tackifying resins. The copolymers were synthesized by the Dexco Polymers (Houston, Texas, USA). The tackifying resins are (1) a solid resin, Escorez® 1310 from the ExxonMobil Chemical Company (Houston, Texas, USA), (2) a liquid resin, Wingtack® 10 from the Goodyear Company (Akron, Ohio, USA). These resins are unentangled oligomers and the glass transition temperatures values are $+47°\mathrm{C}$ for the solid resin and $-28°\mathrm{C}$ for the liquid resin. The resins have a double effect on the isoprene elastomeric sequence of the structurally well-defined copolymers. These effects (thermodynamic effects on glass transition, Tg, topological effect on the plateau modulus) have already been described in previous papers [1, 3]. The resins are not compatible with the styrene sequence and swell only the entanglement network of the elastomeric part (polyisoprene).

The HMPSA blends were prepared in a Z-blade mixer at 145°C by blending the copolymers and tackifying resins for about 45 min.

A series of blends were made with different ratios of diblock copolymer in the blend. The main physical and structural parameters of the pure block copolymers and blends are reported in Tables 1 and 2. We report only the pure copolymers (SI_1 and SIS_1) and pure blends [SIS-SI] in Table 1. All formulations [SIS-SI-resins] are presented in Table 2.

Rheological Experiments

Rheological characterization of pure copolymers, pure resins, pure blends [SIS + SI], and formulations were made by measuring the

TABLE 1 Characteristic Parameters of Pure Copolymers and Copolymer Blends

	%SI	SIS M_w ($g{\cdot}mol^{-1}$)	%S in SIS	SI M_w ($g{\cdot}mol^{-1}$)	%S in SI
SI_1	100	—	—	72000	15
SIS_1	0	118000	18.2	—	—
Sample_1	42	156000	15.1	72000	15
Sample_2	80	143000	13	68000	12.6
Sample_3	50	234000	12.7	68000	12.6
Sample_4	54.3	176000	16.1	86000	16
Sample_5	50	143000	13	65000	28.4
Sample_6	50	143000	13	99000	12.3
Sample_7	80	143000	13	105000	28.1
Sample_8	80	234000	12.7	99000	12.3
Sample_9	80	234000	12.7	65000	28.4
Sample_10	50	234000	12.7	105000	28.1

complex shear modulus (G′ and G″) as a function of frequency, ω, at various temperatures. These mechanical spectroscopy experiments were performed in the frequency range (10^{-2}–$100\ rad{\cdot}s^{-1}$) using a Rheometrics RDA II rotational rheometer (Rheometries, New Castle, Delaware, USA) in parallel-plate geometry. The time–temperature superposition principle can be used to plot the main relaxation domains from the terminal zone region (flow region or secondary plateau region for viscoelastic solids like [SIS]) up to the glassy domain (T_α relaxation) at high frequencies. The plateau diameter was varied from 5 mm to 25 mm, depending on the modulus level, in order to minimize instrument compliance and sample slip effects, particularly in the glassy domain. All master curves are reported at a reference temperature $T_0 = 20°C$, except for Figure 1.

TABLE 2 Characteristic Parameters of the Various HMPSA Formulations

	SIS		SI		SIS + SI	Formulation		
	M_w ($g{\cdot}mol^{-1}$)	%S	M_w ($g{\cdot}mol^{-1}$)	%S	%SI	% Polymer	% Solid resin	% Liquid resin
HM_1	118000	18.2	—	—	0	31	42	27
HM_2	176000	16.1	86000	16	54.3	31	42	27
HM_3	154000	15.1	72000	15	19	31	42	27
HM_4	156000	15.1	72000	15	42	30	27	43
HM_5	156000	15.1	72000	15	42	31	27	42
HM_6	156000	15.1	72000	15	42	35	39	26
HM_7	156000	15.1	72000	15	42	31	42	27

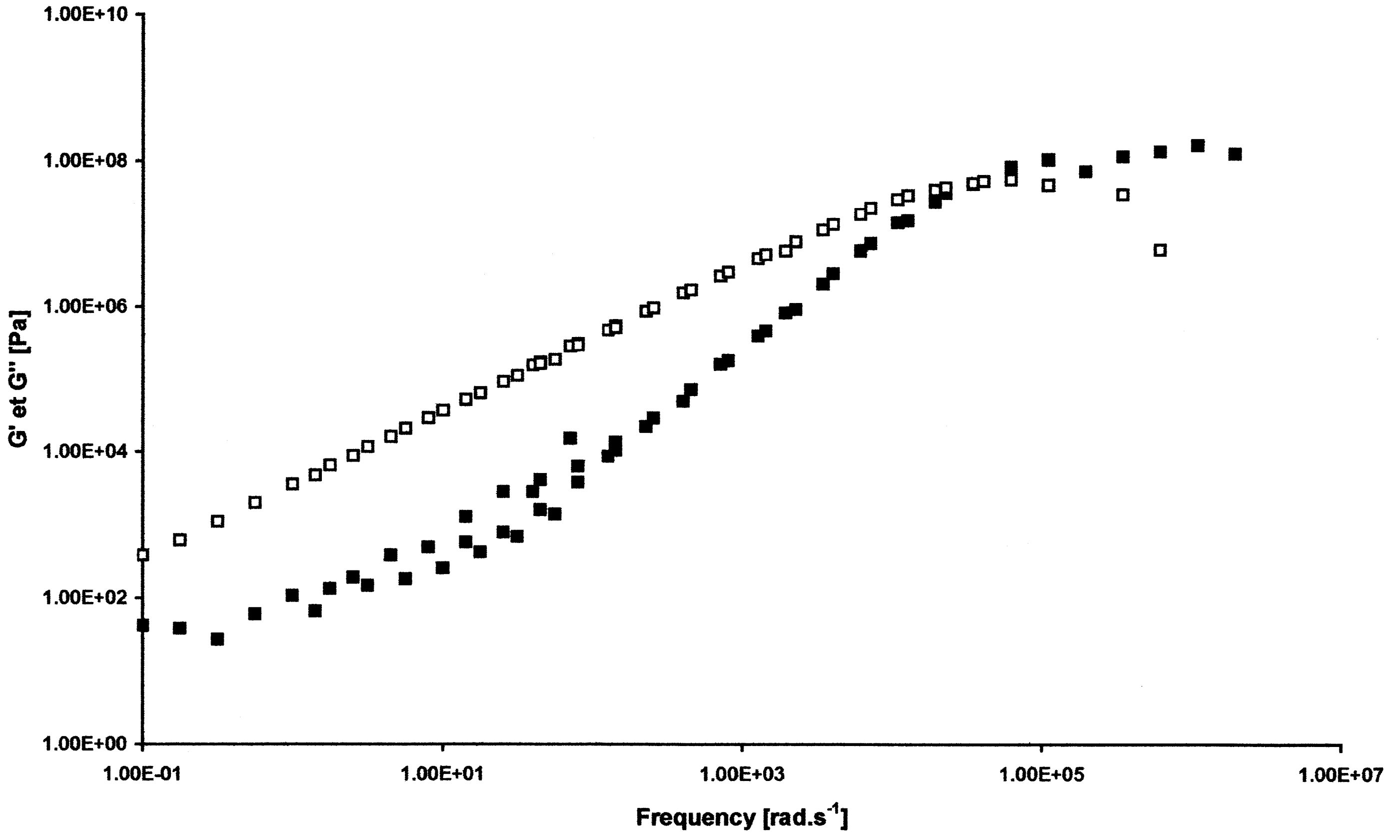

FIGURE 1 Storage and loss moduli *versus* frequency at Tref = 0°C for the Wingtack® 10, liquid resin. ■, G′; □, G″.

EXPERIMENTAL RESULTS: EFFECTS OF THE COPOLYMERS STRUCTURE AND COMPOSITION OF THE BLENDS

All the rheological data were obtained following the method described in the first section. The main structural and composition parameters are (1) the amount of styrene in the [SI] and [SIS] copolymers, (2) the amount of [SI] diblock in [SIS-SI] blends, and (3) the amount of copolymers [SIS] + [SI] in the overall [SIS-SI-resins] formulation.

Experimental results obtained on the pure copolymers and on the various formulations are described below.

Pure Copolymers and Resins

Pure Resins

It can be seen in Figure 1 that the rheological behavior of the liquid resin is typical of an unentangled polymer: the glassy domain at higher frequencies is directly followed by a flow zone at lower frequencies. The behavior of the solid resins is similar but shifted in the frequency scale.

Pure Diblock and Triblock Copolymers

We have plotted on Figures 2 and 3 the variations of the complex shear modulus as a function of frequency, ω, for one pure [SI] diblock copolymer (SI_1), and for one [SIS] triblock copolymer (SIS_1) (see Table 1 for the characteristics of each polymer).

We can observe for the diblock copolymer (Figure 2) four regions corresponding to the usual relaxation domains which are characteristic of the viscoelastic behavior of high molecular weight polymers [5]:

1. a glassy domain for the higher frequency range;
2. a transition region from the glassy domain to the rubbery domain at intermediate frequencies;
3. a rubbery plateau region; and
4. at lower frequencies, one can observe the onset of a flow region which occurs below the cross-over between G' and G''. Then, at the lowest frequencies, the onset of a secondary plateau appears, certainly due to a low quantity (lower than 5%) of very high molecular weight of statistical polymer which has been confirmed by gel permeation chromatography (GPC) analysis.

