The effect of vulcanization additives on the dielectric response of styrene-butadiene rubber compounds

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HIGHLIGHTS

- Understanding vulcanization mechanisms using molecular dielectric dyes.
- Effect of the vulcanization additives on the dielectric response of rubber compounds.
- Filler-accelerator interaction in vulcanized rubber compounds.
- In situ monitoring of vulcanization process by means of dielectric spectroscopy.

ARTICLE INFO

ABSTRACT

Rubber compounds are usually vulcanized in order to improve their mechanical properties. Although vulcanization has been largely studied in the literature, it is not completely clear how the different additives interact among them and how these affect the final properties of the compounds. Here, we present a systematic study using a combination of different experimental techniques, which allows a deeper understanding of the vulcanization mechanisms. We have studied different compounds, with and without silica filler, prepared with styrene butadiene rubber (SBR) of different microstructures and functional end groups. The dielectric response of cured and uncured samples was measured at different temperatures in a wide frequency range. In addition, we analysed the calorimetric and mechanical properties for selected compounds as well as the crosslink density. Furthermore, we performed *in-situ* vulcanization (in the dielectric cell) to analyse the evolution of different contributions to the dielectric spectrum during cure. Based on our results we conclude that the dielectric response of these SBR compounds is strongly affected by the presence of one of the cure accelerators used in the formulation, namely diphenyl guanidine (DPG). However, this does not affect the segmental relaxation time nor the structure of the crosslink network or the mechanical properties. This study shows the potential of broadband dielectric spectroscopy for monitoring and understanding the vulcanization mechanisms.

1. Introduction

Rubber compounds are very important materials due to their wide tunability in properties and their potential applications in several industries. In particular, styrene butadiene rubber (SBR), one of the most used synthetic rubber, is a very versatile material and it has been used for several applications such as tires, footwear, belts and other industrial products. Similar to other rubber materials, SBR is vulcanized to form covalent crosslinks between polymeric chains to produce a three-dimensional network. Vulcanization causes deep chemical changes that increase elasticity and reduce plasticity by the formation of a three-dimensional cross-linked molecular network. The "vulcanization package" includes vulcanization agents (being sulphur or organic peroxides the most used), accelerators and activators which have a pronounced effect on the vulcanization rate as well as on the crosslink distribution. Although vulcanization has been used for more than a century and it has been largely studied over the last decades [1–5], a fundamental understanding of its complex mechanisms remains as one of the most scientific challenges in the rubber community [6].

The dynamics of unvulcanised as well as cross-linked (cured)

rubbers is normally characterized by means of either mechanical [7–9] or dielectric spectroscopy [4,10–12]. In particular, dielectric characterization of polymers has shown to be a useful technique that provides relevant information about the dynamics of polymers in a wide frequency and temperature range. In addition, dielectric spectroscopy can be a very versatile and successful technique to obtain a deeper insight into the vulcanization mechanisms. These processes usually involve a cascade of chemical reactions whose behaviour is strongly affected by complex interactions among the different additives and also with silica (in the case of filled compounds). The effects of many of these processes are, in some cases, not detectable by means of mechanical measurements, but they are observable using dielectric spectroscopy. Thus, this technique can be used to monitor the vulcanization process and to understand in more details the complexity of the vulcanization mechanisms.

In this work, we performed a systematic study to analyse the effect of the different vulcanization additives (with special emphasis on the accelerators) on the dielectric response of rubber compounds. In addition to dielectric spectroscopy, we used a combination of experimental techniques such as calorimetry, rheometry and mechanical dynamical analysis. By analysing neat SBR as well as uncured and cured compounds of SBR we were able to get insight in the understanding of the interactions among different ingredients and how this affects the segmental dynamics and the mechanical properties.

2. Experimental section

2.1. Materials

We investigated the dynamics of both styrene butadiene rubber (SBR) and chain-end functionalized styrene butadiene rubber (fSBR) with an alkoxysilane group and at least one of a primary amine group and thiol group (Trinseo SLR4602). SBR and fSBR have the following composition (or microstructure): 21% styrene, 11% 1,4 cis, 18% 1,4 trans and 50% vinyl monomer. The baseline formulation is given in Table 1 from which the formulations of the here studied compounds are derived. Additional fSBR samples were prepared in which each of the vulcanization additives (listed in Table 1) was systematically removed only one at a time. These samples are labelled fSBR without "name of the removed additive".

Furthermore, we also studied filled compounds on a second polymer, labelled SBR2, with a different microstructure (SBR2: 15% styrene, 27.5% 1,4 cis, 27.5% 1,4 trans and 30% vinyl monomer). The filler used was 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 (d50) of 127 nm. Table 2 shows the formulations for these samples which in addition contain antioxidant (2.5 phr), stearic acid (3 phr), ZnO (2.5 phr), DPG (2 phr), CBS (2.3 phr) and Sulphur (1.5 phr).

Rubber compounds were prepared using an internal mixer. All the ingredients (except sulphur and accelerators) were added in a first step and mixed until the batch reached 423 K. In a second mixing step,

Table 1
Full formulation [phr[a]] of both SBR and fSBR.

