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Multiscale properties of polymeric insulating materials: from microscale polarizability to macroscale permittivity

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Multiscale properties of polymeric insulating materials: from microscale polarizability to macroscale permittivity

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Abstract- **This article presents an innovative and easy way for the calculation of the real part of permittivity for some of the most common insulating materials used for electrical applications, namely: polyethylene (PE), polypropylene (PP), polytetrafluorethylene (PTFE), ethylene-propylene diene monomer (EPDM), polyamide-imide (PAI), and epoxy resin (EP). This is achieved by the implementation and validation of the additivity approach for polarizability, along with the derivation of molecular volumes by means of chemical calculations involving real density of the considered materials. The proposed approach significantly reduces the computational time and effort for the calculation of macroscopic permittivity. Simulated values show good accordance with experimental results, thus validating the approach.**

I. INTRODUCTION

Permittivity is one of the macroscopical constitutive properties of materials, giving information about microscopical polarization mechanisms occurring inside the materials once they are subjected to external electric fields. For this reason, it is widely used for design of electrical equipment as capacitors, cables, and bushings [1].

The pioneering research on understanding the relation between the polarization mechanisms with the macroscopical quantity was led by Clausius and Mossotti during the end of the XIX century [2]. The Clausius-Mossotti (CM) equation relates some of the microscopical properties of the material, i.e., polarizability and volume, with the macroscopical permittivity. This equation results to be valid only on linear, homogeneous, and isotropic materials, which is hardly obtainable in real conditions. Nonetheless, it is found that the formula may still be applicable to gasses thanks to the so-called "Lorentz-Mossotti hypothesis", which equals the external electric field applied with the internal one acting on the gas molecules [2].

Only over the past decade, thanks to the development in computational physics and chemistry, new methodologies for the calculation of permittivity have been developed, also for solids [3,4]. As an example, *Natan et al.* [3] proposed an innovative way for the calculation of macroscopical permittivity of thin layer solids by means of the same microscopical properties as in the CM formula. This approach is found to be valid for some species of interest as biphenyl, p-quaterphenyl and alkyl group molecules. This latter can be considered as a good representation of the polyethylene (PE) chains, opening the possibility to apply the proposed procedure for other polymer groups.

Nonetheless, long computational times are usually required due to the complexity of solid materials. However, the recent advances in the study of first-principles calculations via density functional theory (DFT) with periodic boundary conditions resulted in faster calculations for simple polymeric materials, as PE [5–7].

As known, polymers are characterized by the repetition of the same chemical groups (methylene, in the case of PE), also called constitutive repetitive units (CRUs). In the case of additive properties i.e., polarizability and volume, it is possible to significantly diminish the computational time by reducing the simulation analysis form the macromolecule to its CRU.

With reference to the molecular volume, chemical simulation software permits the estimation of the Van Der Waals (VDW) volume. This latter is related to the sphere surrounding the atom described through the VDW radius. The VDW volume may be incorrect in the case of solids since it neglects the interaction among adjacent molecules which ensures the solid state of the material. On the other hand, the calculation of molecular volumes, through the real density of the considered solid materials, brings to more realistic values.

In this article, the authors attempt to overcome some of the issues related to the calculation of macroscopical permittivity in solids by proposing a novel approach which requires very little computational effort. Hence, the aim of this article is twofold. On the one hand, a validation of the additivity approach is presented by calculating the microscopical properties of the CRUs of various polymers used as electrical insulating materials. On the other hand, the introduced hypotheses are verified by comparing the permittivity values, simulated through the proposed approach, with experimental ones.

II. MODELLING APPROACH

A. Calculation of permittivity in solids

Susceptibility χ is a quantity which indicates the degree of polarization of a dielectric under the effect of an electric field.

Under Clausis and Mossotti's hypotheses, it is possible to write the susceptibility as a function of two microscopic quantities: polarizability α and volume v [2]. As in:

$$\chi = \frac{\alpha/v}{1 - 4\pi\alpha/3v} \qquad (1)$$

The polarizability vector P is defined by the product between the susceptibility and the local electric field. This latter is the electric field acting on a narrow part of the dielectric e.g., a single molecule acting as a polarizable point dipole (PPD). The local electric field is then given by the external field as well as the field created by the induced dipoles of the adjacent molecules [3,4].

