

Extended Adam–Gibbs Approach To Describe the Segmental Dynamics of Cross-Linked Miscible Rubber Blends

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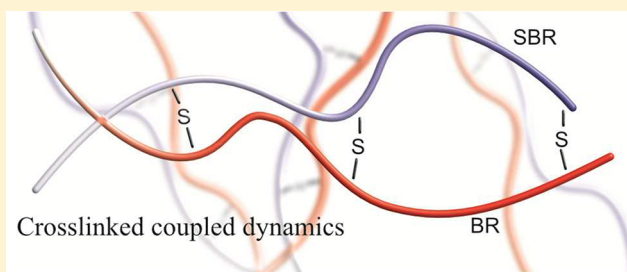
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Supporting Information

ABSTRACT: We present an extension to the Adam–Gibbs (AG) model to describe the segmental dynamics of miscible polymer blends with strong interactions. We studied the segmental dynamics of cross-linked styrene–butadiene rubber (SBR)/butadiene rubber (BR) blends of different microstructure, chain-end functionalization, and composition both unfilled and filled with precipitated silica by means of broadband dielectric spectroscopy (BDS). Contrary to what is observed for athermal miscible blends, the dynamics shows only a single segmental relaxation process due to the strong intermolecular interaction given by the cross-links. The temperature dependence of the relaxation times has been described and analyzed within the framework of a modified AG approach that takes into account the strong interactions between blend components due to the presence of the cross-links. The accuracy of the proposed model facilitates a deepened understanding of the dynamics of polymer blend systems based on the dynamics of its neat components.



1. INTRODUCTION

The segmental dynamics of miscible polymer blends shows some peculiar features making its study very attractive from both scientific and technological point of view. On the one hand, athermal polymer blends display heterogeneous dynamics at the length scale of the segmental relaxation, showing the presence of two relevant time scales.^{1–5} However, for strongly interacting polymer mixtures, like hydrogen-bonded systems or cross-linked rubber blends, the dynamical heterogeneity is broken, and single dynamics are observed.^{6–11} On the other hand, polymer blends provide useful material properties for engineering applications since their physical properties can be continuously varied between each of its components. The study of the polymer dynamics is relevant because the properties as well as the processability of polymer blends are related to chain motions. However, there has been minimal work done dealing with models to account for the dynamics of such blends. Therefore, systematic investigation of the temperature dependence of the segmental dynamics of cross-linked polymer blends will help enhance the understanding of physical fundamentals of the associated relaxation processes in rubber blend systems.

In previous studies^{4,9,12–14} different extensions of the Adam–Gibbs (AG) theory¹⁵ have been proposed to account for the segmental dynamics of polymers, polymer blends, and polymer/plasticizer mixtures under different conditions. By combination of the AG theory with the self-concentration concept, it is possible to account for the component segmental

dynamics of noninteracting miscible polymer blends. This approach has also provided an excellent description of the temperature dependence for the component segmental relaxation time in concentrated polymer/solvent athermal mixtures at atmospheric pressure¹⁴ and also for polymer/plasticizer binary mixtures at different temperatures and pressures.⁹ Only for the latter case the interactions between components were taken into account. However, the strong interactions between components in vulcanized polymer blends (provided by the cross-links) significantly affect the dynamics, and therefore a new framework is necessary to describe it. We propose here a further extension of the AG theory to include the effects of these interactions.

The aim of this work is to explore the ability of an extended AG model to describe the cross-linked polymer blend segmental dynamics as measured by dielectric spectroscopy at different polymer microstructures, temperatures, and blend compositions. The AG approach has been modified to take into account the effect of strong interactions between components due to the presence of the cross-links. The proposed model gives an excellent fitting of the experimental relaxation times of different unfilled and silica filled SBR/BR blends over a broad range of compositions and temperatures.

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2. MODEL

We will briefly summarize the theoretical background of the AG theory and the proposed extension to describe the dynamics in cross-linked polymer blends. For more details the reader is referred to previous studies.^{4,9,12–14}

The Adam–Gibbs (AG) theory relates the increase of structural relaxation time (τ) to the reduction of configurational entropy (S_c) by¹⁵

$$\tau(T) = \tau_0 \exp\left(\frac{C_0}{TS_c}\right) \quad (1)$$

where τ_0 is the relaxation time at very high temperature and C_0 is a constant which depends on the polymer type. The configurational entropy is not experimentally accessible, and therefore it is usually estimated^{12–14} from the excess entropy ($S_c \propto S_{ex} = S_{melt} - S_{crystal}$). Thus, S_c can be written as

$$S_c(T) = gS_{ex}(T) = g \int_{T_k}^T \frac{\Delta C_p(T')}{T'} dT' \quad (2)$$

where $\Delta C_p(T)$ is the excess heat capacity and T_k is the Kauzmann temperature. As shown in Figure 1, a linear

