Research Article

Le Qi, Zhongliang Ma*, Jiahao Liang, and Zhongliang Xiao

Effect of Solid Additives on the Rheological Property of Nitroglycerin Plasticized Nitrocellulose

https://doi.org/10.1515/arh-2020-0002
Received Jul 02, 2019; accepted Feb 21, 2020

Abstract: The rheological properties of energetic materials comprising nitroglycerin plasticized nitrocellulose were studied using rheological tests in a parallel plate rheometer. The Carreau-Yasuda equation was applied to calculate the zero-shear viscosity, and the dependence of solid additives, temperature and solvent content on zero-shear viscosity was developed. One can study flow characteristics of the energetic materials by observing the zero-shear viscosity instead of the effect of solid additives, temperature and solvent content. Additionally, the relationship between zero-shear viscosity and additives concentration was studied. The Kissinger-Akahira-Sunose (KAS) method was used to obtain the viscous flow activation energy, and the equation to describe the relationship between solid additives concentration and viscous flow activation energy was represented. The Zero-Shear Viscosity (ZSV) test showed that temperature was the predominant effect on the ZSV value at low solvent content, as the concentration of solid additives increased, the ZSV value decreased at low solvent content but increased at high one, however, there is an opposite trend when graphene concentration is above 0.1%. The viscous flow activation energy showed different changing trends with solid concentration that increased at different solvent content. The master curves were obtained by Time-Temperature Equivalence Principle, the viscosity prediction model has been established and showed a good agreement with the experimental data, compared with the test results, the viscosity prediction model is more accurate at low temperature (15°C-25°C). The obtained knowledge of the different equations will form a contribution to the research on extrusion process of this energetic material containing Cyclotrimethylenetrinitramine (RDX) and graphene, and the results obtained by this research have certain practical significance of the extrusion process for this energetic material.

Keywords: Rheometer, Zero-shear viscosity (ZSV), Viscous flow activation energy, Carreau-Yasuda equation, master curve

1 Introduction

Energetic materials can be defined as metastable materials with high energy density containing a high amount of stored chemical energy that can be released. Nitrocellulose (NC) is an important energetic material for some specific applications, such as explosive and propellant. Its combination with nitroglycerin (NG) makes it possible for a broader range of applications [1–4]. Mixtures of NC and NG show good performance in terms of thermal stability and energy performance [5]. Extrusion molding is the preferred method for processing mixtures of NC and NG, and numerous works have been completed to study the process [6, 7]. While most previous works have studied the process from the extrusion step to forming, only a few studies have focused on the flow properties of the materials. Rheology is affected by factors such as temperature, shear rate and the concentration of additives. In order to explore the relationship between rheological properties of materials and these factors during extrusion, rheological method is used to investigate the viscosity change of this material during the extrusion process.

While apparent viscosity of a NC and NG mixture, as a non-Newtonian fluid, is one of the important factors in the operability of the extrusion process, for solid-like energetic materials it is in most instances replaced by complex viscosity [8–10]. The relationship between temperature and viscosity is very well described by the Arrhenius equation which has been shown to be valid for a broad
Effect of Solid Additives on the Rheological Property of Nitroglycerin Plasticized Nitrocellulose

range of non-Newtonian fluids and solid-like (viscoelastic) fluids. The Zero-shear viscosity (ZSV) is a phenomenological parameter that is derived, actually extrapolated, from the shear viscosity as a function of shear rate curves (rheogram). The ZSV value can be calculated from shear rate or strain rate curves. In addition, ZSV value is calculated under the same shear rate or shear stress, while frequency or shear rate scanning are more suitable for solid-like materials. ZSV is a time-independent parameter that reflects the microscopic properties of a fluid and is an important basic parameter for evaluating fluid viscosity and chemical properties of polymer solutions. ZSV is a common parameter for evaluating the end-use of polymers in food, road construction and with other polymeric materials to characterize the flow characteristics during their processing, such as obtaining starch intrinsic viscosity at different temperatures or evaluating the conditions of using asphalt [11–16]. In the evaluation system for the performance of asphalt at different shear rates and temperatures, the zero-shear viscosity is used to replace the previous $G'$/$\tan \delta$ as the evaluation criterion [17]. Some researchers have explored starch solutions at different concentrations, hence the values of ZSV were obtained by the Carreau-Yasuda equation, providing a fundamental background on the starch-ionic liquid rheology [12]. Since zero-shear viscosity is difficult to measure directly, many researchers have proposed different models to calculate the zero-shear viscosity, such as the Power Law, Cross, and Carreau-Yasuda equations. Because the models have different scope of application and precision, one should choose the appropriate model for calculations of ZSV according to their needs [18–25]. Also, the viscous flow activation energy can be used to characterize the dependence of viscosity on temperature, reflecting the viscous flow characteristics of a material and its temperature dependency [26, 27]. From viscosity curves and the viscous flow activation energy, master curves can be obtained. It is possible to obtain flow information over a wide temperature and shear rate range with a small amount of experimental data using master curves, which is very advantageous for material characterization [28–32]. Although beneficial trials showed that master curves give an advantage in studying the rheological properties and processing of materials, little research effort has so far been given to the rheological properties of nitroglycerin plasticized nitrocellulose with solid additives.

