**Solid Freeform Fabrication 2018: Proceedings of the 29th Annual International**
**Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference**
**Reviewed Paper**

# Additive Manufacturing of Energetic Materials

M. Chiroli*, F. Ciszek*, and B. Baschung*

*French-German Research Institute of Saint-Louis, 5 rue du Général Cassagnou, 68301 Saint-Louis CEDEX, FRANCE

## Abstract

Over the last decade, additive manufacturing gained a lot of interest within the defense industry. However, printing energetic materials such as explosives or solid propellants remains a challenge. A research work with the aim to suggest appropriate materials and associated 3D printing techniques to produce energetic materials, is currently carried out. In interior ballistics, improved weapon performance ends in reaching higher muzzle kinetic energy. This can be achieved by adjusting the gas pressure released during the ballistic cycle by using specific propellant grains. A former study (Baschung, MRS Symposium H, Boston, 2005) highlighted the advantages of using co-layered propellant grains to achieve this goal. The difficulties in producing such kind of propellants can now be bypassed thanks to 3D printers. Our approach consists in deposing a viscous energetic paste, containing a solvent, with an adapted machine. The layer formation and the adhesion between them are investigated in this work.

## 1. Introduction

In recent years, additive manufacturing (AM) technologies have experienced considerable growth. The various existing techniques enable to produce parts with different materials, such as metal alloys, polymers, ceramics or even concrete [1] [2] [3] [4]. Thus, for example, 3D printing techniques can now be used to produce airfoils for aerospace applications, automotive parts or medical implants [5]. This wide range of possibilities led the defense sector to take a close interest in this process. For this reason, an increasing number of studies are currently carried out to use additive manufacturing within the defense industries [6].

An energetic material (EM) is a chemical substance that can release its stored energy in a very short time. Once initiated, these materials undergo self-sustaining exothermic reactions. They can be classified as explosives, propellants and pyrotechnics. The latter can be used in countermeasure decoy flares for the safety of military aircrafts [7] or in fireworks. Propellants can be used in airbag systems [8] and in space launchers [9]. They can also be used in interior ballistics which is the branch of applied physics dealing with the motion of the projectile in the gun until it exits the barrel. The final performance of energetic materials is linked to their chemical composition and geometry.

The main current issue within the field of interior ballistics consists in increasing the weapon performances. To achieve this goal, it is necessary to raise the muzzle kinetic energy of the projectile propelled. One of the most intuitive ways consists in adjusting and controlling the combustion gases released from the energetic material during the ballistic cycle. This can be achieved thanks to the use of specific solid propellant grains such as multi-material propellants (co-layered propellants) [10]. Quite difficult to manufacture before, it appears that the production of this type of solid propellant can now be easier to handle thanks to 3D printing technologies.

The use of inert materials combined with slightly modified machines can be of interest to print energetic materials. Indeed, it is possible to adapt material extrusion based machines to print highly viscous materials. For example, Yang *et al.* [11] mounted a jet valve on a Fab@Home v2 3D printer while Hong *et al.* [12] linked a screw extruder to feed the extruder of the printer. In order to produce ceramic parts, Faes *et al.* [13] developed and tested an additive manufacturing process based on the extrusion of a composition which has the capacity to cross-link under UV light. Recently, scientists from the Massachussets Institute of Technology (MIT) investigated the additive manufacturing of cellulosic materials. Pattinson and Hart [14] succeeded in developing a simple process, operating at room temperature, for the 3D printing of cellulose. They dissolved cellulose acetate (CA) powder in acetone and modified a commercial-off-the-shelf fused deposition modeling (FDM™) machine (Printrbot Simple Metal) to meet their objectives. Studies directly concerning energetic materials are currently emerging. Indeed, Fleck *et al.* [15] prepared a reactive filament made of aluminum (Al) and polyvinylidene fluoride (PVDF) that can be printed on an unmodified FDM™ 3D printer. The Dutch research center TNO started working on AM of energetic materials in 2013 [16]. After having successfully printed trinitrotoluene (TNT) with a FDM™ printer, because of the expected performance gain, TNO focused on the 3D printing of gun propellants. They succeeded in printing multi-perforated gun propellants containing up to 75 wt% of energetic material [17] by using a stereolithography based printer.

