

POSSIBILITIES FOR FABRICATING POLYMER DIELECTRIC LASER ACCELERATOR STRUCTURES WITH ADDITIVE MANUFACTURING*

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Abstract

We report the results of recent studies of new materials designed for the additive manufacturing of accelerating structures for dielectric laser accelerators (DLAs). Demonstration of a stand-alone practical DLA requires innovation in design and fabrication of efficient laser accelerator structures and couplers. Many complicated three-dimensional structures for laser acceleration (such as a long woodpile structure with couplers) are difficult to manufacture with conventional microfabrication technologies. LANL has a large effort focused on developing new materials and techniques for additive manufacturing. The materials for DLA structures must have high dielectric constant (larger than 4), low loss in the infrared regime, high laser damage threshold, and be able to withstand the electron beam damage. This paper discusses the development of novel infrared dielectric polymer materials that are of interest for laser acceleration and are compatible with additive manufacturing.

INTRODUCTION

The woodpile accelerating structures for laser acceleration confine the accelerating mode in a narrow channel (hollow waveguide at the center) with transverse dimensions of the order of a wavelength (typically 1-2 microns [1]). Unlike photonic band gap fibers, the three-dimensional nature of the woodpile structures allows integration of ancillary devices such as power couplers and diagnostics, which are necessary for successful operation of an accelerator. A dielectric laser accelerator requires woodpile structures fabricated with high precision, made of vacuum compatible dielectric materials with a relatively high dielectric constant ($\epsilon > 4$), low losses ($\tan \delta < 10^{-3}$), and the ability to withstand high accelerating gradients.

LANL is now utilizing a Nanoscribe Photonic Professional GT [2], a direct laser-writing device capable of maskless lithography and additive manufacturing. The Nanoscribe can print at sub-micron resolution by focusing ultra-short, 760 nm laser pulses into a resin. The flux is only high enough for two-photon polymerization (2PP) at the focal point, allowing for lateral and vertical resolutions of 300 nm and 800 nm, respectively. There are numerous reports in the literature on the use of a Nanoscribe to create photonic structures. We have produced the woodpile struc-

tures of the relevant dimensions with Nanoscribe's proprietary IP-Dip resin [3]. However, these structures cannot be employed for laser acceleration, because of the low dielectric constant of IP-Dip. We are conducting research to develop novel resins compatible with the Nanoscribe that are applicable for production of various dielectric structures for laser acceleration.

Table 1: Laser breakdown thresholds of some 3D printable dielectric materials. The breakdown thresholds in Si and SiO₂ are shown for comparison.

Material	F _{th} (J cm ⁻²)	Previously measured F _{th} (J cm ⁻²) [4]
Ormocomp + Napthalene	0.85	
Ormocomp	0.68	
Pentaerythritol triacrylate (PETA)	0.69	
5% Ge NP in Ormocomp	0.22	
IP-Dip	0.0086	
Si		0.18
SiO ₂	2.8	3.5

LASER DAMAGE THRESHOLD TESTING OF 3D PRINTABLE MATERIALS

We conducted laser damage threshold measurements of some existing materials amenable to the 2PP polymerization at the SLAC National Accelerator laboratory. Thin films of materials were illuminated with an ultrashort 67 fs laser pulse with a wavelength of 800 nm. White-light generation at the entrance and exit surfaces of the material served as a proxy for damages. While some materials that are compatible with the Nanoscribe laser-writing device (such as the Nanoscribe's proprietary IP-Dip) tested to have relatively low laser damage threshold, some other materials, such as Ormocomp demonstrated damage threshold more than 3 times higher than the damage thresholds of silicon commonly used in many high gradient laser acceleration experiments (Table 1).

Dielectric properties of the high performing materials Ormocomp and PETA were measured with infrared interferometry. However, the dielectric constant for both materials was found to be around 2, which is lower than what is required for the fabrication of the functional woodpile structure. Therefore, the search for other higher dielectric constant materials that are amendable to the radical polymerization has been initiated.

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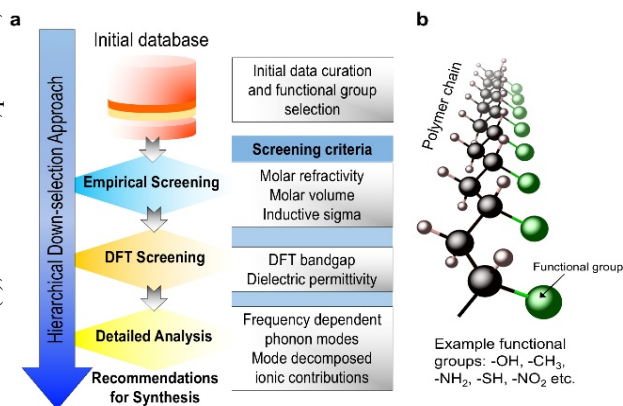


Figure 1: (a) An overview of the hierarchical down-selection strategy adopted in the present computational framework to identify the most promising functional groups leading to desired polymer dielectric performance. (b) Schematic showing an atomistic model of a functionalized polyethylene chain.

