Analysis of the Viscoelastic Behaviour of Silica Filled Rubber : Prediction of the Interphase Properties

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Summary : The aim of this work is to analyse the influence of both silica content and the presence of a silane coupling agent on the viscoelastic behaviour of silica filled rubber. It is well-known that changes in the dynamic mechanical properties of filled rubber could result from either the mechanical coupling between phases and/or *interface effects*. Micromechanical modelling, taking morphological analysis into account, will be used to separate these two effects and allows us to assess the actual properties of the polymer close to the silica surface.

Introduction

In order to optimise rolling resistance and wet grip performances of tires, carbon black has been replaced by precipitated silica in tread compounds.[1-2] However, because of the strong intermolecular hydrogen bonds between hydroxyl groups, agglomerates of silica appear in the absence of surface treatment of the filler. In order to decrease the filler-filler interactions and thus promote the dispersion of silica aggregates in the rubber matrix, silane coupling agents are used. [2-3]

The influence of both silica content and the presence of a silane coupling agent on the linear and non-linear viscoelastic behaviour of a Styrene-Butadiene Rubber (SBR) filled with various volume fraction of silica is analysed. Many studies show that changes in the dynamic mechanical properties of composites could result from either the mechanical coupling between phases and/or interface effects. [4-5] To separate these two effects, and thus assess the actual properties of the polymer close to the silica surface, micromechanical modelling is required.

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Materials Analysed and Differential Scanning Calorimetry Measurements

The elastomer used in this study is a Styrene Butadiene Rubber. The gum contains 25 % of styrene and is extended with 37.5 phr of oil. Moreover, additional products are introduced in the compound, such as accelerators ZnO or vulcanising agents. The filler chosen in this study is a highly dispersible precipitated silica (Zeosil 1165MP from Rhodia). To promote the dispersion of such a polar filler within the apolar elastomer, a silane coupling agent is used (Si69 from Degussa). Details of the compound formulation in parts per hundred rubber (phr) are shown in table 1 accompanied with the values of T_g and ΔC_p^* determined from the thermograms of SBR reinforced by silica.

Table 1. Characteristics of silica filled SBR compounds studied

	SBR	SBR5	SBR5S	SBR10	SBR10S	SBR15	SBR15S
Silica	0	20	20	40	40	70	70
C.A.[a)]	/	N	Y	N	Y	N	Y
V_f[b)]	0	5.7	5.7	10.0	10.0	15.0	15.0
T_g[c)]	-37.5°C	-37.9°C	-37.8°C	-37.8°C	-37.7°C	-37.9°C	-38.1°C
ΔC_p^*	*0.15*	*0.17*	*0.17*	*0.14*	*0.15*	*0.13*	*0.13*

a) Presence or not of the silane coupling agent (C.A.) in the different compounds analysed
b) Volume fraction of silica (V_f), evaluated through thermogravimetry measurements
c) Glass transition temperature (T_g) evaluated at 10°C/min.

It can be observed that the reinforcement of the vulcanised elastomer by both raw and silane-coated silica does not induce significant changes either in the glass transition temperature or in the specific heat jump. Such a result could be due to the weak physico-chemical interaction between filler and the copolymer or to the weak sensibility of this experimental technique to changes in molecular motion of SBR chains at the vicinity of the silica surface.

Quantitative Morphological Analysis

The morphology of the different composites is analysed using experimental techniques such as Small Angle X-ray Scattering (SAXS-CEA Saclay) or Atomic Force Microscopy (AFM). From SAXS measurements, it has been shown that elementary silica particles are spherical with

an average diameter of 13 nm : their fractal dimension varies from 2.0 to 2.2 for the different composites analysed, thus indicating a relatively smooth surface for the elementary particles. The addition of a silane coupling agent in the different filled compounds does not induce changes in the morphology at this scale.

