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FDM 3D printing of combustible structures: first results

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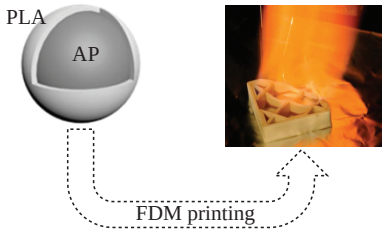
For the first time, complex geometry combustible structures of an ammonium perchlorate–polylactic acid composite have been successfully printed using fused deposition modeling (FDM). The structural and energetic capabilities of the printed structures are demonstrated. Combined with the ability to be produced by FDM printing, these combustible elements could afford many practical applications.



Keywords: fused deposition modeling, additive manufacturing, 3D printing, energetic materials, ammonium perchlorate, polylactic acid, combustible structures.

Additive manufacturing is a revolutionary new technology in the production of energetic materials.[1–5] It allows one to create more complex structures in terms of geometry and precision than those produced by traditional manufacturing technologies. Notably, fine-tuning the structure is beneficial not only from a manufacturing aspect but also for the controlled functioning of reactive structures (some examples can be found in the recent review).[5]

However, standard 3D printing technologies cannot be directly applied to existing energetic formulations for several reasons. First, currently used binders, *e.g.*, hydroxyl-terminated polybutadiene, cannot be used in conventional printing techniques such as fused deposition modeling (FDM). Therefore, several novel binders for composite solid propellants are being considered,[6] including thermoplastic elastomeric materials such as styrene–(ethylene–butylene)–styrene copolymer.[7] Second, the content of solids in energetic formulations is as high as 90 wt%, which again makes it difficult to 3D print by conventional methods such as FDM. Some modifications of conventional printing techniques have been proposed to overcome this problem, *e.g.*, vibration-assisted FDM printing.[8,9] The most critical issue is that energetic materials are inherently hazardous; they usually decompose when heated or extruded. At the same time, such a popular 3D printing technique as FDM involves heating and extrusion of the manufactured sample.

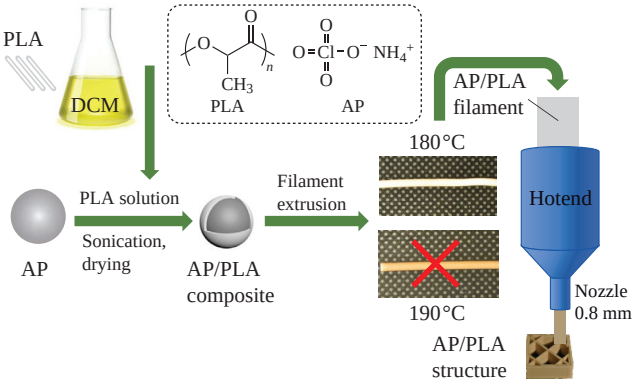


Figure 1 Schematic representation of the three-step preparation of an AP/PLA structure.

To address the above problems, we propose in this work to use an energetic material with high thermal stability, consisting of a commonly used oxidizer, ammonium perchlorate (AP), and polylactic acid (PLA) traditionally used for FDM. PLA is a very convenient matrix for FDM printing due to its low temperatures of glass transition (T_g = 60–65 °C) and melting (T_m = 173–178 °C),[10,11] low shrinkage during curing, high adhesion to the printer platform and high strength.[12,13] Many publications consider the composite materials based on the PLA matrix filled with plastics, metal powders and ceramics[14,15] for the aerospace,[16] medical[17] and automotive[18] applications. However, to the best of our knowledge, there are no published studies reporting successful FDM printing of a highly loaded PLA-based energetic composite. The objective of our study is to assess this possibility.

A three-step 3D printing process (Figure 1) was developed that involved preparing granules,† then extruding the filament and loading it into the printer hotend to fabricate the desired structures by FDM.

First, thermodynamic calculations[19] were performed to guide the selection of a specific energetic composition. The results show that the adiabatic combustion temperature (T_{ad}) reaches 2472 K for a composition of 75% AP and 25% PLA. However, at 75% AP, the filament made for 3D printing turned out to be too brittle.

† Commercial AP powder (average particle size of 30 μm) was dried at 60 °C overnight prior to use. Then, slurry of energetic materials was produced by ultrasonic mixing of the AP powder and a commercial PLA filament (Bestfilament, Russia) solution in dichloromethane (TU 2631-019-44493179-98). After sonication and air drying, the resulting composite of crystalline AP particles encapsulated in a PLA matrix was crushed into granules with 3–5 mm diameter. The burning rate of the pressed energetic granules was measured at a nitrogen pressure of 0.1 MPa to prove the self-burning ability of this material.