The objective of this study is to suggest appropriate materials and associated 3D printing techniques to produce energetic materials, specifically gun propellants. The idea, based on the work of Pattinson and Hart [14], is to use viscous pastes that can be printed on a slightly modified material extrusion based 3D printer. Materials (both inert and energetic) are selected to prepare viscous mixtures ready to be deposited. The approach developed consists in using an inert paste, equivalent to the energetic one, to study the layer formation process and to configure the 3D printer. Different inert compositions in terms of viscosity are prepared. Dynamic viscosity measurements are carried out and the behavior of the pastes during extrusion is analyzed. To understand the layer formation process, deposition and adhesion tests are performed. Once the best inert candidate has been identified and the printer has been configured accordingly, an energetic paste having the same viscosity has to be printed.

## 2. Materials and Experimental setup

To prepare viscous pastes, seven different inert materials were hermetically kept in a solvent for 24 hours (see figure 1). Because of its capacity to reliably dissolve solid propellants, the solvent chosen was acetone (Zundel + Kohler). The considered materials are: ethylene vinyl acetate (EVA) LEVAPREN® 700 HV (Bayer AG); cellulose acetate (CA) (Sigma Aldrich); ethylene vinyl alcohol EVAL™ (Kuraray); polyninyl alcohol Rhodoviol 4/125 (Prolabo); Ultramid® 6A (BASF); polylactic acid (PLA) (Printrbot) and acrylonitrile butadiene styrene (ABS) (Ultimaker).

*Figure 1 : Solubility tests of inert materials in acetone. From left to right: EVA LEVAPREN® 700 HV (1); CA (2); EVAL™ (3); Rhodoviol 4/125 (4); Ultramid® 6A (5); PLA (6) and ABS (7)*

Among the inert materials tested, only two were soluble in acetone: EVA LEVAPREN® 700 HV and CA. Thus, at first, inert pastes were prepared by dissolving 10 g of ethylene vinyl acetate in 6.4 mL of acetone, and 10 g of cellulose acetate in 25.5 mL of acetone. The mixtures were manually mixed and hermetically sealed for 24 hours. Feedstock was then loaded into 30 mL syringes (Nordson EFD) and extrusion were performed thanks a Performus™ V dispenser (Nordson EFD).

The EM considered for this study is an in-house developed formulation. It is made of 54 wt% of nitrocellulose, mechanically mixed with other energetic ingredients. This solid propellant is soluble in acetone, and, depending on the weight percentage, different viscosities of the mixture can be reached. In the same way as it was done for inert pastes, a 30 mL syringe was loaded with an energetic paste initially prepared by dissolving 10 g of solid propellant in 10 mL of acetone. Extrusion tests were performed as well. For both inert and energetic pastes, dynamic viscosity measurements were done thanks to a RM 100 Plus viscometer and its MS-R4 measuring system from Lamy Rheology.

The 3D printer used in this study is a material extrusion based desktop printer (Printrbot Simple Metal). This FDM™ printer has been enhanced by replacing the original filament extruder by the Paste & Food Extruder system from Printrbot. This system enables to use viscous materials loaded into syringes to 3D print parts. Initially designed to use HSW 50 mL syringes, the system has been slightly modified to use 55 mL syringes from Nordson EFD. Furthermore, for pyrotechnic safety reasons, the aluminum parts of the printer are currently being replaced by plastic ones. In case of non-desired reaction of the energetic loading, the plastic parts will generate less dangerous fragments and enable a better deconfinement of the associated pressure wave.

## 3. Results and Discussion

The first step consisted in performing extrusion tests with the three different compositions (EVA/Acetone, CA/Acetone and EM/Acetone). An examination of the material behavior during the extrusion was carried out. During extrusion from the syringe, EVA/Acetone composition showed significant swelling while, in the same conditions, no swelling or shrinkage was noticed with CA based mixture (see figure 2). Furthermore, the extrusion of CA paste was quite similar to the EM/Acetone paste. Indeed, both CA/Acetone and EM/Acetone filaments seemed close in terms of adhesive properties, while the EVA/Acetone filament turned out to be highly sticky. Consequently, the CA/Acetone paste was retained to be used as an inert composition.