Atomic force microscopy reveals that composites exhibit a heterogeneous morphology, characterised by the presence of both :

- silica aggregates constituted by quasi-spherical nanoparticules. The mean size of these entities ranges from 50 to 60 nm,
- agglomerates of silica aggregates. The largest size of these agglomerates, observed for the different materials analysed except for the composite reinforced by 15 vol. % of coated silica, is about 0.7 μm, figure 1.

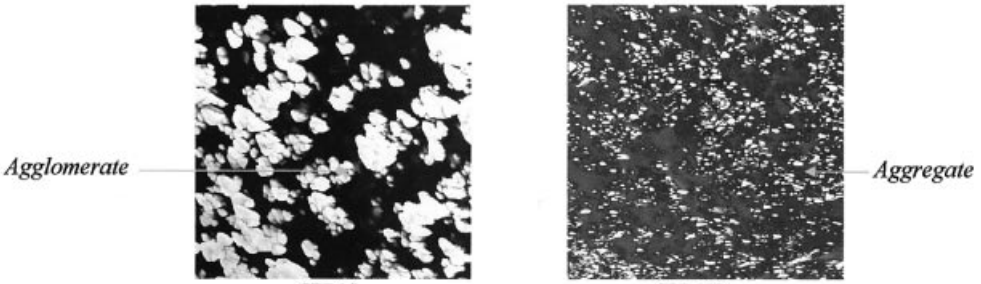

Figure 1. AFM Observations (2 x 2 μm) of 2D geometric arrangement of fillers in composite reinforced by 15 vol. % of silica

Based on these images, statistical analyses are then performed to evaluate different morphological parameters, such as the apparent surface fraction of filler (S_f), the average filler spacing ($\overline{d_{ppv}}$) or the shape factor of filler (κ).[6].

The analysis of these morphological parameters allows us to identify the development of a silica network for composites filled with volume fractions higher than the percolation threshold. Fillers are then connected and the polymer is trapped within the interstices of the filler network. Moreover, the statistical treatment of the distance distribution among filler and its firsts neighbours allows us to show that the presence of the coupling agent improves the dispersion of filler, in particular in the compound filled with 15 vol. % of silica. The coupling agent used, Si69, thus decreases the filler-filler interactions and improves the chemisorption between SBR and the filler.

Viscoelastic Behaviour of Silica Filled SBR (VA4000 Metravib, Limonest, France)

Although conventional dynamic mechanical analysis of CB or silica-filled rubbers gives global information on the viscoelastic properties of heterogeneous systems, the respective influence of the reinforcement effect of polymer induced by active filler or the *interface effects*, can be assessed through the use of micromechanical modelling. For this aim, classical mechanical models, such as Guth, Guth and Gold or Christensen and Lo models [7-8], have been applied in a direct mode and compared to experimental values. The superposition of experimental and theoretical results leads to the following conclusions:

(i) previous mechanical models significantly underestimate the rubbery properties of filled rubber compounds, whatever the value of the Young's modulus of the filler.

(ii) the theoretical magnitude of the main relaxation displayed by the filled rubber compound is overestimated with respect to the experimental one. [9]

Consequently, the discrepancy observed between experimental and theoretical variations of the linear viscoelastic properties *vs.* temperature leads us to revise our point of view and shows the necessity to use micromechanical modelling in a *reverse mode* to assess the viscoelastic properties of the interphase, so-called bound rubber.[5,9] Before determining the dynamic properties of such a phase, it is first required to evaluate the actual properties of the reinforcing phase, constituted by both silica aggregates and the bound rubber, figure 2.

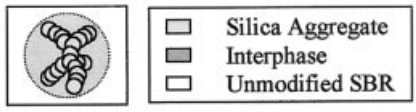

Figure 2 . Schematic representation of the reinforcing phase embedded in SBR

The viscoelastic properties of the reinforcing phase extracted from the overall mechanical properties of the different composites analysed require a knowledge of the amounts of the different phases. To this aim, a kinetic extraction method has been used to determine the amount of the bound rubber, table 2. Thermogravimetric measurements have also been carried out to confirm the silica content in the different composites studied.