On the same figure, we superimposed the rheological behavior of a pure polyisoprene ([I], $M_w = 29000\ \text{g}\cdot\text{mol}^{-1}$). It will be seen that in the high frequency part, [SI] and [I] have the same viscoelastic

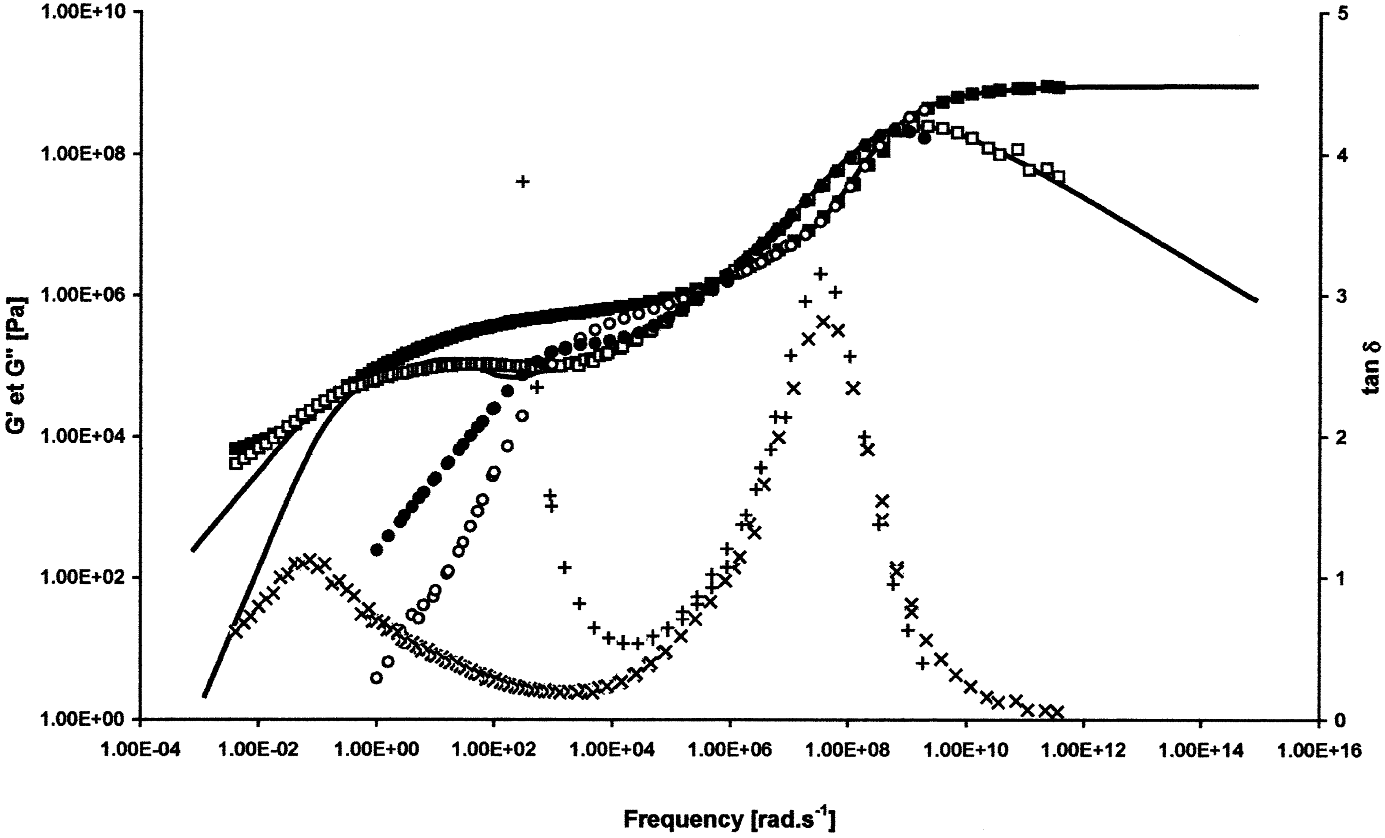

FIGURE 2 Storage and loss moduli *versus* frequency for the SI_1 diblock copolymer and Isoprene polymer. The right scale refers to tan δ. ■, G′ (SI_1); □, G″(SI_1); ●, G′ (I); ○, G″ (I); ×, tan δ for SI; +, tan δ for I. Full line: model.

behavior (hence the same apparent glass transition temperature, T_α). It will also be observed that the values of the plateau modulus, ${G_N}^0$ (defined as the storage modulus value at the minimum of the loss angle, tan δ), are very close for the diblock and pure polyisoprene (${G_N}^0 = 5.8 \times 10^5$ Pa for the diblock copolymer and 4.7×10^5 Pa for polyisoprene). So, we can describe the diblock [SI] copolymer at room temperature as made of an isoprene entangled matrix in which rigid nodules of polystyrene are dispersed. The T_g of polystryrene being close to 100°C, the styrene sequences of [SI] behave like rigid nodules of glassy polymer at room temperature. So the value of the plateau modulus of [SI] is slightly higher than the corresponding value for pure polyisoprene because the styrene sequences play the role of a filler. We will describe that effect quantitatively in the next part.

For the [SIS] copolymer (Figure 3) we observe three relaxation domains corresponding to:

1. a glassy domain at higher frequencies,
2. the transition region from glassy domain down to rubbery domain (at intermediate frequencies), and
3. an elastic plateau region.

The time–temperature superposition principle does not apply, within experimental uncertainty, to [SIS] at temperatures above 30°C, particularly on the loss modulus, G″, showing a physical evolution of the network described above at higher temperatures. So, the experimental temperature range corresponding to the data reported in this paper is −30°C to 25°C.

As for the SI_1 diblock, we observe for the [SIS] triblock copolymers the same rheological behavior as pure polyisoprene in the high frequency range. The value of the plateau modulus is somewhat higher than for pure polyisoprene (${G_N}^0 = 7.7 \times 10^5$ Pa). Again, this corresponds to a viscoelastic solid behavior due to the organization of a physical network of polyisoprene trapped between glassy polystyrene nodules. The isoprene sequences are trapped between styrene sequences and cannot relax as in the diblock copolymers; hence, the triblock architecture makes the flow region disappear.

[SIS - SI] Blends

As previously described and confirmed in the literature [6–9], the styrene sequences create a network of rigid polystyrene dispersion which traps the isoprene sequences of the triblock molecules; the free

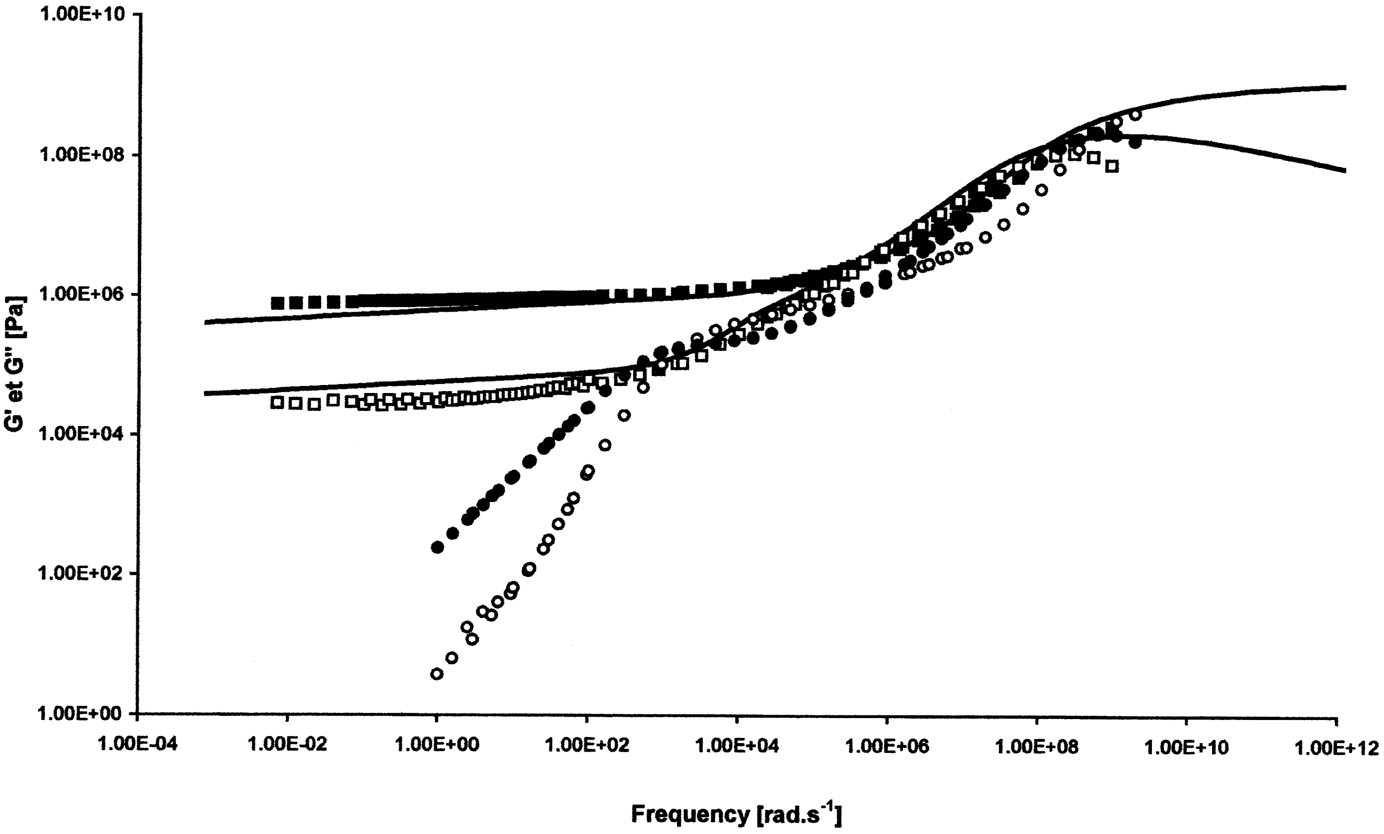

FIGURE 3 Storage and loss moduli *versus* frequency for the SIS_1 triblock copolymer and isoprene polymer. ■, G′ (SIS_1); □, G″ (SIS_1); ●, G′ (I); ○, G″ (I). Full line: model.