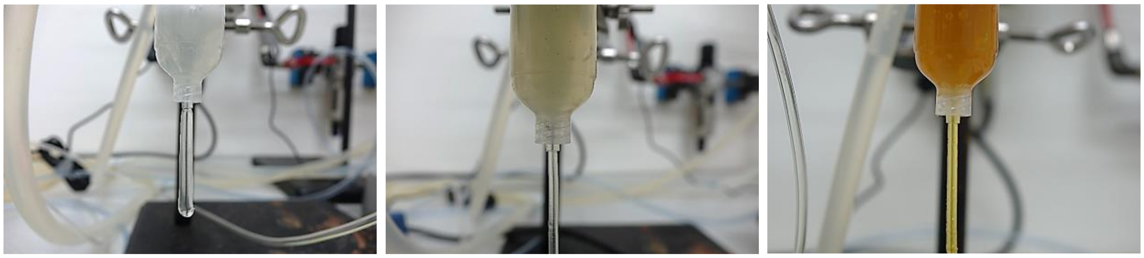


*Figure 2 : Extrusion tests performed with the three compositions. From left to right: EVA/Acetone; CA/Acetone; EM/Acetone*

Therefore, different inert mixtures CA/Acetone were prepared for deeper characterizations. Two different samples of cellulose acetate (sample A: molecular weight $M_n \approx 30{,}000$ by GPC and sample B: molecular weight $M_n \approx 50{,}000$ by GPC) were dissolved from 25 wt% up to 50 wt% in acetone by manual mixing. The details of the prepared samples are given in table 1 and 2. An energetic composition with a charge rate of 60 wt%, looking like the more viscous inert compositions, was also prepared (see table 3).

*Table 1 : CA/Acetone compositions prepared with sample A ($M_n \approx 30{,}000$)*

| **Name** | **Weight CA (g)** | **Volume Acetone (mL)** | **Charge rate (wt%)** |
|---|---|---|---|
| *A25wt%* | 10.01 | 38.4 | 25 |
| *A30wt%* | 12.86 | 38.3 | 30 |
| *A35wt%* | 16.16 | 38.4 | 34.9 |
| *A40wt%* | 20.04 | 38.3 | 40 |
| *A45wt%* | 24.55 | 38.3 | 45 |
| *A50wt%* | 30.01 | 38.3 | 50 |

*Table 2 : CA/Acetone compositions prepared with sample B ($M_n \approx 50{,}000$)*

| **Name** | **Weight CA (g)** | **Volume Acetone (mL)** | **Charge rate (wt%)** |
|---|---|---|---|
| *B25wt%* | 10.01 | 38.3 | 25 |
| *B30wt%* | 12.89 | 38.4 | 30 |
| *B35wt%* | 16.15 | 38.3 | 35 |
| *B40wt%* | 20.00 | 38.3 | 40 |
| *B45wt%* | 24.55 | 38.3 | 45 |
| *B50wt%* | 30.00 | 38.3 | 50 |

*Table 3 : EM/Acetone composition*

| **Name** | **Weight EM (g)** | **Volume Acetone (mL)** | **Charge rate (wt%)** |
|---|---|---|---|
| *EM60wt%* | 45 | 38.3 | 60 |

The dynamic viscosity of the prepared mixtures was measured. As it was not possible to obtain homogenous pastes for highly charged preparations, no viscosity measurements could be conducted for samples A50wt%, B45wt% and B50wt%. The velocity gradient value retained for the measurements was determined thanks to the visually more viscous preparation

(A45wt%). It was set to 4 $s^{-1}$. Measurements were realized at room temperature (22 °C ± 2 °C). Results can be seen in figure 3. Because of the higher molecular weight of sample B of CA, for a same charge rate, compositions prepared with this sample are more viscous than sample A based preparations (see figure 3). This enables to screen a wide range of inert compositions from syrup like fluids to mastic like ones. Furthermore, it is noticed that the dynamic viscosity of the EM60wt% (1126 Pa.s at 4 $s^{-1}$) composition is in the same range than the one of A45wt% (1388 Pa.s at 4 $s^{-1}$) and B40wt% (1238 Pa.s at 4 $s^{-1}$) pastes. In terms of dynamic viscosity, it is thus possible to have an inert composition equivalent to the energetic pastes.

