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Experimental analysis of rheological behaviour of a multi-base energetic material during conventional extrusion

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Abstract

The final quality to be achieved during conventional extrusion of energetic materials depends on diverse factors such as the material formulation, extrusion parameters, characteristics of raw materials and previous stages like mixing process. Process optimization is really complex due to the existence of a great number of factors, and the nature of the distinct phenomena involved. In the present work, the extrusion of a multi-base energetic material is studied, with the purpose of discovering the relation between the main factors of this process and the optimum conditions for this forming stage. The effect of rheological properties of initial compounds, extrusion velocity, extrusion pressure and chemical formulation are evaluated, considering two alternative formulations for a triple-base propellant. The analysis of rheological properties served to deduce the recommended parameters for conventional extrusion of these triple-base propellant, as well as essential information about the process variability and expected quality of final products.

Keywords: Extrusion; Energetic Materials; Oscillatory Rheology; Elastic Modulus; Viscous Modulus

1. Introduction

In the manufacturing of multi-base propellants, the extrusion stage can be remarked as one of the main processes due to its strong influence of the final quality of produced propellants. Not only the process conditions adopted during extrusion but also the previous stage of mixing have a great influence on the expected performance of final products.

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products, because the physical, geometrical, thermal and chemical properties of energetic materials are seriously affected by the levels and distributions of shear stress and shear strain during both manufacturing stages.

For an appropriate understanding and optimization of the conventional extrusion of energetic materials, the supervision of rheological properties of kneaded propellant doughs prior to their processing by the extrusion stage is highly recommended, since the extruded material will be clearly influenced by their complex viscoelastic behavior during this forming process [1]. Propellant doughs present a very high viscosity and a complex rheological response during their processing in semi-solid state, and they also present some specific phenomena such as wall slip and die swell [2]. In many of the works dedicated to the study and improvement of these extrusion processes, the rheological response of these highly viscous special materials is considered.

There are numerous studies dedicated to identifying the rheological and mechanical response of different energetic materials and other related compounds, for its application to distinct manufacturing processes such as mixing, extrusion, lamination or other possible technologies [3-6], as well as other works on the analysis and optimization of material transformation during the extrusion stage, including the experimental study and/or the numerical modelling of this process [6-10].

As an example of the works focused on rheological characterization of energetic materials and experimental techniques for measuring their rheological and mechanical properties, in the study of D.M. Kalyon et al. [3] a new methodology to evaluate the rheological behavior of energetic materials on die walls is presented. The proposed experimental methodology consists in the use of two rectangular slit rheometers, and so the surface to volume ratio can be modified to consider the appropriate wall slip corrections.

S. Ozkan et al. [4] studied the rheological behavior of some propellant simulants subjected to twin-screw extrusion. According to the results obtained by these authors, their elasticity and shear viscosity are reduced as the suspension homogeneity is enhanced. The work of J. Martinez-Pastor et al. [5] evaluated the experimental techniques to be applied for rheological characterization of multi-base propellants and inert simulants related to these propellants, and the limits and applications of these rheological techniques were presented.

F.M. Gallant et al. [7] analysed the burning properties of extruded composite propellants, in order to weigh the possible utilization of new ingredients or formulations for these energetic materials. From the results presented in this work, these authors concluded that burning rate is significantly influenced by propellant ingredients and extrusion conditions, and lower values of burning rate are obtained as extruder speed is increased.

B. Kalaycioglu et al [8] developed a numerical modelling for conventional extrusion of a double-base propellant considering the large deformation elasto-viscoplastic behaviour of extruded compound, and deduced the distribution of hydrostatic pressure and contact stress in order to respect the safety conditions imposed by the nitroglycerine content. Other authors like S. Rahimi et al. [9] were focused on the analytical and numerical modeling of the effect of wall friction on the mean apparent viscosity, wall slip and pressure gradient in conical extrusion flow of gel propellants, and encountered some asymptotic approximations for small cone angles and low friction levels.

In this work, the experimental analysis of conventional extrusion of a multi-base propellant is carried out, in order to clarify the influence of rheological properties of previously mixed compounds, the time that propellant doughs were retained in an intermediate storage and the main parameters of extrusion process, such as the initial and final temperature of extruded products, extrusion velocity and extrusion pressure. The energetic material studied in this work is a triple-base propellant composed by nitrocellulose (NC), nitroglycerin (NG) and nitroguanidine (Ng), and two series of experiments with two different levels of nitroguanidine content are assumed. The effect of rheological properties of propellant doughs to be processed and the factors involved in conventional extrusion are discussed, and guidelines oriented to minimize the dispersion in process parameters and enhance the overall quality of final products are provided.

