World Scientific
www.worldscientific.com

Novel Hybrid Polymer Dielectrics Based on Group 14 Chemical Motifs

Chenchen Wang and Rampi Ramprasad
Materials Science and Engineering, University of Connecticut,
97 North Eagleville Road,
Storrs, Connecticut 06269, USA
rampi@ims.uconn.edu

The present contribution provides a strategy to enhance the dielectric constant of polyethylene by chemical modification while not overly compromising its large band gap. Isolated polyethylene chains are considered and the CH_2 motifs in the backbone are allowed to be substituted by a number of Group 14 motifs, including SiF_2, $SiCl_2$, GeF_2, $GeCl_2$, SnF_2, and $SnCl_2$, in a systematic, progressive, and exhaustive combinatorial manner. Our results indicate that consecutive SnF_2 or GeF_2 motifs in the polyethylene backbone are most desirable, which can lead to systems with dielectric constant as high as 47.

Keywords: Hybrid polymer; group 14 motifs; dielectrics.

1. Introduction

Dielectric materials with high energy density are of great importance for a broad range of applications such as food preservation, nuclear test simulations, medical defibrillators, and hybrid electric vehicles.[1-4] The maximum possible stored energy density of a capacitor is given by $U = 0.5\varepsilon_0\varepsilon E_b^2$, where $\varepsilon_0, \varepsilon$ and E_b are, respectively, the permittivity of free space, the dielectric constant and the dielectric breakdown field. A major subset of high energy density capacitors utilizes polymeric materials as the dielectrics. Compared with ceramic dielectrics, polymer-film capacitors can provide several attractive properties, including ease of processability, high breakdown field, low loss, low cost, and graceful failure.[1] The current state-of-the-art polymer dielectric for high energy density capacitors applications is biaxially oriented polypropylene (BOPP) due to it high breakdown strength and low loss. However, the low dielectric constant (~2.2) of BOPP limits it energy density.[5-7]

In the present work, we consider chemical modifications of polyethylene (which is chemically similar to polypropylene) in order to improve its dielectric constant, while still maintaining its good insulating properties (i.e., large band gap). The σ and π conjugation along the polymer backbone controls the extent of electron delocalization and hence the electronic contribution to the dielectric constant. By introducing other Group 14 elements, Si, Ge, and Sn into the C-based polymer backbones, the σ conjugation along the backbone can be enhanced, which probably will make this class of polymers interesting candidates for polymer dielectrics. Also, substituting C with Si, Ge

and Sn can help ensure the chemical compatibility by preserving the local chemical environment and bonding. In order to achieve high ionic contribution to the dielectric constant, large dipole moments that should easily response to the applied electric field need to be created in the polymers, which can be realized by introducing small atoms with high electronegativity such as F and Cl to the side chain. By considering all these factors, our modification strategy involves the replacement of the CH_2 building blocks of polyethylene by the Group 14 halides, including SiF_2, $SiCl_2$, GeF_2, $GeCl_2$, SnF_2 and $SnCl_2$.

2. Methodology and Model

Our calculations were performed using density functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP).[8] The Perdew, Burke, and Ernzerhof functional (PBE),[9] projector-augumented wave (PAW) frozen-core potentials[10,11] and a cutoff energy of 500 eV for the plane wave expansion of the wavefunctions were used.

The investigation of polymers is confounded by the necessity of a knowledge of the appropriate crystal structure to be used in DFT computations. Moreover, even if such information is available (or can be "guessed"), each computation may be time consuming. In order to reduce the time involved in each such computation, and to obtain rapid estimates of the dielectric constant and band gap values in the absence of reliable crystallographic information, we have developed a method that is based on purely single chain computations.
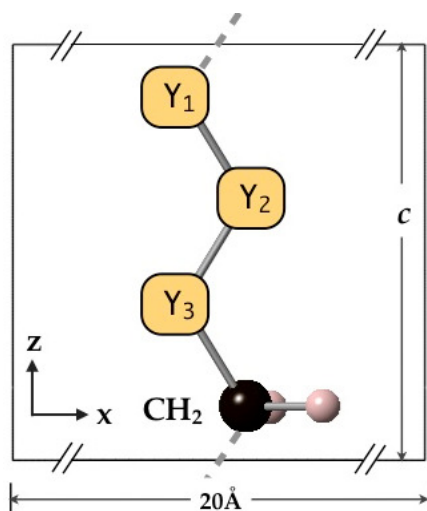

