

Internal Stresses in the Electrostriction Phenomenon Viewed Through Dynamic Mechanical Analysis Studies Conducted under Electric Field

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ABSTRACT

A model for studying the mechanical internal stresses into dielectric materials is developed in the present work. The model takes into account the formalism of inclusions in continuous media. The dielectric material is assumed to be partitioned in different cubes which form a sizeable bulk material in such a way that a given cube can be of the dipolar phase and its neighbor can be of the same phase or the matrix. The behavior of the internal stresses promoted by the electrostriction phenomenon can be monitored by studying the behavior of both the misfit coefficient related to the strain misfit and the transfer of elastic energy process. The equations obtained through the here presented model are calculable using magnitudes from mechanical tests, in particular dynamic mechanical analysis, which is very sensitive to changes in the microstructure. Dynamic mechanical analysis as a function of the electric field is reported, perhaps for the first time in literature, for the study of dielectric materials, giving rise to a useful tool for studying the behavior of internal stresses in dielectric materials.

Index Terms - Dielectric materials, electrostriction, modeling, polymers, rubbers, dynamic mechanical analysis

1 INTRODUCTION

THE application of an electric field to a dielectric material causes small displacements of the positive and negative charges which give induced dipole moments. The field then interacts with these dipole moments to produce a distortion which is proportional to the square of the field strength. The relation between the strain and the electric field is called electrostriction [1, 2]. From an appropriate reciprocity relation, it follows that the application of a mechanical stress may produce a change in the dielectric properties [2, 3]. In fact, the interaction between the electrical and mechanical fields has been proposed as a critical point to be considered for the study of the lifetime of insulating materials. For instance, electrical

forces acting on the polymer chains were proposed as the driving force for controlling the crystalline state in ethylene-propylene-diene M-class rubber (EPDM) insulators, which leads to the modification of the mechanical and dielectric properties [4]. In addition, the mechanical internal stresses and the empty space were reported as the responsible for controlling the behavior of the dielectric strength [5]. Besides this, there exists also works, where the influence of the internal stresses, either thermal or mechanical, on the dielectric behavior have been reported [6-10].

A general and formal treatment of the coupling of the mechanical and electrical properties in materials can be done by resolving the stress state from a general thermodynamic potential equation involving both contributions [2]. However, the mathematical handling of the resulting equations applied to engineering calculations in technological materials is always complicated.

On the other hand, the internal stresses in materials have been studied widely in literature from the point of view of the elasticity theory [11, 12]. In the theory of elasticity one inclusion is a region whose shape is different from the surrounding bulk matrix or where the elastic constant is different from that of the bulk matrix. The formalism of the inclusions into elastic matrix has been used widely for studying the behavior of the internal stresses in materials [11, 13-15]. However, in many cases the resulting equations are also complicated for being used in engineering calculations of materials in service. In contrast, more recently, a model based in a mean field treatment applied to the formalism of the inclusion [15, 16] has been reported, which allows easy calculations of the behavior of the mechanical internal stresses [17, 18]. This model has been applied to study the behavior of the internal stresses when the size and volume fraction of the crystalline zones in EPDM are modified [17, 18].

It should be noticed that, to our knowledge, a model which allows to describe the behavior of the mechanical internal stresses arisen from an electrostriction phenomenon, useful for engineering calculations, was not yet reported.

In the present work, the basic ideas of the model involving the mean field treatment applied to the formalism of the inclusion [17, 18] will be used for describing the behavior of the (mechanical) internal stresses into dielectric materials as a consequence of the electrostriction phenomena, promoted by the appearance of an electric field. The new model allows the calculus of the internal stresses in dielectric materials promoted by the application of an electric field, from electromechanical tests. Results of the model here developed, are successfully applied to dynamic mechanical analysis (DMA) [19] studies under the application of an electric field. Indeed, this work is a very useful tool which brings both the theoretical equations and also an experimental setup, which allow the study of the internal stresses behavior in dielectric materials which arise from the application of an electric field. Moreover, it has to be highlighted that, to our knowledge, it is the first report of DMA studies performed under the application of an electric field for the study of dielectric materials.

2 THEORETICAL BACKGROUND

For better understanding of the work presented here, the essential concepts of the previously reported model based in a mean field treatment applied to the formalism of the inclusion will be summarized. Only the one-dimensional case will be presented in this paper; for more details see [17]. The model takes the idea of partitioning the volume of the sample in small elementary cubes in such a way that each partitioned element is composed by a single phase [17, 18, 20] either inclusion or matrix, in the polymer material we are dealing with.

Figure 1 summarizes the main concepts to take into account. It shows a (z, y) plane of the partitioned sample at $x = v$, where the size of the partitioned matrix, over each axis, was chosen equal to l_{0p} . The model for calculating the

degree of the strain misfit starts with the following considerations:

a) The volume element located at (v, m, j) of the whole partitioned matrix (for more details see [17]), which is plotted by means of full fine lines in Figure 1, is cut and removed out of the matrix; leading to a cubic hole of edge l_{0p} . In other words, a cubic volume is cut from the nondistorted initial cubic lattice.

b) An inclusion of size $l_{0p} + \epsilon l_{0p}$, with $0 \leq \epsilon \leq 1$, plotted by means of broken lines, will be firstly compressed to fit into the hole of the matrix and subsequently placed in.

c) The inclusion is mechanically released and then the boundaries of the hole, in the x , y and z axis, displace to a position $l_{0p} + \beta l_{0p}$, with $0 \leq \beta \leq 1$, where the equilibrium of stresses is achieved. The wide lines in Figure 1 represent this state.

