Investigations of ETPE formulations for additive manufacturing

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Abstract
Additive manufacturing methods are emerging fields that are under investigation for production of propellants and explosives. Fraunhofer ICT investigated GAP-based EPTE formulations as a starting point for energetic filaments that can be processed according to the Fused Deposition Modeling (FDM) method. For high energy content an energetic crystalline filler (e.g. RDX, HMX) content above 50wt% is needed. However, the viscosities of the energetic filament formulations are then too high and these formulations cannot easily be processed by commercial FDM printers. We tested 2,4-dinitroanisole (DNAN) and the energetic ionic liquid 4-amino-1-butyl-1,2,4-triazolium nitrate (C4 N) as an additive to reduce viscosity and therefore enable processability via FDM printers.

Introduction
Additive manufacturing ("3D printing") is a process for the production of three-dimensional solid objects from a digital file. Forms and geometries of energetic materials or formulations can be realized which are not or only very difficultly realized by means of traditional techniques. Additionally, different formulations can be combined in the energetic charge. In the processing of energetic formulations, it is now already intensively investigated.
At Fraunhofer ICT caseless ammunition with foamed propellants are under investigation and manufactured for over 20 years [1, 2]. This approach was based on a reactive binder system filled with RDX and other energetic components and some additives. Mainly polyurethanes were used as reactive binders. The polyol component contains as an energetic part the glycidyl azide polymer GAP and the foamed charges were easily produced by the reaction injection moulding process. The reaction injection moulding (RIM) is an industrial process for the mass production of a wide variety of plastic parts mainly using polyurethanes. However, the control of the pore size distribution and gradient of pore size is limited to a special area shown in Figure 1.

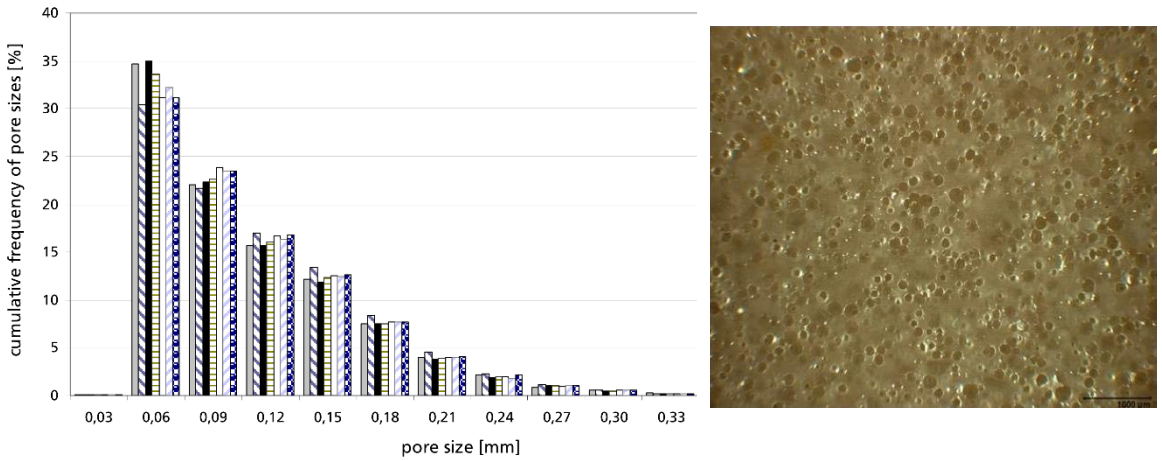

Figure 1. Classical pore size distribution of foamed gun propellants (left) produced at Fraunhofer ICT and microscope image of the propellant (right) [3].

Using additive manufacturing pore size and shape of the propellant can be produced and adjusted in a much wider area than it is possible with the classical RIM process. Therefore, it is possible to produce propellant charges for the first-time task-specific tailored for caseless ammunition. In Figure 2 caseless ammunition using foamed propellants (left) and a model of caseless ammunition manufactured by additive manufacturing (right) is shown.

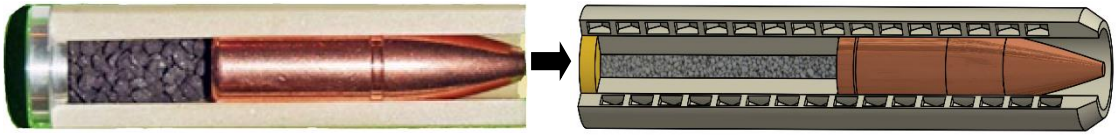

Figure 2. Caseless ammunition manufactured at Fraunhofer ICT (left) [4] and a model of additive manufactured complex shaped caseless ammunition (right).

Depending on the additive manufacturing method, the pores or cavities can be individually adapted to the desired burning behavior and in addition, filled by a second energetic formulation with lower mechanical strength but higher energy content and different burning rates.