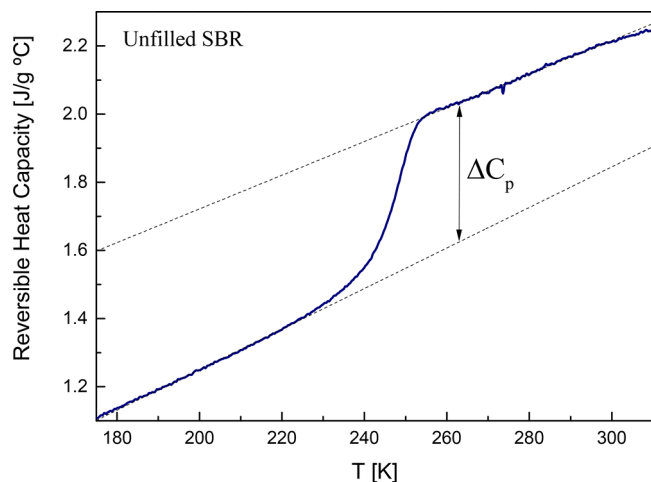


Figure 1. Reversible heat capacity as a function of temperature for unfilled SBR.

dependence of the type $\Delta C_p(T) = a + bT$ can be assumed for the temperature dependence of the excess heat capacity. Then, integrating eq 2 and inserting the result in the eq 1, we obtain the following temperature dependence for the segmental relaxation time:

$$\tau(T) = \tau_0 \exp\left[\frac{C}{T\left(a \ln\left(\frac{T}{T_k}\right) + b(T - T_k)\right)}\right] \quad (3)$$

using $C = C_0/g$ as a constant related to the polymer type. Equation 3 gives a description of the segmental relaxation time for neat polymers with only three fitting parameters (τ_0 , C , and T_k) once a and b are determined from calorimetric experiments.

In the case of polymer blends, an appropriate way to express the excess entropy in the mixture needs to be established. Contrary to athermal mixtures where two different dynamics are observed,^{1–4} cross-linked polymer blends possess single

dynamics. This behavior is commonly observed for interacting polymer blends where both components are dielectrically active.^{6–9} Thus, we can assume that for cross-linked polymer blends the interaction between the two components is strong enough to couple both dynamics. This means that the excess entropy of a blend composed of polymers A and B can be expressed as a linear combination of the corresponding quantity for each component weighted by the relative concentration plus an additional nonlinear term to account for the interactions:

$$S_{ex}^{Blend} = \phi^A S_{ex}^A + (1 - \phi^A) S_{ex}^B + \phi^A(1 - \phi^A)\chi \quad (4)$$

where ϕ^A is the macroscopic concentration of component A , $S_{ex}^{A,B}$ is the excess entropy of each component, and χ is a factor to account for the effects of the interaction between both components. Although in some cases an “effective concentration” is used,^{4,9,13,14} we will see that in the here analyzed case the nature of both the interactions and the polymers (random copolymers) does not allow to define the effective concentration properly. Therefore, we use the macroscopic concentration instead. The interaction factor can display nontrivial dependences with composition and temperature and is empirically defined, following the definition of the Flory interaction parameter,¹⁶ as the sum of two terms:

$$\chi(T) = A + B/T \quad (5)$$

where A is referred to as the “entropic part” and B/T is called the “enthalpic part”. If just one common dynamics exists in the blend, according to the AG theory eq 1, we can write the relaxation time as

$$\tau^{Blend}(T) = \tau_0^{Blend} \exp\left(\frac{C^{Blend}}{TS_{ex}^{Blend}}\right) \quad (6)$$

As a first-order approximation, we can assume that τ_0 and C are not strongly affected by the interactions between the two components, and therefore we can express them as a linear combination of the corresponding values for the neat polymers. Thus, we get

$$\tau_0^{Blend} = \phi^A \tau_0^A + (1 - \phi^A) \tau_0^B \quad (7a)$$

$$C^{Blend} = \phi^A C^A + (1 - \phi^A) C^B \quad (7b)$$

$$S_{ex}^{Blend} = \phi^A S_{ex}^A + (1 - \phi^A) S_{ex}^B + \phi^A(1 - \phi^A)\chi \quad (7c)$$

In order to apply this approach to describe the segmental dynamics of cross-linked polymer blends, the dynamics and thermodynamics of the neat components need to be fully determined. Once this is done, the dynamics of the blend can be described at any temperature and composition by means of two fitting parameters (A and B) to account for the interactions.