Fig. 1. Modeling showing our computation strategy, in which we fill up Y_1, Y_2, and Y_3 in the backbone with any of the seven motifs, CH_2, SiF_2, $SiCl_2$, GeF_2, $GeCl_2$, SnF_2, and $SnCl_2$.

As shown in Figure 1, we consider an isolated infinite polymer chain with four independent blocks in a supercell. In order to break the extend of σ conjugation along the

polymer backbone, one block was always fixed to be CH_2, while the remaining three blocks were filled by any of the seven motifs, CH_2, SiF_2, $SiCl_2$, GeF_2, SnF_2, and $SnCl_2$. This scheme resulted in 175 symmetry unique systems. A vacuum of 20 Å along the x and y directions (normal to a polymer chain) was used to minimize spurious unphysical interactions between the periodic images. A Monkhorst Pack k-point mesh of $1 \times 1 \times k$ produced converged results for a supercell of length c Å along the chain direction (i.e., the z direction).

Density functional perturbation theory (DFPT)[12] was then used to compute their dielectric constants. We note that the dielectric constant calculated from DFPT for such a supercell includes the contributions from the polymer as well as from the vacuum region of the supercell. Treating the supercell as a vacuum-polymer composite, effective medium theory may then be used to estimate the dielectric constant of just the polymer.[13,14] Besides dielectric constant, we also compute the band gap of our polymer systems as a function of chemical modification due the fact that the insulating behavior of a dielectric material correlates with the band gap.

3. Results and Discussion

Figure 2(a), (b) and (c) show the DFT calculated band gap, electronic, ionic, and total dielectric constant of 175 polymers. A near perfect inverse Pareto optimal front relationship between the band gap and the electronic dielectric constant can be seen from Figure 2(a), which imposes a theoretical limit on the electronic part of the dielectric constant as a function of band gap, a limit that can be understood by regarding the electronic part of the dielectric constant response as a sum over electronic transitions from occupied to unoccupied states. While the pristine polyethylene chain has the highest calculated band gap among all the systems explored, additions of the larger Group 14 elements to the chain lead to a progressive decrease in the band gap and increase in the electronic dielectric constant. On the other hand, the ionic dielectric constant is not correlated with the band gap and varies over a much larger range of values as shown in Figure 2(b). The ionic contribution is determined by the infrared active zone center phonon modes (i.e., the modes that display a time-varying dipole moment).[16, 17] The ionic dielectric constant can thus be exploited to increase the total dielectric constant without compromising the band gap.
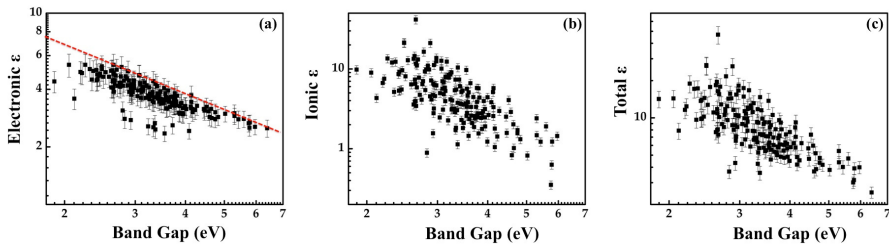

Fig. 2. DFT computed (a) electronic, (b) ionic, and (c) total dielectric constants as a function of the band gap. The axes are in logarithmic scale. Reprinted with permission from Ref. 15.