2. Experimental procedure

In this study, the relation between the main factors of conventional extrusion and rheological properties of multi-base propellants is analyzed. The energetic material considered in these experiments is a triple-base propellant constituted by a mixture of nitrocellulose (NC), nitroglycerin (NG) and nitroguanidine (Ng), and a certain proportion of additives and solvents. The most relevant extrusion parameters such as the room temperature, initial and final
material temperature, extrusion velocity and extrusion pressure were registered during the experiments, as well as the time that mixed compounds were retained during the intermediate storage.

For the measuring of initial and final extrusion temperatures, an ATEX immersion pyrometer with a type-K thermocouple was used. The rheological properties of propellant doughs were registered after both the mixing and intermediate storage stages, in order to know the rheological moduli that correspond to these materials during their mixing from the initial solid and fluid components and also during their forming by conventional extrusion. The extrusion equipment employed in the experimental study of these multi-base propellants consists of industrial scale machinery for manufacturing of these materials, and so the dispersion of process parameters associated to real production can be deduced.

The propellant doughs are examined by rotational rheology using a TA Instruments DHR-1 rheometer with parallel disk geometry of 20 mm diameter and the software TRIOS for processing the rheological data. Due to the usual difficulty of executing flow tests for concentrated suspensions, oscillatory amplitude sweep tests are adopted as a reliable rheological technique to evaluate the viscous and elastic properties of these energetic materials [6].

3. Results

In this work, two different series of experiments with a distinct propellant formulation were carried out. The first series of extrusion tests (identified as extrusion type I) correspond to the regular proportion of nitroguanidine for this triple-base propellant, while a lower nitroguanidine content was considered in the other experiments (extrusion type II). In both series of tests, different values of extrusion velocity and extrusion pressure were considered in order to evaluate the relation among these factors and the rheological properties of propellant doughs.

The storage modulus ($G'$) and loss modulus ($G''$) registered by oscillatory measuring techniques within a certain range of oscillatory angular deformation amplitudes are represented in Figures 1-2 for both series of experiments before extrusion process. The constant values of storage and loss modulus at the range of the linear viscoelastic region (LVR) serve as indicators of elastic and viscous behavior of the sample material, respectively.

![Fig. 1. Rheological moduli within the LVR for mixing type I propellants doughs before extrusion process.](image-url)
As a consequence of the discontinuity between mixing and extrusion stages, the rheology response of propellant doughs was measured after both the mixing and intermediate storage of these compounds, and so the influence of storage time can be quantified. During the intermediate storage, a slight (but not negligible) amount of the solvents leave the mixed material and evaporate inside the antistatic bags in which these compounds are stored, increasing the value of the rheological moduli as can be seen in Figures 3-5.

The storage or viscous modulus ($G'$), loss or elastic modulus ($G''$) and complex modulus ($G^*$) registered in the range of the linear viscoelastic region (LVR) for both mixing and storage stages are represented in Figures 3, 4 and 5, respectively. The rheological moduli for the intermediate storage were registered only a few minutes before the extrusion process, and so describe the viscoelastic behaviour that propellant doughs will exhibit during their forming by conventional extrusion.
If the rheological moduli before and after the storage stage are compared, a good adjustment among these parameters can be found. A logarithmic empirical correlation can be established for the multi-base propellant analyzed in this work, with the mathematical expressions that are shown in Figures 3-5. As can be observed in these figures, both the storage and loss moduli ($G'$ and $G''$) present the same logarithmic tendency. For that reason, the complex modulus ($G^*$) can be adopted as a unique rheological indicator for controlling the storage stage, in order to maintain the desired rheological properties for an optimized extrusion.
The relation obtained between these pairs of rheological properties, can be attributed to the lower capability to evaporate the solvents in propellant doughs with elevated values of rheological moduli. As a consequence, more remarked increments can be originated in the case of reduced rheological moduli prior to the storage stage (equivalent to softer mixed compounds), since they contain a greater amount of solvents in their composition.

