

Dielectric properties of organosilicons from first principles

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Abstract Density functional perturbation theory calculations have been performed to determine the dielectric constant of Si “doped” polyethylene (PE). Substitution of C atoms in PE by Si ranging from 0 to 100% has been considered. Both the electronic and ionic contributions to the dielectric constant increase with increasing Si content. These increases are attributed, respectively, to enhanced σ conjugation and increased IR vibrational intensity of modes involving Si containing bonds (owing to their softness and polarity).

Introduction

The ever-increasing demand for improved high voltage, high energy density capacitors continues [1]. A major subset of high energy density capacitors utilize polymeric materials as the dielectric, which provide several attractive properties, including ease of processability, high breakdown field, and graceful failure [2]. The present state-of-art in such capacitors is dominated by metalized biaxially oriented polypropylene (BOPP) [3], a linear dielectric with electronic polarizability but low dielectric constant (~ 2.2). BOPP provides an energy density of 5 J/cm^3 at breakdown, which occurs at $\sim 720 \text{ V}/\mu\text{m}$ for films $\sim 10 \mu\text{m}$ thick. Several promising approaches to further increase the energy density are currently being pursued, e.g., by increasing the dielectric constant and/or the breakdown field (as the maximum electrostatic energy that can be

stored in a capacitor is proportional to the former and the square of the latter). These include the utilization of ferroelectric relaxors such as copolymers of poly(vinylidene fluoride) [4], multilayer films of differing polymers with increased statistical independence of defects between layers [5], and polymeric films “filled” with high dielectric constant nanoparticles [6, 7].

The present paper constitutes an initial step along a possible new direction to achieve high energy density, namely, one that involves organosilicon compounds. As a reference point, we note that a polymer with properties similar to Si (fast response and a dielectric constant of ~ 12 due to large electronic polarizability), and good dielectric strength would provide an energy density at breakdown of about 27 J/cm^3 . While such a polymer may not be directly and immediately achievable, understanding the impact of introducing Si into the network of a base polymer such as polyethylene (PE) is useful.

In this paper, we consider a range of PE-based organosilicon systems in which C atoms are progressively replaced by Si. In “**Models and methods**” section, we provide details concerning the atomic level models used to study the Si-substituted PE systems, and the first principles computational methodology used. In “**Results**” section, we begin by presenting results concerning expected alterations to the physical structure, Young’s modulus and band gap of PE due to Si-substitution, before moving onto a detailed discussion of the dielectric properties of Si-substituted PE. Finally, our conclusions are summarized in the last section.

Models and method

The primitive (orthorhombic) unit cell of PE contains two chains, each with two CH_2 units as shown in Fig. 1 [8].

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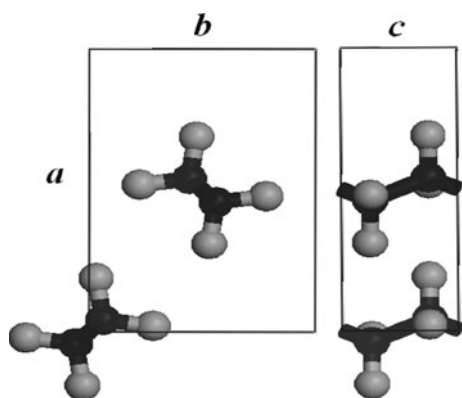


Fig. 1 Unit cell of PE projected normal to the *c* axis (left) and *b* axis (right). Black and gray spheres represent carbon and hydrogen atoms, respectively

Successive replacement of the four C atoms of this unit cell with Si atoms resulted in systems with Si concentration of 25, 50, 75, and 100% (polysilane). Given that the primitive PE unit cell was used as the starting point for such substitutions, all but the 50% Si situation could be constructed in only one way. For the 50% Si situation, two types of substitutions are possible. The first is when the two C atoms in the same chain are substituted by Si atoms, and the second type corresponds to the two substituted Si atoms being in different chains. Since the former has relatively higher total energy than the latter, we report results only for the latter in the following.