1,3,5-trinitro-1,3,5-s-triazine (RDX) is an important explosive of high energy used widely in military applications [33, 34]. As a novel material, graphene is also often used as a solid additive in energetic materials [35, 36]. Both RDX and graphene are important energetic additives for nitroglycerin plasticized nitrocellulose. Adding graphene into a propellant can improve its mechanical properties, such as tensile strength; while adding RDX to a propellant can improve its energy performance. There is no systematic research on the rheological properties of graphene and RDX added to nitroglycerin-plasticized nitrocellulose.

The purpose of this work was to (a) provide a fundamental investigation of the rheological properties of nitrocellulose material plasticized by nitroglycerin, and (b) obtain a viscosity predictive model as an analytical reference for the extrusion process of such material. The ZSV and viscous flow activation energy parameters were investigated to define the flow characteristics of the energetic material, while the master curve was obtained by a rheological method, useful in investigating the viscosity-temperature dependence of the material. The analytical method was chosen to get valuable information to optimize the extrusion process and the end-use properties of the final product.

2 Theoretical background

Viscometry is one of the most widespread methods to investigate and characterize the flow characteristics of energetic materials, yielding significant information for their extrusion process in engineering. Viscometry and rheological measurements have been widely used in investigating engineering and polymeric liquid materials, while more and more works focus on the applications of energetic materials, hence operation of extrusion processes is manifested by their rheological parameters, such as zero-shear viscosity (ZSV) and viscous flow activation energy.

From the rheology point of view, the energetic material in our study belongs to the pseudoplastic fluids class, for which, when flow is very slow, shear viscosity is constant, and its value representing the ZSV. Subsequently, as shear rate increases up to a certain value, viscosity decreases. The flow curves are generally divided into three stages: at the initial phase stage, shear rate approaches zero ($\gamma$ → 0), shear viscosity ($\eta_a$) is constant ($\eta_0$) and $\eta_0$ is the zero-shear viscosity. This stage is called the first Newtonian region. As shear rate increases, the apparent shear viscosity decreases, defining the second shear-thinning region. When shear rate further increases ($\gamma$ → $\infty$), the apparent shear viscosity $\eta_a$ approaches to infinity ($\eta_\infty$) and this stage is called the second Newtonian region. The apparent shear viscosity is the ratio of shear stress to shear rate in a non-Newtonian flow at some shear rate. The second Newtonian region is hard to reach as unstable flow
We selected to use the amplitude sweep test to determine \( \eta \)
Where viscosity-temperature dependence of the material.

The amplitude sweep measurements, the limit of the linear viscoelastic region (LVE region) was first determined. The LVE region indicates the range within which an amplitude sweep test can be carried out without destroying the sample structure and the test can be completed in a short time period. We selected to use the amplitude sweep test to determine the ZSV values of the energetic material samples. Before the amplitude sweep measurements, the limit of the linear viscoelastic region (LVE region) was determined. Considering the high complexity of the viscosity-shear rate curve, the Carreau-Yasuda Equation was used to calculate the ZSV \( \eta_0 \). The Carreau-Yasuda Equation was applied as:

\[
\eta^* (\omega) = \frac{\eta_0 - \eta_\infty}{[1 + (\lambda \omega)^n]^{1/a}} + \eta_\infty
\]

Where \( \eta_0 \) is zero-shear viscosity (ZSV) in Pa·s, \( \eta_\infty \) is the limiting viscosity corresponding to the characteristic time for onset of shear thinning, \( \omega \) is angular frequency in rad/s, \( \eta^* (\omega) \) is complex viscosity in Pa·s, \( \lambda \) and \( a \) are parameters dependent on temperature, \( n \) is the exponent of Ostwald-de Wale law, \( a \) is the non-Newtonian index of the material, and parameters \( a \) and \( n \) are dimensionless.

From the graph of \( \eta^* (\omega) \) as a function of \( \omega \)in a double-logarithmic curve, parameters \( \lambda \), \( a \), \( \eta_\infty \) and \( n \) are calculated to obtain the equation of \( \eta_0 \) at T temperature.

The viscous flow activation energy \( E_\eta \) quantifies the viscosity-temperature dependence of the material. \( E_\eta \) is defined as the minimum energy required to overcome the barrier in the flow process, the displacement from the original position to the nearby “hole”. The relationship between complex viscosity and temperature of soft solids can be described well by Arrhenius Equation,

\[
\eta_0 (T) = K e^{E_\eta / R T}
\]

Where \( \eta_0 (T) \) is ZSV at T temperature, \( K \) is the material constant, \( R \) is the gas constant and \( R=8.314\)·mol\(^{-1}\)·K\(^{-1}\), \( E_\eta \) is the viscous flow activation energy in kJ·mol\(^{-1}\).

Rewritten Eq. 2, one obtains Eq. 3,

\[
\log \eta_0 (T) = \log K + \frac{E_\eta}{2.303 R T}
\]

According to Eq. 3, from the curves of \( \log \eta_0 (T) \) versus \( \frac{1}{T} \), the slope of the curves is \( E_\eta / 2.303 R \), and viscous flow activation energy \( E_\eta \) can be obtained.

The viscosity of the materials depends on temperature and shear rate, and shear rate reflects the flow velocity of materials relative to the radius of the circular passage. Because of the Time-Temperature Equivalence Principle, it can be concluded that the shear viscosity can be converted into a temperature-dependent function at the same amplitude. Therefore, we take the Time-Temperature superposition of the flow curve to form master curves, which can be gathered within a larger temperature and shear rate range. It is a better way to characterize the flow characteristics of energetic materials and optimize their extrusion process.

