

Dielectric permittivity enhancement in hydroxyl functionalized polyolefins via cooperative interactions with water

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Recent experiments have shown that polypropylene (PP) with a small fraction of hydroxyl (-OH) side groups displays a two-fold increase in the dielectric permittivity. It has been suggested that both the -OH groups and trapped water molecules may contribute to the dielectric constant increase. In this first principles computational study, using short polyolefin chains as models of PP, we shed light on the role played by -OH functional groups and the trapped moisture. Our results reveal that the trapped water molecules will inevitably accompany -OH incorporation (due to hydrogen bonding) and that both the -OH groups and water molecules will contribute cooperatively to the increase of the PP dielectric constant. These findings also provide insights into the effects of moisture on other molecularly functionalized materials systems. © 2013 AIP Publishing LLC [<http://dx.doi.org/10.1063/1.4801950>]

The ever-increasing demand for improved high voltage, high energy density capacitors continues, as such capacitors impact an enormous breadth of technologies ranging from hybrid electric vehicles, food preservation, nuclear test simulations, and the defense industry.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 current standard dielectric material for such capacitor applications is biaxially oriented polypropylene (BOPP),³ which has a remarkably high electrical breakdown strength (>700 MV/m) and low dielectric loss (<0.1%), but a small dielectric constant (~2.2).

Recent experiments have shown that polypropylene (PP) with just 4-6 mol. % hydroxyl (-OH) side groups displays an almost two-fold increase in the dielectric constant, with minimal impact on the dielectric loss and morphology.⁴ This finding is significant as it provides a pathway to systematically improve upon the properties of PP, especially its energy density which scales linearly with the dielectric constant. The experimental results also imply that the PP-OH contains roughly 0.5 water molecule per -OH moiety on the chain.^{4,5} On a related note, we point out that molecular functionalization and the accompanying moisture have been shown to impact a plethora of properties (including chemical, mechanical, dielectric, and electronic properties).⁶⁻⁹ In the present work, using parameter-free first principles density functional theory (DFT) computations, we provide further evidence for the presence of water when -OH groups are incorporated in a polyolefin. Furthermore, we also show that the dielectric constant of polyolefins increases successively as -OH groups, and, subsequently, water molecules are added to the polyolefin system.

Since modeling PP or any polyolefin, inclusive of morphological details, is cumbersome using first principles methods, we use a short C₁₁H₂₄ hydrocarbon to model the unfunctionalized polyolefin and C₁₁H₂₂(OH)₂ (with one -OH unit in each of its two ends) to model the -OH functionalized polyolefin. The tendency for hydrogen bond formation was probed using two such hydrocarbon chains within our unit cell, and varying numbers of water molecules were introduced close to the chain ends to interrogate the tendency for water trapping. Similar computations with an even smaller hydrocarbon molecule, namely, ethane (i.e., C₂H₆), were also performed to more exhaustively explore various configurations. These latter computations yielded hydrogen bonding and water bonding results that were similar to those obtained using the longer chains. The optimized geometries obtained using the longer 11C atom hydrocarbon systems were used to determine their dielectric constant using density functional perturbation theory (DFPT)¹⁰ followed by extrapolation of these results to correspond to the volume actually occupied in real polyolefin systems using methods developed recently.^{11,12} We note that the effective -OH content of the modeled systems is higher than considered in past experimental work. Nevertheless, we believe that the present findings, in terms of the tendency for water trapping by -OH species, and trends in the dielectric constant variations are adequately captured in the current treatment.

The DFT computations were performed using the Vienna *ab initio* simulation package (VASP).¹³ The projector-augmented wave (PAW) frozen-core potentials^{14,15} were used to represent the valence electrons, and the quantum mechanical part of the electron-electron interactions was approximated using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.¹⁶ van der Waals (vdW)