Density functional theory (DFT), as implemented in the Vienna *ab initio* simulation package (VASP) [9], was used to optimize the structure of all organosilicon systems. The PW91 generalized gradient approximation (GGA) [10], projector-augmented wave (PAW) pseudopotentials [11, 12] and a cutoff energy of 400 eV for the plane wave expansion of the wavefunctions was used. Density functional perturbation theory (DFPT), also implemented in VASP, was then used to determine the elastic and dielectric constant tensors. Large Monkhorst–Pack *k*-point sampling meshes of $(2 \times 4 \times 8)$ were required in order to obtain converged DFPT results.

Results

Basic properties of Si-substituted PE

Figure 2a summarizes our results concerning the geometry of the modified PE system as a function of Si concentration. The calculated PE *a*, *b*, and *c* lattice constants are in good agreement with the corresponding experimental values [13]. In the Si-substituted PE systems, *a* and *b* are determined by the interchain distance (controlled by weak van der Waals

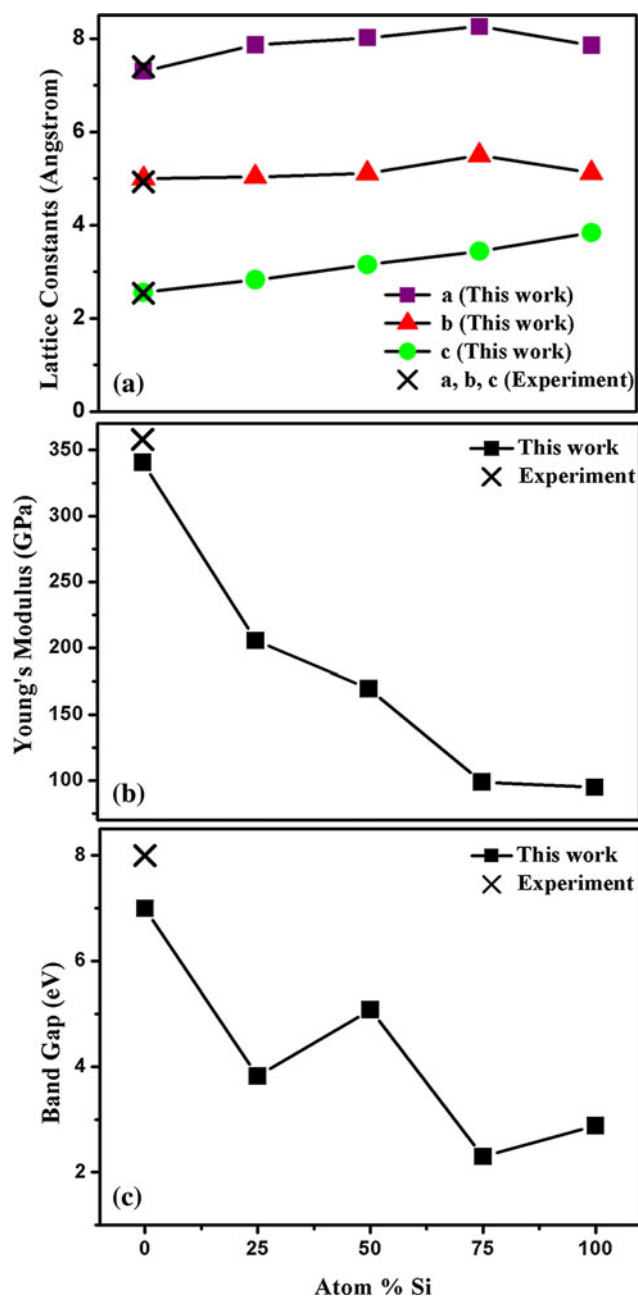


Fig. 2 a Calculated lattice parameters, b Young's modulus along the *c* axis, and c band gap of Si-substituted PE as a function of Si content. The corresponding experimental values for pure PE are also indicated (color online)

