Rheological Behavior of High Solid Content Propellant Substitutes in Extrusion Process Assisted with SC-CO$_2$

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Abstract：In order to solve the problem of high viscosity of high solid content propellants，supercritical carbon dioxide（SC-CO$_2$）has been used as a plasticizer to improve its rheological behavior. The in-line viscosity of the CA/CaCO$_3$ solution was measured by a slit die rheometer during the extrusion process assisted with SC-CO$_2$，and the Power law was used to describe the rheological behavior of CA/CaCO$_3$ and CA/CaCO$_3$/SC-CO$_2$ solutions. Polyflow was utilized to model the dispersive mixing properties of the CA/CaCO$_3$/SC-CO$_2$ solutions. Results show that with the presence of SC-CO$_2$，the viscosity and pressure of the CA/CaCO$_3$ solution decreases significantly. And the viscosity coefficient of the CA/CaCO$_3$ solution at 50℃ decreases by 26.00%，while its non-Newtonian index increases by approximately 16.67%. As the extrusion temperature increases，the viscosity of the CA/CaCO$_3$/SC-CO$_2$ solution decreases，and its shear viscosity is less sensitive to temperature at higher shear rate. According to this simulation results，when the CA/CaCO$_3$/SC-CO$_2$ solution is subjected to the maximum shear stress，the maximum probability density increases by 20.63% at 50 ℃，which confirms that SC-CO$_2$ improves the dispersion mixing properties of the CA/CaCO$_3$ solution.
Key words：High solid content propellant；Supercritical carbon dioxide；Rheological behavior；Dispersive mixing properties.
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1   Introduction

In recent years，reducing sensitivity without decreasing the energy of the propellant has been the main aim of research and development. Therefore，low vulnerability ammunition（LOVA）propellants were developed based on the formulation of solid-filling hexogen（RDX）and non-energetic binders[1-2]. These types of high solid content propellants are normally produced using inefficient and potentially dangerous batch processes that are prone to produce propellants of variable quality [3].

Screw extrusion technology has great potential in the automated industrial production of high solid content propellants. Its major advantages include higher production capacity，fewer operational handling steps and more uniform products. Meanwhile，the automated extrusion process can achieve human-machine isolation，thereby overcoming the harm of energetic/toxic chemicals to operators. Rheological studies of propellants in the extrusion process have been conducted，including safety and capabilities of intensive mixing，which can guide the processing of propellants and identify conditions that lead to improved propellant quality and productivity[4-6].

However，due to the high viscosity of the high solid content propellant，there is a great potential safety hazard in the extrusion process. Meanwhile，complex rheological properties should be found to improve the processes oriented to their manufacture. Organic solvents and energetic plasticizers have been used to improve the rheology of propellants[7]. Nevertheless，these organic solvents are often toxic，environmentally unfriendly and leave residues in the

product，which affects the performance of the final product. Besides，the addition of energy plasticizer increases processing risks. It is important to find an ideal plasticizer to improve the rheology of high solid content propellants in extrusion process.

The application of supercritical fluid（SCF）technology provides an easily removable solvent system that exhibits gas-like diffusivity，liquid-like density and low viscosity，and is suitable for extrusion process[8]. The high diffusion rate of supercritical carbon dioxide（$SC\text{-}CO_2$）enables it to penetrate into the polymer matrix faster than liquid solvents，which reduces the viscosity and promotes faster transport of dissolved solutes throughout the polymer matrix[9-11]. Lee[12] found that $SC\text{-}CO_2$ had a measurable effect on the clay dispersion in the polymer matrix during the extrusion process，accordingly improving its rheology. Besides，Ding[13-15] did a lot of work for gun propellant substitutes assisted with $SC\text{-}CO_2$ in extrusion processing，which proved that the addition of $SC\text{-}CO_2$ lowered the viscosity of propellant substitutes. Indeed，the presence of $SC\text{-}CO_2$ introduced into the barrel of the single-screw extruders improves the performance of the high solid content propellant extrusion process，which is feasible and has enormous potential for development.