Ingredient	[phr]
fSBR or SBR	100
Wax	2
Antioxidant	4
Processing oil	3
Stearic Acid	3
ZnO	2.5
Secondary accelerator (Diphenylguanidine, DPG)	1.6
Primary accelerator (N-Cyclohexylbenzothiazole-2-sulphenamide, CBS)	1.2
Sulphur	1.4
Sulphur-Donor	2

[a] (per hundred rubber; parts in weight per 100 g of rubber).

Table 2
Formulation [phr[a]] of silica filled SBR2 samples.

Ingredient	Unfilled	15 phr	30 phr	50 phr	70 phr	90 phr
SBR2	100	100	100	100	100	100
Silica	–	15	30	50	70	90
Silane	–	1.2	2.4	4	5.6	7.2

[a] (per hundred rubber; parts in weight per 100 g of rubber).

sulphur and accelerators were added and the mixing continued until the batch reached 383 K. Cured square sheets of $100 \times 100 \times 0.7 \, mm^3$ dimensions were obtained in a curing press held at 443 K for 10 min. The samples for calorimetric, mechanical and dielectric characterization were cut from the rubber sheets using dies of 5, 8 and 30 mm of diameter, respectively.

2.2. Experimental techniques

- **Thermal measurements:** Standard differential scanning calorimetry (DSC) measurements were done using a Q2000 from TA Instruments. Cooling-heating cycles between 323 and 423 K at a rate of 10 K/min were performed using nitrogen as transfer gas. The annealing time between cooling and heating runs was 5 min. The glass transition temperature (T_g) was determined at the inflection point of the endothermic curve.

- **Dielectric measurements at atmospheric pressure.** The dynamics of the compounds was studied by broadband dielectric spectroscopy (BDS). To measure the complex dielectric permittivity (ε^*) we have used a high-resolution dielectric analyser from Novocontrol in the frequency range from 10^{-2}–10^6 Hz. The sample temperature was regulated using a Quattro temperature controller with nitrogen gas flow providing a temperature stability better than ± 0.1 K. The measurements were done by performing frequency sweeps at constant temperature, in the temperature range from 253 K to 325 K every third degree.

For neat SBR the α-relaxation is asymmetric (as for most of the polymeric materials [13]) and it depends on the styrene content [14] and not on functionalization [15]. However, when SBR is vulcanized, the α-relaxation becomes symmetric [16,17]. It has been also observed that crosslinking does not affect the local motions (at high frequencies) whereas it slows down the cooperative molecular motions (α-relaxation), broadening the low frequency side of the dielectric loss spectra and thus making the peak more symmetric. Therefore, in the following we analyse the imaginary part of the dielectric permittivity for the segmental relaxation as well as for other contributions using the phenomenological Cole-Cole (CC) function [18].

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + (i\omega\tau)^\alpha} \tag{1}$$

where $\omega = 2\pi f$ is the angular frequency, τ is a characteristic relaxation time, ε_∞ is the unrelaxed dielectric constant, $\Delta\varepsilon$ the dielectric strength and α describes the symmetric broadening of the spectrum. Normally, at high temperatures conductivity effects dominate the dielectric response at low frequencies and therefore a power law term needs to be added ($\sigma/\omega\varepsilon_0$), where ε_0 denotes the vacuum permittivity and σ is the static ionic conductivity.

- **Dielectric measurements under pressure.** The dielectric measurements at elevated pressures were carried out using a pressure cell, in the range 0–250 MPa, supplied by Novocontrol GmbH. The measurements were performed by frequency sweeps (10^{-2}–10^6 Hz) at room temperature (T = 298 K) and constant pressure, with stability better than ± 2 MPa. For more details about the experimental setup see Refs. [19–21].

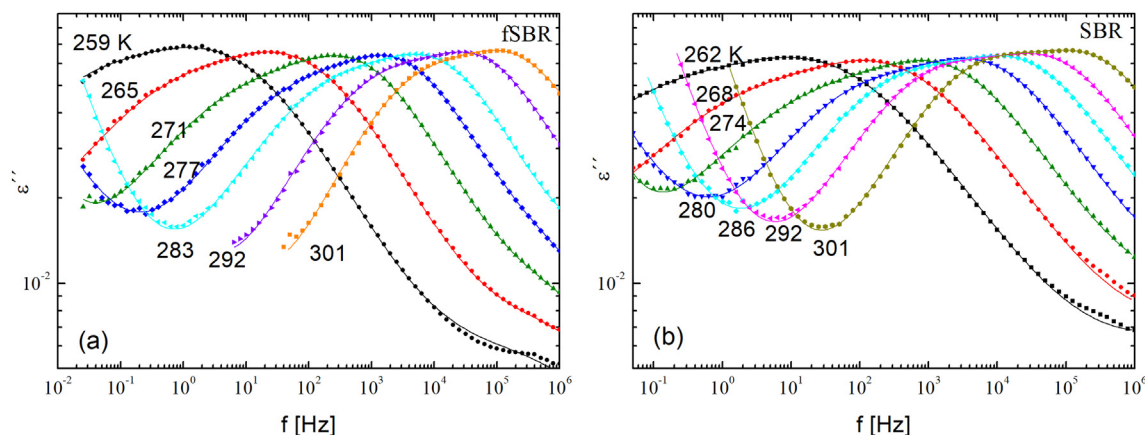- **Mechanical measurements.** For the mechanical characterization, we