Nonetheless, it is possible to define the polarizability vector as a function of the external electric field only, by introducing a new factor, the modified polarizability $\tilde{\chi}$. Hence:

$$P = \chi E_{loc} = \tilde{\chi}E \qquad (2)$$

Under proper hypotheses as reported in [3], the relation between the two electric fields:

$$E_{loc} = E - 4\pi P \qquad (3)$$

where the term $4\pi P$ is given by the potential of the considered polar layer divided by the vertical inter-layer distance.
Combining Eq. 2 and 3, we obtain:

$$\chi = \frac{\tilde{\chi}}{1 - 4\pi\tilde{\chi}} \qquad (4)$$

In the case of gasses, the inter-layer distance is very high so that the term $4\pi P$ vanishes (CM's theory). On the contrary, in a solid molecular film the term is never negligible so that Eq.1 becomes:

$$\tilde{\chi} = \frac{\alpha/v}{1 - 8\pi\alpha/3v} \qquad (5)$$

Eq. 5 relates the microscopical quantities (polarizability α and volume v) of the constitutive molecules of the solid material, with the macroscopical modified susceptibility $\tilde{\chi}$, which considers the external electric field only.
Finally, it is possible to derive the permittivity by means of:

$$\varepsilon = \frac{1}{1 - 4\pi\tilde{\chi}} \qquad (6)$$

B. Polarizability calculation approach

The additive property of polarizability is valid as long as no intermolecular interaction is present. This is the case of the nonpolar molecules e.g., PE or of the high frequency (THz domain) dielectric response. Indeed, in this frequency range, the contribution of dipoles is not present and the molecular relaxation due to the applied electric field is given considering the molecules as standalone (atomic and electronic polarization mechanisms) [2,8].

Nonetheless, in order to validate the additive approach, a parametric study of polarizability was performed on PE chains. Polarizability values of PE chains with increasing length were simulated through the chemical simulation software *Marvin Chemaxon 21.8* (Fig. 1). From the figure, it is possible to notice a linear increase of the property with the chain length. Then, the contribution of the single -CH$_2$- group results to be ~1.9Å^3.
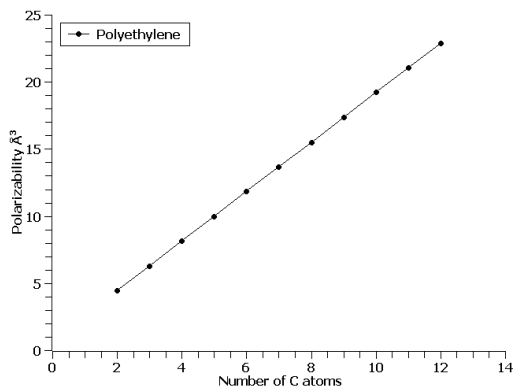

Fig. 1. Polyethylene polarizability values as a function of chain length.

B. Volume calculation approach

In the case of solids, the simulated volumes coming from chemical simulation software are not consistent with the real ones due to the higher density of the solid matter. Inside solids, molecules are more squeezed than in gasses, resulting into lower values than the VDW volume ones. Consequently, consistent calculation of volumes may be derived from solid density. In particular, molecular volumes may be evaluated as follows:

$$v = \frac{M_W/N_A}{\rho} \; (m^3) \qquad (7)$$

where M_W is the molecular weight of the considered CRU, N_A is the Avogadro number and ρ is the density of the considered polymer.

III. MODELLING RESULTS

A. Simulated materials

In this article, the authors investigate some of the most common polymers used as electrical insulators, namely: polyethylene (PE), polypropylene (PP), polytetrafluorethylene (PTFE), ethylene-propylene diene monomer (EPDM), polyamide-imide (PAI), epoxy resin (EP). According to *Section II.B*, it is chosen to consider only the CRUs, whose chemical formulas are reported in Figure 2.
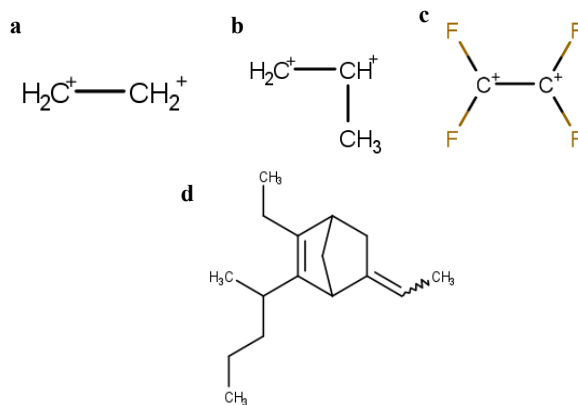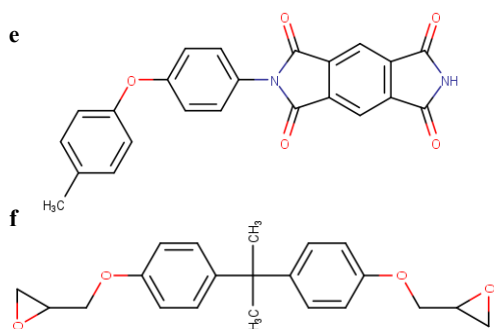
Fig. 2. Chemical formulas of simulated polymers:
(a) PE, (b) PP, (c) PTFE, (d) EPDM, (e) PIA, (f) EP.