LOVA propellants based on the use of solid filler RDX and cellulose acetate（CA）have been proposed as high- energy propellants with good safety[1]. Moreover，RDX is a powerful explosive that is manufactured using extrusion processes that poses a significant explosive or fire hazards. Because the physical properties and surface morphology of calcium carbonate（$CaCO_3$）are similar to those of RDX，they are all white solids and hardly soluble in water and alcohol，so they can be well dispersed in the CA matrix[16-17]. In addition，$CaCO_3$ is often used as a filler in cellulose processing[18]. Therefore，$CaCO_3$ can be considered as a benign replacement for RDX when optimizing extrusion processes.

In this work，experiments were performed by using a slit die rheometer to measure the viscosity of the $CA/CaCO_3$ and $CA/CaCO_3/SC\text{-}CO_2$ solutions dur-

ing extrusion process. Computer modeling was also performed by the modeling software Polyflow to further investigate the rheological and dispersive mixing properties of high solid content propellant substitutes during extrusion. In both methods，the effects of temperature and $SC\text{-}CO_2$ on the dispersion mixing properties and viscosity of the solutions during extrusion process were considered. In the mixture systems，$CaCO_3$ was used as a solid filler，CA was used as an inert propellant binder，and $SC\text{-}CO_2$ was used as a plasticizer. The effects of $SC\text{-}CO_2$ on solution viscosity were studied. Finally，the optimal extrusion process temperature was found.

2　Experimental

2.1　Materials and Devices

CA particles were provided by Xian North Huian Chemical Industry Ltd. $CaCO_3$（analytically pure，AR），ethanol（analytically pure，AR）and acetone（analytically pure，AR）were purchased by Sinopharm Chemical Reagent Ltd. Industrial CO_2（purity≥99.9%）was provided by Nanjing Wenda Special Gas Ltd.

The kneading machine was supplied by Jiangsu Guomao Reducer Group Ltd. The syringe pump（260D）was purchased from American Teledyne ISCO Ltd. The single screw extruder（the length-diameter aspect ratio of the screw is 36）and the slit die rheometer were purchased from Nanjing Yizhong Machinery Ltd.

2.2　Viscosity Measurement

CA（mass fraction of 60%）and $CaCO_3$（mass fraction of 40%）particles were preliminarily mixed together in an acetone/ethanol（1∶1）mixed solvent for 40 minutes at 35 ℃ using the kneading machine. The ratio of the volume of the mixed solvent to the mass of $CA/CaCO_3$ was 1.20 ml·g^{-1}. Then the $CA/CaCO_3$ solution was fed into a single-screw extruder（screw speed of 6 r·min^{-1} to 14 r·min^{-1}），while $SC\text{-}CO_2$ was introduced into the barrel at a constant flow rate of 0.01 mL·min^{-1}. Constant injection pressure was used to maintain above 15 MPa（higher than the critical pressure of $SC\text{-}CO_2$），and processing temperature was used to keep above 40 ℃（high-

er than the critical temperature of SC-CO$_2$). The shear forces generated by the screw resulted in the efficient dissolution of SC-CO$_2$ into the CA/CaCO$_3$ solution phase，then the pressure and the volumetric flow rate of CA/CaCO$_3$/SC-CO$_2$ mixture were measured by a slit die rheometer（Fig.1）.
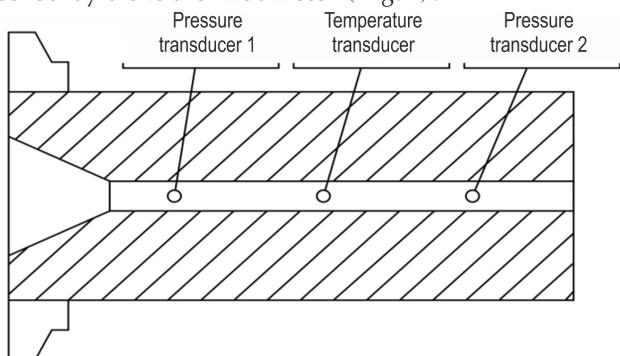
Fig.1　Schematic diagram of the slit die rheometer

Based on the pressure values and the volumetric flow rate，the calculation of shear viscosity of the CA/CaCO$_3$/SC-CO$_2$ solution was calculated by following Equation [19].