polyisoprene ends of the diblock copolymers can relax and swell the polyisoprene network of the triblock part. We can observe for the [SIS-SI] blends the same relaxation domains as for the pure diblocks and triblocks:

1. a glassy domain at higher frequencies,
2. a transition region from the glassy domain down to the rubbery domain (at intermediate frequencies),
3. a rubbery plateau domain,
4. a decrease of the storage modulus corresponding to the relaxation of the isoprene sequence of the diblock copolymers, and
5. a terminal zone corresponding to the secondary plateau modulus (G_s) of the triblock part swollen by the isoprene sequence of the diblock. This domain yields a specific viscoelastic solid behavior to the blend.

In Figure 4 we present an example with sample_1.

[SIS-SI-Resins] Blends

In this part, we will show that (1) the polystyrene sequences, glassy at room temperature, act like a filler of the polyisoprene matrix, (2) the diblock copolymer in the blend acts like a polymeric solvent, and (3) the resin acts like an antiplasticizer in a formulation.

The Effect of Styrene Content in Diblock and Triblock

We can observe in Figures 2 and 3 that the plateau modulus values of [SIS] and [SI] are about the same and close to the plateau modulus value of pure polyisoprene. We know that the plateau modulus scales linearly with the reciprocal of the molecular weight between entanglements, which has a characteristic value for a given polymer. Using the rubber elasticity equation,

$$M_e = \frac{\rho RT}{G_N^0} \tag{1}$$

where M_e is the molecular weight between entanglements, T is the temperature, and G_N^0 is the plateau modulus, we find that $M_e \approx 4000\ g{\cdot}mol^{-1}$, which corresponds to the value of entangled polyisoprene (the M_e of styrene being $18500\ g{\cdot}mol^{-1}$). Thus we can confirm the picture of a polyisoprene matrix with polystyrene acting like a filler.

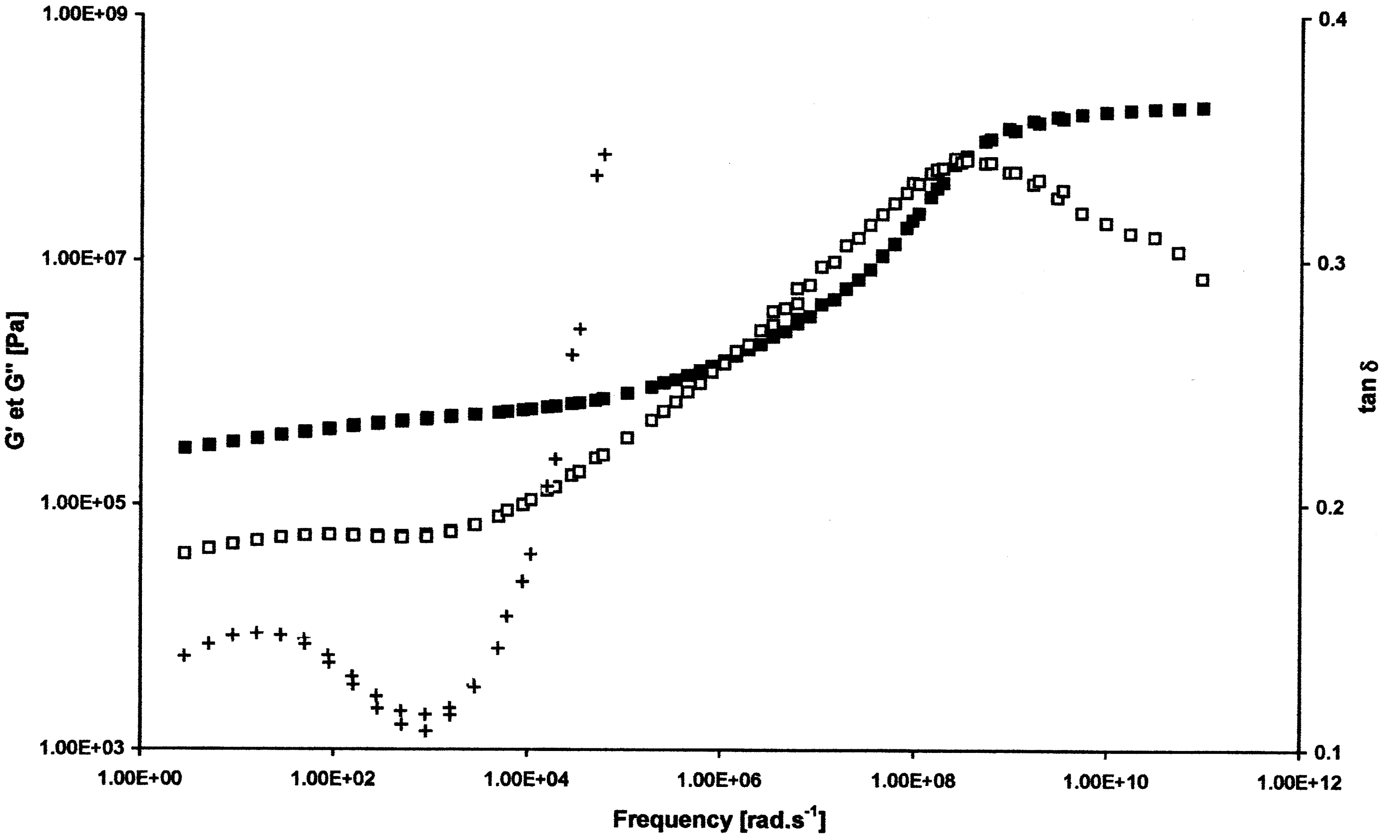

FIGURE 4 Storage and loss moduli *versus* frequency for sample_1. The right scale refers to tan δ. ■, G′; □, G″; ×, tan δ for sample_1.

An equation derived from Einstein's law [10] applied to the blend [SIS + SI] can be written:

$$G^* = f(\Phi_{sty}) \cdot G^*_{polyisoprene\_matrix} \tag{2}$$

where Φ_{sty} is the volume fraction in styrene and

$$f(\Phi_{sty}) = \left(1 + \frac{5}{2}\Phi_{sty} + a \cdot \Phi_{sty}^2\right) \tag{3}$$

The first two terms in the parentheses correspond to Einstein's law, the quadratic term corresponding to two-body (styrene nodules) interactions. One can observe on Figure 5 a reasonable agreement between experimental and calculated values with a value of $a = 10$, which is consistent with literature values for semidilute suspensions in polymers [11–13].

The Effect of [SI] Content in a [SIS-SI] Blends

Figure 6 presents the rheological behavior of sample_2 and _3 corresponding to two different contents of [SI] (50% and 80%) at the same styrene ratio in the blend (13%). We can already observe that the glass transition behavior is practically the same as for pure polyisoprene. The main difference between the two blends concerns the terminal zone. The storage modulus, G', tends toward a limiting plateau value, which depends on the amount of SI in the blend. The plateau level decreases strongly with the amount of diblock in the blend. We also added pure [SIS] data (SIS_1) and pure polyisoprene data on Figure 6 to demonstrate the effect of diblock content.

At this stage, we can observe that the secondary modulus value at lower frequencies changes with the [SIS] concentration in the blend following a power law:

$$G_{SIS/SI}(\omega \to 0) = G_{SIS}(\omega \to 0) \cdot C_{SIS}^2 \tag{4}$$

where C_{SIS} is the volume fraction of SIS in the blend [SIS + SI].

More precisely, we can rewrite this law to take into account the behavior described previously:

$$G_{SIS/SI}(\omega \to 0) = G_{SIS}(\omega \to 0) \cdot C_{I/SIS}^2 \tag{5}$$

where $C_{I/SIS}$ is the volume fraction of isoprene in the SIS part of the [SIS + SI] blends.