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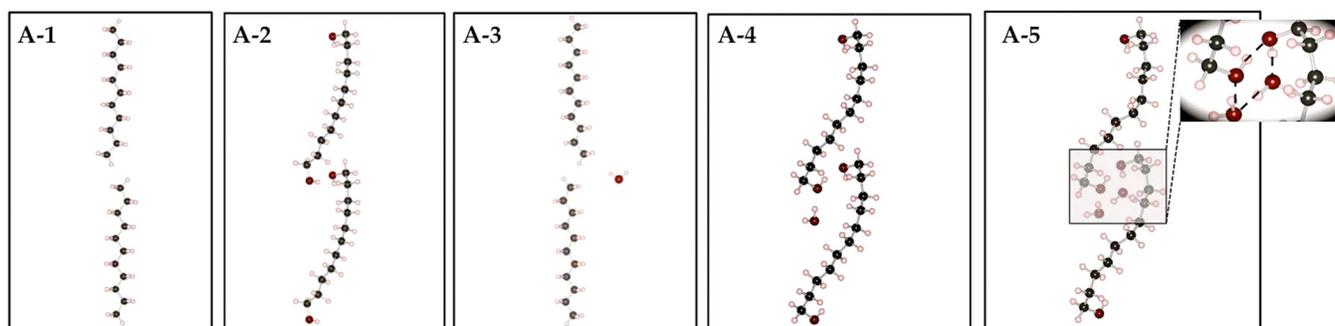


FIG. 1. Optimized structures of complexes A-1, A-2, A-3, A-4, and A-5. Black, white, and red spheres represent C, H, and O atoms, respectively. The inset shows a typical hydrogen bonded ring.

interactions were included by augmenting the PBE functional with the Grimme D2 correction (PBE-D2).^{17,18}

The optimized structures of complexes involving $C_{11}H_{24}$, $C_{11}H_{22}(OH)_2$, and water molecules are shown in Figure 1. The complex A-1 is the system with two $C_{11}H_{24}$ chains in a periodic supercell attempting to interact with each other at the chain ends, and, likewise, the complex A-2 contains two $C_{11}H_{22}(OH)_2$ chains. In complex A-3, where -OH species are absent, complex A-1 interacts with one water molecule, while in complexes A-4 and A-5, one and two water molecules, respectively, interact with the complex A-2, in the vicinity of the -OH species. The interaction between chains, in the presence and absence of -OH species, and the interaction between the chains and water molecules are quantified by calculating the energy of interaction (E_{int}), as defined in Table I. When there is no -OH species, the chain-chain interaction energy is 0.01 eV per CH_3 group, consistent with the weak van der Waals interaction between chains.¹⁸ With the incorporation of -OH species, the chain-chain interaction energy increases to 0.28 eV per -OH group. As can be seen in Figure 1, the relative position and geometry of the two chains get altered dramatically (with respect to the case when there is no -OH species) to accommodate the interchain hydrogen bonding interaction mediated by the -OH groups. These results show that introduction of

hydroxyl groups will increase the interchain interactions significantly due to hydrogen bonding. In order to probe the tendency for water molecules to bind to the chains (in the absence and presence of -OH species), we next explore the larger A-3, A-4, and A-5 complexes with one and two H_2O molecules. When there is one water molecule in the complex, the energy of interaction between the chain and water is 0.09 eV when there is no -OH species present (complex A-3). Presence of the -OH species enhances the chain-water interaction to 0.41 eV per water molecule when one water molecule is present (complex A-4) and to 0.59 eV per water molecule when two water molecules are present (complex A-5). The optimized structure of complex A-5 shows a typical hydrogen bonding ring involving the two water molecules and the -OH species. The strong interaction between H_2O and -OH functionalized polyolefin chains indicates that the trapping of water molecules due to the -OH groups is inevitable.

To further validate the results obtained using our long chain model, a parallel study with a small hydrocarbon system, consisting of C_2H_6 , C_2H_5OH , and water molecules, was also performed. A large number of configurations and complexes involving these species were considered, and the optimized structures of the most stable (and the most relevant) of these complexes are shown in Figure 2. Complexes B-1, B-2, and B-3 are analogous to complexes A-1, A-2, and A-3. Complex B-1 involves the interaction of two hydrocarbons (i.e., C_2H_6), and complex B-2 involves two C_2H_5OH molecules. Likewise, complex B-3 represents the interaction between water and the hydrocarbons (i.e., in the absence of -OH). Finally, complexes B-4, B-5, and B-6 represent three different configurations involving two C_2H_5OH and one water molecule (and hence, analogous with complex A-4). The molecule-molecule interaction energy with -OH species being absent is 0.03 eV per CH_3 group (cf., Table I). When there are -OH species, the molecule-molecule interaction energy increases to 0.20 eV per -OH group due the formation of hydrogen bonding between the two hydroxyl groups. The interaction of water with the hydrocarbons (i.e., when -OH species are absent) is rather weak and is estimated to be 0.06 eV. However, the presence of -OH species dramatically alters this picture. In complexes B-4, B-5, and B-6, we placed the water molecule either near one of two -OH groups (complexes B-5 and B-6) or close to both of the -OH groups (complex B-4). The binding energy of water to the -OH containing molecules is in the 0.51–0.66 eV range depending on

TABLE I. The energy of interaction, E_{int} , between chains and water molecules under various situations. E_X indicates the total energy of either the isolated molecule X or the complex X. Snapshots of the stable complexes are shown in Figures 1 and 2. In the E_{int} formula, the denominator represents the number of interacting groups, such as $-CH_3$, -OH, or water molecules depending on the case.