The shear stress（τ_w）of the CA/CaCO$_3$/SC-CO$_2$ solution on the wall of the slit die rheometer was determined from the Equation（1）:

$$\tau_w = \frac{\Delta P \cdot H}{2L} \tag{1}$$

where H（0.002 m）is the height of the slit die rheometer，L（0.130 m）is the length between the pressure transducers，and ΔP is the pressure drop between the pressure transducers，kPa.

The shear rate（$\dot{\gamma}$）of the CA/CaCO$_3$/SC-CO$_2$ solution at the wall of the slit die rheometer was evaluated using the Equation（2）:

$$\dot{\gamma} = \frac{6Q}{W \cdot H^2}\left(\frac{2a+1}{3a}\right) \tag{2}$$

where Q is the volumetric flow rate，cm$^3 \cdot$s^{-1}，W（0.020 m）is the width of the slit die rheometer，a is the power law index obtained from the slope of the linear plots between lg（τ_w）and lg（$\dot{\gamma}$）using Equation（3），$(2a+1)/3a$ is the Rabinowitsch correction factor，and it compensates the loss of shear rate between Newtonian fluid and shear-thinning fluid.

$$a = \frac{d\left[\lg\left(\tau_w\right)\right]}{d\left[\lg\left(6Q/WH^2\right)\right]} \tag{3}$$

Therefore，based on Equations（1−3），the actual shear viscosity（η）of the CA/CaCO$_3$/SC-CO$_2$ solution can be calculated by Equation（4）:

$$\eta = \frac{\tau_w}{\dot{\gamma}} \tag{4}$$

Due to the ratio of W/H is 10，the measurement errors caused by the bondary effect of slit decrease to less than 5%.

3　Numerical Simulation

3.1　Control and Constitutive Equations

Polyflow provides users with the ability to analyze mixing of material[20]. The flow field inside the material flow in the screw section was simulated by Polyflow[21−22]. After the flow field was computed，a mixing task was executed by using the mixing module program（based on particle-tracking technology）. Then，the mixing characteristic parameters inside the flow domain were analyzed using Polystat statistical module to evaluate the probability and density of the probability functions that corresponding to the maximum shear stress levels of the dispersion mixing processes respectively.

According to the theories of rheology，combining the screwing process and the viscoelastic characteristics of the propellant materials，the basic assumptions are as follows：incompressible polymer fluid is considered to be non-Newtonian properties，generating isothermal，laminar and no-slip flow conditions near the extruder walls. Ignoring the inertia and gravity components，the following control Equations（5−7）can be used to simulate flow performance[23]:

Continuity equation:

$$\nabla \boldsymbol{V} = 0 \tag{5}$$

Momentum equation:

$$\rho \, d\boldsymbol{V}/dt = -\nabla \boldsymbol{p} + \nabla \tau \tag{6}$$

Energy equation:

$$\rho c_v \, dT/dt = -\nabla \boldsymbol{q} + \tau \nabla \boldsymbol{V} \tag{7}$$

where $\boldsymbol{V}$ is the volume velocity vector，ρ is the fluid density，τ is the stress tensor，$\boldsymbol{p}$ is the pressure，T is the fluid temperature，c_v is the constant volume spe-

cific heat capacity of the fluid, q is the heat flux vector, and ∇ is the differential operator.