The total dielectric constant of the Group 14 motifs-based hybrid polymers spans over a large range between 2.5 to 47, with the smallest and largest values corresponding to $-(CH_2)_4-$ and $-CH_2-(SnF_2)_3-$, respectively. In general, it is found that for a given composition and configuration, as the backbone atoms varies from C to Si to Ge to Sn (while all the other units in the chain are held fixed), both the electronic and total dielectric constant increase and the band gap decreases. This result is in line with the fact that among all the seven units considered, and SnF_2 has the largest dipole moment; at the same time Sn-Sn bond rotation has the lowest barrier among all the X-X' (with X or X' = C, Si, Ge, and Sn) bond rotation barriers.

Our analysis also shows that the Group 14 motifs-based hybrid polymers with a large total dielectric constant are always composed of contiguous SnF_2 or GeF_2 motifs in the backbone. In general, in order to enhance the dielectric constant without sacrificing the good insulating properties of polyethylene, it is desirable to incorporate SiF_2, GeF_2, and SnF_2 motifs in the polyethylene backbone. Cholrides of Si, Ge, and Sn usually result in relatively lower band gaps. The order of relative importance of fluorides in improving the dielectric constant is predicted to be $SiF_2 < GeF_2 < SnF_2$. Furthermore, owing to the increased σ conjugation along the chains which in turn leads to an enhanced dielectric constant, it is more desirable to have several concatenated, rather than well separated, SnF_2 or GeF_2 motifs along a polymer chain in polyethylene.

Conclusions

In this work, we use first principles based computations to study the impact of incorporating Group 14 chemical motifs (fluorides and chlorides of Si, Ge, and Sn) on the dielectric constant of polyethylene. Improvement in the dielectric constant by purely increasing electronic contribution tends to degrade the insulating properties, since the electronic dielectric constant correlates inversely with the band gap. The ionic dielectric constant, on the other hand, is not limited by the band gap, and thus can provide more latitude. SiF_2, GeF_2, and SnF_2 have been identified to be promising in terms of increasing the dielectric constant of polyethylene while still maintaining a relatively large band gap, especially when SnF_2 or GeF_2 motifs are arranged in a consecutive manner.

References

1. H. S. Nalwa, Ed., *Handbook of Low and High Dielectric Constant Materials and Their Applications*, Vol. 2, (Academic Press, New York, 1999).
2. J. Ennis, F. W. MacDougall, X. H. Yang, R. A. Cooper, K. Seal, C. Naruo, et al., *Recent Advances in High Voltage, High Energy Capacitor Technology*, 16th IEEE International Pulsed Power Conference, Albuquerque, NM, June 2007.
3. P. F. Flynn, *Meeting the Energy Needs of Future Warriors*, (National Academics, Washington, D. C., 2004).
4. W. J. Sarjeant, J. Zirnheld, F. W. MacDougall, *IEEE Trans. Plasma Sci.* **108**, 1368 (1998).
5. M. Rabuffi, G. Picci, *IEEE Trans. Plasma Sci.* **30**, 1939 (2002).

6. E. J. Barshaw, J. White, M. J. Chait, J. B. Cornette, J. Bustamante, F. Folli, D. Biltchick, G. Borelli, G. Picci, M. Rabuffi, *IEEE Trans. Magn.* **43**, 223 (2007).
7. J. H. Tortain, N. Bonifaci, A. Denat, C. J. Trassy, *Appl. Phys.* **97**, 053304 (2005).
8. G. Kresse, J. Furthmuller, *Phys. Rev. B* **54**, 11169 (1996).
9. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
10. P. E. Blochl, *Phys. Rev. B* **50**, 17953 (1994).
11. G. Kresse, D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
12. S. Baroni, Stefano de Gironcoli, Andrea Dal Corso, *Rev. Mod. Phys.* **73**, 515 (2001).
13. C. C. Wang, G. Pilania, R. Ramprasad, *Phys. Rev. B* **87**, 035103 (2013).
14. G. Pilania, R. Ramprasad, *J. Mater. Sci.* **47**, 7580 (2012).
15. C. C. Wang, G. Pilania, S. A. Boggs, S. Kumar, C. Breneman, R. Ramprasd, *Polymer* **55**, 979 (2014).
16. X. Gonze, C. Lee, *Phys. Rev. B* **55**, 10355 (1997).
17. X. Gonze, *Phys. Rev. B* **55**, 10337 (1997).