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Reinforcement effects in fractal-structure-filled rubber

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Abstract

A quantitative morphological analysis has been performed using AFM and SAXS measurements in order to determine the spatial distribution of fillers in silica SBR composites. The proportion of fillers in agglomerates or aggregates of silica has thus been separated. Additional measurements have been carried out to quantify the amount of modified polymer in the vicinity of the filler surface, i.e. the bound rubber. It is shown that the reinforcing phase, constituting both silica particles and bound rubber, can be considered either as the dispersed or the continuous phase depending on the filler content.

The linear dynamic mechanical properties of composites are then analysed. The variations of the shear modulus as a function of the filler content are then related to either the reinforcement effect induced by fillers or the development of specific additional interactions between phases, i.e. *the interface effects*. To separate the respective contribution of these effects from the overall dynamic behaviour of composites, micromechanical modelling is then performed. In a first step, the viscoelasticity of composites reinforced by 5.7 vol% of silica is predicted with the help of Christensen and Lo's model. For composites filled with 10 and 15 vol% of silica, self-consistent modelling, applied in a reverse mode, confirmed that the reinforcing phase, i.e. silica particles and bound rubber, acts as the continuous phase, in agreement with the morphological analysis. From the predicted dynamic mechanical properties of the reinforcing phase, the bound rubber behaviour is thus extracted as a function of the filler content and compared to that of unfilled SBR.

Keywords: Morphology; Micromechanical modelling; Reinforced elastomers

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1. Introduction

Changing the active filler from carbon black to precipitated silica in rubber compounds enhances the rolling resistance and wet grip performance of tyres [1–4]. However, this change requires the introduction of new additives in the filled rubber compounds in order to decrease the strong filler–filler interactions, associated with the hydrogen bonds between silica particles [4–7]. For example, the addition of the well-known TESPT, so-called Si69, leads to the hydrophobisation of silica particles and promotes the adhesion between silica aggregates and the elastomer with the formation of sulphur bridges [8,9]. ^{1}H NMR experiments have shown that the addition of such a coupling agent in filled SBR leads to the formation of a rigid interphase in the vicinity of the filler surface [9,10]. In fact, two relaxation times have been detected for SBR filled with 'coated' silica which are attributed to the different mobility of chains as a function of the distance from the filler surface. Moreover, Leblanc et al. proposed a 'kinetic extraction method' in order to quantify the thickness of the modified polymer layer [11,12].

The mechanical properties of filled rubber are the subject of many investigations [1–6]. The morphology, i.e. the dispersion state of fillers, the filler geometry [13], and the 'filler–filler' or 'filler–matrix' interactions [3,4,14] strongly affect the mechanical behaviour of such composites. Using a 'cluster–cluster aggregation' model (CCA), Klüppel et al. [15] have shown that the storage shear modulus of the filler network is proportional to $V_f^{3.5}$. According to these authors, the exponent 3.5 reflects the characteristic structure of the fractal heterogeneity of the filler network. The reinforcement effect is thus mainly due to the development of a percolating network by the filler particles. However, many studies have shown that the addition of fillers within a polymer matrix can lead to the formation of a modified polymer layer at the vicinity of the filler surface, the so-called interphase or bound rubber.

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Nomenclature

V	volume fraction of the different phases
ρ	density of the different phases
G'	storage shear modulus of different phases
f, BR, RP	subscript referring, respectively, to filler, the bound rubber and the reinforcing phase
S_{aggl}	respective surface fraction of agglomerates
d_1, d_2	mean diameter of silica aggregates and agglomerates, respectively
tan δ	damping factor of composite materials
tan δ_{max}	maximum of the damping factor
T_α	temperature location of the maximum of tan δ
G'_{u}	glassy storage shear modulus of composites
G'_{r}	rubbery storage shear modulus of composites
M_{BR}	average inter-cross-link chain molecular weight of the bound rubber

The development of such an additional phase could affect the overall mechanical properties of (i) composites reinforced by fibres [16], (ii) polymer blends [17] or (iii) filled rubber compounds [18]. To separate the relative contributions of the individual phases from the overall mechanical behaviour of composites, it is thus proposed to use micromechanical modelling in a reverse mode [16–18].

The present work is focused on the relationships between the filler dispersion and the mechanical properties of a copolymer styrene–butadiene rubber (SBR) filled with precipitated silica. From AFM observations, a quantitative morphological analysis is carried out to define the spatial distribution of the different phases. Based on such a morphological analysis, the viscoelastic properties of the different phases are determined with the help of Christensen and Lo's model applied in a reverse mode. The linear mechanical behaviour of the bound rubber is evaluated and compared to that of the unfilled polymer. Changes in molecular mobility of SBR chains at the vicinity of fillers are also tentatively quantified.

2. Experimental

2.1. Materials

The elastomer used in this study is a styrene– butadiene rubber with 25% of styrene and extended with 37.5 parts per hundred rubber (phr) of oil (BUNA VSL 5025-1 from Bayer). The filler chosen in this study is a highly dispersible precipitated silica (Zeosil 1165MP from Rhodia); three levels of filler volume fraction (V_{f}) have been investigated: 5.7, 10 and 15%. To promote the dispersion of such polar filler within the apolar elastomer and improve the adhesion between filler and polymer, a silane-coupling agent is added in the compounds (Si69 from Degussa). For each volume fraction, a comparison has also been made between 'raw' and 'coated' silica, i.e. silica with and without Si69. Additional ingredients are also introduced in the compounds, such as ZnO and vulcanising agents. The details of the compound formulations in phr are reported in Table 1.

Table 1
Characteristics of silica filled SBR compounds

	SBR	SBR5	SBR5S	SBR10	SBR10S	SBR15	SBR15S
Silica	0	20	20	40	40	70	70
CA[a]	–	N	Y	N	Y	N	Y
V_{f} (%)	0	5.7	5.7	10.0	10.0	15.0	15.0

[a] Presence (Y) or not (N) of the silane coupling agent (CA) in the different analysed compounds.

2.2. Morphology

The filler dispersion morphology has been characterised by means of small angle X-ray scattering (SAXS) measurements, atomic force microscopy (AFM) and by extraction experiments.