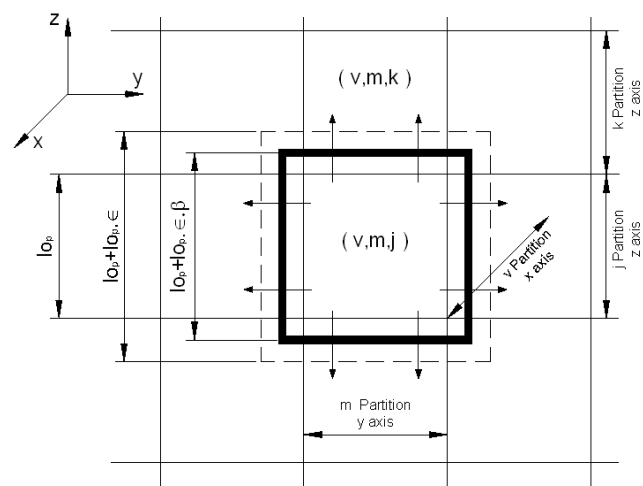


Figure 1. Accommodation of the misfit strain by the appearance of an inclusion into the material matrix, case: inclusion larger in size than the size of the hole. Fine full line: Initial size of the base of the cube of the partitioned material. Broken line: Size of the inclusion free of stresses. Wider full line: Equilibrium position of the boundary between the inclusion and the matrix, after location of the inclusion into the matrix hole (see details in the text). Arrows in the Figure indicate the compression effect of the inclusion on the matrix. Taken from [17].

The movement of each boundary is considered in each axis as a plane front, which moves until the equilibrium of stresses in each axis is reached.

The movement of the boundary in the z -axis, produced by the inclusion located at (v, m, j) , and its effects over the neighbor matrix element (v, m, k) , will be considered now, see Figure 1. The displacement of the boundary of the element (v, m, j) from the initial position (cube in dashed line in Figure 1) after the inclusion is forced into the hole and released mechanically achieving the mechanical equilibrium, leads to the movement of the front from the solid line to the wider line, Figure 1.

It is considered that the inclusion and the matrix are homogeneous and isotropic media, and due to the symmetry of the problem the centre of the inclusion will

not change its position during the deformation process and the reaching of the stresses equilibrium [17]. Then any point inside the inclusion between the initial state (original size, free of stresses, state represented by the dashed line in Figure 1) and after forcing the inclusion into matrix and subsequent achievement of the mechanical equilibrium, moves from $(z + z \in)$ to $(z + z \in \cdot \beta^z)$, where β^z means the misfit coefficient along the z-axis. This leads to a displacement in the z-axis, $u_i(z)$, that is

$$u_i(z) = (z + z \in) - (z + z \in \cdot \beta^z) \quad (1)$$

$$u_i(z) = z \in (1 - \beta^z) \quad (2)$$

Consequently the mean strain inside the inclusion (averaged by the mean field approximation) in the z-axis, ε_i^z , results,

$$\varepsilon_i^z = \frac{\partial u_i}{\partial z} = \varepsilon (1 - \beta^z) \quad (3)$$

Hereafter, the magnitudes corresponding to the inclusion or to the matrix, will be noted with a subscript i or m , respectively. In addition, in order to keep the same style of the mathematical notation used in the work of [17], either the direction for the strain misfit coefficient, β , and for the number of inclusions or matrix elements (N) will be denoted through a supra-subscript.

On the other hand, we obtain now the resulting mean strain inside the matrix element. Let consider that there exists an inclusion concentration lying in the z-axis N_i^z/N_m^z (where N_i^z and N_m^z are the number of inclusions and the number of matrix elements, respectively, which satisfy the condition $N_i^z + N_m^z = N^z$), the N_i^z inclusions move the boundaries of the N_m^z partitions, in such a way that to the partition (v, m, k) the following displacement corresponds: $z + z \in \beta^z N_i^z/N_m^z$. Then, the displacement in the z-axis for the matrix elements can be written,

$$u_m(z) = z \in \cdot \beta^z \left(\frac{N_i^z}{N_m^z} \right) \quad (4)$$

Therefore, the strain inside the matrix element in the z-axis, ε_m^z , results,

$$\varepsilon_m^z = \frac{\partial u_m}{\partial z} = \varepsilon \cdot \beta^z \left(\frac{N_i^z}{N_m^z} \right) \quad (5)$$

By working equation (5) we obtain,

$$\varepsilon_m^z = \varepsilon \cdot \beta^z \left(\frac{N_i^z / N^z}{N_m^z / N^z} \right) = \varepsilon \cdot \beta^z \left(\frac{f r_i^z}{f r_m^z} \right) \quad (6)$$

where $f r_i^z$ and $f r_m^z$ are the volume fraction for the inclusions and matrix element in the z-axis, respectively; which satisfy $f r_i^z + f r_m^z = 1$.

From the mechanical equilibrium conditions at the boundary between the adjacent elements (v, m, j) and (v, m, k), according to the Reuss approximation [11, 17], and by applying the Hooke's law; the misfitting coefficient in the z-axis, β^z , can be obtained as a function of the Young moduli, M , and volume fractions of both, inclusions and matrix,

$$\beta^z = \frac{1}{1 + \left(\frac{M_m}{M_i} \right) \cdot \left(\frac{f r_i^z}{f r_m^z} \right)} \quad (7)$$

Moreover, considering that the distribution of inclusions is random in the bulk (homogeneous and isotropic) matrix, it can be demonstrated easily that [17]

$$\beta^z = \beta^x = \beta^y = \beta \quad (8)$$

Indeed, β is the misfit coefficient, which relates the inclusion strain caused by the matrix or vice versa, i.e. the matrix strain caused by the inclusion.