Fig. 1. Imaginary part (ε") of the complex dielectric permittivity ($\varepsilon^*(f)$) of the vulcanized fSBR (a) and the vulcanized SBR (b) at temperatures above the glass transition. The main feature is composed of two contributions. Solid lines represent the least-squares fits as explained in the text.

used two experimental setups. On the one hand, we measured the rheometric properties at T = 423 K using an MDR2000 rheometer from Alpha Technologies according to the ASTM D2084 standard. On the other hand, the dynamical mechanical measurements were done using an Anton Paar MCR 302 rheometer with a plate-plate configuration of 8 mm in diameter. Specimen in the shape of circular discs of the same diameter were cut from vulcanized sheets of 0.7 mm thickness. The measurements were done in oscillatory rotational shear with a strain of 0.05%, a frequency of 1 Hz and a heating rate of 2 K/min, starting at 238 K going up to 318 K.

3. Results and discussion

3.1. Dynamics of neat and vulcanized SBR

Fig. 1 shows the frequency dependence of the imaginary part (ε´) of the complex dielectric permittivity (ε^*) of the functionalized and the non-functionalized SBR (fSBR and SBR) at different temperatures. In both cases, we observe that it is not possible to describe the main feature (typically associated with the α-relaxation) by a single process. Instead, it is composed of at least two distinct contributions.

Fig. 2 shows ε´ as a function of the frequency for the neat SBR (only polymer without additives) and two vulcanized samples (SBR and fSBR) at fixed temperatures above T_g (see plot). The neat SBR (Fig. 2a) displays a single peak corresponding to the α-relaxation as normally

observed for most polymers. However, when mixing SBR with the corresponding additives and vulcanizing, the main feature has to be fitted by two processes (Fig. 2b). For the fitting of these samples (with additives), two Cole-Cole (CC) functions were used. Since both peaks are rather close to each other, the fitting parameters of the two CC functions are strongly coupled and therefore there are different sets of parameters that fit the total dielectric response. Hence, we established some criteria to constrain these parameters: both the frequency and the relaxation strength for the α-process were set as high as possible. It is important to note that the relaxation time at $\tau = 100s$ gives a dielectric estimation of the glass transition temperature, $T_{g,100s}$. Therefore, we can identify the faster process in Fig. 2 (b and c) as the α-relaxation of the compounds since the $T_{g,100s}$ coincides with the calorimetric T_g.

Fig. 2c shows the superposition of the three curves after normalizing both the frequency and the intensity. On the high frequency side, very small differences are observed among the three samples. However, on the low frequency side, a clear change between neat and cured samples is observed. From these figures, it is evident that the presence of additives and/or the vulcanization process (presence of the additives, products of vulcanization or chemical changes in the polymer chains) are related to the origin of the slow dielectric mode.
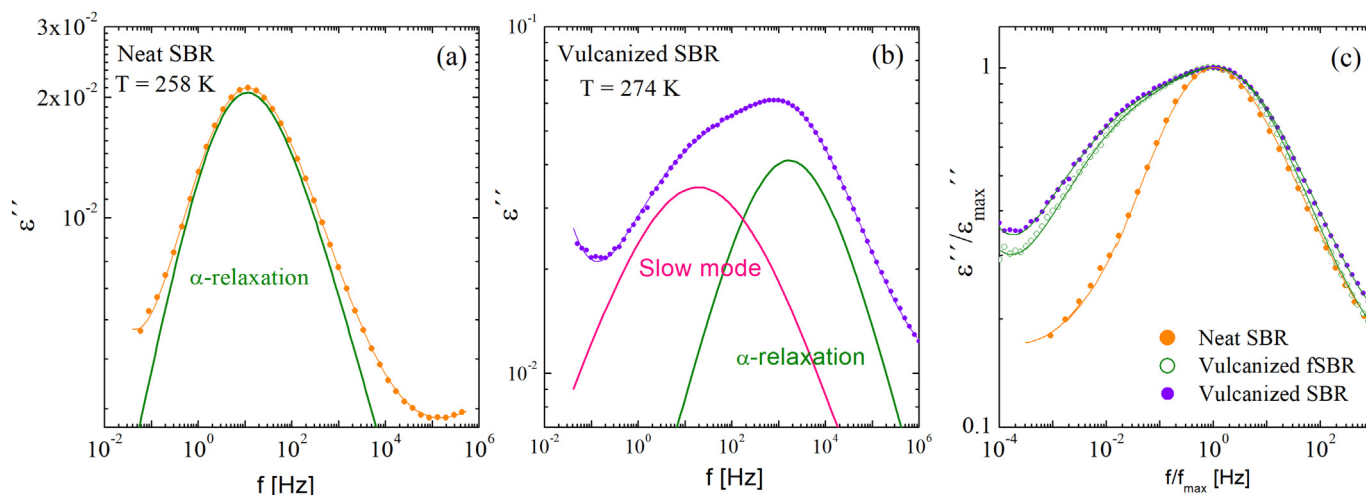

Fig. 2. Imaginary part (ε´) of the complex dielectric permittivity as a function of the frequency. (a) Neat SBR, (b) Vulcanized SBR and (c) normalized response of SBR and fSBR compounds and neat SBR. After vulcanization the main peak is composed by two contributions where the fastest corresponds to the α-relaxation (see text).