B. Polarizability results

Once the CRU chemical formulas are drawn inside the chemical simulation software (*Marvin Chemaxon 21.8*), the corresponding values of polarizability may be calculated. Results are reported in Table 1.

TABLE I
SIMULATED POLARIZABILITY OF INVESTIGATED POLYMERS

Polymer	Polarizability ($Å^3$)
PE	3.8
PP	5.8
PTFE	4.8
EPDM	28.3
PIA	37.4
EP	38.4

As expected, as the size of the molecule increases, the polarizability raises. It may be demonstrated that the resulting polarizability is given by the sum of the different polarizabilities of the atoms constituting the molecule [9,10]. However, it is not possible to define a unique value of polarizability per each atom since the resulting atomic polarizability is function of the characteristics of the chemical bond e.g., the grade. As an example, Figure 3.a and Figure 3.b report the atomic polarizability of a carbon atom simply bonded with a hydrogen (as in PE) and with another carbon through double bond (as in the benzene ring inside EP), respectively. From the figure, it can be noticed that the presence of the double bond increases the carbon atomic polarizability from ~1.12 $Å^3$ up to ~1.36 $Å^3$, modifying, as a consequence, the global molecular polarizability.
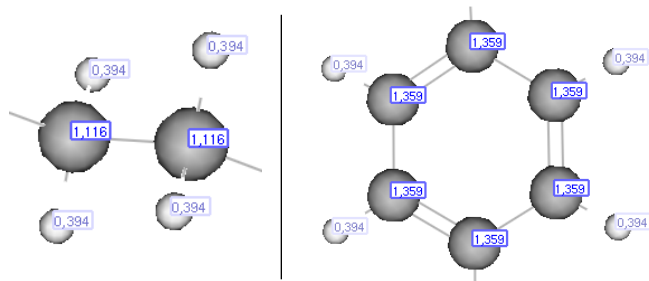

Fig. 3. Atomic polarizability closeup as a function of the grade of bonds.
(a) Simple bond, (b) Double bond.

C. Volume results

Molecular volumes are calculated according to Eq. 7 for the different simulated species. Molecular weight values are obtained by simply addition of the weights of the atoms inside the considered CRU, while density values are easily available in base chemistry books. Input data and calculated molecular volumes are reported in Table 2.

TABLE II
CHEMICAL PROPERTIES AND MOLECULAR VOLUMES OF INVESTIGATED POLYMERS

Polymer	Density (g/cm^3)	Molecular weight of CRU (g/mol)	Molecular volumes (m^3)
PE	0.92	28	$5.0 \cdot 10^{-29}$
PP	0.90	42	$7.8 \cdot 10^{-29}$
PTFE	2.20	102	$7.7 \cdot 10^{-29}$
EPDM	1.50	218	$24.1 \cdot 10^{-29}$
PIA	1.42	354	$41.4 \cdot 10^{-29}$
EP	1.15	340	$49.1 \cdot 10^{-29}$

D. Permittivity results

Once the microscale properties, namely molecular polarizability and volume, for the different CRUs are obtained, the macroscopical permittivities can be derived according to Eq.6. Results are reported in Table 3 and Figure 4, along with experimental values coming from literature.

It is worth noting that calculated permittivity values are very close to the experimental ones, claiming the effectiveness of the proposed approach. Although, few deviations are present, and these may be related to scattered signal given by the very high testing frequencies and/or nonuniquely defined density for the simulated material.

Finally, a schematic of the overall multiscale modelling approach is reported in Figure 5.