3 EXPERIMENTAL

3.1 SAMPLES

Rubber samples were prepared with raw SBR (styrene-butadiene rubber, cold emulsion polymerization, 23.5% bound styrene). Two different grades of SBR were used: SBR 1502 (typical Mn 140000 Da, Mw 500000 Da) and SBR 1712 (typical Mn 210000 Da, Mw 710000 Da, 27.5% added extender oil). The latter contains a highly aromatic oil from the type DEA (distilled aromatic extract), with typical composition: 38% aromatic carbons, 26% naphthenic carbons, 36% paraffinic carbons (according to ASTM D2140), and viscosity value of 32 cSt (at 373 K).

Rubber compounds were prepared in an open mill with roll temperature at 323 K (± 5 K), according to ASTM D3182. Compound formulae were taken from ASTM D3185 (see Table 1). To obtain vulcanized rubber sheets, the massed compounds were passed through the mill to give a thickness of about 2.2 mm, and were cooled on a flat metal plate. After conditioning at 296 K (± 3 K) for 4 h each sheet was cut in squared pieces of 150 mm side, and the direction of the milling was marked. Pieces were placed in a mold and vulcanized in a press (35 min, 418 K), after which they were immediately cooled on a water bath and conditioned for 18 h at 296 K (± 3 K). This procedure provided the rubber vulcanized sheets ready for mechanical measurements [21].

Table 1. SBR compound formulae for vulcanized samples (ASTM D3185).

Material (in phr, parts per hundred rubber)	SBR 1502 (Formula 1A)	SBR 1712 (Formula 2B)
Raw SBR	100.00	137.5*
Zinc oxide	3.00	3.00
Sulfur	1.75	1.75
Stearic acid	1.00	1.00
Oil furnace black	50.00	68.75
Accelerant (N-tBu-2-benzothiazolesulfenamide)	1.00	1.38

(*) Raw SBR 1712 contains 37.5 phr of highly aromatic oil

Samples of vulcanized SBR 1502 and 1712 were cut with a bistoury in a single pass. The direction for sample extraction from the whole sheet was parallel to the rolling direction. Samples after the cut were examined with magnifying glass (X100) in order to check the sharp of the resulting cut. Sample dimensions for DMA studies were 40mm length, 9mm width and 2 mm thickness.

3.2 MEASUREMENTS

DMA test, loss tangent (damping or internal friction), $\tan(\phi)$, and dynamic shear modulus, G' , were measured as a function of the applied electrical field, E , in a mechanical spectrometer working in torsion at temperature of 318 K (± 0.25 K), in air. The resonance frequency was around 1.5 Hz. Damping was determined by measuring the relative half width of the squared resonance peak for a specimen driven into forced vibration using equation (9) [22]:

$$\tan(\phi) = \frac{\omega_2 - \omega_1}{\omega_0} \quad (9)$$

where ω_0 is the resonance frequency, and ω_1 and ω_2 are the frequencies at which the amplitude of oscillation has fallen to $1/\sqrt{2}$ of the maximum value. The errors of $\tan(\phi)$ and G' , being proportional to the squared oscillating frequency, are less than 1%. The maximum oscillating strain on the surface of the sample was 2×10^{-4} .

The electric field was produced by two electrodes placed at the sample position, lying in parallel direction to the torsion axis of the spectrometer, i.e. the resulting electric field is perpendicular to the torsion axis, Figure 2. Electrodes were connected to a variable DC high voltage power supply, giving rise to E values up to 430 kV/m, at the sample location. Details of the assembled of this novel device are reported elsewhere [23].

Samples usually employed for DMA testing could have a large variety of sizes. Some equipment allow measurements in samples of size as small as around 10 μm of thickness. Nevertheless, to measure thinner samples of only a few microns of thickness could be also possible in composite

samples, where the sample of interest is deposited on the surface of a substrate with a comfortable thickness for the equipment operation [24, 25]. Deposition can be done by means of the usual procedures, e.g. reaction synthesis or cathode vapor deposition, etc.

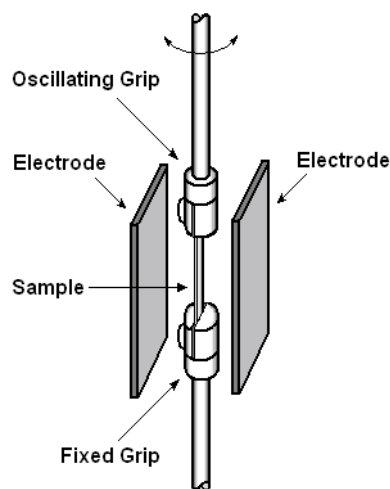


Figure 2. Schematic representation of the positioning of electrodes in the DMA equipment.

4 RESULTS AND DISCUSSION

4.1 THE MODEL

The dielectric material will be partitioned in different cubes which form a sizeable bulk material, similarly to the procedure described in Section 2, in such a way that a given cube can be of the dipolar phase and its neighbor can be of the same phase or the matrix.