CA/CaCO$_3$ and CA/CaCO$_3$/SC-CO$_2$ solutions exhibit the characteristics of pseudoplastic fluids. The Power model based on the constitutive Equation (8) is the ideal model that describes the relationship between the shear viscosity (lnη) and the shear rate (ln$\dot{\gamma}$):

$$\eta = K(\lambda\dot{\gamma})^{n-1} \tag{8}$$

where η is the viscosity, k·Pas, K is the viscosity coefficient, kPa·s^n, λ is the relaxation time, $\dot{\gamma}$ is the shear rate, s^{-1}, and n is the non-Newtonian index.

3.2 Rheological Parameters

The rheological parameters of the propellant substitutes were obtained from the experiment of the viscosity measurements and Equation (8), shown in Table 1. These experimental datas was used as parameters to simulate dispersion mixing.

Table 1 Rheological parameters of the propellant substitute

solution	T / ℃	K / kPa·s^n	n
CA/CaCO$_3$	50	34.00	0.18
	40	37.43	0.18
	45	30.45	0.19
CA/CaCO$_3$/SC-CO$_2$	50	25.16	0.21
	55	21.01	0.21
	60	16.50	0.24

3.3 Geometric Model

During extrusion process of CA/CaCO$_3$ solution assisted with SC-CO$_2$, the material flow of the screw section has an important influence on the plasticizing process between CO$_2$ fluid and material. Therefore, this paper mainly focuses on the numerical simulation of the material flow in the screw section. A schematic diagrams of the single-screw and fluid channel used in this paper were shown in Fig.2. The
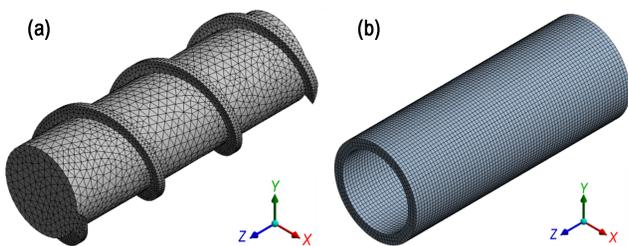
Fig.2 Schematic diagrams of (a) single-screw and (b) flow channel

length, diameter and gap of the single-screw are 78 mm, 30 mm, 26 mm, respectively. The groove depth, outer diameter and inner diameter of fluid channel are 3 mm, 30 mm, 24 mm, respectively.

4 Results and Discussion

4.1 Rheological Behaviors of CA/CaCO$_3$/SC-CO$_2$ Solution

The in-line rheological behavior of the CA/CaCO$_3$ and CA/CaCO$_3$/SC-CO$_2$ solutions can be calculated from the above Equations (1) to (4) and data measured by the slit die rheometer. Fig.3 shows the flow curves [ln shear rate (ln$\dot{\gamma}$) vs ln shear viscosity (lnη)] of the CA/CaCO$_3$ and CA/CaCO$_3$/SC-CO$_2$ solutions at 50 ℃ with screw speeds ranging from 6 r·min^{-1} to 14 r·min^{-1}. It was found that the viscosity level decreased with increasing shear rate. Since ln$\dot{\gamma}$ has a significant linear relationship with lnη, it demonstrates that the rheological behavior of both CA/CaCO$_3$ and CA/CaCO$_3$/SC-CO$_2$ solutions can be described by the Power law.
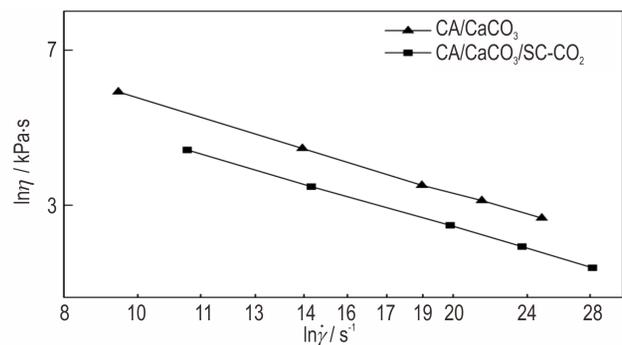
Fig. 3 Rheological curves of CA/CaCO$_3$ and CA/CaCO$_3$/SC-CO$_2$ solutions at 50 ℃