3. EXPERIMENTAL SECTION

Materials. We investigated the dynamics of miscible blends of high *cis*-butadiene rubber (BR), styrene–butadiene rubber (SBR) with different microstructures, and chain-end-functionalized styrene–butadiene rubber (fSBR). The microstructure of the polymers is listed in Table 1. For the filled samples, 120 phr (per hundred rubber; parts in weight per 100 g of rubber) of precipitated amorphous silica (Hi-Sil 315 G-D from PPG) with a BET N_2 specific surface area of 125 m^2/g and a mean aggregate size (d_{50}) of 127 nm was used. Tables S1–S4 in the Supporting Information show the complete formulation for all rubber compounds.

Table 1. Microstructure of the Polymers Used in This Work (M_w Is the Molecular Weight)

	styrene	cis-	trans-	vinyl-	M_w [kg/mol]
SBR	21	11	18	50	288
fSBR	21	11	18	50	288
SBR(2)	15	27.5	27.5	30	300
BR		96	2	2	480

Sample Preparation. Rubber compounds were prepared by mixing the polymers, filler, and additives in a lab-scale internal mixer. All ingredients except sulfur and cure accelerators were added in a first stage where the batch attains 150 °C. In a second subsequent stage, sulfur and accelerators were added, and mixing continued until the batch reaches 110 °C. Cured square sheets of 100 × 100 × 0.7 mm³ dimensions were obtained in a curing press held at 170 °C for 10 min. From these cured sheets the samples for dielectric and calorimetric measurements were punched out using a die with the appropriate size for each experiment. Samples prepared following this protocol were divided into six groups according to their composition: SBR/BR, fSBR/BR, and SBR(2)/BR both filled and unfilled. Each group is composed of blends with SBR/BR ratios of 100/0, 75/25, 60/40, 50/50, 40/60, 25/75, and 0/100 (60/40 and 40/60 samples were skipped for SBR(2)).

Differential Scanning Calorimetry (DSC). The calorimetric measurements were performed on a Q2000 TA Instruments DSC in the modulated mode, with a period of 100 s, amplitude of 0.5 K, and underlying heating rate of 0.25 K/min. In order to remove the thermomechanical history, the samples were annealed above T_g . Figure 1 shows the reversible heat capacity (C_p) as a function of the temperature for the neat unfilled SBR compound. The lines represent the extrapolated C_p above and below the glass transition temperature. Similar curves were obtained for fSBR, SBR(2), and BR (filled and unfilled) as shown in the Supporting Information.

According to Figure 1, and as it was previously observed for many polymers,^{13,14} the temperature dependence of the excess heat capacity can be described by means of a linear equation of the form $\Delta C_p(T) = a + bT$. Table 2 shows the corresponding values of a and b for both filled and unfilled neat SBR, fSBR, SBR(2), and BR. In the case of all SBR samples used, we observe negative values for b (Table 2) indicating that ΔC_p decreases with increasing temperature (as shown in Figure 1 and Figure S1). In the case of BR samples (for both filled and unfilled compounds) the opposite trend is observed (see Figure S2); i.e., ΔC_p increases with increasing temperature. Although negative values of b are usually found for most of polymers, we have previously observed the opposite trend for PVC,¹⁷ for instance.

Dielectric Measurements. The dielectric measurements were performed using a broadband dielectric spectrometer (Alpha Novocontrol GmbH) in the frequency range 10^{−2}–10⁷ Hz and a Quatro cryosystem as temperature controller with a precision better

than 0.1 K. According to a previous study,¹⁸ the low-frequency contribution can be removed from the experimental frequency window by drying the samples prior to the measurement. Therefore, before measuring, the filled samples were dried in two steps to remove water molecules attached to the silica surface: first at 100 °C for 4 h and then at 60 °C for 2 h under a nitrogen atmosphere. The dielectric measurements were done by performing frequency sweeps (10^{−2}–10⁷ Hz) at constant temperature. For more details about the experimental setup, the reader is referred to refs 4, 12, 13, and 18.