Figures 3 summarize the main concepts to take into account for this new case of dielectric materials. It shows a (z,y) plane of the partitioned sample at $x = v$, where the size of the partitioned matrix, over each axis, was chosen equal to l_{op} . The model now starts with the following considerations:

a) The volume element corresponding to a dipolar phase, located at (v,m,j) of the whole partitioned matrix, which is plotted by means of full fine lines in Figure 3a, is cut and removed out of the matrix; leading to a cubic hole of edge l_{op} .

b) An electric field is applied to this extracted dipolar zone, then it stretches from l_{op} to $l_{op} + \epsilon l_{op}$, with $0 \leq \epsilon \leq 1$, see broken lines in Figure 3b. It is easy to recognize that the mismatch parameter ϵ is the strain misfit promoted thorough an electrostrictive phenomenon. Indeed, the application of the electric field give rise to the appearance of an inclusion of larger size into the matrix, plotted by means of broken lines.

c) The inclusion of size $l_{op} + \epsilon l_{op}$, with $0 \leq \epsilon \leq 1$, plotted by means of broken lines, will be firstly compressed to fit into the hole of the matrix and subsequently placed in.

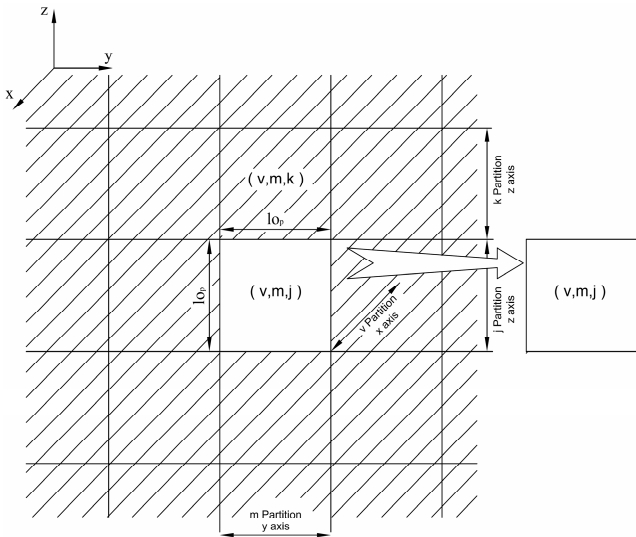


Figure 3a. Initial size of the base of the cubes of the partitioned material (full line), from where a dielectric inclusion (v, m, j) is removed.

d) The inclusion is mechanically released and then the boundaries of the hole, in the x-axis, displace to a position $l_{0p} + \beta \in l_{0p}$, with $0 \leq \beta \leq 1$, where the equilibrium of stresses is achieved. The wide lines in Figure 3c, represent this state.

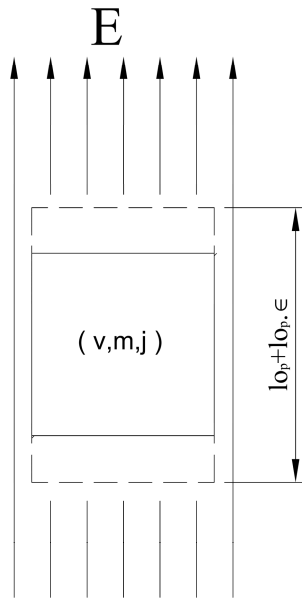


Figure 3b. The isolated dielectric partition (v,m,j) is subjected to electric field, leading to its stretching (broken line).

Therefore, by means of the above described procedure, the elastic misfit promoted by an electric dipole when an electric field is applied, can be studied now using the mathematical formalism of the inclusions theory. In fact, in the present study β is the misfit coefficient, which is related to the matrix strain caused by the stretching of the dipole when the electric field appears. A straightforward analysis,

allows easily to deduce that the mathematical expression for β coefficient which corresponds to the elastic misfit promoted by the stretching of a dipole under the application of an electric field, is similar to equation (7) where the magnitudes related to the inclusion correspond to the dipoles.

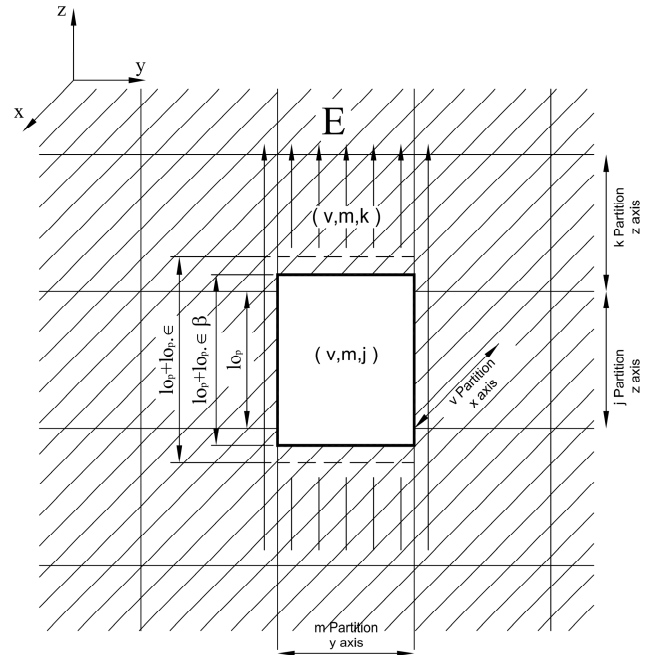


Figure 3c. Equilibrium position of the boundary between the inclusion and the matrix, after location of the stretched inclusion into the matrix hole and release of its constriction. See explanation in the text.

Nevertheless, even if the volume fraction of inclusions can be known, a β coefficient, equation (7), cannot yet be calculated from measured data in mechanical tests, due to the modulus of the inclusion is unknown. In fact, to know the elastic modulus of the inclusions requires take a relation between the electrical stress and the dielectric strain.

From the general problem of the thermodynamic of deformations under the application of an external electric field [2, 3], a thermodynamic potential, FF , can be written in the form [26, 27],

$$FF = F - \frac{ED}{4\pi\epsilon_0} \tag{10}$$

where F is the free energy, D is the displacement electric field vector and ϵ_0 is the permittivity of the empty space.