SAXS measurements are performed at the CEA (DSM—Service de Chimie Moléculaire, Saclay, France) with an apparatus including a rotating anode X-ray generator. A monochromatic beam of incident wave vector k_{i} is selected and is incident on the sample. The scattered intensity (I) is recorded as a function of the so-called scattering angle 2θ. The parameter used to analyse the interaction is the scattering vector q $(= k_{\mathrm{i}} - k_{\mathrm{f}})$, ranging from 1.4×10^{-2} to 4×10^{-1} Å^{-1}. The scattered intensity $I(q)$ is related to the Fourier transform of the pair correlation function, $g(r)$, and corresponds to the probability of finding two scatterers at a distance r apart.

AFM observations are carried out in the tapping mode at Pirelli Pneumatici Spa labs (Italy). Phase and amplitude images of the different materials analysed have been compared. Images (512 × 512 8-bit pixels) were processed using two different programs: *pcv2*® developed by the 'Reconnaissance des Formes et Visions' Laboratory (INSA-Lyon, France) and Scion Image (Maryland, USA). Image analysis provides an accurate characterisation of the 2D geometric arrangement of the filler particles within the elastomer matrix. A statistical analysis of the nearest-neighbour distance or the filler area performed on four images is used to evaluate the uniformity of the filler distribution.

The technique proposed by Leblanc et al. [11,12] was used to determine the amount of bound rubber (BR) in different systems. Bound rubber corresponds to the fraction of polymer that cannot be extracted from uncured silica filled SBR compounds by toluene of the gum elastomer. Around 0.5 g of the sample was cut into small pieces and placed in a steel wire basket previously weighed. The basket was then suspended in toluene at room temperature for one week and the solvent was changed four times during this period. The basket was slowly removed from the solvent and dried for 24 h under vacuum at 40 °C. Drying was considered complete when a constant final weight was achieved. Above certain threshold filler content, a gel, containing both bound rubber and the silica particles, can be detected. The respective fractions of BR and silica can thus be determined through thermogravimetric measurements.

2.3. Dynamic mechanical analysis

Dynamic mechanical spectrometry analysis is carried out on unfilled SBR and composites using a Rheometric Dynamic Spectrometer II at Pirelli Pneumatici Spa labs (Italy). This set-up provides the variation of the storage shear modulus (G') and the damping factor (tan δ) of the different materials analysed as a function of the temperature from -80 to 30 °C at 1 Hz. The same shear strain amplitude is used in all the experiments (0.1%).

3. Results

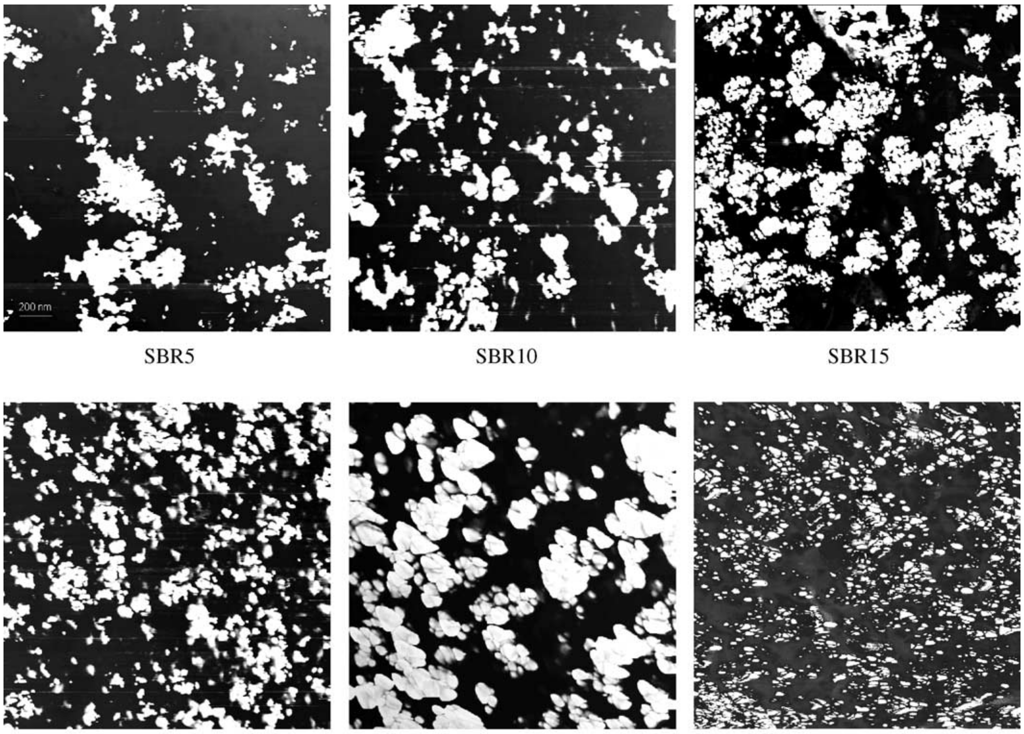
3.1. Morphology

From SAXS measurements, it is shown that the elementary silica particles are spherical with an average diameter of 13 nm [19]. The elementary particles cluster together to form highly structured silica aggregates. From the behaviour of the scattered intensity vs. the scattering vector, the mass fractal dimension of the silica aggregates is determined to be in the range from 2.0 to 2.2 for different composites. SAXS analysis thus suggests that:

(i) elementary particles exhibit a relatively smooth surface;
(ii) with increasing filler content or with the addition of a silane coupling agent, no change in the structure of primary aggregates can be detected at this scale of analysis.

To complete the morphological analysis, and in particular to evaluate the uniformity of the distribution of silica particles within the SBR matrix, atomic force microscopy observations are carried out, Fig. 1. These images reveal that composites exhibit a heterogeneous morphology, characterised by the presence of both silica aggregates and clusters of aggregates, i.e. ‘agglomerates’, except for the composite SBR15S, in which no agglomerates can be detected.