In order to get the superposition master curves at various temperatures, we set \( T_r \) as a reference temperature, then the flow curves at other temperatures were translated and superimposed to the master curve, the translational distance depended on temperature displacement factor \( a_T \),

\[
a_T = \frac{\dot{\gamma}(T_r)}{\dot{\gamma}(T)}
\]

Where \( \dot{\gamma}(T_r) \) and \( \dot{\gamma}(T) \) are corresponding to the same value of shear rate at \( T_r \) and \( T \), respectively.

According to Arrhenius Equation, \( a_T \) can be written as following,

\[
\log a_T = \log \frac{\eta_0 (T)}{\eta_0 (T_r)} = \frac{2.303 E_\eta}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right)
\]

where \( E_\eta \) is viscous flow activation energy, \( R \) is the gas constant and \( R=8.314\)·mol\(^{-1}\)·K\(^{-1}\), \( T_r \) is the reference temperature and \( T \) is the temperature required for the translation curve.

3 Experimental

3.1 Material

Energetic materials 1# (mass percentage NC (nitrocellulose): 70%, NG (nitroglycerin): 29%, C2 (Dimethyl diphenyldiurea): 0.5%, TEGDN (triethylene glycol dinitrate): 0.5%) and energetic material 2# (NC: 80%, NG: 15%, C2: 2%, TEGDN: 3%) were received from North Xingan Chem. Co.,
Table 1: Samples label and description

| Samples label | Sample description |
|---------------|--------------------|
| 1 mL (or 1.5 mL) RDX 0% | 1 g energetic material, 1 mL (or 1.5 mL) mixed solvent |
| 1 mL (or 1.5 mL) RDX 10% | 1 g energetic material, 1 mL (or 1.5 mL) mixed solvent, 0.1 g RDX |
| 1 mL (or 1.5 mL) RDX 20% | 1 g energetic material, 1 mL (or 1.5 mL) mixed solvent, 0.2 g RDX |
| 1 mL (or 1.5 mL) RDX 30% | 1 g energetic material, 1 mL (or 1.5 mL) mixed solvent, 0.3 g RDX |
| 1 mL (or 1.5 mL) graphene 0% | 1 g energetic material, 1 mL (or 1.5 mL) mixed solvent |
| 1 mL (or 1.5 mL) graphene 0.05% | 1 g energetic material, 1 mL (or 1.5 mL) mixed solvent, 0.0005 g graphene |
| 1 mL (or 1.5 mL) graphene 0.10% | 1 g energetic material, 1 mL (or 1.5 mL) mixed solvent, 0.0010 g graphene |
| 1 mL (or 1.5 mL) graphene 0.15% | 1 g energetic material, 1 mL (or 1.5 mL) mixed solvent, 0.0015 g graphene |

Figure 1: Storage modulus vs. strain of RDX and graphene curves at different content.

energetic material 1# and energetic material 2# were dried at 303 K for 72 h. The mixed solvent (volume fraction 1:0.9, ethyl alcohol and acetone) was 200 mL. EC (Ethyl cellulose) was supplied by North Xingan Chem. Co. and dried for 72 h at 303 K. RDX was obtained from North Xingan Chem. Co., graphene was prepared by Nanjing XFNANO. Co., diameter was 0.5-5 µm, thickness was 0.8-1.2 µm.

3.2 Sample preparation

We mixed 1 g energetic materials with 1 mL or 1.5 mL solvent, respectively and added RDX (graphene) creating samples with mass ratio of 0%, 10%, 20% and 30% (0%,0.05%,0.10 and 0.15%) as shown in Table 1.

3.3 Experimental set-up

The rheological experiments were performed using an Anton Paar Physica MCR 302 rheometer where the geometry was 25 mm in diameter and 1 mm in height. To prevent the material from volatilizing, testing samples were covered with a passive hood enclosure. The amplitude sweep experiments were carried out at 15°C, 25°C, 35°C, with angular frequencies from 0.01 s⁻¹ to 300 s⁻¹, and the strain was determined by the limiting value of the LVE region., Results were the average value of 5 repeated tests.

4 Results and discussion

4.1 LVE region

For evaluating storage modulus against strain curve, it is beneficial to use a log-log plot for the diagrams. The am-
amplitude sweep measurements were conducted at $T = +25^\circ C$ and $\omega = 10$ rad/s. The storage modulus vs. strain of containing RDX and graphene curves are exhibited in Figure 1. The left curve represents data containing RDX and the right curve data containing graphene. It can be found that the storage modulus remained the same under low strain conditions, while the storage modulus decreased rapidly with increasing strain, which indicated that the initial structure of this energetic material was damaged under high strain conditions. The LVE region was depicted on the left handside of $\gamma_L$ in the curves, the range with low strain values. The limit of the LVE region is at $\gamma_L = 0.996\%$ and $\gamma_L = 0.337\%$ for samples containing RDX and graphene, respectively. These values represent the lowest strains hence amplitude sweeps were carried out without destroying the structure of the samples. Consequently, amplitude sweeps experiments were carried out at these corresponding shear rates, respectively.

It is noteworthy that adding either RDX or graphene reduced the storage (elastic) modulus $G'$, but adding RDX and graphene had different tendency to increase storage modulus $G'$. It can be found that the increase of storage modulus caused by adding graphene is greater than that caused by adding RDX. The reason is that RDX can be regarded as a liquid additive, while graphene is a solid additive. Solid additives in dispersions induce higher storage modulus than liquid additives, therefore, the storage modulus of energetic materials containing graphene is higher than that of energetic materials containing RDX. However, when the concentration of graphene is more than 0.15%, because of the lamellar structure and a large specific surface area, graphene is prone to agglomeration and it is not easily dispersed. Uneven dispersion of graphene affects the increase of storage modulus of the energetic materials.