The average values that correspond to storage, loss and complex moduli ($G'$, $G''$ and $G^*$) for each series of extrusion tests are shown in Table 1, as well as the dispersion of these rheological properties in terms of standard deviation. According to the results contained in this table, the second series of experiments (with a reduced amount of nitroguanidine) presents lower values for the totality of rheological moduli, both in the case of rheological properties registered after mixing and intermediate storage stages.

Table 1. Rheological moduli of propellant doughs for different propellant formulations.

| Mixing Moduli | Extrusion Moduli |
|---------------|------------------|
| **Experiment Type I** | | |
| $G'$ (Pa)     | 9.08E+05 ± 0.91E+05 | 9.72E+05 ± 7.80E+04 |
| $G'' (Pa)$    | 3.08E+05 ± 0.23E+05 | 3.37E+05 ± 2.25E+04 |
| $G^* (Pa)$    | 9.59E+05 ± 0.93E+05 | 1.03E+06 ± 8.11E+04 |
| **Experiment Type II** | | |
| $G'$ (Pa)     | 8.45E+05 ± 0.63E+05 | 9.61E+05 ± 4.39E+04 |
| $G'' (Pa)$    | 2.81E+05 ± 0.21E+05 | 3.24E+05 ± 7.79E+03 |
| $G^* (Pa)$    | 8.91E+05 ± 0.66E+05 | 1.01E+05 ± 4.31E+04 |

Table 1 represents the average values of complex modulus ($G^*$) that should be maintained during the production of these multi-base energetic materials in order to guarantee the desired conditions in mixed compounds to be subject to the extrusion process, and also to reduce the dispersion associated to the extrusion parameters and to provide a higher accuracy in the physical, geometrical and ballistic properties of final propellants.

The possible deviations in the complex modulus of propellant doughs that result from the mixing stage could be corrected if a different value of storage time is employed. A lower time of intermediate storage will provide a more moderate complex modulus for extrusion stage, or by the contrary a higher increment in this theological indicator could be achieved from an increased storage time.

If excessive deviations in rheological properties of mixed compounds are detected, the mixing energy (or mixing time) can serve to correct these variations. In other cases, the extrusion velocity and pressure should be modified to make possible the adequate forming of these materials, although a higher dispersion could be registered in these extrusion parameters and it could also provoke greater fluctuations in the final properties of extruded propellants.

Figures 6 and 7 illustrate the extrusion pressure required for a convenient performance of extrusion and cutting processes, according to the hardness and viscoelastic properties of kneaded compounds to be extruded. As depicted in these figures, a progressive increase of extrusion pressure is needed at the start of each extrusion operation, while an almost uniform pressure level can be maintained during the intermediate time interval, and finally a certain pressure reinforcement is required at the end of extrusion.

According to the results illustrated in Figures 6 and 7, the steady extrusion pressures for experiments with propellant formulation type I are between 140 and 180 bar approximately, while in the case of extrusion tests type II a lower range between 150 and 170 bar is sufficient. In addition, a lower pressure peak is required at the beginning of each extrusion operation for the second series of experiments. The lower levels of extrusion pressure associated to experiments type II correspond to safer extrusion conditions, and so the utilization of this new propellant formulation could be interesting to minimize the safety risks in this forming stage.
On the other hand, the diminished dispersion that is demonstrated in steady extrusion pressures for the second series of experiments can help to obtain more accurate final properties in the propellants manufactured by conventional extrusion. Nevertheless, further experiments should be carried out in order to prove the convenience of using a new propellant formulation as assumed in extrusion tests type II, and the ballistic performance must be also considered.
4. Conclusions

Two series of extrusion experiments were carried out for a triple-base propellant constituted by nitrocellulose, nitroglycerin and nitroguanidine, with two different chemical formulations in terms of the amount of nitroguanidine in the mixture. The effect of several factors such as the rheological properties of mixed material, extrusion velocity and extrusion pressure was studied. The rheological behaviour of propellant doughs to be subject to conventional extrusion was measured before each extrusion experiment by oscillatory testing techniques, and the required extrusion velocity and pressure for the adequate performance of extrusion and cutting processes were evaluated. The relation between the rheological moduli and process parameters during extrusion of multi-base propellants was analysed for both series of extrusion experiments, and the obtained results were employed to deduce guidelines for reducing the variability in extrusion pressure and achieving more uniform physical, geometrical and ballistic properties in the final propellants.

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