Based on these 2D observations, a statistical analysis was performed to define the extent of dispersion or the possible connectivity of fillers. To this aim, different morphological parameters were examined [19]. For example, the distribution of filler areas was determined. The evaluation of this parameter allows us to quantify the proportion of silica in agglomerates, S_{aggl}. It can be seen in Fig. 2a that the composite filled with 5.7 vol% of ‘coated’ silica exhibits a bimodal distribution of the filler areas. This behaviour has been observed for all the analysed composites, except SBR15S for which only one population of aggregates can be detected (Fig. 2b).



SBR5 SBR10 SBR15

SBR5S SBR10S SBR15S

Fig. 1. AFM observations of the (2D) geometric arrangement of fillers in composites filled with 5.7, 10 and 15 vol% of silica with and without the CA.

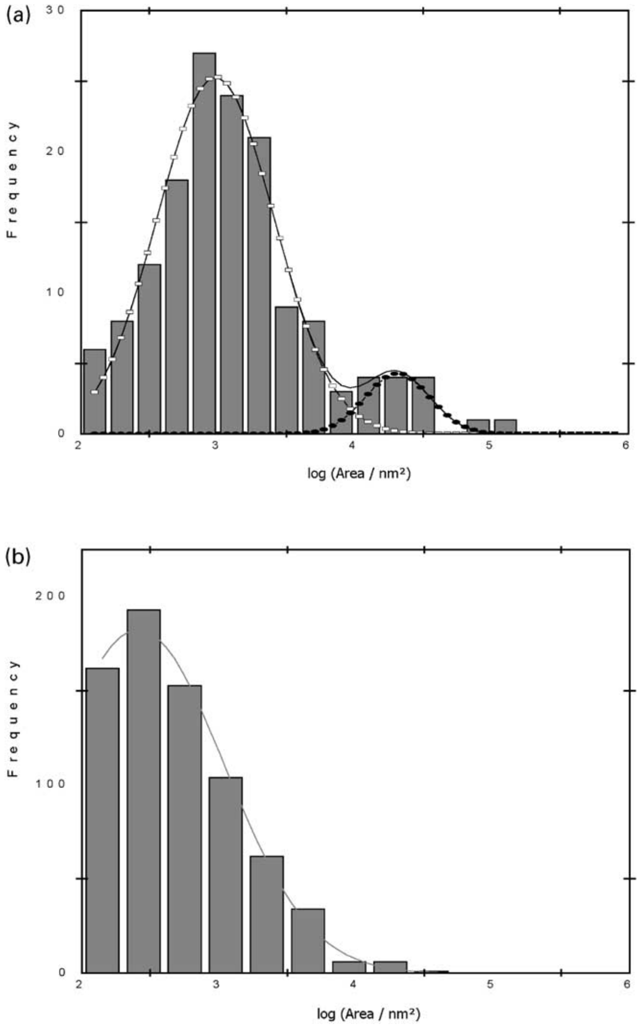


Fig. 2. Distribution of the filler area measured from AFM images for composite filled with 5.7 (a) and 15 (b) vol% of 'coated' silica.

Moreover, by assuming that fillers exhibit a quasi-spherical shape, the mean diameters of silica aggregates, d_1, and agglomerates, d_2, can be quantified from the maximum of the two fitted Gaussians (Table 2).

The analysis of the different morphological parameters leads to the following conclusions:

(i) the mean size of the silica aggregates ranges from 25 to 45 nm for all the analysed composites;

(ii) the proportion of agglomerates is low, ranging from 4 to 7 vol% of the total filler content.

Table 2
Mean diameters of silica aggregates (d_1) and agglomerates (d_2) in the filled rubbers analysed

	SBR5	SBR5S	SBR10	SBR10S	SBR15	SBR15S
S_{aggl} (%)	5	7	6	4	7	0
d_1 (nm)	44	38	30	42	30	25
d_2 (nm)	430	210	190	220	205	–

S_{aggl} corresponds to the respective amount of agglomerates/overall filler content.

The decrease in agglomerate sizes for filler contents higher than 5.7 vol%, can be attributed to the break-down of the silica agglomerates during the mixing process, as shown by Seyvet et al. [20]. With increasing filler content, the inter-particle distances decrease and the probability of collision between agglomerates is enhanced during the mixing of silica with the SBR. The absence of agglomerates in SBR15S could be due to the addition of the silane coupling agent, hindering the (re)agglomeration of fillers.

Such a morphological analysis allows us to distinguish the different populations of fillers present in the analysed composites. However, as proposed by others authors [11, 12], a third phase, the so-called 'bound rubber', can be present in filled SBR in the vicinity of the filler surface. To reveal and to quantify the amount of such a third phase, extraction measurements have been carried out using toluene. Experimental results of the amount of bound rubber remaining in different samples after one week are reported in Table 3.

For composites filled with 10 and 15 vol% of silica, such experiments reveal the presence of a gel, containing both silica aggregates and bound rubber. In contrast, for composites filled with 5.7 vol% of silica, no gel can be detected.

Based on the observation of a gel for V_{f} above 5.7%, it is proposed that a percolating network of the reinforcing phase, i.e. silica plus bound rubber, is presented for the composites filled with $V_{\mathrm{f}} > 5.7$ vol%, Fig. 3. This would imply that the silica particles can be considered as being connected by a layer of bound rubber for composites filled with 10 and 15 vol% of silica, forming a 3D network. This result is confirmed by both the modelling of the linear viscoelastic behaviour, see after, and the analysis of the non-linear mechanical properties of the composites filled with $V_{\mathrm{f}} > 5.7$ vol%, where the Mullins effect has been observed [19].