Taking into account that in a solid FF is a function of all the components of the strain tensor ϵ_{im} , the electric field and the absolute temperature, T , that is,

$$FF = FF(E, T, \epsilon_{im}) \tag{11}$$

Differentiating with respect to the components of the deformation tensor ϵ_{im} and operating, the components of the

stress due to the combined application of the electric and mechanic fields can be obtained, such that

$$\sigma_{ik} = \sigma_{ik}^{(0)} + (2\varepsilon_0 - a_1) \frac{E_i E_k}{8\pi \varepsilon_0} - (\varepsilon_0 + a_2) \frac{E^2 \delta_{ik}}{8\pi \varepsilon_0} \quad (12)$$

where $\sigma_{ik}^{(0)}$ is the stress tensor free of electric field, which is determined by the elasticity modulus and a_1 and a_2 are the constants of the second rank dielectric tensor, ε_{ik}^d , constructed of linear mode from the components of the strain tensor [2, 3, 27], that is

$$\varepsilon_{ik}^d = \varepsilon_0 \delta_{ik} + a_1 \varepsilon_{ik} + a_2 \varepsilon_{ll} \delta_{ik} \quad (13)$$

Coefficient a_1 and a_2 are related to the physical driving force for coupling the electrical and the mechanical field.

It was previously explained that although equation (12) is a function of the type of the crystalline structure of the solid, it is always possible to find a non-vectorial relationship in the case of non-crystalline solids, using the mean field approximation [2, 3, 26, 27]. As it can be inferred, to handle mathematically equation (12) for obtaining the elastic modulus of the dipolar phase, even in an average approximation of a mean dependence with the square of the electric field, is not easy.

In contrast, a more friendly solution for eliminating the appearance of the elastic modulus of the inclusion in equation (7) can be done taking into account the relationship that exists between the elastic modulus of the whole material, M , and the moduli of the matrix and inclusion parts, when a Reuss condition is considered [11, 20],

$$\frac{1}{M} = \frac{f r_m}{M_m} + \frac{f r_i}{M_i} \quad (14)$$

Then, by working mathematically equation (14), results

$$M = \frac{M_m \cdot M_i}{M_i \cdot f r_m + M_m \cdot f r_i} \quad (15)$$

$$M = \frac{1}{\frac{f r_m}{M_m} \cdot \frac{1}{1 + \frac{M_m \cdot f r_i}{f r_m \cdot k_i}}} \quad (16)$$

Remembering the mathematical form of β , then equation (16) can be written as

$$M = \frac{M_m}{f r_m} \cdot \beta \quad (17)$$

from where β coefficient can be now calculated, despite of unknowing the elastic modulus of the dipolar zone, that is

$$\beta = f r_m \frac{M}{M_m} \quad (18)$$

It should be highlighted the powerful of equation (18) here deduced since it makes possible to calculate the misfit coefficient in dielectric materials, or two-phase polymers, knowing the elastic modulus of the matrix, free of electrostrictive effects, its volume fraction and the elastic modulus of the whole material, when the electrostrictive effects appears.

It should be stressed, that the above discussion which involves the Eshelby's inclusion theory [11, 16, 17] has been performed taking in consideration a homogeneous and isotropic media. However, the model here described can be also applied to anisotropic materials. In fact, β coefficient obtained corresponds to the one-dimension rearrangement of strains between the matrix and the inclusion. So, by applying an electric field in a given direction we can obtain β for each direction. Where β is an average misfit coefficient that takes into account the contribution of all the anisotropic effects of both the matrix and the inclusion. Nevertheless, the three-dimensional case formerly reported for two phase polymer [17] cannot be used in anisotropic media.

On the other hand, the above procedure can be easily applied to the study of the mechanical energy transfer related to the electrostriction phenomenon. In fact, by following the work in [18], we can write the expression for the whole elastic energy available to be transferred to one matrix element over the z-axis, such that

$$W_T^z = \frac{1}{2} M_i \cdot \varepsilon^2 \cdot V_p \cdot \left(\frac{f r_i^z}{1 - f r_i^z} \right) \quad (19)$$

where V_p is the volume of the (v,m,j) partition. In addition, the energy in the partition corresponding to the matrix element results

$$W_m^z = \frac{1}{2} M_m \cdot \varepsilon^2 \cdot \beta^2 \left(\frac{f r_i^z}{1 - f r_i^z} \right)^2 \cdot V_p \quad (20)$$

Consequently, the ratio between the elastic energy transferred to the matrix and the whole available one is

$$\frac{W_m^z}{W_T^z} = \frac{M_m}{M_i} \beta^2 \left(\frac{f r_i^z}{1 - f r_i^z} \right) \quad (21)$$

It is convenient to mention that the transfer of elastic energy is due to the movement of the borders of the inclusion into the matrix from its initial compressed state up to the achievement of the mechanical equilibrium condition. So, the ratio given by equation (21) is very intuitive regarding the competition of the moduli values between the inclusion and the matrix, until the equilibrium condition is achieved.

By replacing the value of M_i obtained from equation (14), equation (21) can be written as function of measurable values in mechanical tests and the value of β , that is

$$\frac{W_m^z}{W_T^z} = \frac{M_m - M f_{rm}}{M} \beta^2 \frac{1}{f_{r_m}} \quad (22)$$

4.2 EXPERIMENTAL RESULTS-APPLICATION OF THE MODEL

Dynamic mechanical analysis (mechanical spectroscopy) measurements were used in the present work as the mechanic test for the application of the model developed in Section 4.1, due to DMA is very sensitive to the changes occurring in the structure of materials [19]. Indeed, DMA can detect at ppm of micromechanisms in movement giving rise to relaxation phenomena [19]. In addition, DMA has been also applied widely to the study of both magnetomechanical damping and magnetostriction phenomena [19, 26]. In contrast, as it was mentioned in the Introduction, to our knowledge, there is not reported works on DMA in which an electric field is applied during the measurements, for the study of dielectric materials.