GAP-based ETPE

A promising approach for developing new, powerful gun propellants is the application of thermoplastic elastomers (TPEs) as binders. These materials are composed of thermoplastic hard segments and elastomeric soft segments. Due to the combination of hard and soft segments in the matrix these polymers have special properties. When external stress is applied the materials respond with a deformation, returning to their original form when the stress is removed. This implies an insensitive material behavior, for example in the case of impact stress.

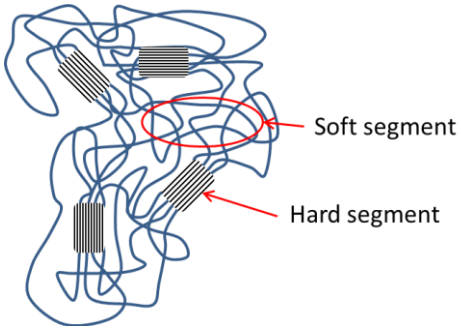

Figure 3. Schematic view of a thermoplastic elastomer composed of hard and soft segments.

Fraunhofer ICT has expertise in all the areas which are essential for the development of a new generation of plastic-bonded gun propellants, from the synthesis of applicable elastomers with energetic functional groups (ETPE), the combination with different energetic plasticizers and the formulation with energetic fillers to the manufacturing and subsequent characterization of the new gun propellants [5].

Processing temperature

In order to produce additive manufactured propellants via the FDM process according to applicable regulations and requirements the processing temperature of the energetic filament/formulation should be between 90 °C and 110 °C. In this case, the melting temperature is well above the melting point of TNT, which is in some applications too low and below the maximum temperature for processing energetic materials of 120 °C according to DGUV (German Social Accident Insurance Regulation) [6].

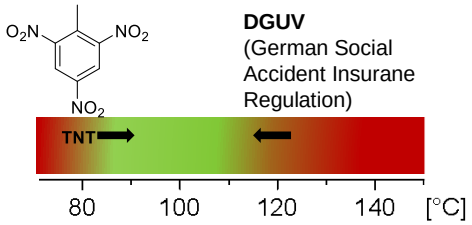

Figure 4. Target processing temperature (green) for energetic filaments using FDM process.

Processing viscosity

The available modified FDM Printer can process filaments between 10^3 and 10^7 Pas at a shear rate of 1 s^{-1} to 10 s^{-1} at the corresponding processing temperature. Due to the need of high energetic crystalline filler content in the filaments above 50wt% the processing viscosity of the filament formulation will drastically increase and therefore additives are needed to lower the viscosity.

Additives

In order to reduce the viscosity of the GAP-based ETPE we were choosing two different kind of additives. The energetic ionic liquid 4-amino-1-butyl-1,2,4-triazolium nitrate (C4 N) and the well-known 2,4-dinitroanisole (DNAN), which is liquid at processing temperatures (T_m = 95 °C).

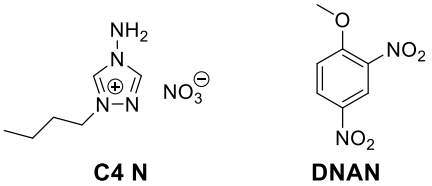

Figure 5. Structural formulas of the selected additives C4 N and DNAN for GAP-based ETPE.

In contrast to in use energetic plasticizers like Bu-NENA, BTTN, TMETN, BDNPA/F and DNDA57, C4 N does not evaporate upon heating in nitrogen flux up to 120 °C (TGA) due to its ionic nature (see Figure 6).

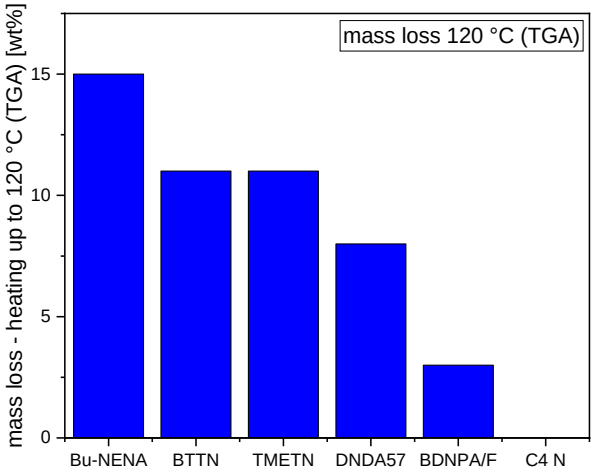

Figure 6. Mass loss of different energetic plasticizers and C4 N upon heating in a nitrogen flux (25 mL/min) up to 120 °C.

Therefore, an energetic ionic liquid like C4 N should be suited to be part of a filament formulation for additive manufacturing as the entire polymer formulation needs to be heated/melted twice, once during filament production and subsequently during the additive production process.