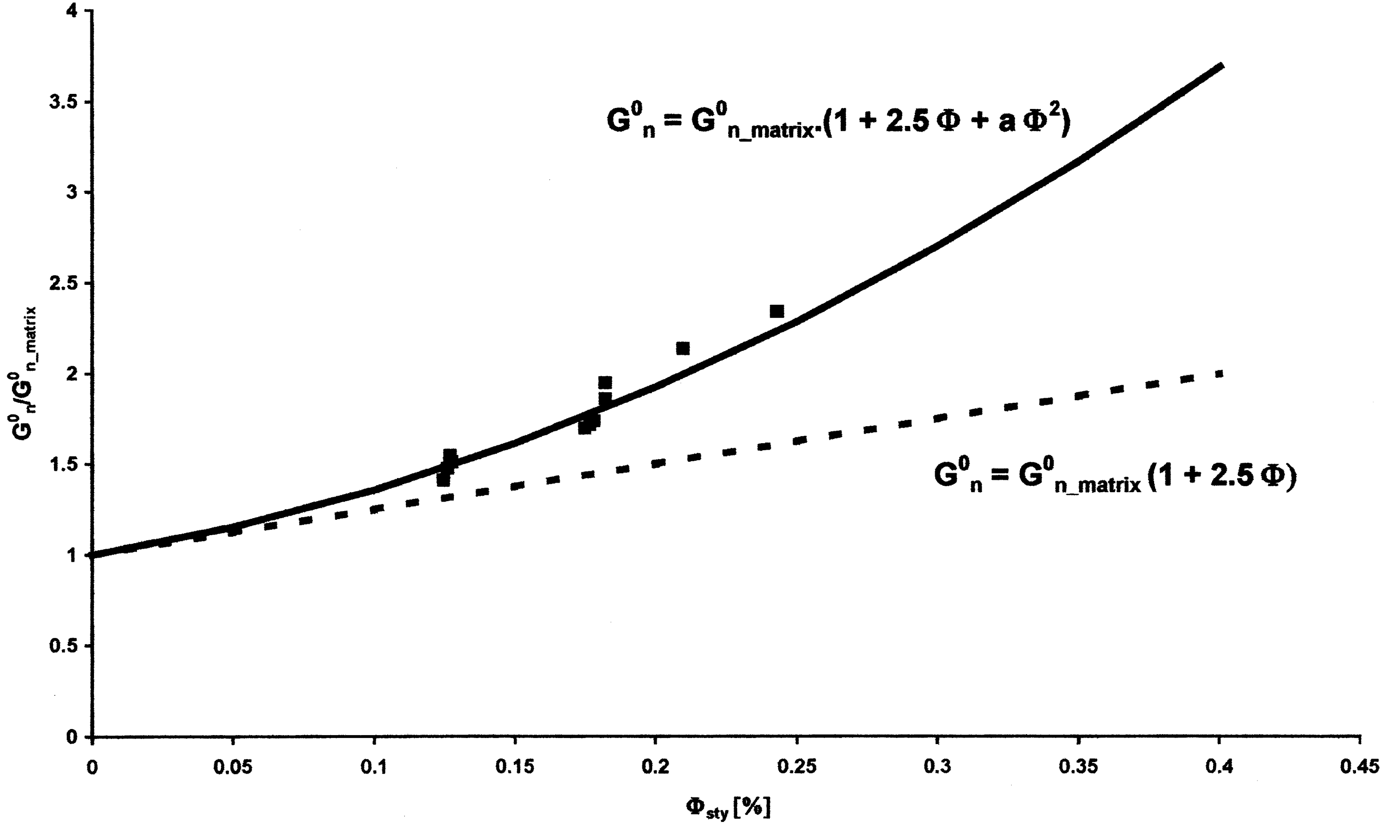

FIGURE 5 Plateau modulus of samples 1 to 10 normalized by the plateau modulus of pure polyisoprene as a function of average volume fraction of styrene Φ_{sty}. Full line: Equation (16).

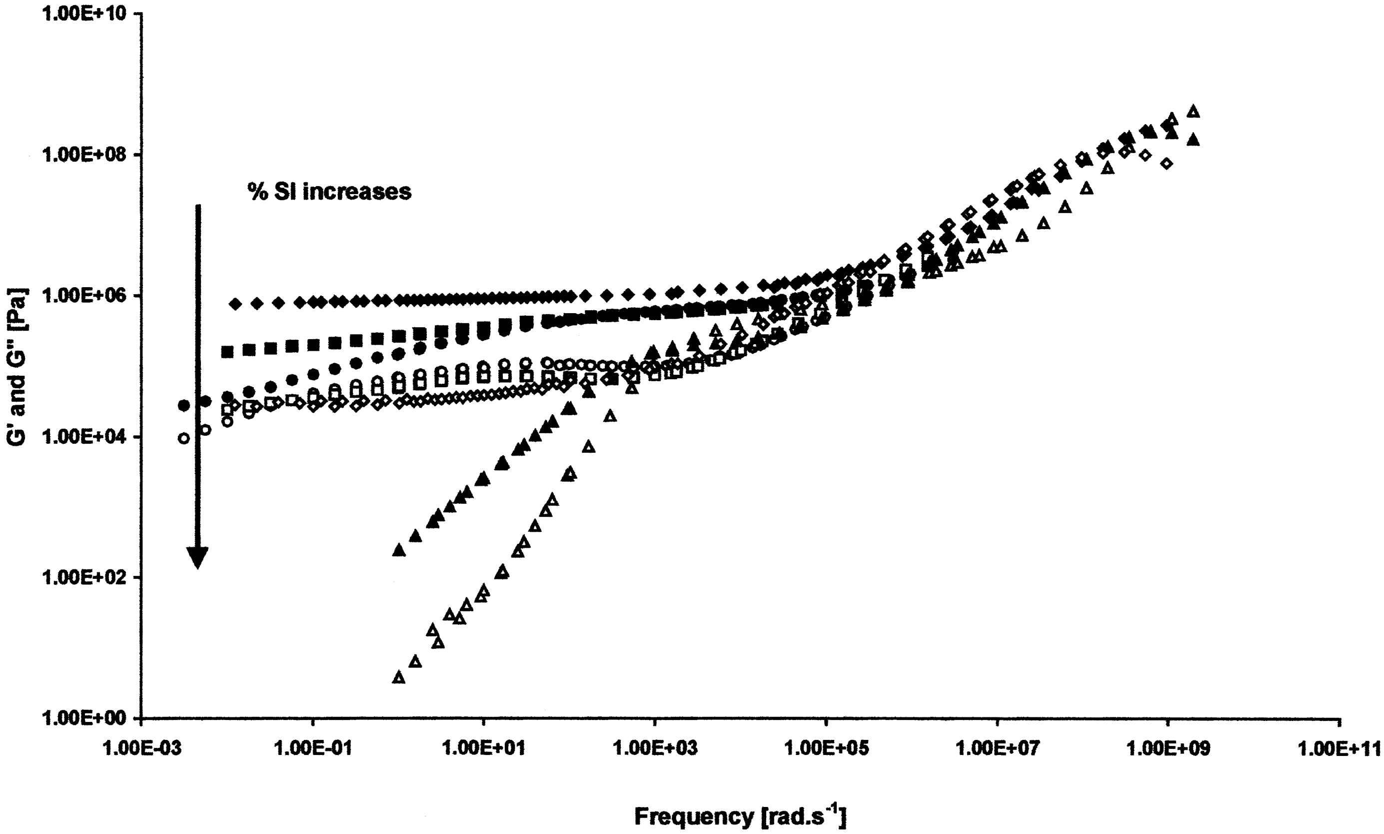

FIGURE 6 Storage and loss moduli *versus* frequency for samples 2 and 3 compared with SIS_1 (pure triblock) and pure polyisoprene. ◆, G′; ◇, G″, SIS_1; ■, G′; □, G″, sample_3; ●, G′; ○, G″, sample_2; ▲, G′; △, G″, polyisoprene.

Two limiting conditions can be written with respect to the experimental observations:

$$G_{SIS}(t) = G_{SI}(t) \tag{6}$$

at short time (high frequency) and

$$G_{SIS/SI}(t) = G_{SIS}(t) \cdot C_{SIS}^2 \tag{7}$$

at long time (low frequency), taking into account the effect of %SI.

These two limiting conditions are in agreement with the quadratic blending law that we will use in the next part [14–16].

We have reported in Figure 7 the variations of the secondary plateau (G_s) as a function of polyisoprene volume fraction in the pure SIS part of [SIS-SI] blend (*i.e.*, without resin). We can verify the power law described previously. The experimental power law exponent is 1.9, in agreement with the above microstructural description. We assume that the free polyisoprene ends of the diblock copolymers explore the network of [SIS], which behaves like an entanglement network trapped by nodules of glassy styrene at room temperature. We will refine this "blending law" while describing the model in the next section, A Model of the Rheological Behavior of the Formulations.

A Model of the Rheological Behavior of the Formulations

We have reported in Table 2 all the formulations studied, referenced as HM_x. The reference formulation used in this work is: 31% of [SIS-SI] pure polymer, 42% of solid resin, and 27% of liquid resin. For all these formulations, we observe a secondary plateau in the terminal zone. The analysis of the viscoelastic properties in this domain shows that the level of the secondary plateau decreases with the volume fraction of isoprene contained in the SIS part. Figure 8 shows that for blends HM_1 to 4, the isoprene part of the [SI] diblock acts like a solvent of the isoprene contained in the [SIS] part. It is important to notice that the concentration of resin is the same for all 4 formulations, so this curve describes the swelling effect of the diblock contained in the formulation. We have reported the secondary plateau values as a function of isoprene in the [SIS] part of the formulation; one can observe a power law exponent close to 2, which is the same as what was observed in Figure 7 for pure [SIS - SI] blends. So, the behavior described previously remains of the same nature, even in the complete formulation.