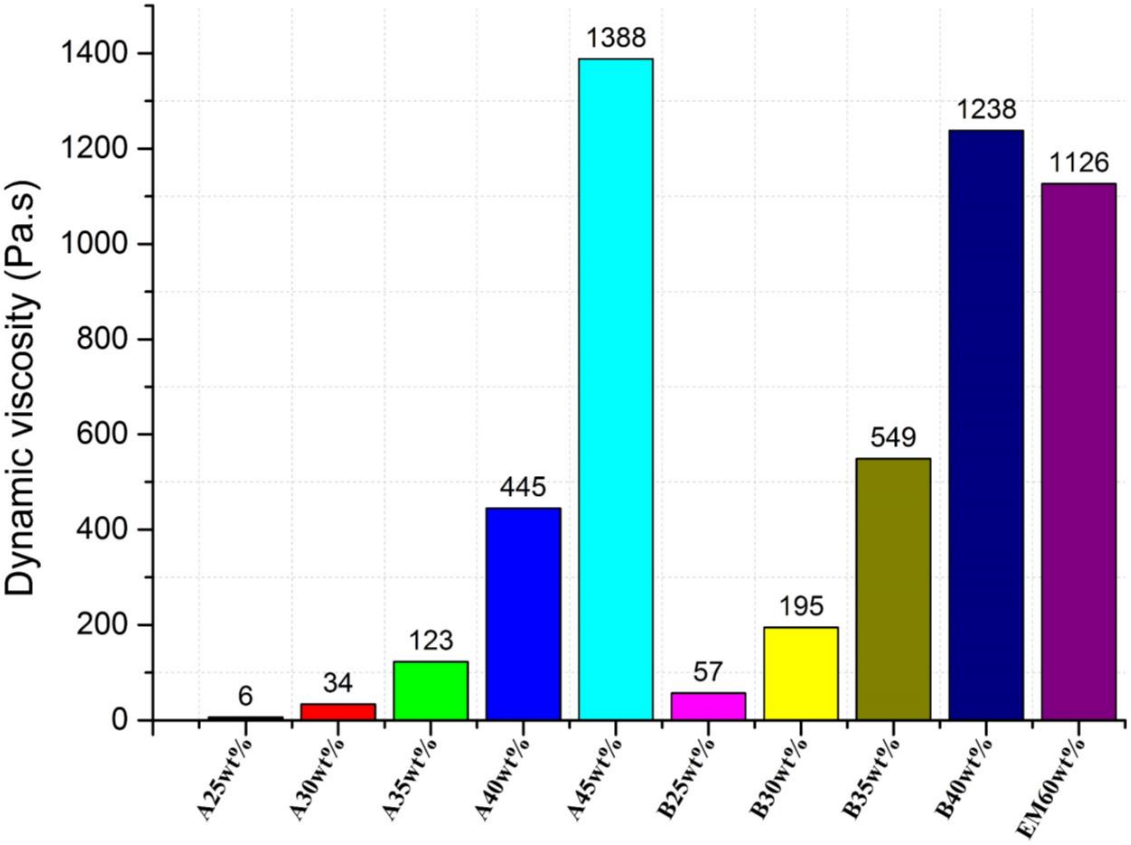


*Figure 3 : Viscosity measurements of CA/acetone compositions*

In order to study the layer formation process, extrusion and deposition tests were performed. Thus, the prepared pastes were extruded through different tapered tips (Nordson EFD, diameter Φ from 0.84 mm to 0.25 mm) to obtain a paste filament that can be manually deposited onto glass microscope slides, simulating the build plate. For both the energetic and inert mixtures, the extruded paste filaments were sticky when acetone was still present, but they solidified with the acetone evaporation. Kapton® covered glass slides showed better adhesion than bare glass. Indeed, when deposited on bare glass, the materials first adhere, but rapidly slide with the solvent evaporation. The pressure needed to extrude the compositions through the different types of tips was measured. The tests were considered as successful if it was possible to vertically deposit the extruded filament on the microscope slides. Results for the peak viscosity values as well as for an intermediate one are given in table 4. EM based paste results can be seen in table 5. A green box means that the test was successful while a red one means that it failed.

*Table 4 : Pressure needed to extrude the inert pastes*

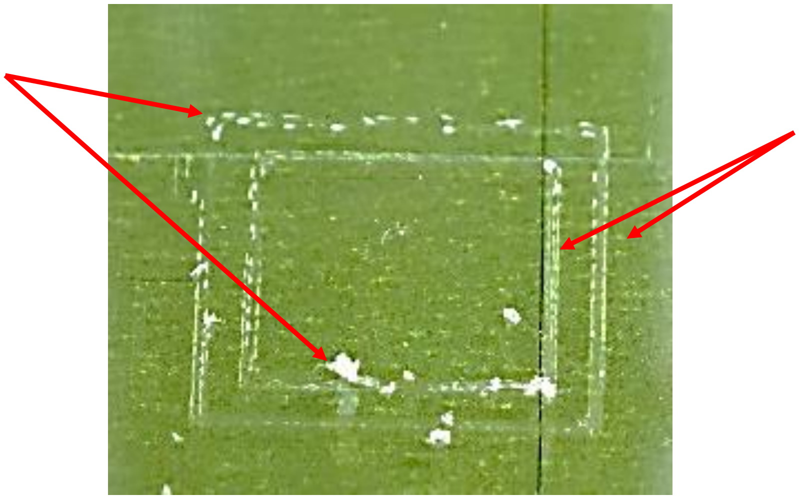
| **Pressure (bar)** | CA/Acetone A25wt% | | | | CA/Acetone B35wt% | | | | CA/Acetone A45wt% | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Φ tip (mm) | | | | Φ tip (mm) | | | | Φ tip (mm) | | | |
| | 0.84 | 0.58 | 0.41 | 0.25 | 0.84 | 0.58 | 0.41 | 0.25 | 0.84 | 0.58 | 0.41 | 0.25 |
| 2 | 🟩 | 🟩 | 🟩 | 🟩 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 |
| 3 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 |
| 4 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟥 | 🟥 | 🟥 |
| 5 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 |
| 6 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 |
| 7 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 |