Figure 2 shows the dielectric loss as a function of the frequency at different temperatures for unfilled SBR(2). A main peak is observed

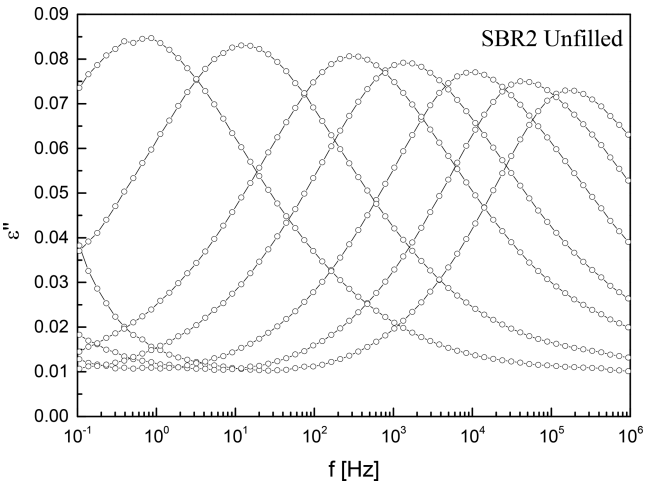


Figure 2. Dielectric loss as a function of the frequency at different temperatures (from left to right: 220, 226, 235, 241, 250, 259, and 268 K) for neat unfilled SBR(2) compound.

together with an additional contribution at lower frequencies due to the conductivity. It is worth noticing here that whereas for non-cross-linked BR and SBR the segmental relaxation uses to be asymmetric,^{19,20} in the case of cross-linked polymers symmetric peaks are observed in the dielectric loss spectra as shown in Figures 2 and 6. It has been observed²¹ that cross-linking does not affect the local motions (high frequencies) of polymers whereas it does slow down the long-range molecular motions, broadening the low-frequency side of the dielectric loss spectra becoming the curve more symmetric. Thus, solid lines in Figure 2 represent the best fit of the experimental data by means of a Cole–Cole function to account for the segmental relaxation according to²²

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (i\omega\tau)^\alpha} \quad (8)$$

Table 2. Thermodynamics and Segmental Dynamics Parameters for the Neat Compounds^a

polymer	T_g [K]	segmental dynamics parameters			thermodynamics parameters	
		$\log(\tau_0$ [s])	C [kJ/mol]	T_k [K]	a [J/(K mol)]	b [J/(K ² mol)]
			unfilled samples			
SBR	249.1 ± 0.2	−11.3 ± 0.2	35.1 ± 1.1	209 ± 2.3	42.6	−0.061
fSBR	251.1 ± 0.1	−10.5 ± 0.2	32.0 ± 1.0	215 ± 1.8	52.5	−0.091
SBR(2)	217.6 ± 0.1	−11.3 ± 0.2	35.6 ± 0.9	175 ± 1.5	59.5	−0.155
BR	172.1 ± 0.1	−10.3 ± 0.2	27.7 ± 0.7	113 ± 3.7	−6.1 ± 1.3	0.135 ± 0.03
			filled samples			
SBR	242.5 ± 0.2	−9.6 ± 0.4	47.2 ± 2.6	220 ± 2.3	96.1	−0.120
fSBR	243.6 ± 0.1	−12.0 ± 0.2	122.8 ± 2.7	194 ± 1.8	86.7	−0.057
SBR(2)	218.5 ± 0.1	−11.9 ± 0.3	53.3 ± 1.9	175 ± 1.9	69.3	−0.169
BR	175.2 ± 0.1	−13.7 ± 0.4	112.9 ± 5.9	100 ± 5.7	29.8 ± 7.3	0.006 ± 0.004

^aErrors are lower than ±1 × 10^{−3} of the least significant digit unless specified.

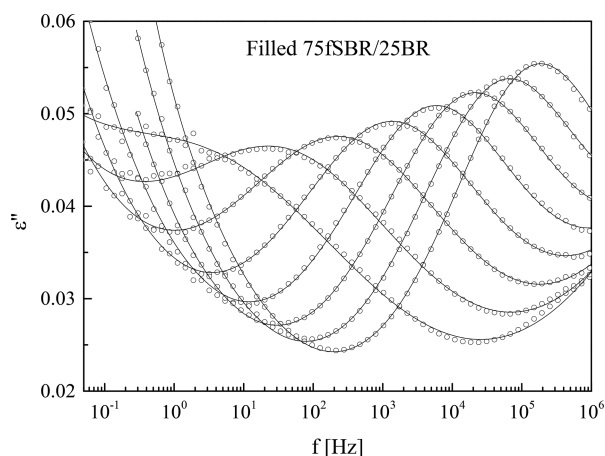


Figure 6. Dielectric loss (ϵ'') as a function of frequency at different temperatures (from left to right: 241, 247, 253, 259, 265, 271, 277, and 283 K) for the 75/25 fSBR/BR filled sample.

where $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$, being ϵ_0 and ϵ_∞ the unrelaxed and relaxed values of the dielectric constant, τ is the relaxation time, $\omega(2\pi f)$ is the angular frequency, and α is a shape parameter to account for the broadening of the relaxation peak. In addition, a power law to account for the conductivity contribution was added at high temperatures. In the following, we focus on the segmental relaxation time.