Moreover, as shown in Table 3, the amount of bound rubber increases from 8 to 15 vol% for composites filled with 10 and 15 vol% of 'raw' particles. Such a tendency is enhanced by the addition of the silane-coupling agent in filled rubber compounds and could result from the increase of the specific surface induced by the better dispersion of fillers. Consequently, in the following parts of this paper, the reinforcing phase will not be considered as just the silica particles but by the combination of silica plus bound rubber,

Table 3
Volume fractions of the bound rubber (BR) and the corresponding reinforcing phase (RP)

	SBR	SBR10	SBR10S	SBR15	SBR15S
V_{BR} (%)	0	8.3	13.3	15.1	23.9
V_{RP} (%)	–	18.3	23.3	30.1	38.9

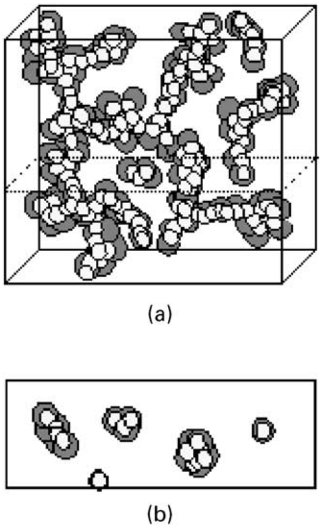


Fig. 3. Schematic representation of the spatial distribution of an interconnected network of 'fillers' in 3D (a) and its appearance in cross-section (b).

as in the work of Medalia [21]. Thus, for SBR15S, the corresponding volume fraction of the reinforcing phase, V_{RP}, is equal to about 39%, corresponding to a thickness of bound rubber layer close to 5 nm.

The morphological investigations of silica filled SBR lead to the following conclusions:

(i) all the analysed composites, except the SBR15S, exhibit a bimodal distribution of the filler particle sizes, related to the presence of silica aggregates and agglomerates;
(ii) for the composite SBR15S, only one population of aggregates is detected. This result indicates that the addition of a silane coupling agent in highly filled rubber compounds seems to hinder the (re)formation of agglomerates;
(iii) for composites filled with 10 and 15 vol% of silica, a gel is detected in contrast to the composites reinforced by 5.7 vol% of silica;
(iv) increasing the volume fraction of fillers or adding the silane coupling agent, augments the amount of bound rubber.

The decrease in the distance between filler particles, accompanied by the increase in the thickness of the bound rubber layer favours the 3D connectivity of the silica particles 'coated' by the bound rubber and leads to the development of a percolating network of the reinforcing phase. For composites SBR5 and SBR5S, it has been proposed that the volume fraction of the filler and the thickness of the bound rubber layer are not sufficient to connect distant filler particles and to form a gel.

In light of this morphological analysis, it is now of interest to analyse the linear dynamic mechanical properties of silica filled SBR in order to give some qualitative indication on the relative contributions of filler–filler interactions and filler–polymer interactions. With this in mind, micromechanical modelling will be used in a reverse mode, in order to determine the contribution of the individual phases. The viscoelastic properties of the bound rubber can thus be evaluated and compared to that of the unfilled SBR.

3.2. Experimental viscoelastic behaviour

3.2.1. Influence of the filler content

The influence of the silica content on the storage shear modulus, G', and the damping factor, tan δ, of 'raw' silica filled SBR is depicted in Fig. 4. Values of the glassy modulus, G_u, evaluated at -70 °C, the rubbery modulus, G_r, determined at 20 °C, the temperature at the maximum of

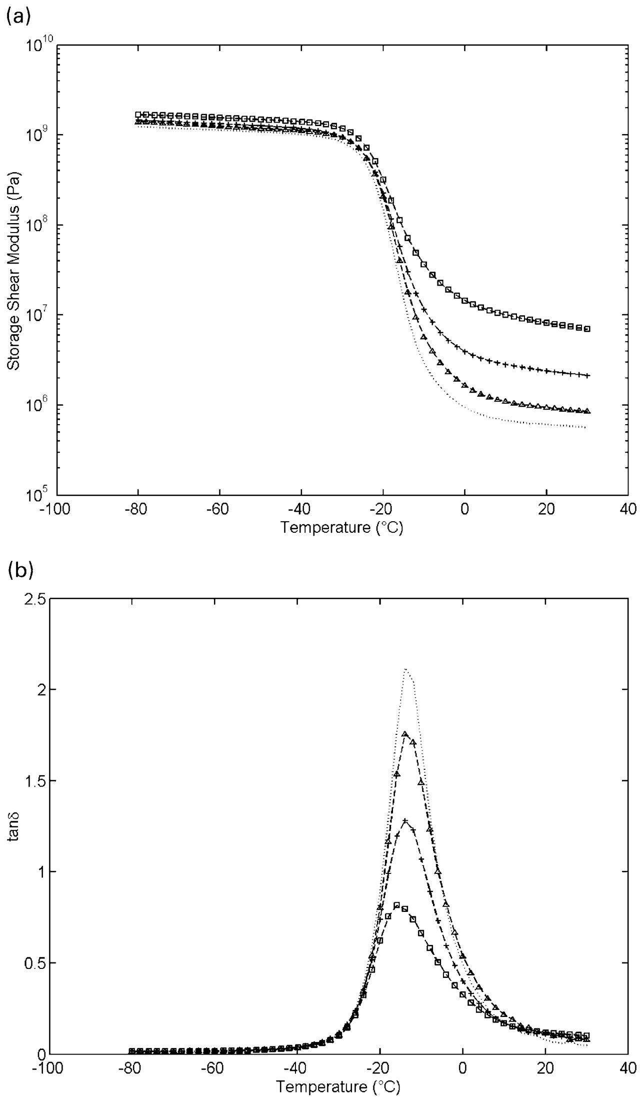


Fig. 4. Experimental plots of (a) G' and (b) tan δ versus temperature at 1 Hz for the unfilled rubber (- - -) and composites with $V_f = 5.7$ (-▲-), 10 (- + -) and 15 (-□-) vol% of 'raw' silica.

Table 4
Experimental viscoelastic properties of unfilled SBR and composites

	G_u (GPa)	G_r (MPa)	T_α (°C)	tan δ_{max}
SBR	1.2	0.6	− 13.5	2.14
SBR5	1.3	0.9	− 13.4	1.77
SBR5S	1.4	1.0	− 12.2	1.60
SBR10	1.4	2.4	− 13.8	1.22
SBR10S	1.4	2.0	− 13.8	1.20
SBR15	1.6	8.2	− 15.6	0.82
SBR15S	1.5	6.8	− 15.6	0.79

tan δ, T_α and the height of the maximum damping factor tan δ_{max}, are reported in Table 4.