TABLE III
CALCULATED PERMITTIVITIES OF INVESTIGATED POLYMERS

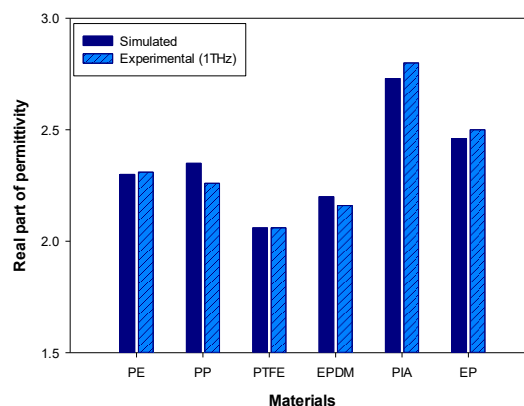| Polymer	Permittivity (calculated)	Permittivity (experimental)	Ref.
PE	2.30	2.30	[9,10]
PP	2.35	2.26	[13]
PTFE	2.06	2.06	[11]
EPDM	2.20	2.16	[14]
PIA	2.73	2.8	[15]
EP	2.46	2.50	[16]

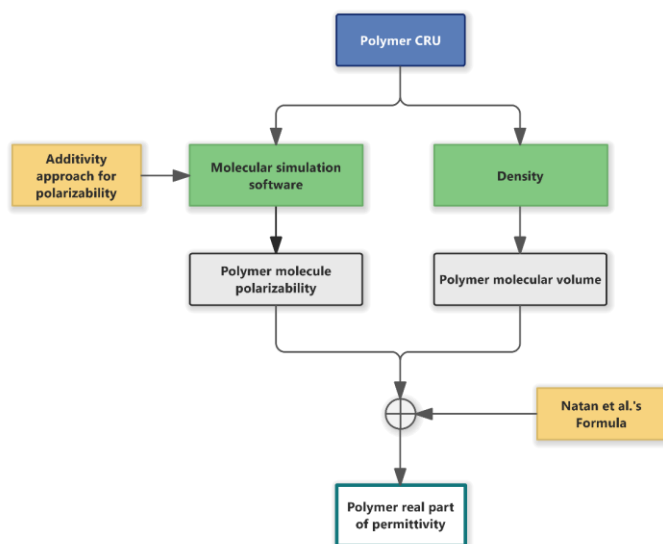Fig. 4. Comparison between simulated and experimental values of permittivity for the investigated polymers.

Fig. 5. Schematic of the multiscale modelling approach presented.

III. CONCLUSIONS

The proposed multiscale model permits the a priori evaluation of the macroscopical permittivity of several common polymeric dielectric materials through their microscopical properties i.e., molecular polarizability and volume.

In particular, calculations of complex macromolecule structures, e.g., polymer chains, are performed through chemical simulation software by considering just the characteristic CRU of the investigated materials. Indeed, it is demonstrated, through a parametric study, that the polarizability of the considered macromolecule is given by the sum of the polarizability of the different CRUs (additivity approach). This method deeply simplifies the complexity and computing resource consumption of the software simulation.

Moreover, the molecular volumes obtained by chemical calculations, involving the molecular weight and density of the solid matter, showed to provide realistic output values.

Finally, calculated permittivity is validated through comparison with experimental values, depicting good agreement. Though, in some cases, little inconsistences between the two sets of data are present and associated to non-uniquely defined density values for some investigated polymers.

Future works on this topic will include the estimation of the evolution of the polymer permittivity trend as a function of aging through calculation of permittivity for degradation species e.g., ketones and hydroperoxides.

ACKNOWLEDGMENT

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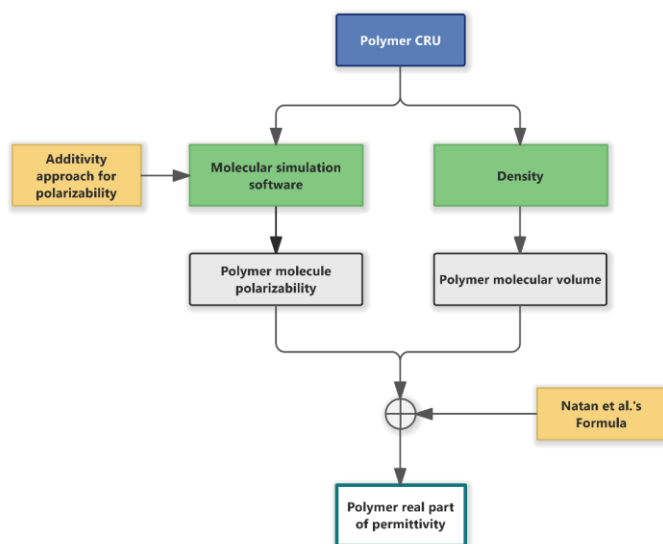
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