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The rational design of polyurea & polyurethane dielectric materials

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ABSTRACT

When designing polymeric capacitors, it is important to understand the structure–property relationship between chemical functionalities and dielectric properties to tailor materials for specific applications in terms of dielectric constant, dielectric loss, band gap, breakdown strength, etc. Herein, we report a clear structure–property relationship with dielectric constant and dielectric loss in a series of polyurea and polyurethane thin films. We demonstrate that the dielectric constant systematically increases and the dielectric loss decreases as the number of carbons between polarizable functional groups decreases. Our syntheses are guided with data obtained from high-throughput density functional theory calculations. By modeling 382 polymer systems, we have determined that a dielectric constant >4 is achieved with at least one aromatic group and at least one of the following moieties: –NH–, –C(=O)–, or –O–.

1. Introduction

The development of high energy density capacitors is driven by their importance in various applications, including hybrid electric vehicles, the electric propulsion of ships [1] and electromagnetic railguns [2]. In terms of polymeric materials, biaxially oriented polypropylene (BOPP) is the current industrial standard. BOPP boasts a remarkably high electrical breakdown strength and large band gap, in addition to its ease of processability, high breakdown field and graceful failure [3]. BOPP has a dielectric constant at room temperature of ~2.2 across a broad frequency range and a dielectric loss in the neighborhood of 10^{-3}–10^{-4} [4]. To add to the existing body of work in this field [5–8], we aim to understand the structure–property relationship between chemical functionalities and dielectric properties, through the paradigm of rational capacitor design. Ultimately, this level of understanding should allow for the tailoring of materials for specific electronic applications.

In the present study, we consider a large number of polymer systems with different functionalities, with the intent of identifying new polymer dielectric materials that have better dielectric properties than BOPP without sacrificing its already remarkable insulating properties. In an attempt to identify promising polymer subclasses we use first principles computations based on density functional theory (DFT) to perform an initial combinatorial screening. This initial screening has helped us to identify organic building blocks such as aromatic rings, –NH–, –CO–, –O–, etc., (i.e., those that make up ureas and urethanes) as promising ones. Polymers containing these functionalities are synthesized and their dielectric properties are characterized and compared with the DFT results.

2. Computational guidance

As a first step, we used DFT computations in a high-throughput mode to identify promising cases that may lead to a high dielectric constant and high band gap; we note that the former property leads to a larger energy density, and the latter is an indicator of a good insulator (and high breakdown strength). Fig. 1 captures the computational model adopted in our strategy. In essence, we consider an all-trans single polymer chain containing four independent blocks with periodic boundary conditions along the chain axis. We allow each block in the polymer backbone to be one of following units: $-CH_2-$, –NH–, –C(=O)–, $-C_6H_4-$ (benzene), $-C_4H_2S-$ (thiophene), –C(=S)–, and –O–. Different combinations of these units form traditional polymers, including polyesters, polyamides, polyethers, polyureas, *etc*. This scheme results in 382 symmetry unique systems.

Density functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP) [9] was used to determine the structural and electronic properties of the 382 polymer chains. The Perdew, Burke, and Ernzerhof functional (PBE) [10,11], projector-

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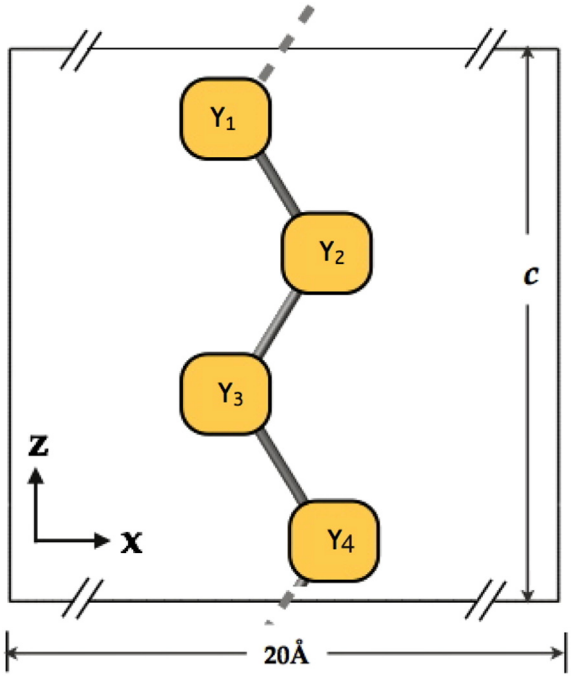

Fig. 1. Model showing our computational strategy, in which we substitute different functionalities into the four blocks. These calculations operate at the atomic scale, and therefore neglect interchain interactions.

augumented wave (PAW) frozen-core potentials [12] and a cutoff energy of 400 eV for the plane wave expansion of the wave-functions were used. The optimized geometry was then used to determine the electronic (high frequency, or optical) and total (low frequency, or static) dielectric constant tensor of the polymer chains density functional perturbation theory (DFPT) [13], followed by extrapolation of these results to correspond to the volume actually occupied in real polymeric systems using methods developed recently [14,15].