With HM_5 and _7 we can see the solid and liquid resin effect. For these two blends we inverted the ratio of solid and liquid resins and kept the ratio of polymer constant. Figure 9 shows that the "dilution effect" is the same, so the secondary plateau is the same in the two

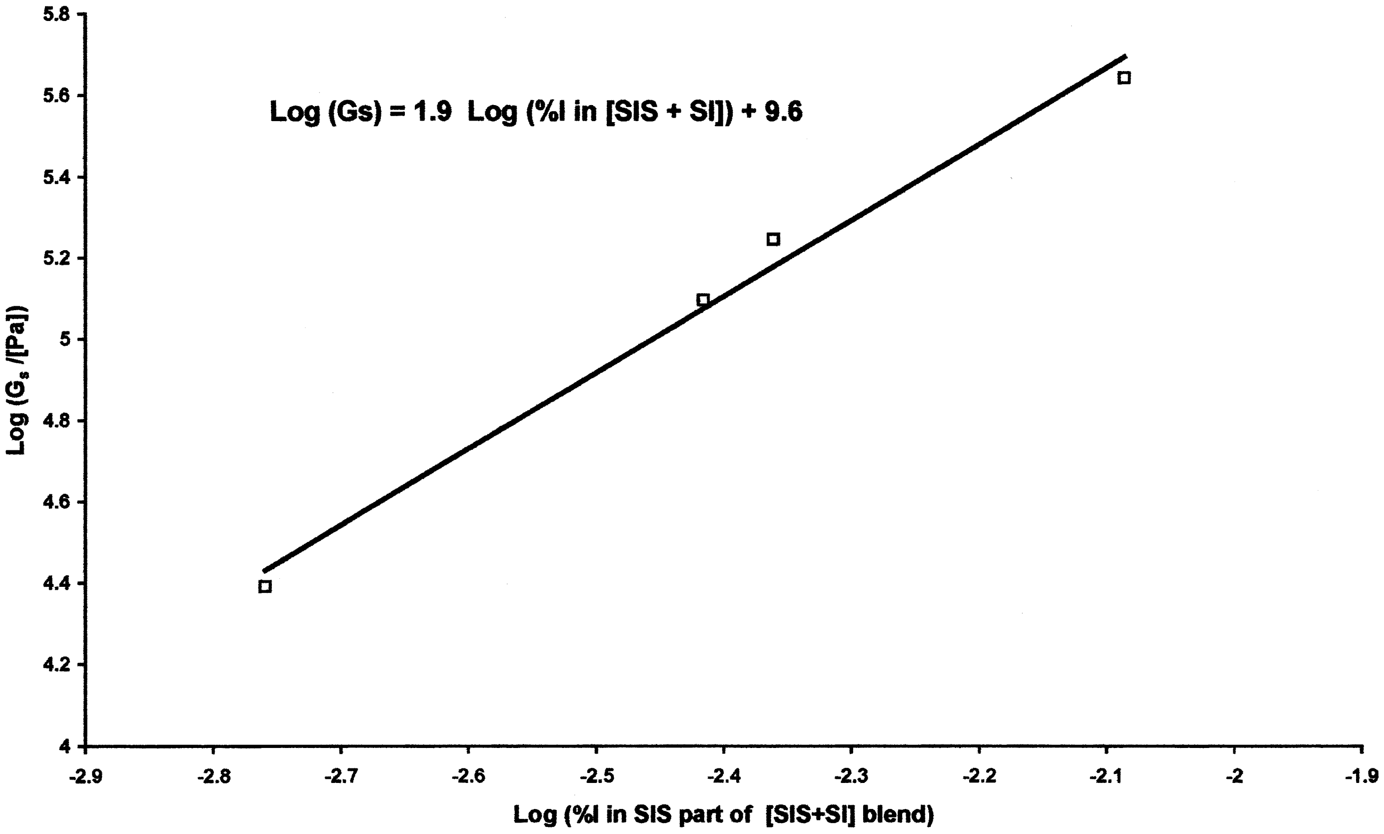

FIGURE 7 Secondary plateau modulus of SIS_1, samples 2, 4, and 5 versus polyisoprene volume fraction.

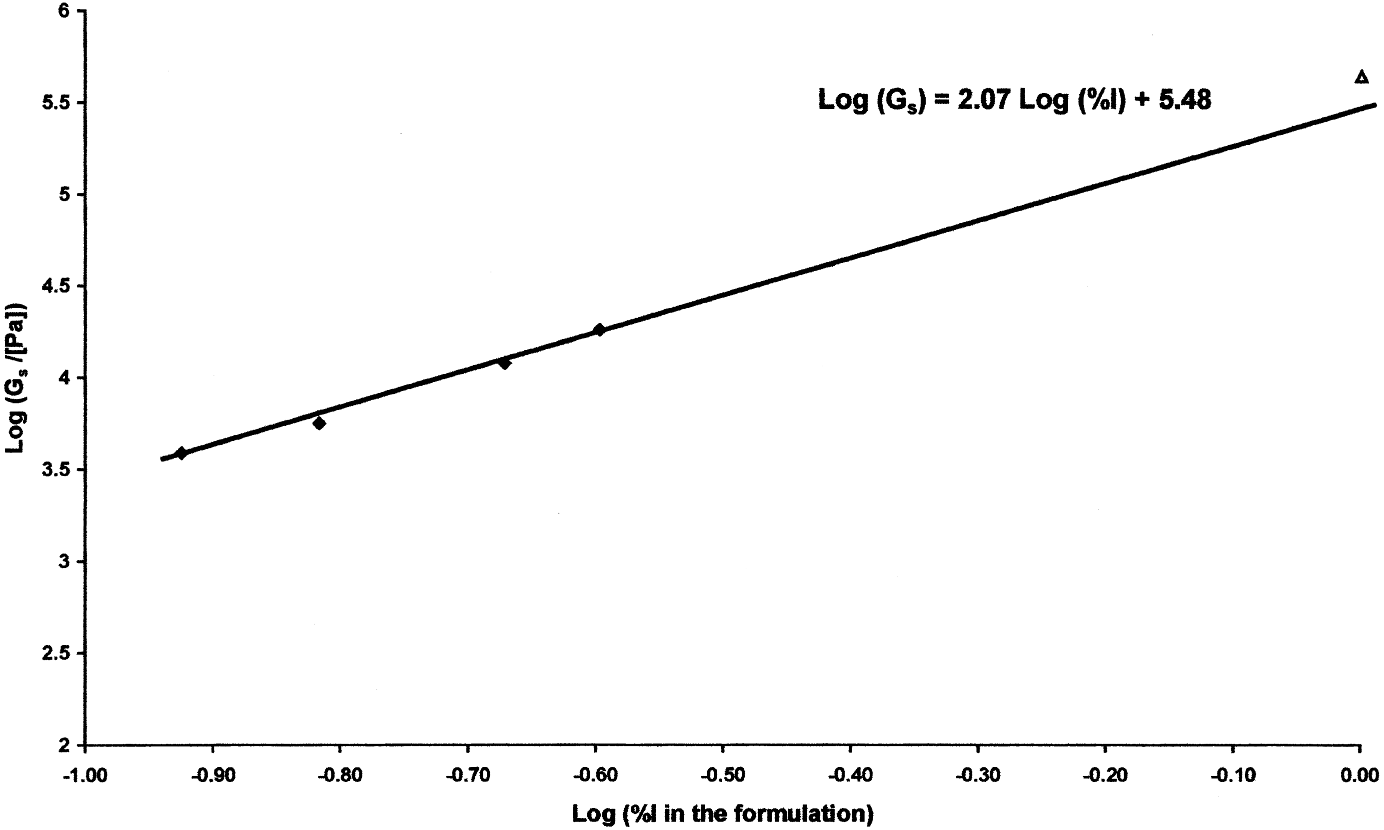

FIGURE 8 Secondary plateau modulus *versus* isoprene volume fraction in the HM_1, 2, 3, 4 at same resin content and different diblock ratio. (△), pure polyisoprene.