Figure 3 shows the relaxation maps for unfilled and filled SBR/BR at different blend compositions. Dots represent the experimental data

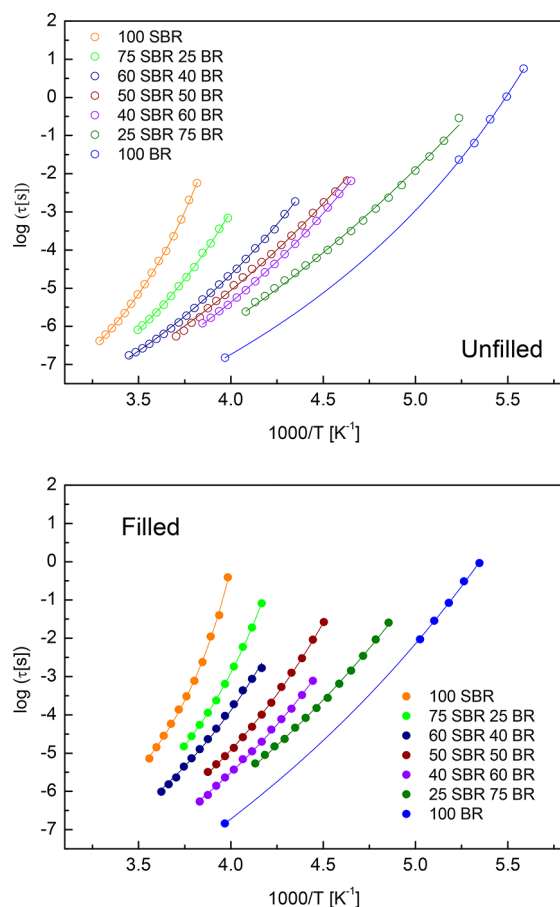


Figure 3. Relaxation map for unfilled and filled SBR/BR at different blend compositions. Solid lines represent the best fit by means of the AG approach using eqs 5–7 (see text).

and solid lines are the best fits by means of the AG approach (eqs 5–7) here proposed as described in the next section. Because of the partial crystallization of neat BR, the relaxation time is not experimentally accessible for some temperatures as shown in Figure 3 (blue line).

4. RESULTS AND DISCUSSION

Dynamics of Neat Components. Once the calorimetric response of the neat components is known, eq 3 can be used to fit the corresponding segmental relaxation times. Orange and blue lines in Figure 3 show the excellent agreement between the experimental data and the AG model for neat unfilled and filled SBR and BR, respectively. Figures 4 and 5 show the relaxation maps for fSBR/BR and SBR(2)/BR blends. The fitting parameters for all neat compounds are listed in Table 2.

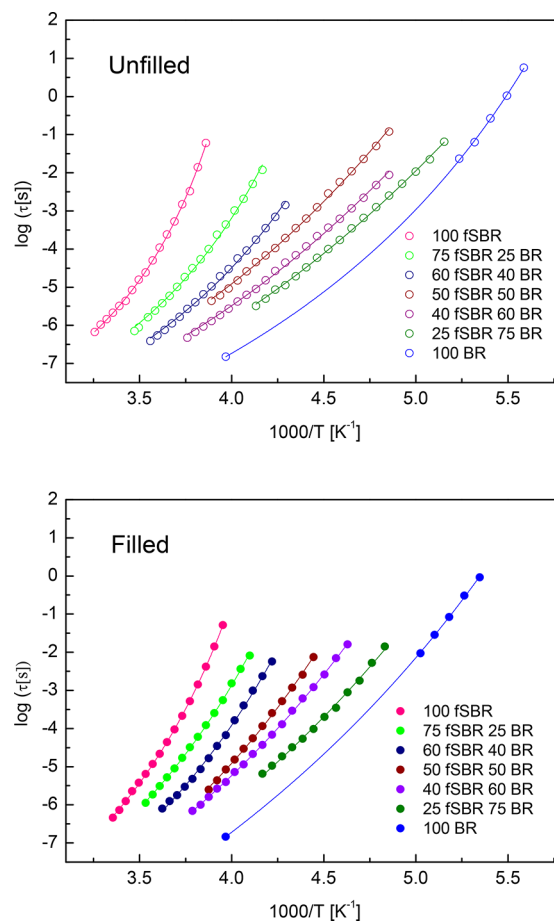


Figure 4. Relaxation maps for unfilled and filled fSBR/BR at different blend compositions. Solid lines represent the best fit by means of the AG approach using eq 5–7 (see text).