It can be observed that the viscoelastic characteristics of composites strongly depend on the amount of filler. Increasing the volume fraction of precipitated silica leads to:

(i) a significant rise in the storage shear modulus over the analysed temperature range, accompanied by a decrease in the height of the main relaxation related to the T_g of SBR;
(ii) a shift towards the lower temperatures of the main relaxation of the composites filled with 15 vol% of silica.

The first result can be attributed solely to the reinforcement effect induced by the introduction of hard spheres into a polymer matrix [23].

The shift of the main relaxation towards the lower temperatures has been attributed by some authors to an increase in the molecular mobility of the polymer in the vicinity of the filler surface [23]. However, previous differential scanning calorimetry measurements have shown that the glass transition temperature of composites is insensitive to the filler content and the presence or absence of a coupling agent [19]. Moreover, recent studies by NMR spectroscopy on filled rubber have shown that the presence of fillers does not induce an increase in the molecular mobility of chains close to the filler surface but leads, in contrast, to the development of a low mobility layer [22]. Accordingly, the shift of T_α towards the lower temperatures could be due to a particular mechanical coupling effect between the three phases present; silica particles, bound rubber and unmodified SBR.

3.2.2. Influence of the coupling agent

From the analysis of the experimental data reported in Table 4, it can be concluded that the presence of the coupling agent does not strongly affect the viscoelastic properties of composites. As an example, it can be observed that the viscoelastic behaviour of SBR15S is similar to that of composite filled with the same content of 'raw' silica.

The similar behaviour could result from the opposing effects induced by the addition of the coupling agent in the filled rubber compounds. It has been previously shown that the addition of the coupling agent promotes the development of a bound rubber layer at the vicinity of the filler surface, increasing the reinforcement effect. On the other hand, the presence of the Si69 favours the dispersion of fillers thus, decreasing the storage shear modulus [23].

To separate these two opposing effects, micromechanical modelling has been performed. This kind of modelling, applied in a direct mode, allows the prediction of the overall dynamic mechanical behaviour of composites filled only with dispersed silica particles, i.e. composites reinforced by 5.7 vol% of silica. Used in a reverse mode, the viscoelastic properties of the individual phases can be evaluated. In particular, the behaviour of the bound rubber behaviour in composites filled with 10 and 15 vol% of silica will be assessed and compared to that of the unfilled rubber.

3.3. Modelling

3.3.1. Modelling in a direct mode

The prediction of the complex moduli of filled rubber is usually based on phenomenological laws, such as Smallwood–Guth–Gold models [24,25], variational methods [26], or self-consistent schemes [27], extended to describe the viscoelastic behaviour through the correspondence principle.

Previous work has shown that either the phenomenological law or the variational methods are not able to predict the evolution of the viscoelastic properties of silica filled SBR [19]. Accordingly, in this work, rigorous self-consistent schemes are applied in order to predict the dynamic mechanical behaviour of the composites. To a first approximation, based on the Christensen and Lo's model and the following assumptions:

(i) the inclusions are randomly dispersed in the matrix;
(ii) each phase is homogeneous and isotropic;
(iii) bonding between neighbouring phases is considered as perfect.

the complex shear modulus of the composite, G_c^*, is determined by the resolution of the following equation [27]

$$A\left[\frac{G_c^*}{G_m}\right]^2+B\left[\frac{G_c^*}{G_m^*}\right]+D=0 \tag{1}$$

where the subscripts m and c refer to the unfilled polymer and the composite, respectively.

Modelling in a direct mode is applied to predict the viscoelastic behaviour of SBR reinforced by 5.7 vol% of silica, that displays only two phases; silica particles and unmodified SBR. The corresponding representative volume element is thus composed of two concentric spheres embedded in the equivalent homogeneous medium. The

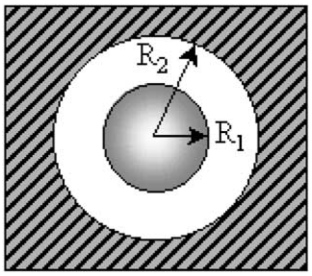


Fig. 5. Representative morphological motif of composites reinforced by 5.7 vol% of silica particles. Phase 1 is the silica particles and phase 2 is the SBR matrix.

central core of this RVE, i.e. the silica particles, is surrounded by a shell of unmodified SBR (Fig. 5).

Comparison between experimental and theoretical dynamic mechanical properties of SBR5 is reported in Fig. 6. It can be observed that there is good agreement between the theoretical and experimental glassy shear modulus. In contrast, the experimental rubbery plateau is underestimated and the magnitude of the main relaxation T_α is overestimated by the micromechanical modelling. These differences can be attributed to the development of the bound rubber layer at the vicinity of the filler surface which is not taken into account in such modelling. Previous morphological analyses have suggested that, whatever the filler content is, the polymer located at the vicinity of the filler surface exhibits different properties from that of the bulk polymer. For the composites reinforced by 5.7 vol% of silica, the thickness of this bound rubber layer cannot be experimentally determined because of the absence of gel.