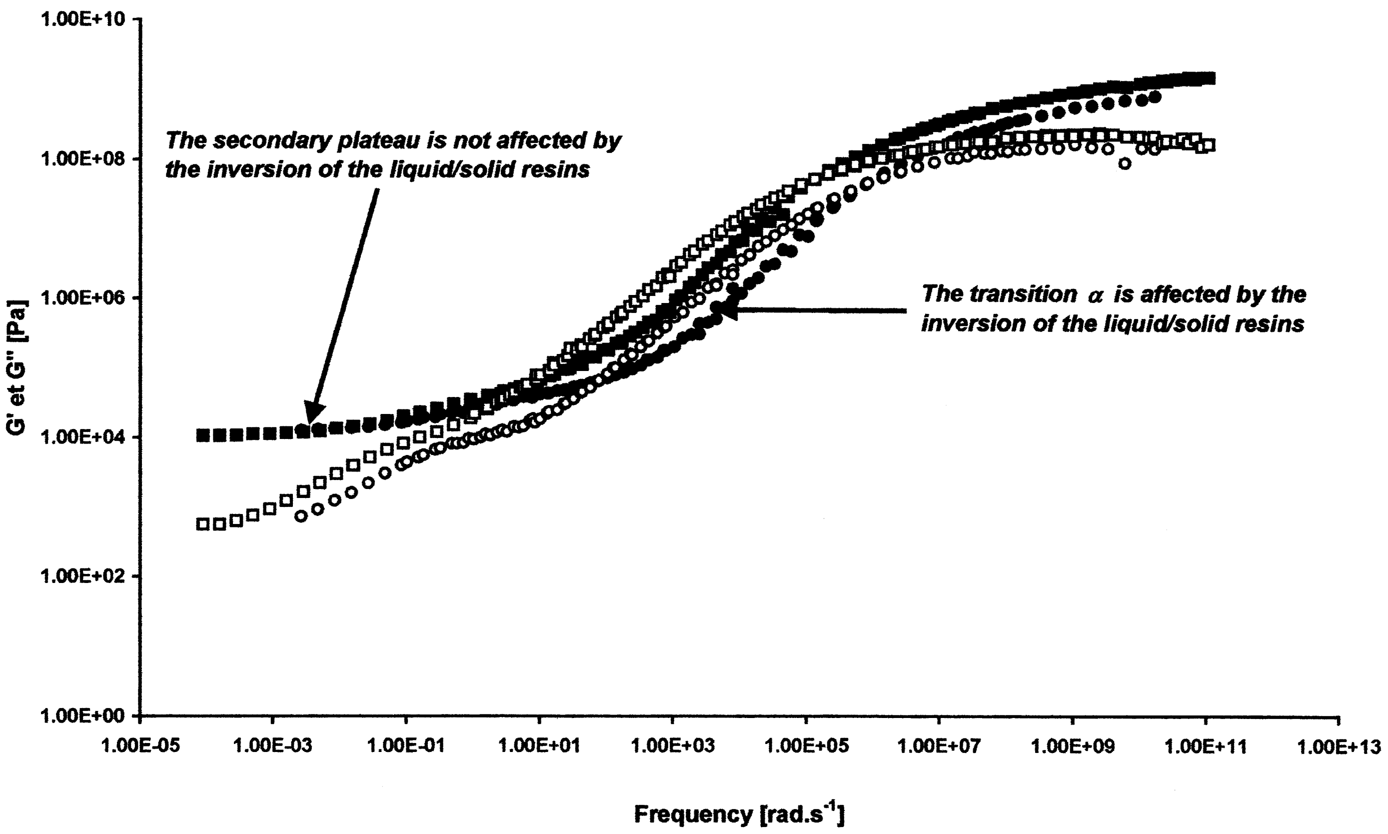

FIGURE 9 Storage and loss moduli *versus* frequency for HM_5 et HM_7. ■, G′; □, G″, HM_5; ●, G′; ○, G″, HM_7.

cases. We observe a shift of the α transition between the two formulations, due to the shift in the glass transitions (the 2 resins have different T_α).

We can see for HM_4, _6, and _7 the effect of the concentration of resin in the blend. The data fits a power law (see Figure 10):

$$G^0_{n,HM} = G^0_{n,SIS\text{-}SI} \cdot \Phi^{2,48}_{SIS\text{-}SI} \tag{8}$$

where $\Phi_{SIS\text{-}SI}$ is the volume fraction of polymer in the formulation. We obtain a power law exponent close to what has been already observed for model and commercial blends in previous works [1, 2].

We have presented in this section the rheological properties of the formulations and the effect of the formulation composition. We have described the elasticity of the blend as a function of the volume fraction of each part. We have concluded that the isoprene part of the [SI] diblock acts like a solvent of [SIS] in the pure blends as well as in the complete formulation; besides, the behavior at the lowest frequencies corresponds to the relaxation of the polyisoprene of the [SI] diblock copolymers that explore the trapped network of [SIS]. We can consider this description to be valid for concentrations of [SI] below 75%. On the other hand, the polystyrene of the [SI] and [SIS] copolymers has been demonstrated to act like a filler. The volume fraction of the resin in the blend is about the same as in the [SI] diblock. The two resins (solid and liquid) are compatible with the polyisoprene phase at the concentrations studied (*i.e.*, lower than 70%). There is only one apparent glass transition and the power law exponent of the plateau moduli as a function of polymer volume fraction corresponds to what is given by models of molecular dynamics for the swelling of entangled polymers by oligomers or low molecular weight polymers. So it should be possible to describe the observed rheological behavior of these formulations by extending models of molecular dynamics (reptation in concentrated solutions and melts, Rouse relaxations of entangled species, relaxation of star polymers).

In the next section, we will present a model which yields quantitative results and can be used to calculate rheological properties from the composition of the blend.

A MODEL OF THE RHEOLOGICAL BEHAVIOR OF THE FORMULATIONS

The linear viscoelastic behavior of the pure polymer and blends has already been quantitatively described by using concepts of molecular dynamics based on the reptation model [16]. The analytical approach of Benallal *et al.* [17] was selected and improved in the present work.

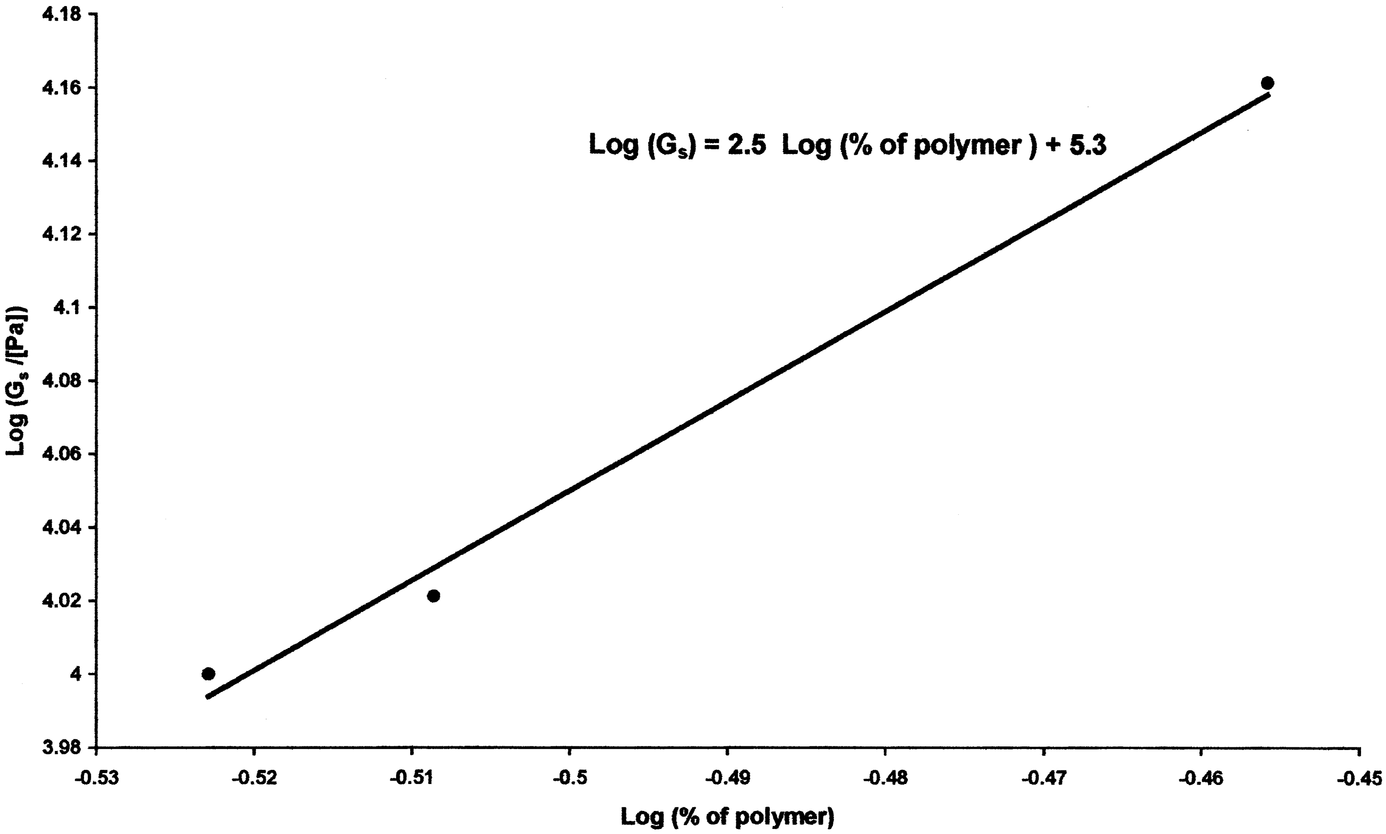

FIGURE 10 Secondary plateau modulus of HM_4, 6, 7 *versus* polymer volume fraction in the formulation.

Benallal et al. describe the relaxation function, G(t), of linear homopolymers as the sum of 4 independent relaxation processes: the α relaxation (glass transition) at very short times; two Rouse relaxation processes at intermediate times (A and B); and the terminal relaxation process at long times (process C), which is the signature of reptation. This model has been adapted to the case of diblock and triblock copolymers and their blends. For diblock copolymers, the relaxation of the isoprene sequence is treated like the relaxation of the arm of a star polymer. The triblock copolymers are modeled as critical gels with a low critical exponent. In both cases, this terminal relaxation domain replaces the reptation term. The resin is considered as an antiplasticizing solvent of the isoprene matrix, which is treated as a concentrated polymer solution [1, 2, 18]. This theoretical analysis is detailed in the following section.