interaction) while *c* depends on the intrachain C–C, Si–Si or C–Si bond lengths along the backbone (controlled by strong primary bonding). We thus expect *c* to depend the strongest on the Si content, with this lattice parameter expected to increase with increasing Si content owing to the larger covalent radius of Si relative to C. Consistent with these expectations, *c* rises monotonically with increasing Si content (cf. Fig. 2a), while the relative fluctuations in *a* and *b* are minor without any particular trend.

Figure 2b shows the Young's modulus (calculated from the elastic constant tensors) along the chain axis (i.e., *c* axis) of Si-substituted PE systems. For comparison, the corresponding experimental [14] result for PE is also shown. With increasing Si content, the Young's modulus along the chain decreases drastically (by a factor of more than 3 on complete substitution of C by Si). This rapid reduction in the Young's modulus is consistent with the intuition that Si–Si bonds are much “softer” than C–C bonds.

The band gap of Si-substituted PE is presented in Fig. 2c. The band gap of pure PE is underestimated with respect to the corresponding experimental value [15] of 8.0 eV by 12.5%, a discrepancy typical of approximations within DFT. It can be seen in Fig. 2c that with increasing Si content the band gap of Si-substituted PE decreases drastically, albeit not monotonically. This drop in band gap with increasing Si content may be attributed to enhanced σ conjugation, a well-documented attribute of organosilicons in general, and that of polysilanes in particular [16] (also see below). The small Young's modulus and band gap values for PE with large Si content are critical factors one may have to consider from the point of view of actual applications using organosilicons.

Dielectric properties of Si-substituted PE

Dielectric constants along three principal axes of Si-substituted PE systems are presented in Fig. 3. As can be seen, for pure PE, the ionic contribution to the dielectric constant is negligible, and the electronic contribution along each of the three principal axes is about 2.4, in good agreement with the experimental value of ~ 2.2 [17]. With increasing Si content, both the electronic and ionic contributions to the dielectric constant increase.

The increase in the electronic contribution to the dielectric constant with Si content may be understood in terms of increased intrachain σ conjugation between Si and/or C atoms (which also results in band gap lowering). The degree of σ conjugation between Si and C follows the order: Si–Si > Si–C > C–C [18]. The σ conjugation controls the extent of delocalization of σ electrons [19] and thus tends to enhance the electronic contribution to the dielectric constant. Increased electronic contributions to the dielectric constant with Si content along *b* and *c* axes may be due to interactions between Si and H orbitals.

In order to understand the increased ionic contribution to dielectric constant with Si content, we present the following analysis. The ionic contribution to the dielectric constants is purely controlled by the infrared (IR) active zone center phonon modes (i.e., modes that display a time-varying dipole moment) [20, 21]. The extent to which each

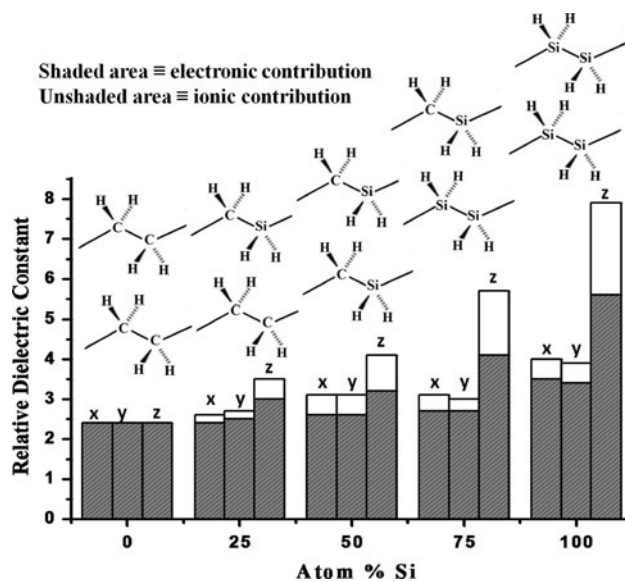


Fig. 3 Dielectric constants along the three principal axes as a function of Si content. Shaded and unshaded areas represent the electronic and ionic contributions, respectively