### 4.2 Zero-Shear Viscosity

ZSV as a function of temperature is an important technical material feature for the extrusion process of a propellant: thermal heating during the extrusion process has a great influence on safety, therefore, evaluation of extrusion process safety can be simplified by using the easily measured ZSV. The value of $\eta_0$ were obtained from the Carreau-Yasuda model according to Eq. 1 and Eq. 2. The curves in Figure 2 and Figure 3 show the complex viscosity as a function of angular frequency at different temperatures for energetic material blends containing RDX and graphene, respectively.

Table 3 and Table 5 show the corresponding probability deviations for the ZSV values from Table 2 and Table 4. It can be seen that the deviation of test results did not exceed 5%. The deviation values under high temperature test conditions are slightly higher than in tests under lower temperature because it is difficult to control the concentration of solvent in samples at higher temperatures. The flow curves of different samples were fitted by Eq. 1. This viscoelastic model fits well as the values of R-square were all greater than 0.99. The values of ZSV for different samples were also calculated from Eq. 1 and the results are represented in Table 2 and Table 3. ZSV values are greatly affected by the RDX concentration, temperature and solvent ratio. ZSV values of samples without additives (con-
Table 2: ZSV of energetic materials contenting RDX at different temperature (×10^6 Pa·s, 1mL/g).

|        | 0%      | 10%     | 20%     | 30%     |
|--------|---------|---------|---------|---------|
| 15°C   | 2.88576 | 2.77767 | 2.65310 | 2.48317 |
| 25°C   | 2.82349 | 2.27514 | 1.86911 | 1.57202 |
| 35°C   | 2.74645 | 1.77720 | 1.34051 | 1.10864 |

Table 3: The probability deviation of ZSV corresponding to the test results is shown Table 2 (×10^-4 Pa·s, 1mL/g).

|        | 0%      | 10%     | 20%     | 30%     |
|--------|---------|---------|---------|---------|
| 15°C   | 1.00979 | 4.47695 | 6.63490 | 12.58810|
| 25°C   | 2.81774 | 6.96150 | 10.34090| 1.28152 |
| 35°C   | 5.01443 | 7.20322 | 2.02019 | 0.94678 |

Table 4: ZSV of energetic materials contenting RDX at different temperature (×10^6 Pa·s, 1.5ml/g).

|        | 0%      | 10%     | 20%     | 30%     |
|--------|---------|---------|---------|---------|
| 15°C   | 1.23918 | 1.24978 | 1.57904 | 1.61951 |
| 25°C   | 1.08871 | 1.16101 | 1.47810 | 1.57402 |
| 35°C   | 1.02571 | 1.08973 | 1.42771 | 1.45666 |

Table 5: The probability deviation of ZSV corresponding to the test results is shown Table 4 (×10^-4 Pa·s, 1.5mL/g).

|        | 0%      | 10%     | 20%     | 30%     |
|--------|---------|---------|---------|---------|
| 15°C   | 5.13415 | 7.30129 | 5.09031 | 7.31665 |
| 25°C   | 4.19747 | 4.35684 | 5.11033 | 5.71649 |
| 35°C   | 3.67903 | 4.28484 | 5.25622 | 4.31690 |

The concentration of solvent in 1 mL/g were basically the same at different temperatures because energetic materials had less free volume under the low solvent concentration, and therefore, solvent concentration became the main factor which restricted free volume of energetic materials, and the temperature increase had less influence on its ZSV. It was found that as the temperature increased, ZSV value of samples decreased. The reason is that high temperature intensified the irregular thermal motion of the molecule, hence the molecular spacing increased, and more space caused more “holes” (Free Volume Theory) inside the materials, making the molecule easier to move and therefore, ZSV value of materials decreased. The influence of temperature dominated for the values of ZSV at 1mL/g, but the temperature and RDX concentration have the same degree of influence at 1.5mL/g. Results show that temperature becomes the predominant factor when the solvent content is low. As the Free Volume Theory, solvent consists of small molecular substances, which have more opportunities to perform activities and their end groups have more oscillations and movements. Thus small molecules have more potential free volume than macromolecules. When the temperature increases, there are more “holes” in the high solvent content materials than the low solvent content materials. Therefore, temperature is the predominant influencing factor for the ZSV value when the solvent concentration is low.

When the concentration of RDX increased, the value of ZSV decreased at all temperatures (15°C, 25°C, 35°C) with 1mL/g, however, ZSV value increased with increase in the concentration of RDX at the same temperature (15°C, 25°C, 35°C) with 1.5mL/g. RDX and this mixed solvent are all small molecular substances, and the materials were dissolved by the mixed solvent first. When the solvent concentration was low, the free volume of solvent was not enough to make the energetic materials molecules to move freely, and it needed the added RDX to provide extra free volume, thus, the viscosity of samples decreased when the RDX concentration increased. When the solvent content increased to 1.5mL/g, according to Free Volume Theory, there many spaces between the molecules and the spaces can be regarded as “holes” in molecules. The “holes” of solvent
were sufficient for the samples to have more opportunity to move freely, but the RDX occupied the free volume from solvent, which decreased the free volume of samples. Therefore, as the RDX concentration increased, the viscosity of samples decreased at high solvent content.