COMPUTATIONAL SEARCH FOR HIGH DIELECTRIC CONSTANT POLYMERS

In light of the ever-increasing role played by theory and simulations in rational materials design and discovery the goal of this part of the effort was to harness the predictive power of electronic structure theory based methods, such as the density functional theory (DFT) [5] to identify candidate polymer dielectric materials for additive manufacturing of accelerator structures. Starting with a large number of candidates, we used a hierarchical down-selection approach (as schematically illustrated in Fig. 1(a)) consisting of (i) empirical screening, (ii) DFT-based screening and finally (iii) a detailed analysis of frequency dependent mode-decomposed ionic contributions to the dielectric permittivity to identify a set of potential polymer dielectrics. While the adopted computational framework is general and capable of assessing any given polymer, for practical reasons we limited the scope of our first exploration to simple polymers formed by functionalized polyethylene chains (see Fig. 1(b)).

Our computational screening effort started with a large dataset of diverse functional groups, containing 530 different groups in total [6], which were subjected to an empirical screening process based on three criteria: (1) molar refractivity, (2) functional group volume, and (3) estimated tendency or susceptibility to radical polymerization. Since we are primarily interested in large dielectric constant materials (note that in the frequency range of interest, the square root of the electronic part of the dielectric constant is also frequently referred to as the refractive index, n), we naturally looked for compact and polarizable functional units. Further, to quantify susceptibility to radical polymerization, we use the concept of captodative effect, which involves the stabilization of a free radical on a geminally-substituted carbon by the synergistic effect of an electron-withdrawing and an electron-donating functional group

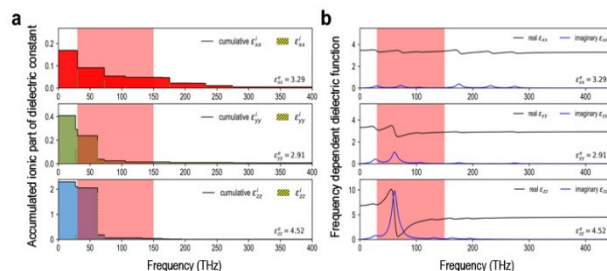


Figure 2: Diagonal components of the (a) net accumulated mode-decomposed ionic contributions to the dielectric permittivity tensor and (b) complex dielectric function, modelled via IR-active lattice mode oscillator strengths as Lorentzian oscillators vs. frequency. The targeted frequency range (30-150 THz) is highlighted.

substituent in free radical reactions, as quantified by the sigma inductive constants [6].

A selected set of 35 top-ranked functional groups from the empirical screening round was next subjected to a DFT-based screening process, where we used the selected functional groups to construct 3-dimensional polymer models of the functionalized polyethylene chains in a supercell geometry using periodic boundary conditions. Unlike conventional DFT computations, we explicitly accounted for inter-chain van der Waals (vdW) interactions [7]. Density functional perturbation theory (DFPT) was used to compute dielectric permittivity tensors (including both electronic as well as lattice/ionic contributions) [8] and Heyd-Scuseria-Ernzerhof (HSE) hybrid functional was used for an accurate description of the polymer bandgaps [9]. We note that the required refractive index $n > 2$ is above that of conventional optical polymers [10]. Therefore, to achieve the high dielectric constant we resorted to ionic contributions to the dielectric permittivity in addition to the electronic response. Next, while the majority of crystalline polymers studied in this round of screening satisfied our band gap screening criterion (i.e., bandgap > 1.6 eV), only seven of these met the requirement of dielectric constant > 4.0 [11].

In a subsequent screening step, these systems were further investigated for their frequency dependent dielectric response and dielectric losses associated with the lattice absorption. The frequency dependence of the ionic component of the dielectric permittivity tensor was analyzed by decomposing the net ionic response in terms of the contributions arising from the individual normal phonon modes and computing the normal mode vibrational frequencies. As an example, Figure 2(a) shows the diagonal components of the net accumulated mode-decomposed ionic contributions to the dielectric permittivity tensor as a function of frequency for a thiol (-SH) functionalized polyethylene, one of the most promising candidate system identified in this exploration. To further account for the resonance effects and to get a reasonable estimate of the dielectric loss, we modeled the IR-active lattice mode oscillator strengths as Lorentzian oscillators [12] to compute the real and im-

imaginary parts of the frequency dependent complex dielectric function (Fig. 2(b)). This analysis was carried on the entire set of polymers screened in the previous round of the DFT-screening.