3.2. The role of the vulcanization additives on the dielectric response of fSBR

In the previous section, we have seen that the dielectric spectrum of both fSBR and SBR after vulcanization showed a new contribution, which is slower than the α-relaxation. It therefore follows that some of the chemicals added for vulcanization or some products formed during vulcanization are related to the origin of this slow dielectric mode. We have noticed that some of these ingredients have associated a relative strong dipole moment that could be easily detected by dielectric spectroscopy. For instance, the accelerators CBS and DPG have a dipole moment of 2.90 and 3.99 Debye (D) respectively [22], which is big enough to be detected by means of dielectric spectroscopy even though the quantity used in the formulation is small.

Vulcanization causes deep chemical changes in which the C-H bonds adjacent to C-C double bonds, are replaced by chains of sulphur atoms that link with a cure site of another polymer chain. Furthermore, after the vulcanization reaction, some of the additives might not be fully consumed and remain in the network or even are converted into other products. Therefore, the first step is to remove the residual products after vulcanization by extraction of fats, waxes, and other organic compounds by using a good solvent, like pyridine. Fig. 3 shows the imaginary part of the dielectric permittivity before (a) and after (b) pyridine treatment. It is clear from the figure that by fixing the parameters of the α-relaxation in both plots, the dielectric strength of the slow mode is strongly reduced after extraction (b). Pyridine is able to remove molecules which are not covalently linked to the polymer chains, which therefore do not contribute anymore to the dielectric response. It is worth noticing that the relaxation time of the α-relaxation is basically unaffected by the presence of the slow mode (in fact, the same CC curve for the segmental relaxation (purple line) was used in both cases).

Based on this result, we proceeded with removing the vulcanization additives systematically, one at a time, and analysed the corresponding dielectric response. Fig. 4 shows the results at $T = 289$ K. The slow mode is still clearly visible for all the compounds except for the one "without accelerators" where the intensity of the slow process has significantly decreased showing that the accelerators are involved in the molecular origin of the slow mode.

3.3. The effect of the accelerators on the dielectric response of fSBR

We now focus on the influence of accelerators (DPG and CBS) on the dielectric response of fSBR. The vulcanization recipe used in this section is the same as before (see Table 1) but varying both DPG and CBS contents as shown in Table 3.

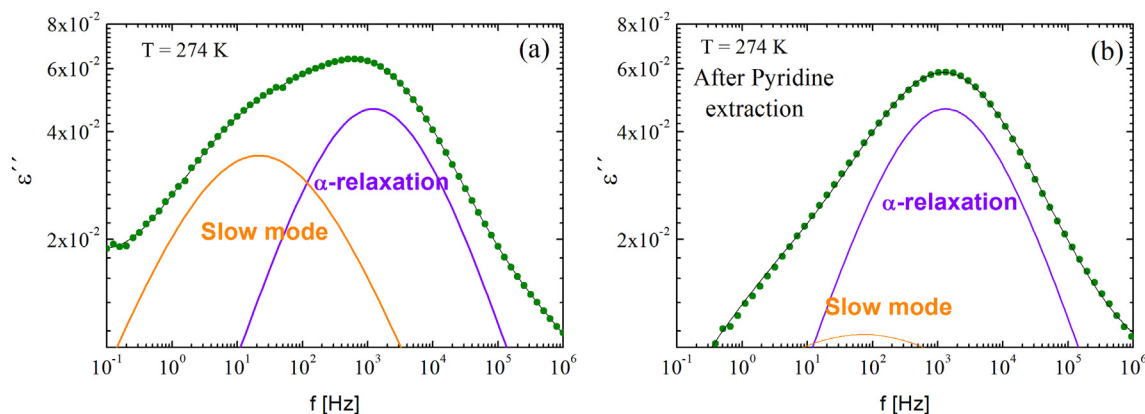The value of T_g is approximately constant for these six samples (about ~250 K), independently of the type and amount of accelerator used in the formulations. Therefore, we do not expect strong shifts of the α-relaxation corresponding to these compounds. In addition, using equilibrium-swelling measurements (in toluene at 25 °C), the crosslink density (μ) was determined [23,24] being of the same order of magnitude for all the compound analysed (see Table 3). This result indicates that the accelerators content within the studied range ($0 \leq$ DPG ≤ 1.2 and $1.0 \leq$ CBS ≤ 1.6) has a weak impact on both the crosslink density and the dynamics. However, DPG has a strong impact on the shape of the dielectric loss as shown in Fig. 5. Decreasing the DPG content, the intensity of the slow mode decreases and it is very small when DPG is not present in the formulation; the residual peak is most likely due to the presence of CBS.

From Fig. 5 it is clear that DPG has a much stronger impact on the slow mode than CBS. On the other hand, neither DPG nor CBS have a significant effect on the segmental dynamics (almost unaffected T_g) or on the network structure (almost constant crosslink density).

3.4. In-situ vulcanization

Although it is evident from the previous results that DPG is related to the origin of the slow mode in the dielectric response, it is still not clear whether this process is due to DPG itself or due to vulcanization products related to it. In order to clarify this point, we have measured two uncured samples as well as the same samples at different levels of vulcanization. The first sample has all the ingredients (full formulation) whereas the second one does not have any accelerator (neither DPG nor CBS).