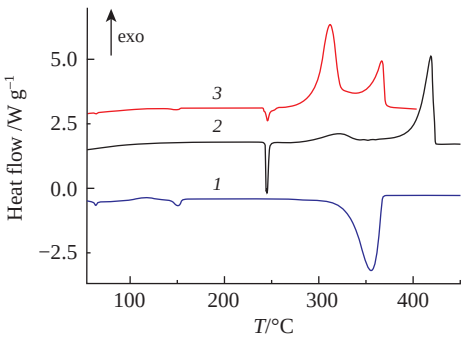


Figure 2 DSC curves of (*1*) PLA, (*2*) AP and (*3*) the AP/PLA composite at a heating rate of 5 K min^{-1}. Curves are shifted for clarity.

Therefore, we tested the mechanical properties of the filaments, reducing the AP content in steps of 5%. At an AP concentration of 65% (T_{ad} = 2108 K), a compromise was reached between the ability of the composite to self-sustained combustion and its mechanical parameters. The adiabatic temperature for this composition is much higher than the value proposed by Merzhanov[20] for the self-sustained combustion of the material (1800–2000 K).

The thermal behavior of the pure components and the selected composite was investigated[‡] to determine if the materials were compatible and could be heated during manufacturing. The DSC profile for PLA is consistent with its known behavior: glass transition is found at 65 °C, followed by cold crystallization at 120 °C, melting at 173 °C and evaporation terminating at 370 °C (Figure 2). Pure ammonium perchlorate is stable up to 240 °C, where a phase transition occurs from the orthorhombic phase to the cubic phase. Then, the thermal decomposition of AP begins as two global processes[21] starting at 310 and 400 °C (see Figure 2). When granules consisting of AP particles encapsulated in the PLA matrix are heated at the same heating rate of 5 K min^{-1}, below the phase transition temperature of AP, several observed thermal events are the sum of the thermal effects of each component, without indicating interaction. The thermal decomposition of the composite above the phase transition temperature of AP indicates the presence of such an interaction. For AP/PLA granules, two AP thermal decomposition peaks are retained, but a considerable increase in heat release at the low-temperature AP decomposition peak is observed along with a significant (by about 50 °C) decrease in the onset of the high-temperature AP decomposition peak. At the moment, without a detailed kinetic analysis, it can be assumed that upon short exposure to heat, the composite is stable up to the AP phase transition (240 °C).

During the production of filament for FDM printing, we noticed that a slight change in extrusion temperature dramatically affects the properties of the filament. The optimal value was found to be 180 °C at an extrusion rate of 1–2 mm s^{-1}, since at lower temperatures, the composite was not plastic enough for extrusion, while at higher temperatures, *e.g.*, 190 °C (see Figure 1), the resulting AP/PLA filament changed its color thus showing the signs of degradation.

For 3D printing, the temperature in the hotend was selected experimentally.[§] Finally, some resolved complex structures, square mesh and gyroid (Figure 3), have been successfully 3D printed and tested for combustion ability. Both charges show complete combustion in the open air, without any residue forming.

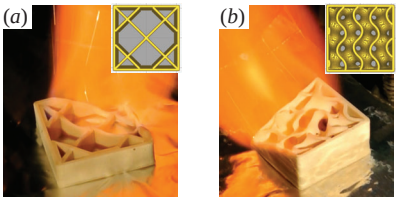


Figure 3 Combustion of 3D printed structures in the open air: (*a*) a square grid and (*b*) a gyroid structure.

To further optimize the composite printing process, two tasks are to be solved in future research. The first is extending the range of energetic formulations components suitable for 3D printing. The second is a detailed analysis of the thermal response of the energetic composite, that is, the kinetic description of the degradation and interaction of components during heating. As follows from the results presented, during DSC analysis, the AP/PLA mixture starts to decompose above 240 °C, while during extrusion, the evidence of degradation was observed at a much lower temperature of 190 °C. Mechanical stimulation seems to play a role here, but this will subject of future research.

This paper demonstrates the possibility of using an AP/PLA composite in FDM printing. The composite with 65% AP has been found to provide printed structures that can burn in a self-sustained mode and has mechanical properties that allow it to be processed by extrusion technique. To facilitate extrusion and printing operations, the AP particles were encapsulated in a PLA matrix prior to feedstock filament preparation. The appropriate temperature and speed for safe extrusion were experimentally determined during the filament fabrication and final printing stages. The energetic capabilities were shown by demonstrating the combustion of energetic granules and printed structures. The proposed printing technology makes it possible to produce adequate combustible structures with high solids loadings without adding solvents to reduce viscosity and special binders to reduce thermal softening. Also, it allows the fabrication of products with complex geometry.

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[‡] Thermal stability was assessed by differential scanning calorimetry (DSC) using a Netzsch STA 449 F3 simultaneous thermal analyzer and a Netzsch DSC 409 HP differential scanning calorimeter. Samples of AP, PLA and their composite weighting 2–5 mg were placed in corundum crucibles and heated at a constant rate of 5 K min^{-1} in an inert gas flow.

[§] The hotend temperature should be low enough not to cause material degradation but high enough to print through a 0.8 mm nozzle with a 0.2 mm layer height at given speed values. For the first layer at a print speed of 2 mm s^{-1}, a temperature of 190 °C was accepted, while for printing subsequent layers at a speed of 5 mm s^{-1}, a value of 200 °C was applied.

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