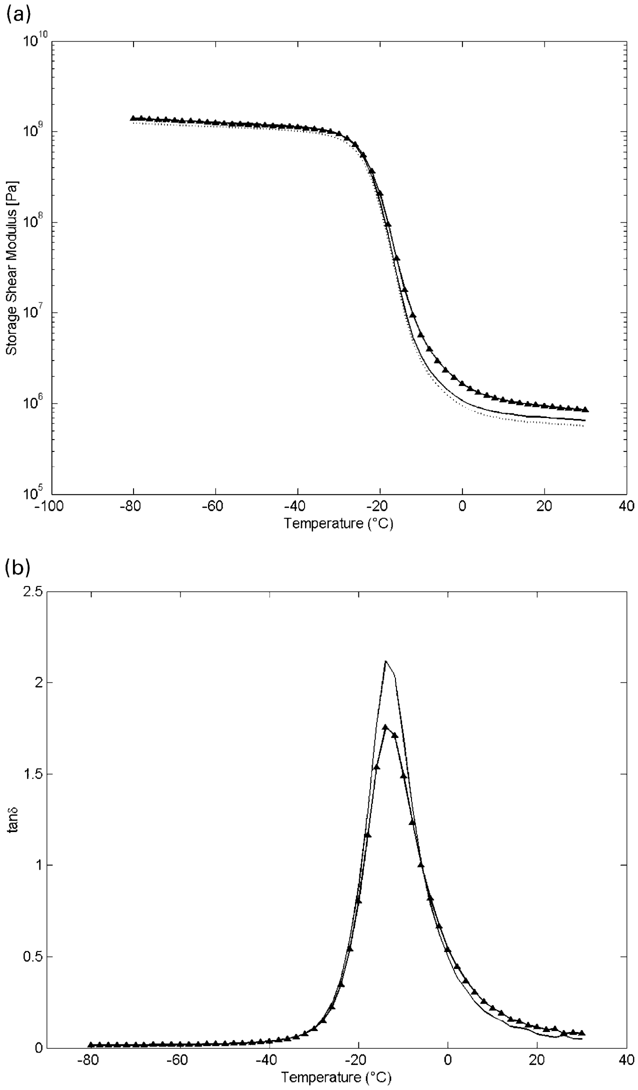


Fig. 6. Comparison between experimental (-▲-) and theoretical (—) (a) storage shear modulus and (b) damping factor of composites filled with 5.7 vol% of silica. Unfilled SBR is superimposed for comparison (···).

For the composites filled with 10 and 15 vol% of silica which show a gel, the respective volume fractions of the three phases, i.e. silica, bound rubber and the unmodified polymer, can be evaluated (Table 3). Accordingly, from the knowledge of the amount of different phases and by using micromechanical modelling in a reverse mode, the dynamic mechanical properties of, first, the reinforcing phase and, in a second step, the bound rubber are determined for composites filled with 10 and 15 vol% of silica.

3.3.2. Modelling in a reverse mode

The use of micromechanical modelling in a reverse mode was recently proposed and applied with success to predict the viscoelastic behaviour of the different phases in polymer blends [17], usual composites [16] or filled rubber compounds [18,19].

Based on the morphological analysis presented here, such an approach should allow the determination of the bound rubber behaviour for the composites filled with 10 and 15 vol% of silica. However, before determining the mechanical properties of the bound rubber, so-called 'modified polymer' in the next part of this work, it is first necessary to evaluate the mechanical behaviour of the reinforcing phase, composed of both silica particles and the bound rubber.

(a) Mechanical properties of the reinforcing phase (silica particles and bound rubber). The viscoelastic properties of the reinforcing phase is extracted using the 3-phase model in a reverse mode. Such a modelling requires the definition of a representative volume element accounting for the spatial distribution of the different phases. Previous work has shown that if we assume that the reinforcing phase is well-dispersed within an unmodified SBR, theoretical data diverge in the viscoelastic and rubbery regions [19]. This result suggests that the RVE chosen does not take into account the actual morphology of composites. In fact, the morphological analysis has shown that, for composites filled with 10 and 15 vol% of silica, a percolating network of the reinforcing phase occurs. Accordingly, the reinforcing phase, i.e. both silica plus bound rubber can be considered as the continuous phase and the unmodified polymer is the dispersed phase. The corresponding RVE then consists of a two-layered spherical

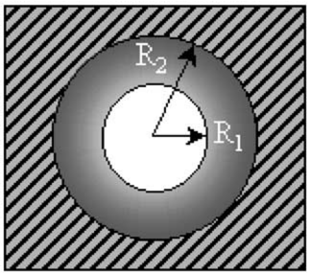


Fig. 7. Representative morphological motif of composites filled with 10 and 15 vol% of silica. Phase 1 is the unmodified SBR and phase 2 is the reinforcing phase constituted of silica particles and BR.

inclusion, in which the central core, the unmodified polymer, is surrounded by the reinforcing phase (Fig. 7).

Based on this RVE, the viscoelastic properties of the reinforcing phase can be extracted over the entire temperature range for the composites filled with 10 or 15 vol% of 'raw' silica (Fig. 8). It can be noted that the glassy storage shear moduli of the reinforcing phase ranges from 2 to 3 GPa and is almost constant for the different analysed composites. In contrast, the rubbery plateau or the maximum of the main relaxation of the reinforcing phase depends on the filler content.

(b) Mechanical properties of fillers and the bound rubber. In a second step, the bound rubber behaviour can be separated from the reinforcing phase by using again Christensen and Lo's model in a reverse mode. By assuming that silica particles are embedded within a shell of bound rubber, we have used a new RVE, consisting of a two-layered spherical inclusion, in which the central core, constituted by silica particles, is surrounded by the bound rubber (Fig. 9).

The prediction of the bound rubber properties requires a knowledge of the elastic properties of fillers. This is performed by assuming that the glassy shear modulus of the modified elastomer is close to that of unfilled copolymer.

The equivalent elastic properties of fillers, G'_a, has been evaluated for the composites filled with 10 and 15 vol% of silica. It has been previously shown that with increasing filler content, the elastic properties of the silica particles increased. Moreover, for composites reinforced by silane-coated silica, the properties of the fillers is proportional to $V_f^{3.5}$, in agreement with Klüppel et al. [15]. In contrast, a lower exponent (1.0) has been found for composites filled with 'raw' particles. This particular behaviour could be due to the different morphologies displayed by composites filled with 'raw' or 'coated' silica.

From the mechanical properties of the reinforcing phase and the equivalent stiffness of fillers, the bound rubber behaviour can now be extracted. As an example, the viscoelastic properties of the bound rubber is depicted in Fig. 10 for composites filled with 10 and 15 vol% of 'raw' silica particles.

With increasing volume fraction of fillers, it can be seen that a significant increase in the rubbery plateau of the bound rubber, accompanied by a decrease in the height of the main relaxation takes place. For example, the rubbery plateau of the bound rubber of SBR15 is 100 times higher than that of unfilled polymer. This result is consistent with the formation of a rigid interphase.