Phenomenology of the Blend Dynamics. Figure 6 shows the dielectric loss (ϵ'') as a function of the frequency at different temperatures for 75/25 fSBR/BR filled blend. The main feature in these spectra is the presence of a single segmental relaxation. A similar behavior is observed for all investigated blends. It is important to mention here that both components are dielectrically active having comparable dielectric strengths. Therefore, the presence of a single peak indicates that both components are relaxing with the same (or very similar) relaxation times. This behavior is typical for interacting polymer blends^{6–9} and random copolymers.¹⁹ For

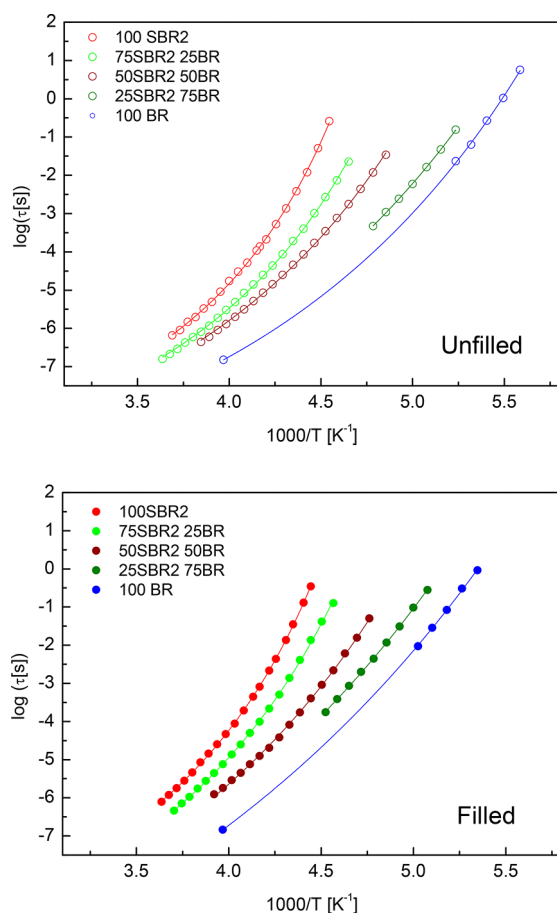


Figure 5. Relaxation maps for unfilled and filled SBR(2)/BR at different blend compositions. Solid lines represent the best fit by means of the AG approach using eq 5–7 (see text).

noninteracting miscible blends, with large enough dynamical contrast (i.e., a large difference of T_g), two different dynamics are usually observed showing the so-called dynamical heterogeneity.^{1–4}

Effect of the Interactions. Figure 7 shows the relaxation map for unfilled fSBR/BR at different blend compositions. At low temperatures, the dynamics of the blend (symbols) are faster than that predicted by the AG approach (with $\chi = 0$ in eq 7c) neglecting the interactions between both polymers (solid lines). According to eq 6, lower values of the excess entropy give higher relaxation times. This means that the real excess entropy should be higher than that resulting from the linear combination of the excess entropy of its components. Thus, the interaction term χ (at least at low temperatures) is expected to be positive and therefore to increase the total excess entropy in the blend. In fact, an increase in the excess entropy would be expected due to the presence of the cross-links, which “freeze” part of the polymer leading to a poor packing of the polymer chains. This would result in increasing the excess entropy of the polymer blend with respect to the noninteracting case, giving lower relaxation times. In addition, one can observe from Figure 7 that the difference between the relaxation times predicted by the noninteracting AG approach and the experimental ones increases upon decreasing temperature.

On the basis of the above, we added a new term to the excess entropy to account for the effect of the interaction between both polymers as stated in the Model section. Thus, our

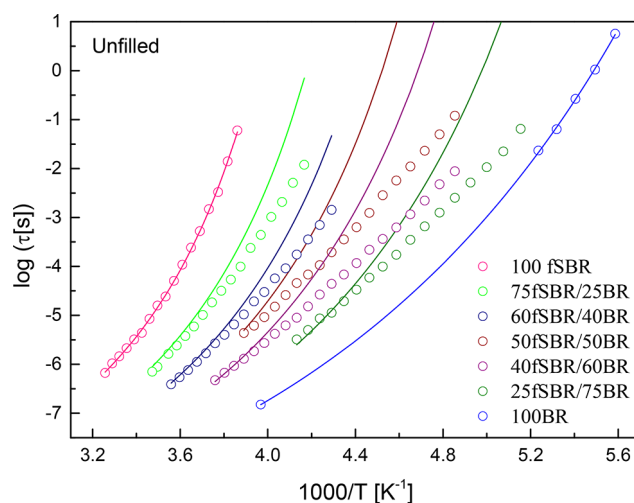


Figure 7. Relaxation map for unfilled fSBR/BR at different blend compositions. Solid lines show the failure of the AG approach without taking into account the interactions (see text).