IR-active phonon mode contributes to the dielectric tensor is determined by the IR intensity, I_i^{IR} , of the corresponding zone center mode (labeled by *i*), which is given by [22, 23]

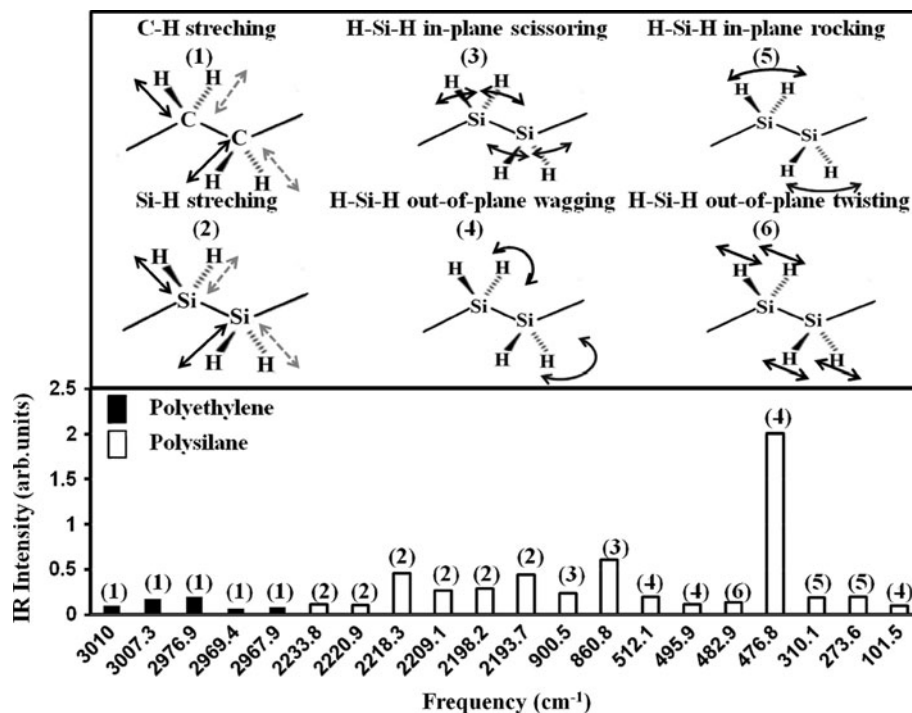
$$I_i^{\text{IR}} \propto \sum_{\alpha} \left| \sum_{k\beta} Z_{k,\alpha\beta}^* X_i(k\beta) \right|^2 \quad (1)$$

In the above expression, *k* labels atoms, and α and β are Cartesian coordinates. $Z_{k,\alpha\beta}^*$ and $X_i(k\beta)$ represent appropriate components of the Born effective charge and the phonon mode eigenvector, respectively. For IR-inactive phonon modes, this intensity vanishes.

In order to determine the reason for the increase of the ionic contribution to dielectric constant with Si content, we consider PE and polysilane, the endmembers of the systems considered here. The zone center phonon modes and frequencies were computed for these two systems, and the IR intensities determined. Results of these computations are summarized in Fig. 4 in the form of histograms that capture the dominant IR-active modes for both systems.