Table 7 and Table 9 are the corresponding probability deviation for the ZSV values from Table 6 and Table 8. It can be found that the deviation of test results did not exceed 5%. Because of the electrostatic entanglement of graphene and low graphene concentration in the test, there is some probability deviation in weighing a small amount of graphene, so the probability deviation of some samples is slightly higher. ZSV for energetic materials contenting graphene at different temperature and solvent concentration are shown in Tables 4 and 5. Three different temperature tests were performed at four concentrations. It can be seen that the values of ZSV were decreased at the concentration range from 0.05% to 0.10%, but increased at the 0.15% concentration. When the concentration of graphene was less than 0.10%, the layered structure of graphene reduced the friction between molecules of this energetic materials, and as relative movements are more likely to occur between molecules, viscosity of the samples decreased. However, when the concentration of graphene is above 0.15%, entanglement between graphene molecules occurred, which hinders the movement and slip of neighboring molecular chains. Thus, bulk viscosity increased when the concentration of graphene was at 0.15%. By increasing the solvent concentration to 1.5g/mL, the viscosity of samples increased as the graphene concentration increased. Because of excess solvent, the graphene in the sample was dispersed evenly because the graphene solids reduce the fluidity of energetic materials, the viscosity of samples increased with the graphene concentration up to the concentration of 0.15%.

4.3 ZSV-concentration dependence

In order to further analyze the effect of RDX concentration on ZSV, $\eta_0$ was observed for different RDX concentrations and temperature, as shown in Figure 4. It can be observed...
that different solvent concentration resulted in opposite change trend with increasing RDX concentration for \( \eta_0 \). For a solvent ratio of 1 mL/g, it can be observed that \( \eta_0 \) decreased when the RDX concentration increased, and the ZSV value of the sample at 35°C decreased more than others. This implies that the effect of RDX concentration on ZSV is more impactful at high temperatures. Because of higher temperature, according to Free Volume Theory, it leads to more free volume. However, when the solvent ratio is 1.5 mL/g, the value of \( \eta_0 \) increased a little as the RDX concentration increased, and the trend of change in ZSV value was the same. Because graphene was dispersed into the solvent, its molecule occupied some free volume and the values of \( \eta_0 \) showed an upward trend, its molecule occupied some free volume and the values of \( \eta_0 \) showed an upward trend.

From Figure 5, ZSV value of samples with increasing graphene concentration represented a trend of decreasing first and then rising solvent concentration to 1 mL/g, the ZSV value varied most at 35°C. Because of the Free Volume Theory, the change in \( \eta_0 \) at high temperature is more pronounced. When the graphene concentration is above 0.1%, the graphene molecules appear tangled, and the viscosity of the samples increased. When the proportion of solvent increased to 1.5 mL/g, it increased the free volume, therefore, the viscosity of samples increased with the graphene concentration raising. Because of more free volume, the ZSV increased when graphene concentration increased.

### 4.4 Viscous Flow Activation Energy

The KAS lines for ZSV of samples at different concentration of RDX are showed in Figure 6. The left figure is the \( \lg[\eta_0/(\text{Pa·s})] \) against \( 1/T \) at different concentration of RDX in solvent concentration of 1 mL/g, and the right figure is the \( \lg[\eta_0/(\text{Pa·s})] \) against \( 1/T \) at different concentration of RDX in solvent concentration of 1.5 mL/g Figure 8 shows that the experimental dependence of \( \lg[\eta_0/(\text{Pa·s})] \) vs. \( 1/T \) can be considered linear within the experiment errors (R-Square R > 0.99, The degree of linear fitting correlation indicates that the degree of agreement between practice and theory is well). The slope value of each curve is equal to the \( E_\eta \) of its corresponding sample, the results are represented in Table 6. It can be observed that \( E_\eta \) increased with the concentration of RDX, and the material constant (K) decreased with the concentration of RDX.

The values of \( E_\eta \) not only reflected the difficulty of material flow, but more importantly demonstrated the temperature sensitivity of the changes in material viscosity. As the concentration of RDX increased from 10% to 30%, the value of \( E_\eta \) increased by 9 to 16 times at solvent concentration is 1 mL/g. However, \( E_\eta \) decreased as the addition level of RDX increased to 1.5 mL/g. \( E_\eta \) is mainly related to the structure of molecular chains of the polymers; when the concentration of solvent is low, RDX is not dissolved by the solvent, therefore, the chain of RDX molecules exhibit high polarity, and the value of \( E_\eta \) was higher than the value in the case of 1.5 mL/g, so the values of \( E_\eta \) increased with RDX concentration. However, when the solvent concentration was over 1.5 mL/g, most of RDX dissolved and the RDX molecular chains showed flexibility therefore, the value of \( E_\eta \) was comparatively low, and it decreased with the RDX concentration.

\[
E_\eta = E_\eta (0) + bC^n
\]
Table 10: Viscous flow activation energy and material constant of energetic materials containing RDX at different solvent concentration.

| Sample | 1 mL/g | 1.5 mL/g |
|--------|--------|----------|
|        | $E_\eta$ (kJ·mol$^{-1}$) | Fitted value | $E_\eta$ (kJ·mol$^{-1}$) | Fitted value |
| 0%     | 1.82357 | 1.82357 | 6.98717 | 6.98717 |
| 10%    | 16.4607 | 16.63714 | 5.06154 | 5.05109 |
| 20%    | 25.2010 | 24.42969 | 4.29470 | 4.33496 |
| 30%    | 29.8042 | 30.41417 | 3.85431 | 3.82390 |

Figure 6: $\lg[\eta_0/(\text{Pa} \cdot \text{s})]$ vs. $1/T$ at different concentration of RDX.