In order to apply the model developed in Section 4.1, SBR rubbers were chosen as samples for the present work. Indeed, SBR 1502, free of oil, was an appropriate reference dielectric material with negligible electrostriction effects, at the field intensities used in the present work, as it will be shown in the next paragraphs. In addition, the composition of SBR vulcanizates can be controlled at will for the authors. Then, the addition of the highly aromatic oil to the raw SBR polymer, giving rise to SBR 1712 samples is an excellent mode of introducing a given volume fraction of dipoles (inclusions) into a known matrix. As it can be seen from Table 1, the aromatic oil in SBR 1712 is the only material different from those included in SBR 1502 formulation. Consequently, the results which will be obtained for β coefficient and the ratio W_m^z/W_T^z through the developed model, give an accurate measurement of the behavior of the strain misfit into the matrix caused by electrostrictive effects promoted by changes in the electric field strength.

It has to be mentioned that in all the calculations made in the present work, the dynamic elastic shear modulus,

G' , instead of the Young modulus, has been used. Nevertheless, this will not diminish nor obstruct the subsequent analysis made here, since the material under study is considered through a mean field approximation.

Figure 4 shows the behavior of damping and dynamic modulus as a function of the applied electric field for the SBR 1712 sample, measured during the field increase. As it can be seen from the Figure, damping (circles) decreases and dynamic modulus (triangles) increases as the strength in the electric field increases. During the decrease in the electric field intensity, after having reached its maximum, a hysteretic behavior in both damping and modulus was not found, i.e. measured values are in good agreement with those measured during the increase in the field intensity.

In contrast, SBR 1502 samples do not show any dependence on the strength of the electric field, giving rise to an independent damping and modulus behavior as a function of the applied electric field, E.

A summary of the damping and modulus values measured at nil electric field for SBR 1502 and SBR 1712 is shown in Table 2.

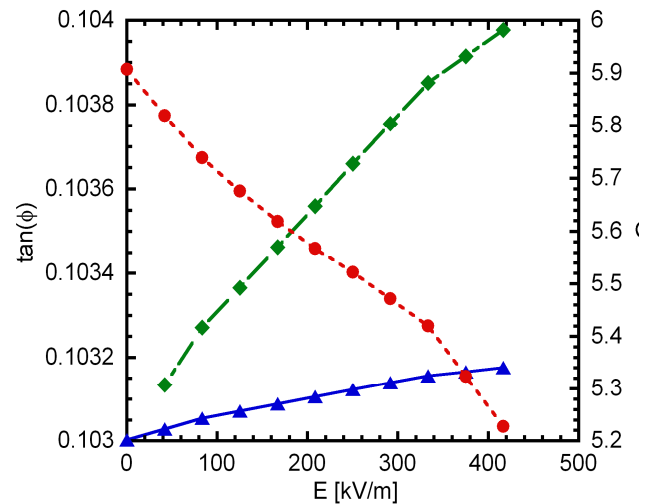
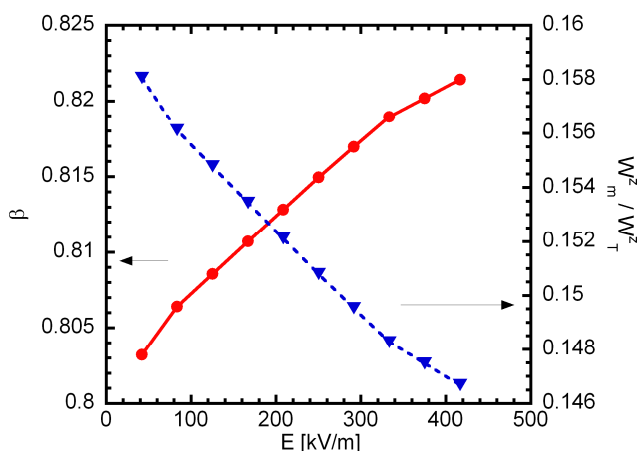


Figure 4. $\tan(\phi)$ (circles) and G' (triangles) as a function of the electric field strength for SBR 1712. Diamonds: dynamic modulus for the dielectric inclusion calculated from equation (14), see explanation in the text. Lines joining points are a guide for the eyes.

Table 2 indicates that the addition of oil to the samples increases the damping values, as it could be expected due to the enhancement of the movement capability of the frictional micromechanisms [28, 29]. In fact, the addition of oil plays a role similar to that of low molecular weight plasticizers into a polymer sample, increasing the whole frictional contribution of the polymer matrix [28-30]. In addition, the elastic modulus is smaller for 1712 than for 1502 samples, in agreement with the above mentioned role of the oil into the matrix.

Table 2. $\tan(\phi)$ and G' measured at nil electric field in SBR 1502 and 1712.

	SBR 1502	SBR 1712
$\tan(\phi)$	0.092	0.104
G' (MPa)	5.5	5.2

**Figure 5.** misfit coefficient β (left axis) and W_m^z/W_T^z (right axis) as a function of the electric field strength calculated for SBR1712. Lines joining points are a guide for the eyes.