In all the expressions given below, τ_0 is the elementary relaxation time of the Kuhn segment, N is the number of entanglements of a given sequence or macromolecular chain, N_e is the number of monomers between entanglement points, and N_a is the number of monomers per chain.

A Viscoelastic Model for Diblock Copolymers

The viscoelastic model for the α, A, and B relaxation processes is described in detail in Benallal et al. [17].

High Frequency Behavior (α Relaxation or Glass Transition)

In this relaxation domain (very high frequencies or very short times), only local relaxation is observed. We have used the phenomenological description of Ngai and Plasek [19], which gives a good fit in the glassy region. If G_{HF} is the glassy modulus of the polymer, the relevant relaxation modulus is given by:

$$G_{HF}(t) = G_{\infty} \exp\left(-\frac{t}{\tau_{0hf}}\right)^{\beta} \qquad (9)$$

where the two parameters G_{∞} and τ_{ohf} can be adjusted to the experimental data. The adjusted values are very close and can be considered identical within experimental uncertainties for the pure polymer and the formulations. The power law exponent β is close to 0.5.

Behavior at Intermediate Frequencies

The A relaxation process describes the Rouse modes of the equilibration of the chain between entanglement points; its characteristic time is:

$$\tau_A = \frac{1}{6}\tau_0 N_e^2 \tag{10}$$

which leads to the relevant relaxation modulus:

$$G_A(t) = G_n^0 \sum_{p=1}^{N_e} \exp\left(\frac{-p^2 t}{\tau_A}\right) \tag{11}$$

The B relaxation process corresponds to the retraction of the chain along its tube to recover the equilibrium length. The relevant characteristic time and the modulus is given by:

$$\tau_B = \frac{1}{3}\tau_0 N_a^2 \tag{12}$$

$$G_B(t) = G_n^0 \sum_{p=1}^{N_e} \frac{1}{N} \exp\left(\frac{-p^2 t}{\tau_B}\right) \tag{13}$$

Low Frequency Behavior of Diblock Copolymers

In the model of Benallal, the low frequency relaxation domain describes the reptation of a linear homopolymer chain. We consider here that the polyisoprene part of the [SI] diblock copolymer is attached at one end and free to relax on the other end like the arm of a star polymer, which leads to a much longer relaxation time than reptation. Following McLeish [20, 21] this time is given by:

$$\tau_{star}(s) = \tau_0' \exp\left(\frac{6\nu'}{M_e M_b}\left(\frac{s^2}{2} - \frac{s^3}{3M_b}\right)\right) \tag{14}$$

where M_b is the molecular weight of one branch (here the molecular weight of polyisoprene), s ranges between 0 and M_b, and ν^1 has a value close to 0.6.

The elementary time τ_0' is a function of τ_0:

$$\tau_0' = \frac{4}{3}\tau_0 \frac{M_b^2}{M_0^2}\sqrt{\left(\frac{\pi M_e}{\nu' M_b}\right)} \tag{15}$$

The expression of the relaxation modulus is:

$$G_{star}(t) = \frac{2G_n^0}{M_b}\int_0^{M_b}\left(1 - \frac{s}{M_b}\right)\exp\left(-\frac{t}{t(s)}\right)ds \tag{16}$$

which leads also to a distribution of relaxation times which is much broader than the spectrum of linear species. In Equation (16), G_n^0 can be calculated by Equation (1).

The overall relaxation modulus is the sum of the 4 contributions given above. A Fourier transform allows one to shift from the time domain to the frequency domain and yields the complex shear modulus:

$$G^*_{\text{dibloc}}(\omega) = G_{\text{HF}}(\omega) + f(\Phi_{\text{sty}})\cdot\left(G^*_{\text{A}}(\omega) + G^*_{\text{B}}(\omega) + G^*_{\text{star}}(\omega)\right) \qquad (17)$$

where the factor $f(\Phi_{\text{sty}})$ takes into account the filler effect of polystyrene [10–13] (see Equations (2) and (3)).

Low Frequency Behavior of Triblock Copolymers

We assume that SIS triblock copolymers behave like critical or fractal gels at low frequencies/long times. The equation

$$G^*_{\text{gel}}(\omega) = G_n^0(j\omega)^n \qquad (18)$$

fits, within experimental uncertainties, the experimental data measured at low frequencies with a value of the fractal exponent $n = 0.06$. The exponent n is very small indeed, so the behavior could be alternately represented as purely elastic.

Hence, the behavior of the viscoelastic solid which is relevant to the [SIS] triblock copolymers and may be written as:

$$G^*_{\text{tribloc}}(\omega) = G_{\text{HF}}(\omega) + f(\Phi_{\text{sty}})\cdot(G^*_{\text{A}}(\omega) + G^*_{\text{gel}}(\omega)) \qquad (19)$$

[SI-SIS] Blends

We used a quadratic blending law of the " double reptation " type to express the viscoelastic behavior of [diblock + triblock] blends:

$$G^{0.5}_{[\text{SIS-SI}]}(t) = C_{\text{triblock}}G^{0.5}_{\text{triblock}}(t) + (1 - C_{\text{triblock}})\cdot G^{0.5}_{\text{diblock}} \qquad (20)$$

We retrieve the limiting conditions defined in the experimental section:

$$G_{[\text{SIS-SI}]}(t) = G_{\text{triblock}}(t) = G_{\text{diblock}}(t) \quad \text{at short times (high frequencies)}$$

$$G_{[\text{SIS-SI}]}(t) = G_{\text{triblock}}(t)\cdot C^2_{\text{triblock}} \quad \text{at long times (low frequencies),}$$

where the isoprene sequences of the diblock have relaxed.

In using the expressions in Equations (17) and (19) it is possible to calculate the relaxation functions of the diblock and triblock copolymers in pure [SIS-SI] blends. We have determined the relaxation time spectrum using an algorithm based on the Tikhonov method already described in Weese [22] and Leonardi et al. [23], leading to the relaxation function:

$$G^*(\omega) \rightarrow H(G_i, \tau_i) \rightarrow G(t) = \sum_{i=1}^{N} G_i e^{\left(-\frac{t}{\tau_i}\right)} \tag{21}$$

Using the quadratic blending law in Equation (20), we can calculate the relaxation function of a pure [SIS-SI] blend and derive the complex shear modulus using the inversion scheme of Equation (21).

Figures 2 and 3 show the reasonable agreement between the model and the observed rheological behavior of [SI] diblock and [SIS] triblock copolymers. Figure 11 compares the model prediction with experimental data for sample_4 (without tackifying resin).

[SI + SIS + Resin] Blends

Topological Effect of Resins

When one adds some resin in an entangled polymer, the dilution effect decreases the plateau modulus by swelling the entanglement network and increasing the molecular weight between entanglements. The relevant power law is given by

$$G^0_{n,\mathrm{formulation}} = G^0_{n,[\mathrm{SIS\text{-}SI}]} \cdot \Phi^{2.48}_{[\mathrm{SIS\text{-}SI}]} \tag{22}$$

with an exponent value close to that observed for concentrated polymer solutions. This topological effect is similar for the elastomeric phase of both block copolymers. The change in the molecular weight between entanglements of the formulation is

$$M_{e,\mathrm{Isopreneformulation}} = \frac{M_{e,\mathrm{Isoprenein\ SISpart}}}{\Phi_{\mathrm{IinSIS}}} \tag{23}$$

Φ_{IinSIS} being the volume fraction of polyisoprene in the SIS part of [SIS + SI] blend in the formulation, $M_{e,\mathrm{Isoprenein\ SISpart}}$ is the molecular weight of the polyisoprene of the [SIS] triblock part swollen by the tackifying resins.

Thermodynamic Effect of the Resin

The resin changes the glass transition temperature of the isoprene which is, as a first approximation, the T_g of the formulation at low temperatures. As far as rheological data are concerned, this leads (at high frequencies) to a simple shift in the frequency scale. It is possible to translate the master curves by a recalculation of the