Fig. 2 shows the relationship between the electronic (Fig. 2(a)) and total (Fig. 2(b)) dielectric constant and the band gap for the 382 polymer systems. A near perfect inverse pareto-optimal front relationship between the band gap and the electronic dielectric constant can be seen from Fig. 2(a), which imposes a theoretical limit on the electronic part of the dielectric constant that one may be able to achieve (a limit that may be understood by regarding the electronic part of the dielectric response as a sum over electronic transitions from occupied to unoccupied states). Fig. 2(b) shows the variation of the total dielectric constant with the band gap. The total dielectric constant derives its contributions from the electronic and ionic contributions. The latter is, in principle, not constrained by the band gap, and is related to the dipole moment values of the functional groups and the flexibility of bonds that can allow the dipoles to respond to an electric field. From Fig. 2(b), a set of the most promising polymers may be selected based on the criteria that the band gap >3 eV, and total dielectric constant >4. This "promising" region is shown in Fig. 2(b), and corresponds to systems composed of at least one aromatic group and at least one of the following three groups: –NH–, –C(=O)–, –O–.

The DFT-recommended groups provided useful constraints for determining the best functionalities to incorporate into a polymer backbone. We understood that polymers synthesized for electronic applications should be as pure as possible; we sought to eliminate impurities that were both catalytic and inherent in nature. To this end, we ultimately decided on polyureas and polyurethanes derived from the step polymerization of an asymmetrically substituted aromatic diisocyanate and various diols and diamines (Fig. 3) – these systems were harmonious with the results of the DFT calculations, produced no byproducts, and required little or no catalyst.

3. Polymer synthesis

3.1. Materials

Reagents and solvent were purchased from Acros Organics or Sigma–Aldrich, with the exception of the 2,2′-oxybis-ethaneamine, which was purchased from Huntsman. Liquids were purified either by ambient pressure distillation or vacuum distillation and were stored under nitrogen.

3.2. Polyurea and polyurethane syntheses

To a nitrogen-filled, flame-dried 25 mL 3-neck flask equipped with a gas inlet, rubber and glass stoppers and a magnetic stirbar, 10 mL of dimethylsulfoxide was added via cannula needle. Next, 5 mmol of diamine/diol was cannulated; the materials used were: 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, 1,6-diaminohexane, 2,2′-oxybis-ethanamine, 1,2-ethanediol, 1,2-

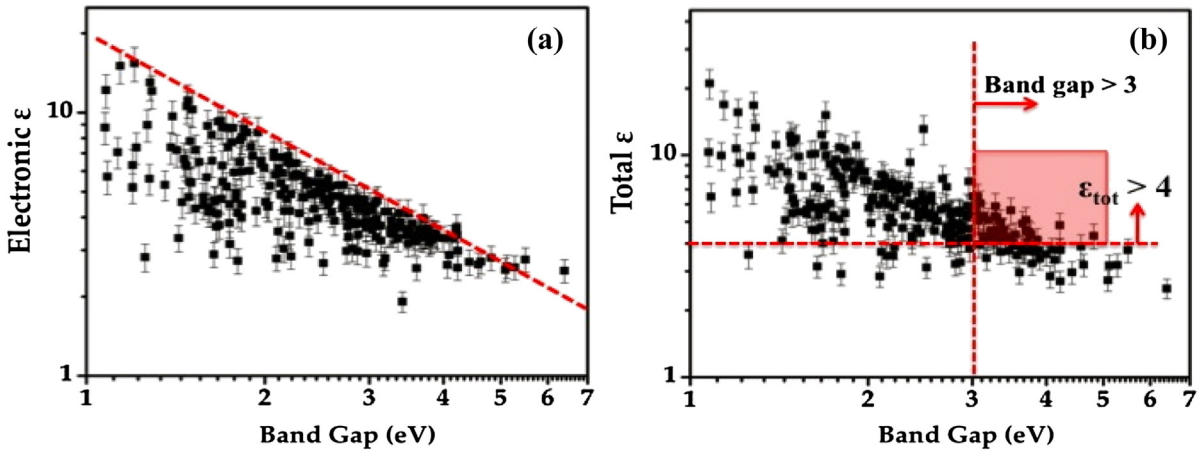

Fig. 2. DFT computed (a) electronic and (b) total dielectric constant along the polymer chain axis as a function of the band gap. The axes are in logarithmic scale.