*Table 5 : Pressure needed to extrude the energetic paste*

| **Pressure (bar)** | EM/Acetone EM60wt% | | | |
|---|---|---|---|---|
| | Φ tip (mm) | | | |
| | 0.84 | 0.58 | 0.41 | 0.25 |
| 2 | 🟥 | 🟥 | 🟥 | 🟥 |
| 3 | 🟥 | 🟥 | 🟥 | 🟥 |
| 4 | 🟩 | 🟩 | 🟩 | 🟥 |
| 5 | 🟩 | 🟩 | 🟩 | 🟩 |
| 6 | 🟩 | 🟩 | 🟩 | 🟩 |
| 7 | 🟩 | 🟩 | 🟩 | 🟩 |

As shown in table 4 and 5, a similar extrusion behavior can be noticed for the EM60wt% and the A45wt% compositions. This reinforces the fact that the CA/Acetone composition can be considered as the inert equivalent to the EM/Acetone paste. To obtain the best surface finishes, the thinner tip (0.25 mm) should be used for the paste extrusion, hence the need of being able to supply 5 bar to extrude the more viscous compositions (see table 5). The pressure needed corresponds to a force of around 300 N applied to the piston of the syringe. This threshold can easily be reached with the Paste & Food Extruder system.

Printing tests were performed with the CA/Acetone compositions. They were conducted at room temperature and no part was heated on the printer (build plate or extruder). For safety reasons, no printing test was carried out with the EM/Acetone mixture until now because prior authorization must be obtained for using EM. The printing parameters used for the first tests are the ones used to print PLA material. No optimization of these parameters was attempted so far. The tests consisted in printing the contours of the first layers of a 3 mm side calibration box. For each inert composition, it was not possible to build a perfect and reliable first layer (see figure 4). This should be solved by optimizing the printing parameters. However, those first attempts seemed encouraging, showing the possibility to reach a good adhesion of the paste on the build plate. Moreover, the hardening of the deposited composition turned out to be in the same time range as compared to standard 3D printing materials. Attempts to build successive layers were made. In order to receive another layer, it seemed that one layer should be completely dried and solidified.



**Impossible to build a perfect first layer with the printing parameters used**

**Very good adhesion of the first deposited layer**

*Figure 4 : First printing tests performed with CA/Acetone paste (contours of a 3 mm box)*

## 4. Conclusion and Future work

In this paper, two different kinds of viscous pastes were prepared with the aim to be printed with a material extrusion based desktop printer. The compositions were obtained by dissolving either an energetic material (EM) or cellulose acetate (CA) in acetone. The CA/Acetone composition was selected as an inert equivalent to the EM/Acetone mixture and should be used to configure the 3D printer. Dynamic viscosity measurements were performed to identify an equivalence between inert and energetic compositions. Extrusion and deposition tests highlighted the similar behavior of both inert and energetic pastes. Specifically, it was found that inert mixtures (A45wt% and B40wt%) resemble the properties of an energetic counterpart (EM60wt%) in terms of dynamic viscosity. Thus, testing and configuring the setup can be conducted with the much safer inert paste. Eventually, first printing experiments carried out with the inert compositions turned out to be encouraging. Furthermore, the necessity to have one layer completely dried and solidified before receiving the next one was noticed.

The next steps of this research work are, first, to optimize the printing of the inert mixture and to identify the best printable inert candidate. Second, an energetic paste, within the same range of dynamic viscosity than the previously identified inert candidate, should be prepared. A first simple shape of solid propellant (*e.g.* flake) should eventually be printed and its performances evaluated.

## 5. Acknowledgements

The authors greatly thanks the French state organization responsible for armament programs, the DGA, for supporting this research. The thanks are also extended to S. Braun, J. Glorian, K.-T. Han and R. Wölbing for their support and advice.

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