As the value of $E_\eta$ show in Table 10, with the concentration of RDX from 0% to 30%, we can fit a correlation equation between $E_\eta$ and concentration of RDX. Linear fitting correlation is greater than 0.96, and the equation is showed below:

1 mL/g: $E_\eta (C) = 1.82357 + 102.83386 \times C^{0.65791}$

1.5 mL/g: $E_\eta (C) = 6.98717 - 8.80306 \times C^{0.48272}$

In the above equations, $n < 1$, which implied that, with respect to rheology, tested samples were pseudoplastic (shear-thinning) fluids. The value of parameter $b$ in Eq. 6 was negative when the solvent ratio was 1.5 mL/g, which shows that when the solvent concentration is different, as RDX concentration was increased, the viscous flow activation energy had the opposite change trend.

The values of viscous flow activation energy with different RDX content are listed in Table 10. $E_\eta$ increased with RDX concentration when solvent concentration was 1 mL/g, but when the solvent concentration increased to 1.5 mL/g, the values of $E_\eta$ decreased. Viscous flow activation implied viscosity-temperature dependence of materials. Therefore, when the solvent concentration was 1 mL/g, the viscosity-temperature interdependence increased with raised RDX concentration, which means that the influence of temperature on viscosity increased with the increased RDX concentration. However, the value of $E_\eta$ significantly decreased when the RDX concentration increased over 1.5 mL/g, the effect of temperature on viscosity slightly decreased with increasing RDX concentration. $E_\eta$ significantly changed with RDX concentration from 0% to 20%, but there were less changes in $E_\eta$ with RDX concentration from 20% to 30%.

Data from Table 11 were used to plot $\lg[\eta_0/(\text{Pa} \cdot \text{s})]$ against $1/T$, hence the linear correlation coefficients of obtained curves in Figure 7 were greater than 0.99. For samples containing graphene, Eq. 6 is not applicable to the fitting of the viscous flow activation energy. The viscous flow activation energy of graphene-containing samples depicted two stages when graphene concentration increased. In the case of less solvent, when the graphene content was less than 0.1%, $E_\eta$ increased with graphene concentration; when the graphene content was greater than 0.1%, $E_\eta$ de-
Table 11: Viscous flow activation energy and material constant of energetic materials containing graphene at different solvent containing.

| Sample | 1 mL/g $E_\eta$ (kJ·mol$^{-1}$) | Fitted value | 1.5 mL/g $E_\eta$ (kJ·mol$^{-1}$) | Fitted value |
|--------|-------------------------------|--------------|-------------------------------|--------------|
| 0%     | 1.82357                      | 1.82357      | 6.82270                       | 6.82270      |
| 0.05%  | 22.06306                     | 23.88649     | 6.77904                       | 6.77903      |
| 0.10%  | 25.39753                     | 27.25907     | 5.60264                       | 5.60263      |
| 0.15%  | 23.79300                     | –            | 8.66944                       | –            |

Results show that the relationship between $E_\eta$ and concentration of graphene (C) is linear, with a fitting correlation greater than 0.97, and it is consistent with previous test results. However, the predictive equation for the viscous flow activation energy is not suitable for material systems with high graphene concentration (i.e., graphene concentration > 0.1%). The reason is that, because of graphene molecular entanglement at high graphene content, the viscosity of the energetic system becomes very high and the material is unprocessable.

4.5 Master curves

According to the time-temperature equivalency principle, flow curves can be transformed to obtain master curves at a reference temperature. Figures 8 and 9 are the master curves of samples containing RDX and graphene at 25°C, respectively. The master curves in Figure 8 with different RDX concentrations are substantially parallel lines; the master curves obtained by moving a set of curves along a line with a slope of $-1$ and superimposing them. The
Table 12: Test value and calculated values of ZSV at different concentrations of RDX.

|       | 10% RDX             | 20% RDX             |
|-------|---------------------|---------------------|
|       | \( \alpha_f \)     | Fitted value        |
|       | \( \eta_0(C) / \text{Pa·s} \) | Fitted value        |
| 15°C  | 6.4923              | 2.8058 \times 10^6  |
|       | 2.7777 \times 10^6  | 2.6531 \times 10^6  |
| 35°C  | 0.1750              | 1.7789 \times 10^6  |
|       | 1.7772 \times 10^6  | 1.3405 \times 10^6  |

Figure 8: Master curves of different RDX concentration at reference temperature is 25°C.

The viscosity prediction model containing graphene is as follows

\[
\log \frac{\eta^\gamma(c)}{\eta_0} = [1 + f(C) \cdot \log(\gamma \cdot \eta_0)]^{-\frac{1}{\alpha}}
\]

Where \( f(C) = 133.93329 - 319956.28667 \times C + 5.86309E8 \times C^2 - 2.61461E11 \times C^3 \), \( C \) represents the concentration of graphene.