Interaction	-OH species	E_{int} formula	E_{int} (eV)
Chain-chain interaction	Absent	$\frac{2E_{C_{11}H_{24}} - E_{A-1}}{4}$	0.01
Chain-chain interaction	Present	$\frac{2E_{C_{11}H_{22}(OH)_2} - E_{A-2}}{4}$	0.28
Chain-water interaction	Absent	$E_{A-1} + E_{H_2O} - E_{A-3}$	0.09
Chain-water interaction	Present	$E_{A-2} + E_{H_2O} - E_{A-4}$	0.41
Chain-water interaction	Present	$\frac{E_{A-2} + 2E_{H_2O} - E_{A-5}}{2}$	0.59
Molecule-molecule interaction	Absent	$\frac{2E_{C_2H_6} - E_{B-1}}{2}$	0.03
Molecule-molecule interaction	Present	$\frac{2E_{C_2H_5OH} - E_{B-2}}{2}$	0.20
Molecule-water interaction	Absent	$E_{B-1} + E_{H_2O} - E_{B-3}$	0.06
Molecule-water interaction	Present	$E_{B-2} + E_{H_2O} - E_{B-4}$	0.66
Molecule-water interaction	Present	$E_{B-2} + E_{H_2O} - E_{B-5}$	0.56
Molecule-water interaction	Present	$E_{B-2} + E_{H_2O} - E_{B-6}$	0.51

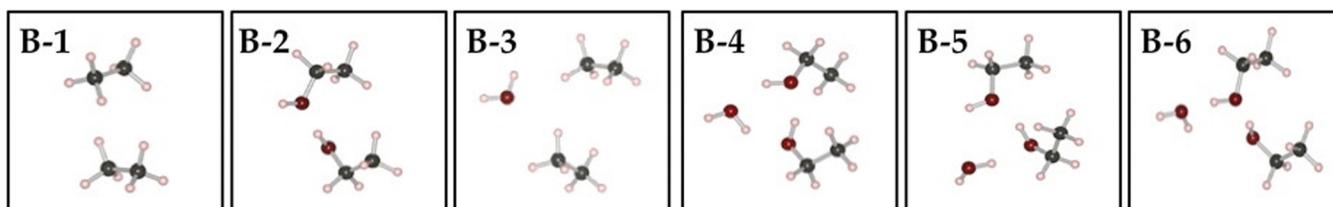


FIG. 2. Optimized structures of complexes B-1, B-2, B-3, B-4, B-5, and B-6. Black, white, and red spheres represent C, H, and O atoms, respectively.

TABLE II. The trace of the dielectric constant tensor of complexes A-1, A-2, A-4, and A-5. ϵ^{elec} represents the electronic part of the dielectric constant, while ϵ^{tot} is the total dielectric constant (i.e., including electronic and ionic contributions). The error bars indicate the uncertainty inherent in the procedure used to extrapolate the computed value to the correct volume.

Complex	ϵ^{elec}	ϵ^{tot}
A-1	2.4 ± 0.4	2.4 ± 0.4
A-2	2.4 ± 0.4	3.3 ± 0.2
A-4	2.4 ± 0.4	3.7 ± 0.7
A-5	2.4 ± 0.4	4.3 ± 1.5

the configuration. These findings are consistent with our longer chain model (cf., Table I). Our DFT results clearly demonstrate that when there are hydroxyl groups present in the system, water molecules have a strong tendency to form hydrogen bonding with the hydroxyl groups and will be trapped in the -OH containing environment.

Next we present the dielectric constant results pertaining to the A-1, A-2, A-4, and A-5 complexes. The trace of the dielectric constant tensor corresponding to both the electronic (the high frequency or optical part) and total (electronic plus ionic or the static) values for these systems is presented in Table II. For complex A-1, the dielectric constant is almost entirely due to electronic contributions, and the predicted value is close to the experimental value of polyethylene.¹⁹ Successive increases in the dielectric constant values can be seen due to the introduction of the -OH species and, subsequently, due to the introduction of

one and two water molecules. The increase in the dielectric constant due to the introduction of -OH groups (without and with water molecules) is entirely due to the ionic contributions.