For composites filled with 15 vol% of silica, it can be

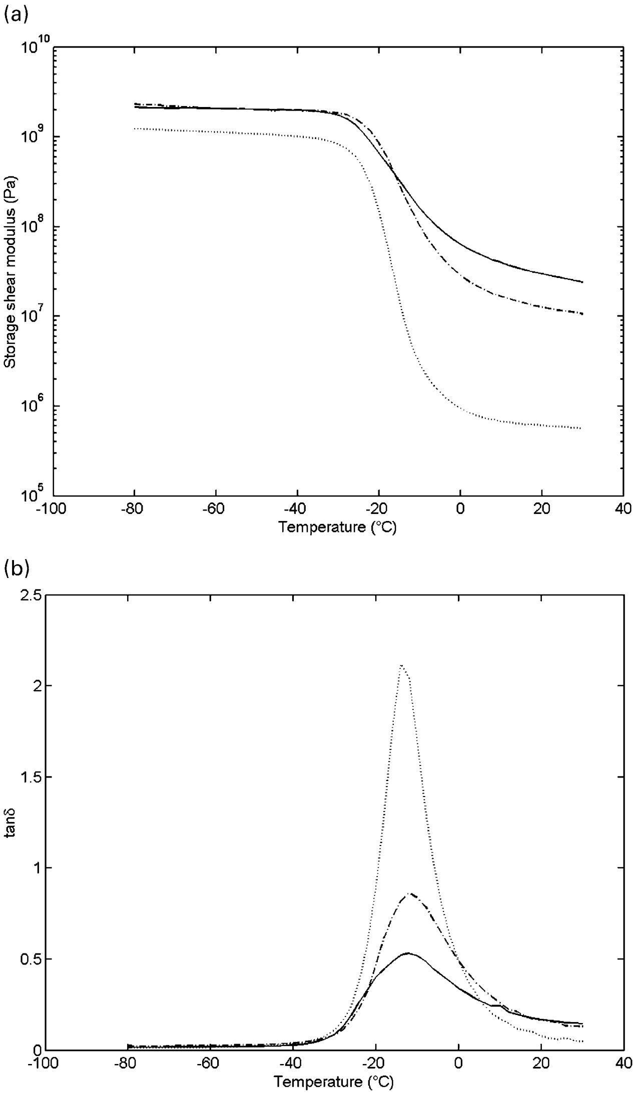


Fig. 8. Theoretical viscoelastic properties of the reinforcing phase for composites filled with 10 (--) and 15 (—) vol% of silica.

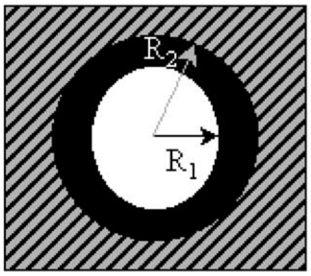


Fig. 9. Representative morphological motif of the reinforcing phase in composites filled with 10 and 15 vol% of silica particles. Phase 1 is the silica particles and phase 2 is the bound rubber shell.

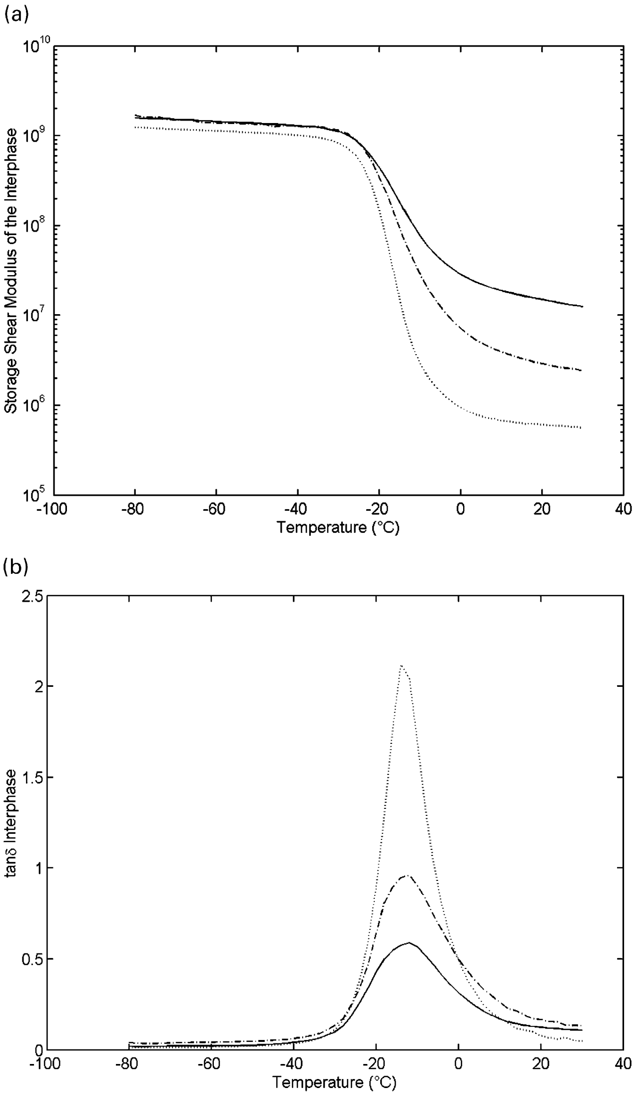


Fig. 10. Theoretical dynamic mechanical properties of the bound rubber for composites filled with 10 (-·) and 15 (—) vol% of raw silica.