PE displays only five (weak) IR-active modes at 3010, 3007.3, 2976.9, 2969.4, and 2967.9 cm^{-1} , all of which are C–H stretching modes. On the other hand, polysilane displays about 15 modes with relatively strong IR intensity. Among these, six are Si–H stretching modes (2233.8, 2220.9, 2218.3, 2209.1, 2198.2, and 2193.7 cm^{-1}), two are H–Si–H in-plane scissoring modes (900.5 and 860.8 cm^{-1}), four are H–Si–H out-of-plane wagging modes (512.1, 495.9, 476.8, and 101.5 cm^{-1}), two are H–Si–H in-plane rocking modes (273.6 and 310.1 cm^{-1}), and one is twisting mode (482.9 cm^{-1}). The character of each mode is also

Fig. 4 IR intensity of the dominant IR-active zone center phonon modes of PE and polysilane. The character of the IR-active modes are illustrated in the *top* using schematics



shown schematically in Fig. 4. It can be seen that most of the IR-active modes of polysilane have higher intensity than those of PE thereby explaining the larger ionic contribution to the dielectric constant in the case of polysilane. Furthermore, the H–Si–H out-of-plane wagging mode at 476.8 cm^{-1} has a particularly large intensity. This mode contributes directly to an oscillating dipole moment along the chain axis, and thus leads to the large ionic contribution along this direction.

Summary

In summary, we have attempted to understand the impact of introducing Si atoms in a PE network on several properties relevant for high energy density applications. Both the electronic and ionic contributions to the dielectric constant of Si-substituted PE increases steadily with increasing Si content, with the total dielectric constant displaying an almost fourfold increase along the chain axis with complete Si-substitution of all the C atoms. However, concomitant with this increase, both the band gap and the Young's modulus of these systems decrease with increasing Si content. The latter factors will be critical when designing new classes of high dielectric constant organo-silicon compounds for energy storage materials.

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References

- Yang C, Lin YH, Nan CW (2009) Carbon 47:1096
- Nalwa HS (1999) Handbook of low and high dielectric constant materials and their applications, Vol. 2, Chapter 9. Academic Press, New York
- Barshaw EJ, White J, Chait MJ, Cornette JB, Bustamante J, Folli F, Biltchick D, Borelli G, Picci G, Rabuffi M (2007) IEEE Trans Magn 43:223
- Chu B, Zhou X, Ren KL, Neese B, Lin M, Wang Q, Bauer F, Zhang QM (2006) Science 313:334
- Wolak MA, Pan M-J, Wan A, Shirk JS, Mackey M, Hiltner A, Baer E, Flandin L (2008) Appl Phys Lett 92:113301
- An AL, Boggs SA (2006) What is 'Nano' in the Context of a Filled Dielectric. In: Proceedings of the 2006 IEEE international symposium on electrical insulation, Toronto
- Tomer V, Randall CA (2008) J Appl Phys 104:074106
- Miao MS, Zhang ML, Van Doren VE (2001) J Chem Phys 115:11317
- Kresse G, Furthmuller J (1996) Phys Rev B 54:11169
- Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiol-hais C (1992) Phys Rev B 46:6671
- Blöchl PE (1994) Phys Rev B 50:17953
- Kresse G, Joubert D (1999) Phys Rev B 59:1758
- Kavesh S, Schultz JM (1970) Polym Sci A 2:8243
- Schaufele RG, Schimanouchi T (1967) J Chem Phys 42:2605
- Fujihira M, Inokuchi H (1972) Chem Phys Lett 17:554
- Miller RD, Michl J (1989) Chem Rev 89:1359
- Bicerano J (2002) Prediction of polymer properties, Chapter 9, 3rd edn. Marcel Dekker, Inc
- Isaka H, Teramae H, Fujiki M, Matsumoto N (1995) Macromolecules 28:4733
- Schepers T, Michl J (2002) J Phys Org Chem 15:490
- Gonze X, Lee C (1996) Phys Rev B 55:10355
- Gonze X (1996) Phys Rev B 55:10337
- Giannozzi P, Baroni S (1994) J Chem Phys 100:8537
- Porezag D, Pederson MR (1996) Phys Rev B 54:7830