Experimental Section

General

Safety precautions for the handling of energetic materials must be applied. Thermogravimetric analysis (TGA) was done on a TA Q500 apparatus with a scan rate of 10 K/min in a platinum 100 µL pan under nitrogen flux (25 mL/min). Rheological measurements were done with a parallel plate rheometer Physica MCR 501. SET Test was performed with a heating rate of 5 °C/min and 0.2 g of sample mass. GAP based ETPE was used produced out of 74wt% GAP-Diol, 5.5wt% ethylenglycole and 20.5wt% hexamethylene-1,6-diisocyanate as described in literature [5b] with other chain extenders.

Characterization

To be capable to measure pure GAP-based ETPE in rotation mode the ETPE had to be measured at 120 °C showing a viscosity of 1.4 10^7 mPas at a shear rate of 1 s^{-1}. A mixture of 70wt% DNAN and 30wt% GAP-ETPE showed at 100 °C already a viscosity of only 1.4 10^3 mPas (Figure 7) providing the possibility to substitute energetic crystalline nitramine filler.

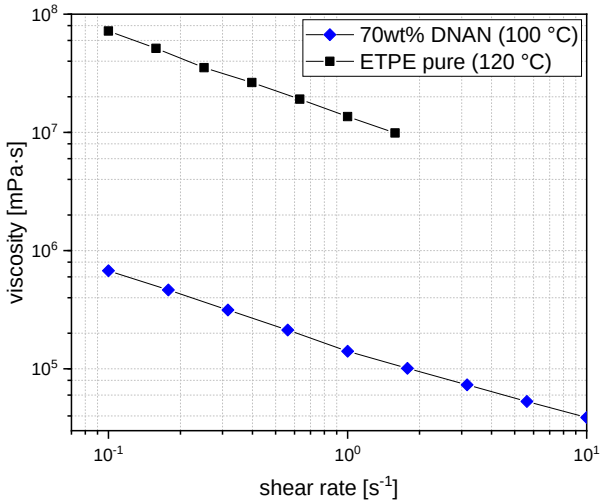

Figure 7. Viscosity of GAP-based ETPE and filled with 70wt% DNAN content at different shear rates.

However, the mixture is too brittle to be processed as a filament. From our former work C4 N was already investigated as a mixture with the methyl analog of C4 N (50:50wt%) in polyester-based polyurethane elastomers and showed an increased strain capability combined with higher maximum tensile strength [7]. We investigated the viscosity decrease of the GAP-based ETPE through addition C4 N as a plasticizer. At a typical processing temperature of 110 °C the viscosity was measured with 5, 10 and 15wt% addition of C4 N at a shear rate of 1 s^{-} (Figure 8). The viscosity of the ETPE/ C4 N (15wt%) mixtures was almost four times lower than pure ETPE at 120 °C (1.4 10^7 mPas vs 3.6 10^6 mPas). The next step for tailored energetic filaments is using DNAN and C4 N in GAP-based ETPE to provide sufficient low viscosity in order to add energetic crystalline filler content like RDX or HMX. Moreover, C4 N can reduce processing viscosities during the production of energetic formulations and due to its high thermal stability combined with its low vapor pressure, processing operations at elevated temperatures can be performed much safer.

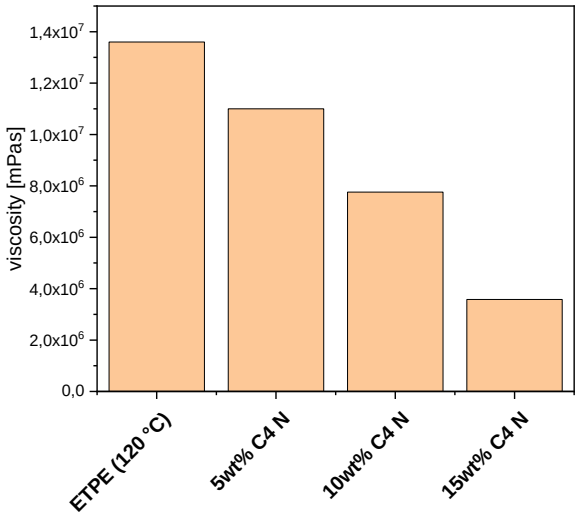

Figure 8. Viscosity of GAP-based ETPE with increasing C4 N content at a shear rate of 1 s^{-1} and 110 °C.

Conclusion

For energetic GAP-based filament formulation with good energy content energetic crystalline filler content above 50wt% is needed. However, the processing viscosity of the filament formulation will drastically increase and therefore additives were investigated to lower the viscosity. DNAN and C4 N showed promising results in the viscosity reduction of a GAP-based ETPE providing the path for advanced energetic filament formulations containing crystalline filler content. Next step will be both additives examined together in a formulation with RDX or HMX to achieve a processable high energy filament formulation.

Acknowledgments

We would like to thank J.-B. Müller for sample preparation, U. Förter-Barth for viscosity measurements and M. Mandt for drawing the 3D Model. General funding by the German Ministry of Defense is gratefully acknowledged.

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