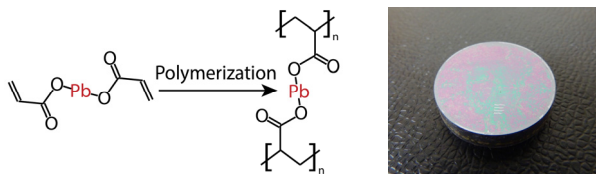


Figure 3: The chemical process of polymerization of Pb acrylate (left), and the resulting polymer film (right).

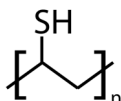


Figure 4: A schematic of poly(vinyl mercaptan).

Based on our computational screening analysis, we identified sulphur (S) containing functional groups as the most promising functional groups to meet the desired requirements. Guided by the theoretical results, efforts are currently underway to explore S-based insulating polymers that contain highly polarizable inorganic metal ions, such as Pb^{+2} and Bi^{+3} .

SYNTHESIS OF NEW POLYMER DIELECTRICS

The inclusion of metal ions with significant electron density, such as Pb^{+2} and Bi^{+3} , offers a potential route to raising the refractive index of composites. By using monomers which bind these metals, such as acrylic acid, uniform blends with high metal density have been obtained (Fig. 3), with characterization of optical properties ongoing. However, previous research into these materials suggests that through this strategy we may expect to boost the refractive index by at most 0.15 [13,14], significant, but only sufficient if the polymer matrix itself has a high refractive index. Towards this goal, we are also investigating preparation of poly(vinyl mercaptan) (Fig. 4), which is predicted to have a refractive index as high as 1.9, and will also readily bind metal ions.

A more likely way to reach the requisite index of refraction is to incorporate high- n inorganics, in the form of nanoparticles, into the material [15]. The very high refractive index of some inorganic semiconductors, in particular Ge and PbS, would enable a composite with $n > 2$ at reasonable nanoparticle loading levels. Such composites might be formed either through blending functionalized nanoparticles with a Nanoscribe-compatible resin, or, in the case of PbS, in-situ nanoparticle synthesis by exposure of a Pb-polymer composite of the type described above to H_2S gas [16,17]. The latter method potentially offers a route to very high nanoparticle loading levels. One potential issue with nanoparticle composites is the loss tangent requirement, as

both Ge and PbS absorb well into the near-infrared. Fortunately, this absorbance may be tuned through the size of the nanoparticle, by quantum confinement effects [18]. These effects, however, will also lower the refractive index

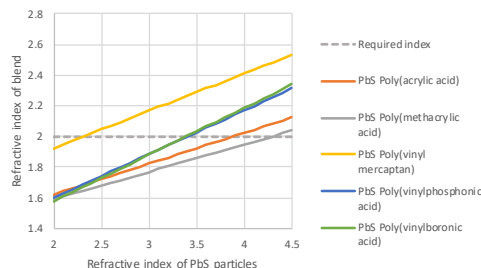


Figure 5: The refractive index of various polymer-nanoparticle hybrids, related to the index of the incorporated particles. Index of the blend is calculated by the volumetric fraction of its constituents, assuming H_2S conversion to PbS from a polymer complex fully loaded with Pb(II).

[19], so the requisite refractive index of the particles must be investigated. As shown in Fig. 5, the required refractive index of the particles depends on what polymer it is blended with. For acrylate-based composites, the particle index must be nearly 4, whereas some other candidates have much more forgiving requirements, either by featuring higher refractive index themselves or by supporting a higher Pb(II) concentration.

Ultimately, candidate materials must also be screened for requirements such as the laser breakdown threshold, however the breakdown fluence may depend not only on the bulk properties but also on impurities [20], and as such is better reserved for a later phase of screening.

CONCLUSION

At LANL we have an ongoing material science effort to identify 3D printable materials that are of interest for advance acceleration. The immediate beneficiary of this effort is the dielectric laser acceleration project where we are investigating means for the fabrication of the woodpile structures that are designed to increase the efficiency of laser acceleration. However, new dielectric materials may find multiple other applications for accelerators and components, wherever there is a need for a dielectric component of a complicated shape that is hard to fabricate by conventional machining or other means. We plan to identify, synthesize, and test several high refractive index low loss polymer dielectric materials and use them for production of simple accelerating structures by additive manufacturing.

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