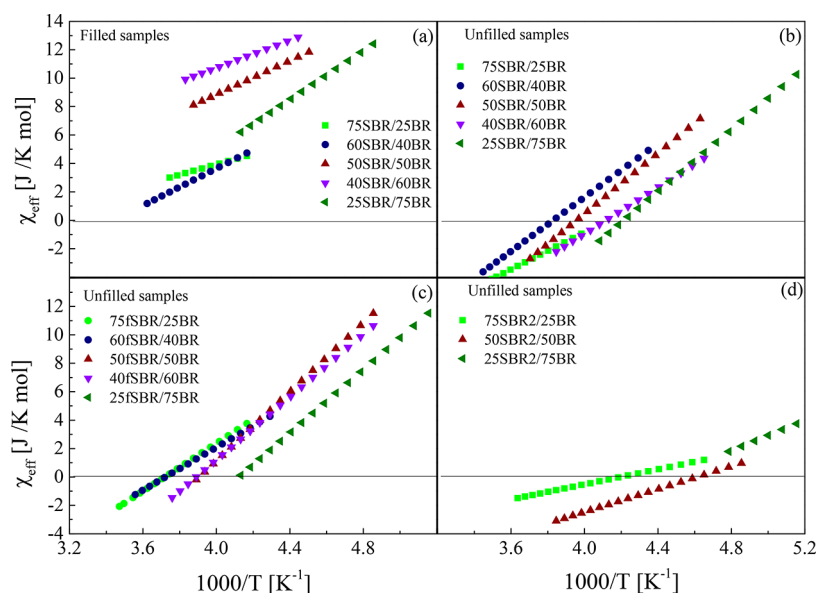
approach consists of an addition of an interaction term to the expression of the entropy in the proposed AG equation as stated in eqs 5 and 7c where the parameters A and B account for the effects of the interactions due to the cross-links. Those have to be determined from the fitting of the experimental data. We will see below that this simple modification of the AG model is sufficient to account for the blend dynamics in cross-linked polymer blends and gives an excellent description of the temperature dependence of the relaxation time for both unfilled and filled compounds with different blend compositions.

Fitting the Dynamics of the Blends. Once a full characterization of the neat blend components has been performed, we can explore the ability of the proposed extended AG model to describe the dynamics of filled and unfilled cross-linked polymer blends. Equation 6 gives the temperature dependence of the segmental relaxation time for each blend whereas the corresponding parameters are given by eqs 7a–7c with $\chi(T) = A + B/T$. Since the dynamics of the neat polymers as well as the concentration of each component are known, only two free parameters (A and B) are necessary to fit the dynamics of each blend. The parameters A and B depend on the interchain monomer–monomer interaction,²³ and since the composition changes in the different blends, one would expect that the local environment that each monomer “sees” slightly changes as well. For this reason, we left A and B to vary as free parameters. Figures 4–6 show the fit results performed for the experimental relaxation times of different SBR/BR filled and unfilled blends. As shown in these figures, we obtained an excellent fitting of the experimental data for both filled and unfilled blends. The corresponding parameters A and B are listed in Table 3.

Figure 8 shows the interaction parameter ($\chi(T) = A + B/T$) as a function of inverse temperature for different blends and compositions. As commented before, the interaction factor, at least at low temperatures, is positive and therefore increases the entropy of the blend compared to athermal mixtures. Negative values of the interaction parameter mean a lower entropy compared to the corresponding athermal mixture most likely due to a more efficient packing of the monomers. By comparing filled and unfilled SBR/BR (Figure 8a,b), we can observe higher values of the interaction and a higher composition dependence

Table 3. Fitting Parameters *A* and *B* for Unfilled and Filled SBR/BR, fSBR/BR, and SBR(2)/BR at Different Blend Compositions (Parameter *A* in J/(K mol) and *B* in J/mol)