The uncured sample with full formulation was measured at 288.15 K where all relevant dielectric contributions fit well into our experimental frequency window. The spectrum is shown in Fig. 6a (open symbols). After the measurement, the sample was cured inside the dielectric cell at 453 K. Then, a new spectrum was measured at 288.15 K as shown in Fig. 6a (full symbols). For the uncured sample, three processes can be clearly observed in the spectrum. The one at around 10 Hz, which is not present in the raw polymer, completely disappears in the cured sample and most likely corresponds to additives which are totally consumed during the vulcanization. The other two processes correspond to the segmental relaxation (at higher frequencies) and to the slow mode discussed in this work. Both processes remain in the cured sample. It is important to note here that the slow mode process is observed in the uncured sample and therefore it is related to DPG itself and not to a product of the vulcanization.

For the sample without accelerators, the dielectric response for the uncured case was first measured at room temperature (open symbols). After that, the sample was cured inside the dielectric cell by applying several cure cycles at different temperatures from 309 to 463 K. After
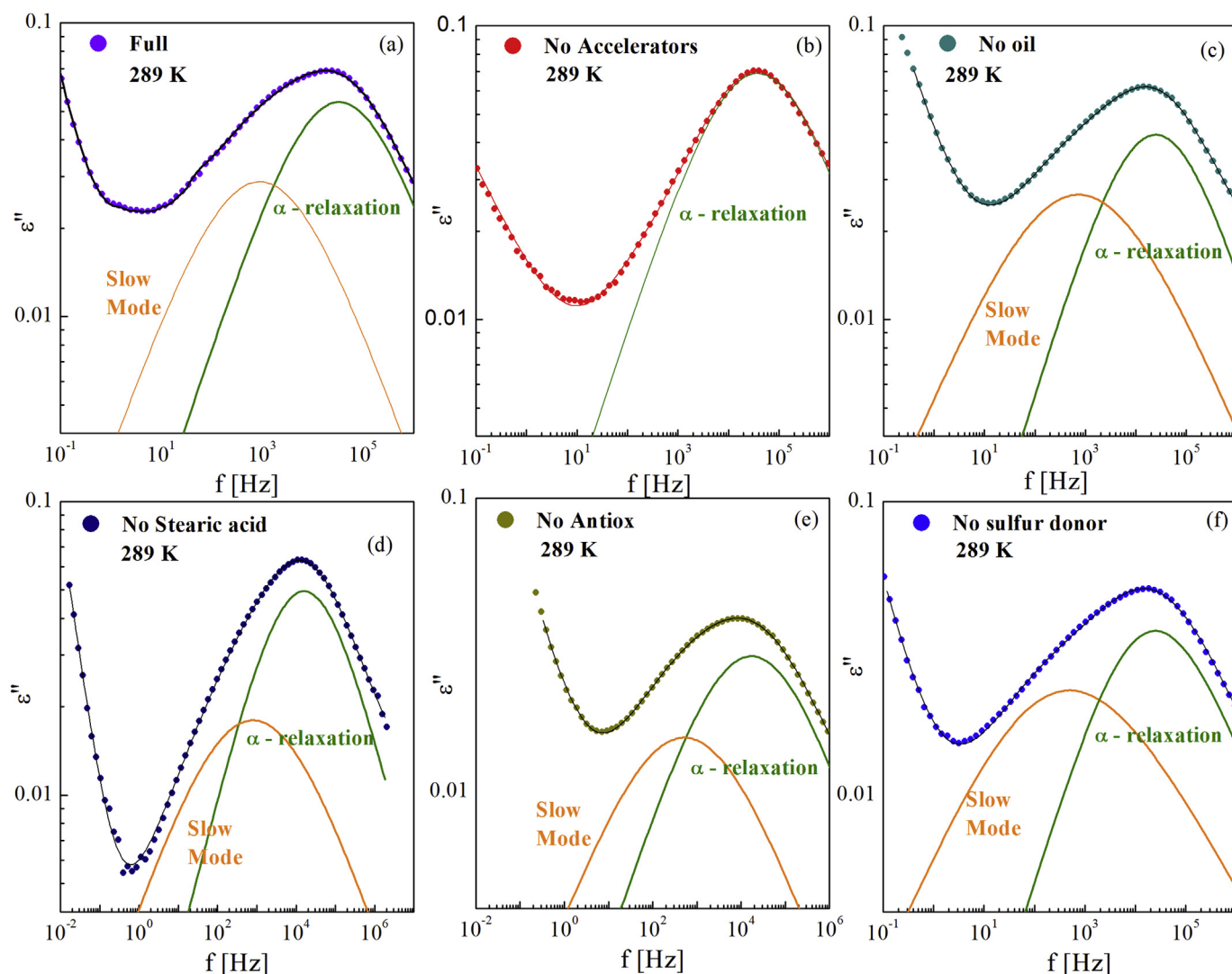

Fig. 3. Imaginary part (ε'') of the complex dielectric permittivity as a function of the frequency at T = 274 K. (a) Vulcanized fSBR, (b) vulcanized fSBR after extraction using pyridine.