Table 2.Volume fractions of the bound rubber (V_{br}) and the reinforcing phase (V_{RP}) in the composites filled with 15 vol. % of silica

	SBR	SBR15	SBR15S
V_{br}(%)	0	15.1	23.9
V_{RP}(%)	0	30.1	38.9

It can be observed that the presence of the coupling agent favours the development of the bound rubber.

It is now of interest to predict the viscoelastic properties of thereinforcing phase in the different composites. Based on previous morphological analysis, two distinct Representative Volume Elements (RVE) are considered.[8] First, we assumed that the reinforcing phase is perfectly dispersed within the polymer matrix. However, the discrepancy (not shown) observed between the experimental and calculated results for the composites filled with 10 or 15 vol. % of silica leads us to consider that the reinforcing phase could act as the continuous phase, *i.e.* a macroscopic phase inversion occurs in these materials. [9] Based on such a RVE, a well-defined representation of dynamic properties of the reinforcing phase can be reached in the whole temperature range, figure 3. This result is consistent with:

(i) previous morphological analysis which gives evidence of the presence of a silica network for the composite filled with 10 and 15 vol. % of silica

(ii) the analysis of the non-linear dynamic mechanical properties. A filler network has been indeed revealed with the stress-softening of composites reinforced by 10 and 15 vol. % of silica.

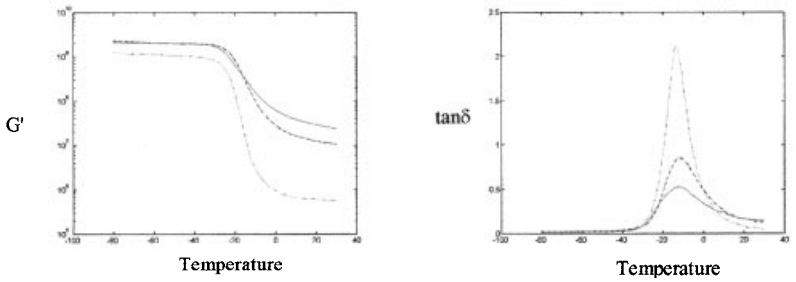

Figure 3 . Theoretical variations of G' and tanδ *vs.* temperature displayed by the reinforcing phase extracted from composite filled with 10 (--) and 15 (—) vol. % of silica Unfilled polymer is superimposed for comparison (···)

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.

Based on the knowledge of both the viscoelastic properties of the reinforcing phase and the amount of the different phases, the dynamic behaviour of the interphase can be determined.[9] By assuming that silica particles are embedded by a shell of interphase, the viscoelastic properties of the interphase can be evaluated from the dynamic mechanical behaviour of the composite filled with 15 vol. % of raw or coated silica, figure 4.

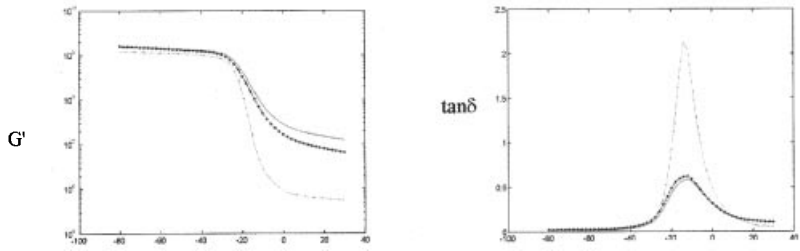

Figure 4 . theoretical variations of (a) G' and (b) tanδ *vs.* temperature displayed by the interphase extracted from composite filled with 15 vol. % of raw (+) and coated (—) silica

The viscoelastic properties of the interphase increase with increasing filler content (not shown).[9] Such a reinforcement effect is enhanced for composites filled with "coated" silica, where the rubbery plateau of the interphase of composites filled with "coated" silica is greater than that displayed by composite reinforced by "raw" silica, figure 4. This last result indicate that the addition of the silane coupling agent in the filled rubber compounds increases not only the thickness of the bound rubber layer (table 2) but also increases its stiffness, due to additional chemical bounds between the silica particles and SBR.

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