Following the theoretical representation of the model developed in Section 4.1, the oil will be considered as cubes embedded into the rubber matrix accordingly to the corresponding volume fraction. The increase in the electric field promotes the stretching of dipoles along the direction of the electric field leading to the appearance of an inclusion, see Figures 3, i.e. the original cube of the partition was modified towards a parallelepiped-shaped inclusion, as it was shown in Section 4.1. Indeed, the increase in electric field leads to higher modulus in the inclusion due to the increase in the stretching of the dipoles, until saturation. Perhaps, an orientation contribution of the dipoles could contribute also to the increase in the modulus. In fact, an increase in the electric field promotes a strong pinning of the oriented dipoles along the field direction. The alignment direction is perpendicular to the torsion axis of the spectrometer (see Figure 2), so a larger anchorage of the dipoles could lead to higher torsion modulus of the inclusions, as the field increases. Then, the increase in the moduli of the inclusions (or second phase), leads to an increase in the modulus of the whole matrix, as it is well known in the mechanical properties of composite and two phase materials [11, 16, 31]. Therefore, as the electric field increases, the modulus of the inclusions increases, leading to the increase of the modulus of the sample, in agreement with the reported results in Figure 4.

As the viscosity of the oil (see Section 3.1), i.e. the dipolar phase, is high enough in such a way that this phase can be considered as a viscoelastic solid [28, 32], at both the frequencies and temperature used in the present work, the behavior of the elastic modulus of

inclusions can be easily obtained from equation (14). In Figure 4, the behavior of dynamic modulus for the dipolar phase (inclusions) is plotted as a function of the electric field by means of diamonds. A clear increase in the elastic modulus of the dipolar phase, with an increase in the electric field intensity can be observed, according to what was mentioned above.

The decrease in damping values as the electric field increases is also in agreement with the increasing modulus of the dipolar phase and the appearance of internal stresses in the matrix. An increase in the modulus of the dipolar phase and the appearance of internal stresses lead to a decrease in the capability of movement of the dissipative micromechanisms, polymer chains in the case of polymers, giving rise to a decrease in the damping values. As the internal stresses into the matrix increases, polymer chains, similarly to dislocation lines, are forced to overcome a higher energy saddle point to begin the movement [5]. The decrease in the damping values related to the modulus increases of the matrix due to the hardening by the appearance of inclusions or second phases, has been widely verified either in metallic alloys and polymeric materials [19, 28, 33, 34].

Figure 5 shows the behavior of β coefficient and W_m^z/W_T^z , as a function of the applied electric field, calculated by means of equations (18) and (22), respectively. Plotted values start from the first stage in electric field, due to the model can be applied after the appearance of the inclusion promoted by the electric field application, see Figure 3 in Section 4.1. As it can be seen from the Figure 5, β increases and W_m^z/W_T^z decreases, as the electric field increases. In fact, β and W_m^z/W_T^z show the inverse dependence among them, in agreement with previous reported works [18].

The increase in β values, indicates that the increase in the strain misfit is mainly accommodated by the matrix, i.e., $\beta \rightarrow 1$ leads to $l_{o_p} + l_{o_p} \in \beta \rightarrow l_{o_p} + l_{o_p} \in$ (see Figure 3), so the strain misfit is mainly accommodated by the matrix. The electric field increase, leads to an increase in the modulus of the inclusion (see Figure 4); forcing the matrix to accommodate higher strain misfit, so leading to an increase of β . It is convenient to mention, that the behavior of β and consequently the behavior of the internal stresses shown for this case is different to the previously reported for EPDM, where the volume fraction of inclusions was the predominant changing phenomenon [5, 17, 18].

In order to make easier the interpretation of β behavior shown in Figure 5, theoretical curves of β coefficient were calculated by means of equation (18), Figure 6, where the M modulus was calculated through equation (14), i.e. both contributions M_m and M_i were taken into account. Curves were calculated as a function of the modulus of the inclusion, for different volume fraction of inclusions, considering an arbitrary modulus for the matrix to be equal

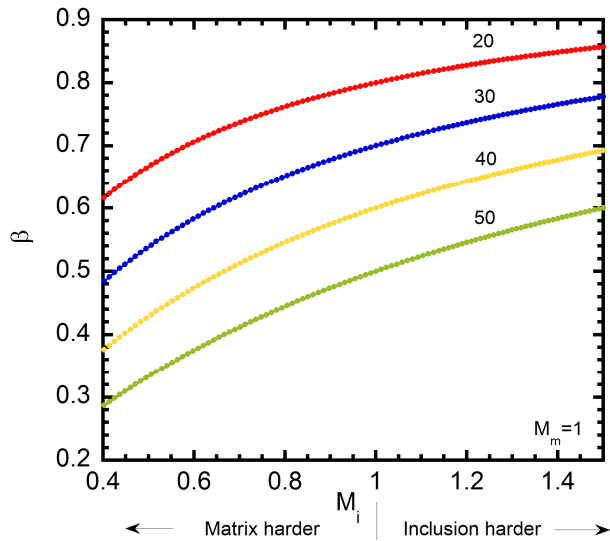


Figure 6. Theoretical curves of the misfit coefficient β as a function of the modulus of the inclusion for different volume fraction of inclusions. $M_m = 1$. See explanation in the text.

to one, $M_m = 1$. So, from the x-axis, a percentage variation between M_m and M_i can be easily determined. As it can be seen from the Figure an increase in the modulus of the inclusion leads to an increase in β values, for all the calculated volume fractions, in agreement with the experimental results here reported. In contrast, if the modulus of the inclusion is constant and the change is produced in the volume fraction, then the β values decrease as the volume fraction increases. This is in agreement with previously reported works related to the modification of the crystalline zones in EPDM [5, 17, 18].