Fig. 4. Imaginary part (ε'') of the complex dielectric permittivity as a function of the frequency at T = 289 K for fSBR: full formulation (a), no accelerators (b), no oil (c), no stearic acid (d), no antioxidants (e), and no sulphur donor (f). Solid lines represent the fit to the experimental data. In all the cases, two dielectric processes are observed with the exception of the sample without accelerators where a single relaxation is observed. (For the sake of clarity, the conductivity contribution is not shown).

Table 3
Calorimetric T_g and crosslink density (μ) for fSBR compounds with different amount of DPG and CBS (the rest of the formulation remains the same as in Table 1).

Sample	DPG [phr]	CBS [phr]	T_g [K]	μ [$\times 10^{-5}$mol/cm3]
fSBR1	0.0	1.6	250.5 ± 0.2	3.5 ± 0.1
fSBR2	0.3	1.6	250.9 ± 0.2	4.0 ± 0.1
fSBR3	0.6	1.6	250.4 ± 0.2	3.8 ± 0.1
fSBR4	0.9	1.6	250.6 ± 0.2	4.0 ± 0.1
fSBR5	1.2	1.6	250.8 ± 0.2	3.9 ± 0.1
fSBR6	1.2	1.0	250.6 ± 0.2	3.3 ± 0.1

each vulcanization cycle, the dielectric response was measured at 298 K as shown in Fig. 6b. In this case, no additional slow mode to the segmental relaxation is observed in the spectrum. This means that in the absence of accelerators, neither other additives nor products of the vulcanization lead to a contribution in the frequency range of the slow mode studied in this work.

These results allow us to conclude that the origin of the slow dielectric mode is due to the DPG itself and it is not related to any product of the vulcanization. In addition, this phenomenon does not affect the

relaxation time nor the structure of the crosslink network.

3.5. The effect of the pressure on the dynamics of SBR

The effect of pressure variation on the dynamics of the different relaxation processes can be very useful to investigate both thermal and density effects [25–27]. In many cases, pressure can be a helpful thermodynamic parameter especially in separating dynamic processes [28–31]. In our particular case, the idea is to use pressure to see whether the slow mode and the α-relaxation have the same activation volume, i.e. the same pressure dependence of the relaxation times. Fig. 7a shows the dielectric loss as a function of the frequency, at room temperature and at different pressures and Fig. 7b shows an example of the fitting. As it is clear in these figures, the relaxation time of each process increases with increasing pressure. This pressure dependence is plotted in Fig. 7c for the whole range showing that both processes move with pressure at the same rate. This means that the activation volume is the same for the two processes emphasizing the hypothesis that the slow mode is due to the dielectric dipole of some additive coupled to the segmental dynamics of the SBR and not due to an independent relaxation process.
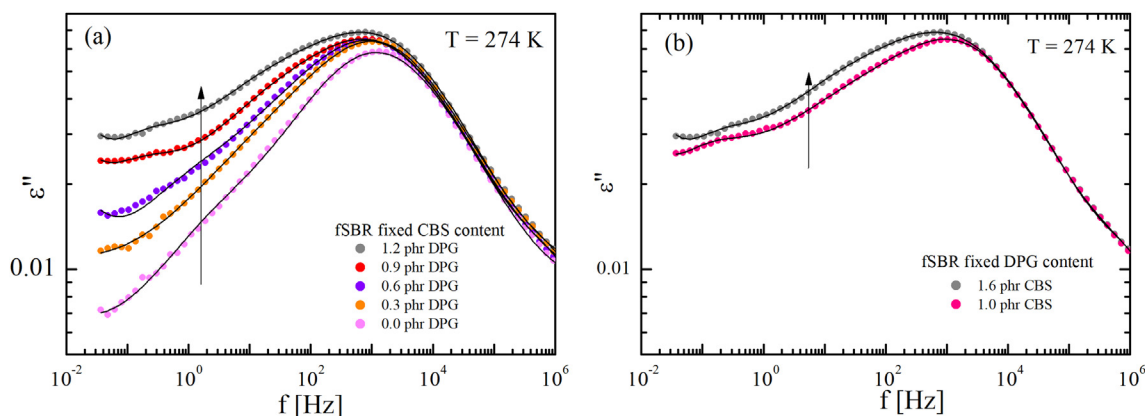
Fig. 5. Imaginary part (ε'') of the complex dielectric permittivity as a function of the frequency at T = 274 K for a) samples with constant CBS (1.6 phr) and different amounts of DPG and b) samples with constant DPG (1.2 phr) and different amounts of CBS.

3.6. DPG in silica filled SBR2 compounds

The analysis of the unfilled compounds allowed us determining that DPG is the main responsible for the slow mode in the dielectric response. We move now to study filled compounds to analyse whether this low frequency process can provide us some insight into the filler-accelerator interaction. In order to do this, we prepared samples with different amounts of silica as shown in Table 2.