SBR/BR		75/25	60/40	50/50	40/60	25/75
unfilled samples						
SBR	<i>A</i>	-10.5 ± 1.9	-22.5 ± 4.6	-14.9 ± 1.4	-8.6 ± 2.2	-29.3 ± 1.2
	<i>B</i>	3605 ± 469	6534 ± 1162	5936 ± 329	4834 ± 532	8592 ± 435
fSBR	<i>A</i>	-47.1 ± 2.6	-13.8 ± 3.1	-23.1 ± 2.6	-42.1 ± 1.0	-34.0 ± 3.5
	<i>B</i>	12712 ± 671	4446 ± 782	8078 ± 605	12221 ± 233	9915 ± 769
SBR(2)	<i>A</i>	-11.1 ± 1.2		-18.6 ± 1.7		-23.4 ± 2.3
	<i>B</i>	2653 ± 312		4031 ± 307		5266 ± 398
filled samples						
SBR	<i>A</i>	-27.0 ± 1.6	-36.4 ± 1.0	-42.1 ± 1.2	-33.6 ± 0.5	-46.4 ± 1.4
	<i>B</i>	6538 ± 416	9503 ± 162	10638 ± 282	8159 ± 96	10915 ± 288
fSBR	<i>A</i>	-31.3 ± 2.3	-28.0 ± 1.7	-47.5 ± 1.0	-43.0 ± 1.0	-46.0 ± 1.0
	<i>B</i>	8415 ± 591	7519 ± 410	12156 ± 181	11049 ± 235	11159 ± 192
SBR(2)	<i>A</i>	10.3 ± 1.5		-3.6 ± 0.8		-18.8 ± 1.9
	<i>B</i>	-2687 ± 235		929 ± 87		3993 ± 512

**Figure 8.** Interaction parameter as a function of inverse temperature for several compositions for (a) filled SBR/BR, (b) unfilled SBR/BR, (c) unfilled fSBR/BR, and (d) unfilled SBR(2)/BR blends.

for filled compounds. In the case of unfilled compounds with SBR and fSBR (Figure 8b,c), similar values of the interaction parameter as well as a comparable composition dependence are observed. However, when comparing SBR (or fSBR) with SBR(2) much lower values of the interaction parameter are observed for the latter (see Figure 8d). This is directly related to the microstructure of SBR(2) which has less styrene and vinyl groups. According to Sakurai et al.,²³ the interaction between BR and SBR is dominated by the interaction with the styrene groups. Thus, by lowering the amount of styrene, one should expect a lower interaction between both components.

In addition, it is most likely that the reduction of “bulky” groups (styrene and vinyl) does not greatly affect the packing between both polymers, and therefore the entropy is not much affected compared to the athermal case.

It is also interesting to note that parameters *A* and *B* are coupled in the sense that the ratio *B/A* is approximately constant for each blend. This would allow reducing even more the number of free parameters by writing the interaction parameter as $\chi(T) = A(1 + k/T)$, *k* being a constant parameters independent of the composition. Figure S3 shows an example

of the fitting obtained for fSBR/BR blends by keeping *k* constant and leaving *A* free. Moreover, it has been shown²³ that the Flory–Huggins interaction parameter can be obtained by means of small-angle neutron scattering (SANS) or even predicted using the theory of random copolymer mixtures developed by Tenbrinke et al.²⁴ and by Paul and Barlow.²⁵ It is worth noticing that the here presented interaction parameter (χ), though analogous, is different from the Flory–Huggins interaction parameter. Whereas the latter refers to an actual energy interaction term, the former is related to the difference in the entropy arising from the interaction of the mixture in the melt with respect to the glassy state. Even though, it is expected that χ could be related (or scaled) with the Flory–Huggins interaction parameter. In this case, the proposed AG model would become completely predictive, and one could estimate the dynamics of a blend given the microstructures, molecular weights, and composition of the neat components.

5. CONCLUSIONS

We have presented in this work an extension of the Adam–Gibbs model to account for the dynamics of cross-linked

polymer blends with different microstructures at several temperatures and compositions. We have included in the model a single term which accounts for the strong polymer/polymer interaction due to the cross-links created during vulcanization. This additional term in the expression for the excess entropy suffices to obtain an excellent description of the temperature dependence of the experimental relaxation time for both filled and unfilled blends.

The simplicity and accuracy of the model make it very attractive from both a scientific and technological point of view.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.macromol.7b02432](https://doi.org/10.1021/acs.macromol.7b02432).

Tables S1–S4: the full formulation of the studied blends; Figures S1 and S2: calorimetric curves for SBR and BR unfilled and filled; Figure S3: relaxation maps with the best fit by means of the AG model with fixed values of k and parameter A left free (see text); Table S5: the corresponding values for k and A (PDF)

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Notes

The authors declare no competing financial interest.

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