In order to understand the increased ionic contribution to the dielectric constant with substitution of a H atom by a hydroxyl group and the presence of bound water molecule(s), we present the following analysis. The ionic contribution to the dielectric constant (total minus electronic) is purely controlled by the infrared (IR) active zone center phonon modes (i.e., the modes that display a time-varying dipole moment).^{20,21} The extent to which each IR-active phonon mode contributes to the dielectric tensor is determined by the frequency of the mode (smaller the frequency larger the dielectric constant) and the IR intensity (I_i^{IR}) of the corresponding zone center mode (larger the IR intensity, larger the dielectric constant), which is given by^{22,23}

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

where i labels the modes, k labels atoms, and α and β are the cartesian coordinates. $Z_{k,\alpha\beta}^*$ and $X_i(k, \beta)$ represent appropriate components of the Born effective charge tensor and the phonon mode eigenvector, respectively. For IR-inactive phonon modes, this intensity vanishes. The zone center phonon modes and frequencies were computed for the complexes A-1, A-2, A-4, and A-5, and the IR intensities determined. Results of these computations are summarized in Figure 3 in the form of histograms

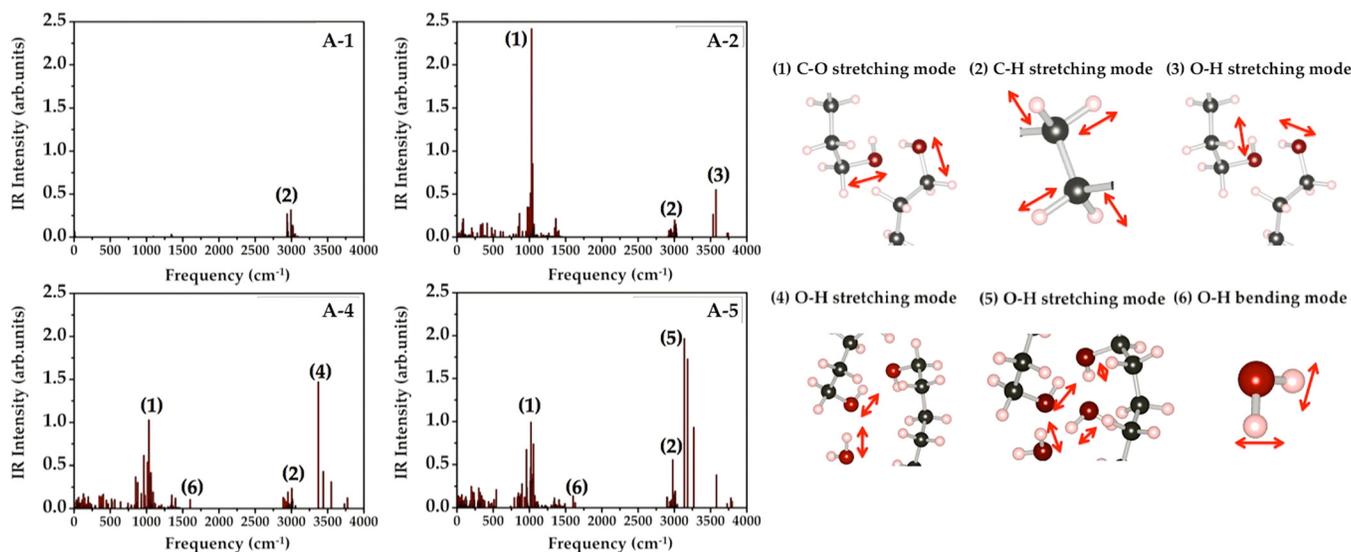


FIG. 3. IR intensity of the dominant IR-active zone center phonon modes of complexes A-1, A-2, A-4, and A-5. The character of IR-active modes is illustrated using schematics.