Fig. 8a shows the dielectric loss for SBR2 silica filled compounds with different filler loadings. We can observe the presence of the slow mode for the unfilled sample (0 phr) and the reduction of its dielectric strength with increasing silica content. We note that increasing the filler content has a similar effect on the dielectric response as decreasing the DPG content as shown in Fig. 5a. It is worth to mention here that DPG molecules are normally adsorbed on the nanopores of precipitated silica particles [32] and therefore, increasing the silica content decreases the effective amount of DPG in the rubber. To prove this, we have measured the cure time (T90) from torque curves as described in the experimental section. The results are shown in Fig. 8b. The cure time increases almost linearly with increasing silica content (starting at 30 phr) indicating that, as part of the DPG is adsorbed on the silica surface and therefore the effective amount of DPG is reduced in the polymer, the curing process takes longer.

Fig. 8b shows that the relaxation strength for the segmental relaxation decreases with increasing silica content. In addition, the relaxation strength for the slow mode decreases with increasing silica content and becomes negligible at around 40 phr. This means that above this silica loading, either the DPG is entirely adsorbed on the silica particles or the fraction of DPG that is not adsorbed is completely consumed during vulcanization.

3.7. Mechanical response

We finally wonder if the feature due to the DPG observed in the dielectric spectrum can be also observed by mechanical spectroscopy. Fig. 9 shows the tan (δ) curve obtained from mechanical spectroscopy as a function of the temperature for SBR with two different quantities of DPG (0 and 1.2 phr).

In Fig. 9 we can observe that tan (δ) is basically the same for both samples, specially at high temperatures where the additional contribution due to DPG is expected to be. Therefore, we can make two important conclusions: on the one hand, the presence of DPG does not affect the mechanical response of the cured compound; this is because the remaining DPG after vulcanization does not further react chemically and does not disturb the mechanical behaviour due to its small amount (< 1% in volume). On the other hand, although the mechanical behaviour is unaffected by DPG, it strongly affects the dielectric response. This is due to its high dipole moment (3.99 D) which makes its detection possible even for very small quantities (less than 1% in volume) in the compound. The fact that DPG does not affect the mechanical response but it is detectable in the dielectric spectra makes possible to use it as a molecular dye showing the possibilities of the broadband dielectric spectroscopy for monitoring and understanding the vulcanization process.
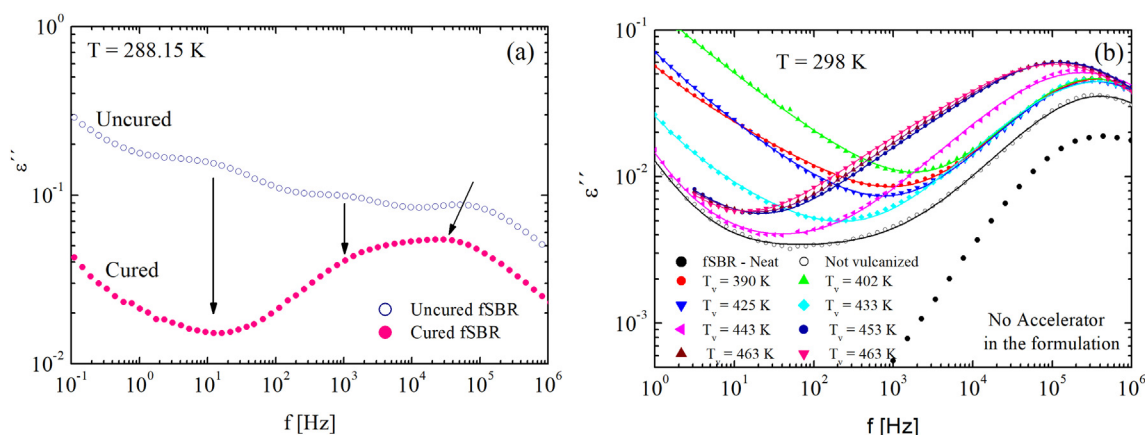

Fig. 6. Dielectric loss as a function of the frequency for uncured, partially cured and fully cured samples. a) Sample with the full formulation and b) sample without acceleratos.
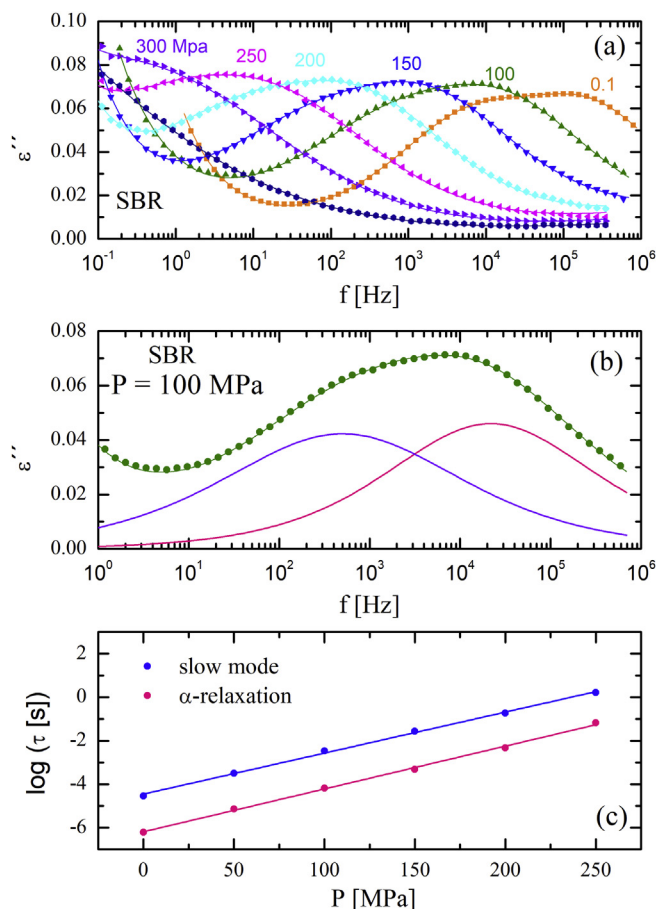
Fig. 9. *tan (δ)* as a function of temperature, at f = 1 Hz for SBR without and with DPG (1.2 phr).