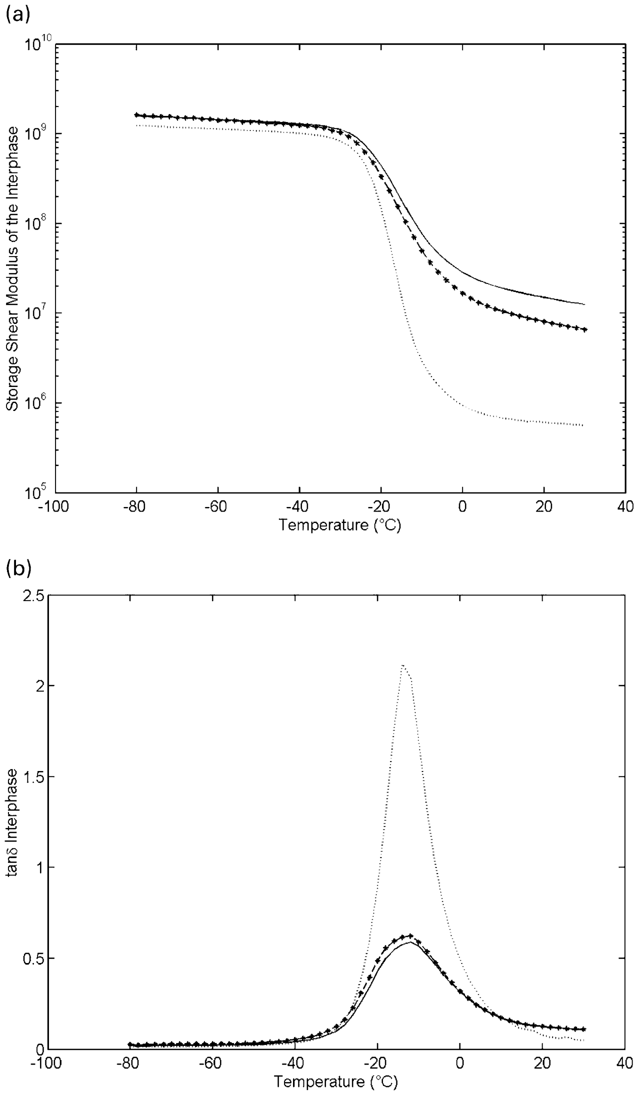


Fig. 11. Influence of the addition of the silane coupling agent on the storage shear modulus (a) G' and (b) tan δ of the bound rubber for composites SBR15 (-◆-) and SBR15S (—).

seen in Fig. 11 that the rubbery plateau of the modified rubber of composites filled with 'coated' silica is greater than that displayed by composite reinforced by 'raw' silica.

This result indicates that the addition of the silane coupling agent in the filled rubber compounds increases not only the thickness of the bound rubber layer but also increases its stiffness, due to additional chemical bounds between the silica particles and SBR.

To quantify these additional interactions, the average cross-link molecular weight of the bound rubber, M_{BR}, is evaluated at 20 °C using the following expression:

$$M_{\mathrm{BR}} = \frac{RT\rho_{\mathrm{BR}}}{G_{\mathrm{BR}}} \tag{2}$$

where T is the temperature (K), G_{BR}, the rubbery shear modulus of the bound rubber and ρ_{BR} is the bound rubber density.

By assuming that the density of the bound rubber is close to that of unfilled SBR, specific interactions between filler and polymer can be quantified by the evaluation of the parameter Δ, defined by the ratio of $M_{\text{unfilled SBR}}/M_{\mathrm{BR}}$, Table 5.

Analysis of Δ values leads us to conclude that:

(i) With increasing filler content, the specific surface of silica rises. This leads to an increase in the number of physico-chemical interactions between silica particles

Table 5
Rubbery shear modulus of the bound rubber, calculated from micromechanical modelling in a reverse mode

	SBR	SBR10	SBR10S	SBR15	SBR15S
G_{BR} (MPa)	0.6	2.6	3.2	8.8	16.3
Δ	1	4	5	15	27

Δ is the ratio $G_{\mathrm{BR}}/G_{\text{unfilled SBR}}$.

and the polymer inducing an increase in the 'effective' cross-link density of the polymer close to the silica surface, i.e. the bound rubber.

(ii) The presence of the silane coupling agent in filled rubber compounds favours silica dispersion, in particular in the composite reinforced by 15 vol% of silica. This effect leads to the development of the bound rubber layer in the vicinity of the filler surface. A greater number of chemical bonds between filler and polymer could thus occur in composites filled with 'coated' silica, leading to the development of a much more rigid interphase.

4. Conclusion

A detailed quantitative analysis of the spatial distribution of the different phases present in silica filled SBR has been carried out as a function of the filler content and comparing systems mixed with and without coupling agent.

It has been shown that:

(i) Silica particles exhibit a bimodal population of aggregates or agglomerates, except for SBR15S for which only one population of aggregates is observed. The addition of the silane coupling agent in the highest filled SBR hinders the (re)formation of agglomerates.

(ii) The composites reinforced by 10 and 15 vol% of silica exhibit a gel shown by means of toluene extraction, in contrast to composites reinforced by 5.7 vol% of silica. The presence of a gel has been related to the presence of a percolating network, composed of both silica particles and the bound rubber, leading to a macroscopic phase inversion.

Based on this morphological analysis, the prediction of the viscoelastic properties of the different phases is performed with the help of a self-consistent model. This 'theoretical' approach first allows us to confirm the role of the individual phases on the overall mechanical behaviour. For composites filled with 5.7 vol% of silica, it is shown that the reinforcing phase, i.e. silica plus bound rubber, is well-dispersed within the unmodified elastomer. In contrast, the reinforcing phase acts as the continuous phase for the composites reinforced by 10 and 15 vol% of silica, in agreement with previous morphological analysis. These results are confirmed by the analysis of the non-linear dynamic mechanical behaviour of silica filled SBR. In fact, the classical Mullins effect has been observed for composites filled with 10 and 15 vol% of silica, showing the presence of a percolating network of 'fillers', contrary to the composites filled with 5.7 vol% [19].

By using again the model of Christensen and Lo in a reverse mode, the dynamic mechanical behaviour of the bound rubber has been determined separately. The viscoelastic properties of the bound rubber increase with increasing filler content. Such a reinforcement effect is enhanced for composites filled with 'coated' silica.

These results are consistent with previous morphological analyses and confirm the development of a rigid interphase or bound rubber in the vicinity of the silica particles. To quantify the additional specific interaction between filler and polymer, the average cross-link molecular weight of the bound rubber, MBR, is evaluated and compared to that of the unfilled rubber. The 'effective' cross-link density of the bound rubber increases with increasing filler content. This effect is enhanced by the addition of silane coupling agent in filled rubber compounds and can be attributed to the development of additional chemical bonds between the silica surface and the polymer due to the coupling agent.

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