that capture the dominant IR-active modes. From Figure 3 we can see that compared with complex A-1, introducing OH groups results in new modes in complex A-2, and the dominant ones are the C-O stretching mode and O-H stretching mode. For the complexes with H₂O (i.e., complexes A-4 and A-5), a new mode at around 1600 cm⁻¹ corresponding to the H₂O O-H bending mode appears. A few new modes appear at around 3200 cm⁻¹ to 3300 cm⁻¹, which are also O-H stretching modes arising from both the hydroxyl group and the H₂O. We are thus persuaded to conclude that -OH functionalizations and the inevitable trapped water act cooperatively to increase the ionic part of the dielectric constant of polyolefins. Although our calculations involve higher -OH content than was considered in past experiments, our main findings pertaining to hydrogen bonding, water trapping, and dielectric constant enhancement are expected to persist under the scrutiny of more realistic computations. Indeed, recent detailed force-field based molecular dynamics simulations, in which the morphological details and the concentration of -OH and trapped water are taken into account, appropriately confirm the current findings.⁵

In conclusion, our first principles calculations indicate that introduction of -OH functional groups will enhance the interaction between polyolefin chains due to interchain hydrogen bonding. Moreover, when -OH groups are present, water molecules tend to be trapped due to the strong interaction between water and the -OH functionalized polyolefin chains. The existence of the -OH groups and water molecules in the system contribute cooperatively to the increase of the dielectric constant of polyolefins. These findings are significant, as they point towards a rational pathway for the tunable control of material properties of polyolefins as well as other related material systems via creative utilization of molecular-functionalization (and moisture).

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- ¹H. Bluhm, *Pulsed Power Systems: Principles and Applications* (Springer, 2006).
- ²W. J. Sarjeant and J. Zirnheld, *Handbook of Low and High Dielectric Constant Materials and Their Applications* (Academic Press, UK, 1999).
- ³E. J. Barshaw, J. White, M. J. Chait, J. B. Cornette, J. Bustamante, F. Folli, D. Biltchick, G. Borelli, G. Picci, and M. Rabuffi, *IEEE Trans. Magn.* **43**, 223 (2007).
- ⁴X. Yuan, Y. Matsuyama, and T. C. Chung, *Macromolecules* **43**, 4011 (2010).
- ⁵M. Agarwal, M. Misra, S. Kumar, C. C. Wang, G. Pilania, R. Ramprasad, X. Yuan, and T. C. M. Chung, "A general methodology for creating improved polymeric dielectrics" (unpublished).
- ⁶A. P. Singh, D. D. Gandhi, E. Lipp, M. Eizenberg, and G. Ramanath, *J. Appl. Phys.* **100**, 114504 (2006).
- ⁷D. Vijayashankar, H. Zhu, S. Gary, R. Teki, R. Ramprasad, M. W. Lane, and G. Ramanath, *Appl. Phys. Lett.* **99**, 133103 (2011).
- ⁸A. P. Singh, P. Victor, P. G. Ganesan, O. Nalamasu, and G. Ramanath, *Appl. Phys. Lett.* **87**, 253506 (2005).
- ⁹S. Garg, B. Singh, R. Teki, M. W. Lane, and G. Ramanath, *Appl. Phys. Lett.* **96**, 143121 (2010).
- ¹⁰S. Baroni, S. de Gironcoli, and A. D. Corso, *Rev. Mod. Phys.* **73**, 515 (2001).
- ¹¹G. Pilania and R. Ramprasad, *J. Mater. Sci.* **47**, 7580 (2012).
- ¹²C. C. Wang, G. Pilania, and R. Ramprasad, *Phys. Rev. B* **87**, 035103 (2013).
- ¹³G. Kresse and J. Furthmuller, *Phys. Rev. B* **54**, 11169 (1996).
- ¹⁴P. E. Blochl, *Phys. Rev. B* **50**, 17953 (1994).
- ¹⁵G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ¹⁶J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ¹⁷S. Grimme, *J. Comput. Chem.* **27**, 1787 (2006).
- ¹⁸C. S. Liu, G. Pilania, C. C. Wang, and R. Ramprasad, *J. Phys. Chem. A* **116**, 9347 (2012).
- ¹⁹J. Bicerano, *Prediction of Polymer Properties*, 3rd ed. (Marcel Dekker, New York, 2002).
- ²⁰X. Gonze and C. Lee, *Phys. Rev. B* **55**, 10355 (1997).
- ²¹X. Gonze, *Phys. Rev. B* **55**, 10337 (1997).
- ²²P. Giannozzi and S. Baroni, *J. Chem. Phys.* **100**, 8537 (1994).
- ²³D. Porezag and M. R. Pederson, *Phys. Rev. B* **54**, 7830 (1996).