the segmental relaxation. The changes in the strength of this slow mode relaxation are ascribed to the available DPG content in the rubber matrix. In addition, this phenomenon does not affect the relaxation time nor the structure of the crosslink network. In the case of filled compounds, we observed that part of the DPG is adsorbed by silica particles lowering the effective amount of DPG in the polymer and therefore increasing the vulcanization time. In addition, the experimental results show that the presence and the strength of the slow mode relaxation does not affect the crosslink density, the segmental dynamics or the mechanical properties. Thus, we have a kind of dielectric probe, which allows us monitoring the curing process without affecting the mechanical properties of the compound, showing that broadband dielectric spectroscopy is an appropriated experimental technique to get a deeper insight into the vulcanization process.

Fig. 7. (a) Imaginary part ($\varepsilon´$) of the complex dielectric permittivity as a function of the frequency at T = 303 K and at different pressures from 0.1 to 250 MPa for vulcanized SBR. (b) Example of the fitting for vulcanized SBR at P = 100 MPa. (c) Pressure dependence of the relaxation times corresponding to α-relaxation and slow mode.

4. Conclusions

The effect of vulcanization additives on the dielectric, calorimetric and mechanical response of styrene-butadiene rubber compounds has been systematically analysed in this work. We have found that the presence of DPG, a cure accelerator often used in the rubber industry, produces a slow mode in the dielectric spectrum at frequencies below
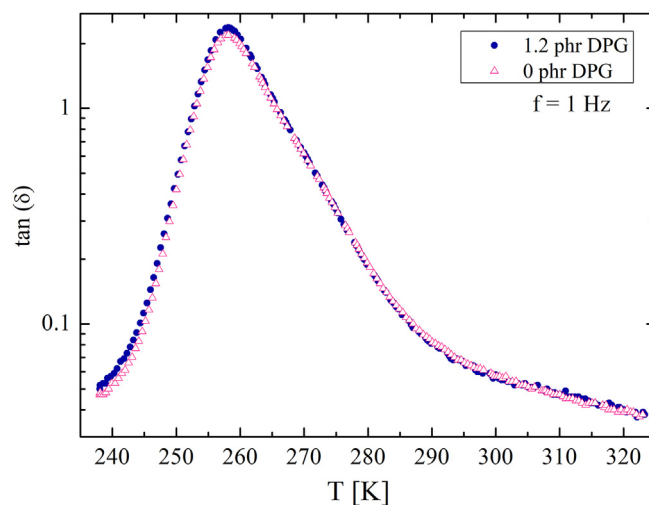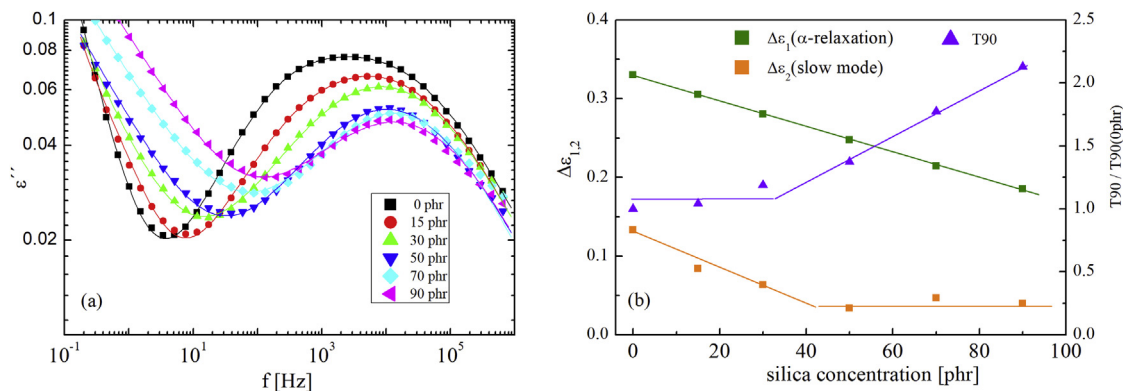
Fig. 8. (a) Imaginary part ($\varepsilon´$) of the complex dielectric permittivity as a function of the frequency at T = 288 K for SBR2 compounds with different filler loadings. The intensity of the slow mode decreases with increasing filler loading. (b) Relaxation strengths of α-relaxation, slow mode and cure time (T90) normalized to T90 for the unfilled sample (0 phr), as a function of silica concentration. As expected, $\Delta\varepsilon\alpha$ drops because the decreasing of the volume fraction of the polymer when increasing silica content. The presence of silica increases cure time and decreases relaxation strength of the slow mode, most likely due to the adsorption of part of the accelerators on its surface. Solid lines are a guide for the eyes.

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