On the other hand, the behavior of W_m^e/W_T^e indicates that the work done in compressing the inclusions from $l_{op} + l_{p\epsilon}$ up to l_{op} for being introduced into the matrix holes, see Figures 3 in Section 4.1, is larger than the work done by the matrix, as the electric field increases. Indeed, a larger work is required for compressing the inclusion in a magnitude ϵ as the electric field increases, due to the increase in the modulus of the inclusion promoted by the increase in the electric field. Therefore, it can be determined that the increase in the modulus promoted by the application of the electric field has a larger effect than the increase in the mismatch parameter ϵ , as the field increases.

Theoretical curves of the ratio W_m^e/W_T^e were calculated by means of equation (22), where β was obtained from equation (18) and M modulus was calculated through equation (14), Figure 7. Similarly to the theoretical calculations for β , curves were calculated as a function of the modulus of the inclusion, for different volume fraction of inclusion and considering an arbitrary modulus for the matrix $M_m = 1$.

As it can be seen from the Figure, an increase in the modulus of the inclusion with respect to the modulus of the matrix leads to a decrease in W_m^e/W_T^e , in agreement with the

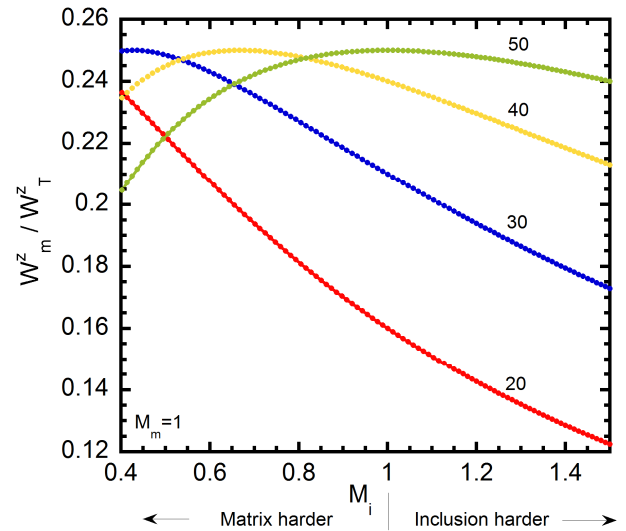


Figure 7. Theoretical curves of W_m^e/W_T^e as a function of the modulus of the inclusion for different volume fraction of inclusions. $M_m = 1$. See explanation in the text.

behavior exhibited from the experimental data. Therefore, it is clear from the Figure, that when the modulus of the inclusion is higher than the modulus of the matrix, for a given volume fraction of inclusions, the ratio W_m^e/W_T^e decreases as the modulus of the inclusion increases. In contrast, for a phenomenon developed at constant values of the modulus of inclusions, where an increase in the volume fraction appears, the ratio W_m^e/W_T^e increases in agreement with previously reported work [18]. Besides this, the maximum in W_m^e/W_T^e for a volume fraction of 50% has been found for an inclusion with the same modulus than the matrix, as it could be expected. In addition, it can be observed from the Figure that a non systematic evolution of the curves can be described for matrix harder than the inclusions around 30%, and also that an increase in the volume fraction of inclusions, for inclusions harder than the matrix, leads to an increase in W_m^e/W_T^e , revealing clearly the interaction processes between the inclusions.

From the mathematical point of view the present model has still the limitation that a group of equations were not yet found in order to get a_1 and a_2 in equation (12) for obtaining the physical magnitudes for the electrostrictive process.

Our model has been developed from a mesoscopic point of view, so it presents limitations for the description of electrostrictive processes at molecular level. For instance, we cannot resolve the movement of single electric dipoles (local movement) embedded into the inclusion at molecular scale when an electric field is applied, since we are studying the average behavior of the whole group of dipoles. In other words, we are studying the internal stress promoted by the electrostriction without the need of knowing the behavior of the dielectric at molecular level. So, we cannot get from our study the dependence of dielectric constant as a function of either molecular polarity, applied electric field, etc..

Nevertheless, it should be pointed out, that the present model give a solution to a crucial point in material science related to the determination of the behavior of the internal stresses in materials immersed in both electrical and mechanical fields.

In another light, DMA measurements conducted under electric field have been performed successfully also in other polymers such as silicon rubbers, EPDM and polyamides. These experiments together with the theoretical results of the new model developed in Section 4.1 will be reported in further works.

5 CONCLUSIONS

A new model based on the theory of inclusions for two phase polymers has been developed for the study of dielectric materials when an electric field is applied.

The behavior of the internal stresses promoted by the electrostriction phenomenon, can be monitored by studying the behavior of the misfit coefficient, β , and the ratio W_m^e/W_T^e as a function of the electric field. The equations obtained through the model for both β and W_m^e/W_T^e are calculable using magnitudes from mechanical tests, in particular dynamic mechanical analysis, which is very sensitive to changes in the microstructure.

Dynamic mechanical analysis as a function of the electric field is reported, perhaps for the first time in literature, for the study of dielectric materials. DMA measurements performed under electric field were verified as a useful tool for studying the behavior of internal stresses in dielectric materials, in particular in this study for styrene butadiene rubbers.

ACKNOWLEDGMENT

This work was partially supported by the CONICET-PIP No. 2098 and 0179, the PID (ING 288) 2010–2013 and the Collaboration Agreement between PETROBRAS ENERGÍA S. A., Puerto General San Martín, Pcia. de Santa Fe and the Instituto de Física Rosario (IFIR) – CONICET, 2008–2012.

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