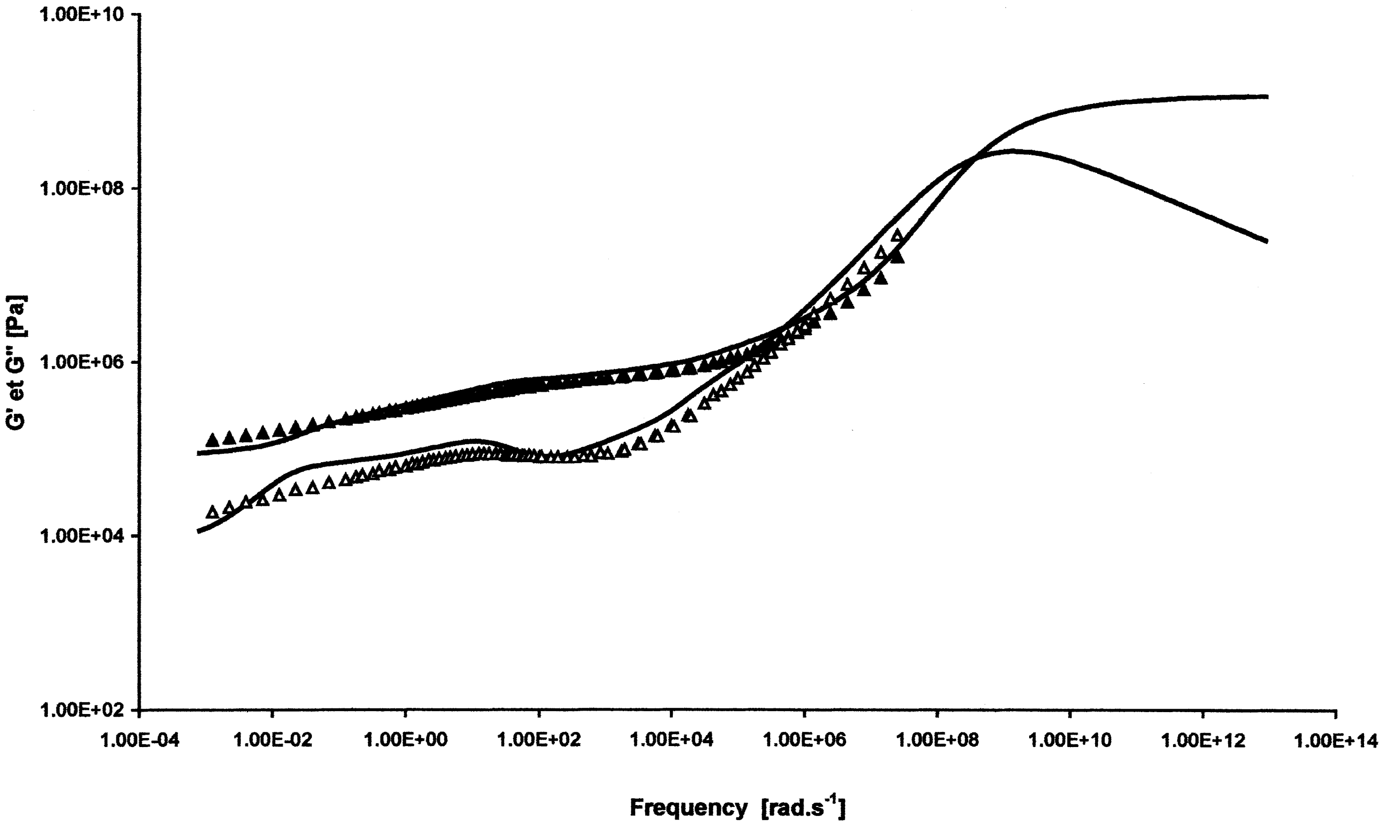

FIGURE 11 Storage and loss moduli *versus* frequency for sample_4. ■, G′; □, G″, sample_4. Full line: model.

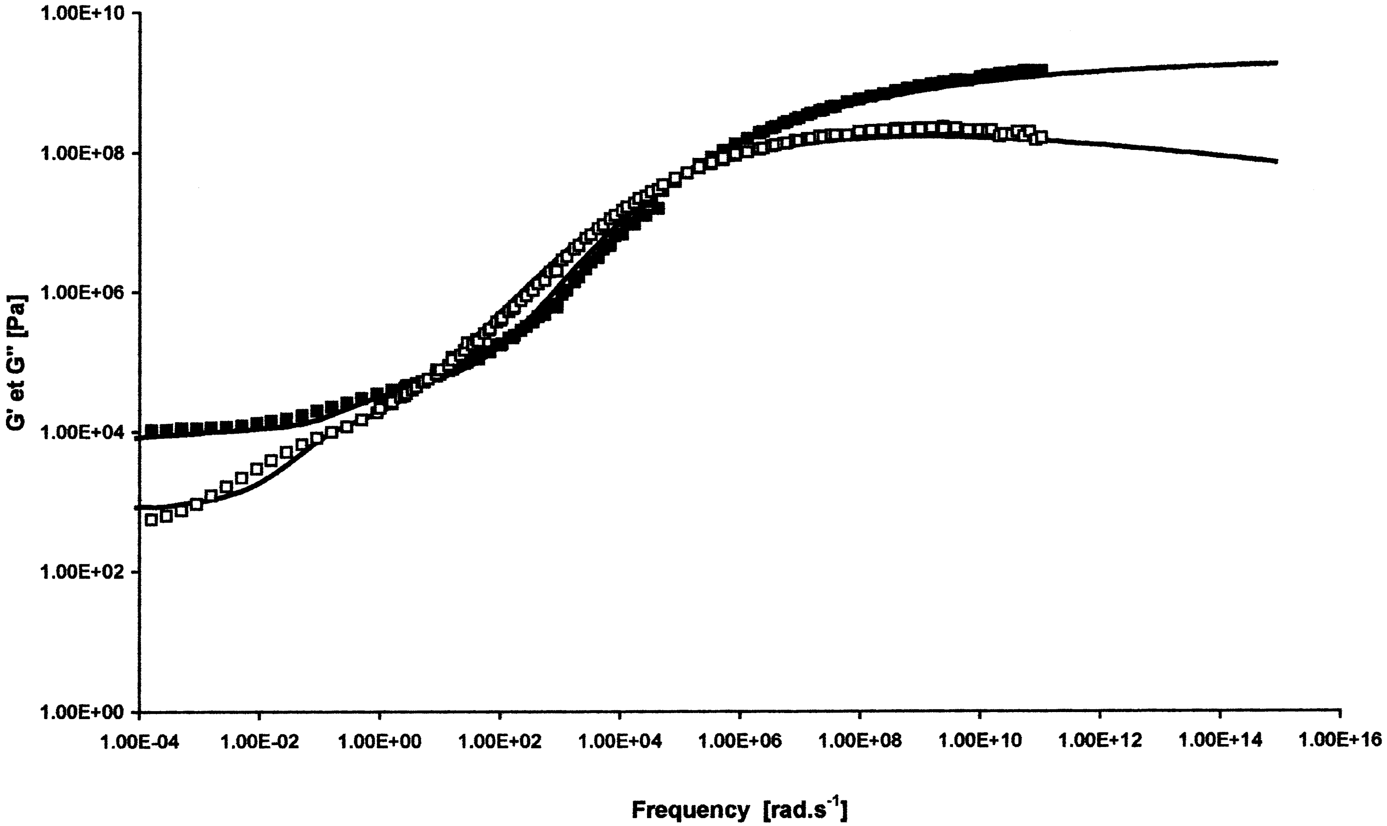

FIGURE 12 Storage and loss moduli *versus* frequency for HM_1. ■, G′; □, G″, HM_1. Full line: model.

elementary times defined above, τ_0 and τ_{0hf}, to take into account the relevant change in friction coefficient.

These concepts, which have already been published in detail [1–4], may be expressed as an increase in the Vogel (hence, glass transition) temperature (T_{inf}):

$$\begin{aligned}\tau_{0hf} &= A\cdot\exp\left(\frac{B}{T_0 - T_{inf}}\right)\\ \tau_0 &= A'\cdot\exp\left(\frac{B'}{T_0 - T_{inf}}\right)\end{aligned} \tag{24}$$

with T_0 the reference temperature (20°C).

Vogel temperature of the formulation is given by:

$$\begin{aligned}T_{inf}(\text{formulation}) = {}& \Phi_{\text{re sin}\,1}\cdot T_{\text{inf,re sin}\,1} + \Phi_{\text{re sin}\,2}\cdot T_{\text{inf,re sin}\,2}\\ &+ \Phi_{[\text{SIS-SI}]}\cdot T_{\text{inf,[SIS-SI]}}\end{aligned} \tag{25}$$

where $\Phi_{\text{re sin}\,1}, \Phi_{\text{re sin}\,2}, \Phi_{[\text{SIS-SI}]}, T_{\text{inf,resin1}}, T_{\text{inf,resin2}}$, and $T_{\text{inf,[SIS-SI]}}$ are respectively the volume fraction of resin part and copolymer part and the Vogel temperature of resin part and copolymer part.

We have confirmed that SI and SIS copolymers have the same characteristic temperatures (T_g, T_{inf}) so the variation of the elementary times is the same in both cases.

Finally, Figure 12 compares the data obtained for a complete formulation HM_1 with the model predictions.

In all cases, one can observe a good agreement between the experimental and the calculated values based uniquely on the data of the molecular weights of the [SI] diblock and [SIS] triblock parts and the percentage of styrene in each copolymer.

CONCLUSIONS

The viscoelastic properties of HMPSA based on blends of [triblock + diblock] copolymers were studied over a wide range of frequencies using time-temperature equivalence. In this first article, we have focused on [SIS-SI] blends, and we described the molecular behavior of the pure polymers and their pure blends. We also described formulations of these blends with 2 tackifying resins, which adjust the tack and adherence properties as well as the glass transition temperature. We demonstrated that the polyisoprene part plays the role of an elastomeric matrix, while the styrene part plays the role of a rigid filler. The resin lowers the elastic modulus of the formulations with a well-defined law while the diblock content lowers the secondary plateau observed at the lowest frequencies. In that case, the onset of the secondary plateau in the frequency scale is governed by the length of the polyisoprene sequence in the diblock.

We quantified concepts of molecular dynamics, which lead to a good description of the viscoelastic behavior over a very wide range of frequencies, covering all time scales relevant for processing and end-user properties of these materials. The complex shear modulus (as well as all other linear viscoelastic functions) can be calculated from the composition of the formulation and the molecular characteristics of the block copolymers.

We will show in following articles how this systematic approach can be extended to other types of adhesive formulations, such as SIS triblock copolymers formulated with SB diblock copolymers. Furthermore, the use of this model as a predictive formulation tool may yield interesting ideas in molecular design of new polymers for HMPSA applications [24].

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