By the same method as above, we can obtain master curves of graphene-containing energetic materials. Fitted curves are shown in Figure 9, and according to calculated ZSV values in Table 13, we can find that the deviation between the results of predicted model and the results of test is less than 5% at 15°C. However, deviation is greater than 30% at 35°C. The main reason is that the high temperature increased the free volume of nitroglycerin, the viscosity of nitroglycerin plasticized nitrocellulose is reduced substantially at 35°C, and the main substance affecting the viscosity is nitroglycerin instead of graphene. Therefore, we only recommend this predictive model for lower temperature ranges. Although there are certain limitations, this viscosity prediction model using at high temperature is slightly lower than that at low temperature and predicted results are consistent with the trendlines of experimental results. The master curves of materials containing graphene can

...
Table 13: Test value and calculated values of ZSV at different concentrations of graphene.

|        | 0.05% graphene |          | 0.10% graphene |          |
|--------|----------------|----------|----------------|----------|
|        | $\alpha_T$ $\eta_0$ (C) / Pa·s | Fitted value | $\alpha_T$ $\eta_0$ (C) / Pa·s | Fitted value |
| 15°C   | 2.0365 | 2.5924×10⁶ | 2.4959×10⁶ | 2.2676 | 2.4359×10⁶ | 2.5138×10⁶ |
| 35°C   | 0.5142 | 1.4247×10⁶ | 1.8982×10⁶ | 0.5651 | 1.2391×10⁶ | 1.8257×10⁶ |

Figure 9: Master curves of different graphene concentration at reference temperature is 25°C.

be used to predicted the viscosity-temperature trend with only a certain precision.

5 Conclusions

We studied the rheological properties of nitrocellulose plasticized by nitroglycerin with different solid additives. The zero-shear viscosity of the energetic materials containing RDX and graphene is described by the Carreau-Yasuda Equation. Results showed that the values of ZSV initially decreased, then increased with more additives under low solvent concentration. When the content of graphene was 0.1%, the ZSV values reached its lowest value over the range of different temperatures tested. According to ZSV test, both temperature and solvent content have effects on ZSV values, and temperature becomes the predominant for the ZSV values at low solvent content. As the concentration of RDX (or graphene) increased, ZSV decreased at low solvent content but increased at high one, however, when the concentration of graphene is above 0.1%, there is an opposite trend. The KAS method was used to yield the viscous flow activation energy. By studying the viscous flow activation energy, when the RDX content increased, $E_\eta$ significantly increased at low solvent content but decreased at high solvent content. The value of $E_\eta$ significantly changed with RDX content from 0% to 20%, but there were less changes in $E_\eta$ with RDX content from 20% to 30%. As the graphene concentration increased, $E_\eta$ demonstrated a trend of first increasing, then decreasing in low solvent content, however, $E_\eta$ exhibited the opposite trend at high solvent content.

Master curves were established by time-temperature equivalency principle, compared with higher RDX concentration materials, this predictive equation is more accurate at low RDX concentrations, and master curves can be used to predict the viscosity-temperature trend of energetic material containing RDX with high precision. This has certain practical significance for the extrusion process of research nitroglycerin plasticized nitrocellulose containing RDX. Also, master curves for graphene were established, however, this predictive equation is more accurate at low temperature range (15°C-25°C) and when the deviation between the results of predicted model and the results of test is less than 5% at 15°C but the deviation is greater than 30% at 35°C. This equation had good agreement with calculations based on experimental results. The viscous flow activation energy $E_\eta$ was applied to obtain the temperature displacement factor $\alpha_T$, according to Arrhenius equation. In the future research, we will use the viscosity prediction model into the actual extrusion molding process, and conduct numerical simulation of the viscosity change of energy-containing materials.

Conflict of Interests: All the authors (Le Qi, Zhongliang Ma, Jiahao Liang and Zhongliang Xiao) declare that they have no conflict of interest. No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication.

References

[1] Baker F S, Privett G J. Dynamic mechanical studies of nitrocellulose/nitroglycerine mixtures[J]. Polymer, 1987, 28(7):1121-1126.
[2] Hsu, P C, Hust, et al. Effect of aging on the safety and sensitivity of nitroglycerin/nitrocellulose mixtures[J]. Office of Scientific & Technical Information Technical Reports, 2013.

[3] Louden J D, Kelly J,Phillipson J. Methylenecentralite concentration profiles in monoperforated extruded nitrocellulose and nitrocellulose/nitroglycerine propellant grains by Raman microspectroscopy[J]. Journal of Applied Polymer Science, 2010, 37(11):3237-3250.

[4] SjöBom R A, Oresten H G. Separation and quantitation of nitrocellulose, nitroglycerin, diethylphthalate, and centralite in double-base powders[J]. 1980, 5(4):105-110.

[5] Ho SY, Fong CW. Relationship between impact ignition sensitivity and kinetics of the thermal decomposition of solid propellants[J]. Combustion & Flame, 1989, 75(2):139-151.

[6] Isayev AI, Miodic M T J. Self-Reinforced melt processible polymer composites: Extrusion, compression, and injection molding[J]. Polymer Composites, 1987, 8(3):158-175.

[7] Yu J C, Chen X X, Hung T R, et al. Optimization of extrusion blow molding processes using soft computing and Taguchi’s method[J]. Journal of Intelligent Manufacturing, 2004, 15(5):625-634.

[8] Cross M M. Rheology of Non-Newtonian Fluids: A New Flow Equation for Pseudoplastic Systems[J]. Journal of Colloid Science, 1965, 20(5):417-437.

[9] Li S, Jarvela P K, Jarvela P A. A comparison between apparent viscosity and dynamic complex viscosity for polypropylene/maleated polypropylene blends[J]. Polymer Engineering & Science, 2010, 43(1):18-23.

[10] Schuch H. Application of a blending rule for the complex viscosity of polymer melts[J]. Rheologica Acta, 1988, 27(4):384-396.

[11] Mckenna G B, Hadziioannou G, Lutz P, et al. Dilute solution characterization of cyclic polystyrene molecules and their zero-shear viscosity in the melt[J]. Macromolecules, 1987, 20(3):498-512.

[12] Liu W, Budtova T. Dissolution of unmodified waxy starch in ionic liquid and solution rheological properties[J]. Carbohydrate Polymers, 2013, 93(1):199-206.

[13] Pishvai M, Grallait C, Mckenna T F, et al. Experimental investigation and phenomenological modeling of the viscosity-shear rate of bimodal high solid content latex[J]. Journal of Rheology, 2007, 51(1):1-51.

[14] Benbow J J, Lamb P. New aspects of melt fracture[J]. Polymer Engineering & Science, 1963, 31(7):1-7.

[15] Stadler F J, Piel C, Kaschta J, et al. Dependence of the zero-shear rate viscosity and the viscosity function of linear high-density polyethylenes on the mass-average molar mass and polydispersity[J]. Rheologica Acta, 2006, 45(5):755-764.

[16] Takahashi Y, Isono Y, Noda I, et al. Zero-shear viscosity of linear polymer solutions over a wide range of concentration[J]. Macromolecules, 1985, 18(5):1002-1008.

[17] Morea F, Aagnusdei J O, Zerbino R. Comparison of methods for measuring zero-shear viscosity in asphalts[J]. Materials & Structures, 2010, 43(4):499-507.

[18] Boyd J, Buick J M, Green S. Analysis of the Casson and Carreau-Yasuda non-Newtonian blood models in steady and oscillatory flows using the lattice Boltzmann method[J]. Physics of Fluids, 2007, 19(9):1311-96.

[19] Padmanabhan K A. Generalisation of activation energy and viscosity relations for superplastic flow[J]. Physica Status Solidi A, 1974, 22(1).

[20] Nobile M R, Bove L, Somma E, et al. Rheological and structure investigation of shear-induced crystallization of isotactic polypropylene[J]. Polymer Engineering & Science, 2010, 45(2):153-162.

[21] Park C K, Noh M H, Park T H. Rheological properties of cementitious materials containing mineral admixtures[J]. Cement and Concrete Research, 2005, 35(5):842-849.

[22] Huspler J D, Ashare E, Holmes J A. Rheological Properties of Three Solutions. Part I. Non km newtonian Viscosity, Normal Stresses, and Complex Viscosity[J]. Transactions of the Society of Rheology, 2000, 12(2):159-179.

[23] Cross M M. Rheology of Non-Newtonian Fluids: A New Flow Equation for Pseudoplastic Systems[J]. Journal of Colloid Science, 1965, 20(5):417-437.

[24] Kumar R U, Reddy P R, Sitaramaraju A V. Role of Viscosity in Hydro-forming Process[J]. Materials Today Proceedings, 2017, 4(2):790-798.

[25] Harboe S, Modigell M. The Influence of Particle Size on Viscosity in Thixo Material[J]. Key Engineering Materials, 2012, 506:333-338.

[26] Ojoivan, Michael I. About activation energy of viscous flow of glasses and melts[J]. MRS Proceedings, 2015, 1757:mrsf14-1757-uu01-10.

[27] Kamimura Y, Kurumada K I, Asaka K, et al. Evaluation of activation energy of viscous flow of sol–gel derived phenyl-modified silica glass[J]. Journal of Non-Crystalline Solids, 2006, 352(30-31):0-3178.

[28] Becker V, Briesen H. A master curve for the onset of shear induced restructuring of fractal colloidal aggregates[J]. Journal of Colloid and Interface Science, 2010, 346(1):32-36.

[29] Lyngaae-Jorgensen J. A phenomenological master curve for viscosity - structure data for two phase polymer systems in simple shear flow (p 610-613) [J]. Polymer Engineering & Science, 2010, 23(11):610-613.

[30] Nakajima N. Examination of a master curve method of characterizing steady-state flow of polymers[J]. 1970, 14(10):2643-2656.

[31] Carrubba V L, Brucato V, Piccarolo S. Isotactic polypropylene solidification under pressure and high cooling rates. A master curve approach[J]. Polymer Engineering and Science, 2000, 40(11):2430-2441.

[32] Chin N L, Chan S M, Yusof Y A, et al. Modelling of rheological behaviour of pummeo juice concentrates using master-curve[J]. Journal of Food Engineering, 2009, 93(2):134-140.

[33] Wang D X, Chen S S, Li Y Y, et al. An Investigation into the Effects of Additives on Crystal Characteristics and Impact Sensitivity of RDX[J]. Journal of Energetic Materials, 2014, 32(3):184-198.

[34] Agrawal P M, Rice B M, Sorescu D C, et al. Models for predicting solubilities of 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazine (RDX) in supercritical CO2: isothermal-isobaric Monte Carlo simulations[J]. Fluid Phase Equilibria, 2001, 187(4):139-153.

[35] Youeda L, Yu L, Dongge Z, et al. Fabrication of Natural Rubber/Chemically Reduced Graphene Oxide Nanocomposites and Nuclear Radiation Resistant Behavior[J]. Chemical Journal of Chinese Universities, 2016, 37(7):1402-1407.

[36] Xu J Z, Chen C, Wang Y, et al. Graphene Nanosheets and Shear Flow Induced Crystallization in Isotactic Polypropylene Nanocomposites[J]. Macromolecules, 2011, 44(8):2808-2818.