The flow equations of the CA/CaCO$_3$ and CA/CaCO$_3$/SC-CO$_2$ solutions can be described by linear fitting Equations (9) and (10):

$$\eta = 33.998 \times (\dot{\gamma})^{-0.82} \tag{9}$$

$$\eta = 25.160 \times (\dot{\gamma})^{-0.79} \tag{10}$$

An increase in shear rate leads to a decrease in shear viscosity, and the phenomenon known as "shear thinning". The n values of the CA/CaCO$_3$ and CA/CaCO$_3$/SC-CO$_2$ solutions are 0.18 and 0.21, respectively, and they are both well below 1, so they

can be treated as non-Newtonian pseudoplastic fluids. Compared with the $CA/CaCO_3$ solution, the K value of the $CA/CaCO_3/SC$-CO_2 solution decreases by 26.00%, and the n value increases by approximately 16.67%. This means that SC-CO_2 decreases the consistency of the $CA/CaCO_3$ solution, which is beneficial to the fluidity of the mixture. Moreover, the viscosity of the $CA/CaCO_3/SC$-CO_2 solution is significantly lower than that of the $CA/CaCO_3$ solution at the same shear rate.

Furthermore, pressure values and volumetric flow rates also important for the overall safety in the extrusion of high solids propellants. The pressure values and volumetric flow rates of the $CA/CaCO_3/$ SC-CO_2 solution can be measured by the slit die rheometer as shown in Table 2. When the screw speed is 10 $r\cdot min^{-1}$, compared with the CA solution, the pressures in the presence of SC-CO_2 decrease obviously, and volumetric flow rate increases by 20.00%. Therefore, the presence of SC-CO_2 significantly reduces the viscosity and pressure of the extruding $CA/CaCO_3$ solution, resulting in a higher fluidity of the mixture solution extruded at an increased volumetric flow rate. These results are consistent with the plasticizing ability of SC-CO_2, which acts as a "lubricant" to improve the swelling ability and motility of the CA molecular chains that leads to a reduction in molecular entanglement and intermolecular forces. The plasticizing effect of SC-CO_2 also promotes more effective mixing of the $CaCO_3$ and CA components, leading to a more uniform dispersion of the system. Consequently, it is promising to extruding high solid content propellants with the solvent of SC-CO_2.

Table 2   Rheological data of $CA/CaCO_3$ and $CA/CaCO_3/$ SC-CO_2 solutions

solution	pressure transducers 1 / kPa	pressure transducers 2 / kPa	volumetric flow rate / $cm^3\cdot s^{-1}$
$CA/CaCO_3$	10642	3200	0.10
$CA/CaCO_3/SC$-CO_2	8540	2351	0.12

4.2   Effect of Temperature on Rheological Behaviors

Temperature has a significant impact on the rheological properties of solid propellant materials,

which is of great significance to the overall safety of the extrusion process. Because the high temperature and high screw speed of the propellant can cause dangerous accidents during the extrusion process, according to the experience of screw extrusion processing of energetic materials, $CA/CaCO_3$ substitutes are more sensitive to the rheological property of the high solid content propellant when temperature is below 70 ℃ and screw speed is below 15 $r\cdot min^{-1}$[24]. The effect of temperature on the extrusion properties of the high solid content propellant substitute are explored at 40 ℃, 45 ℃, 50 ℃, 55 ℃ and 60 ℃, respectively, with Fig. 4 showing the rheological curves of the $CA/CaCO_3/SC$-CO_2 solution at different temperatures that can be calculated from the above Equations（1）to（4）and data measured by the slit die rheometer. At the same shear rate, it was found that the shear viscosity of the $CA/CaCO_3/SC$-CO_2 solution decreases with increasing temperature, which is caused by the better mobility of the CA molecular chains at higher temperatures.
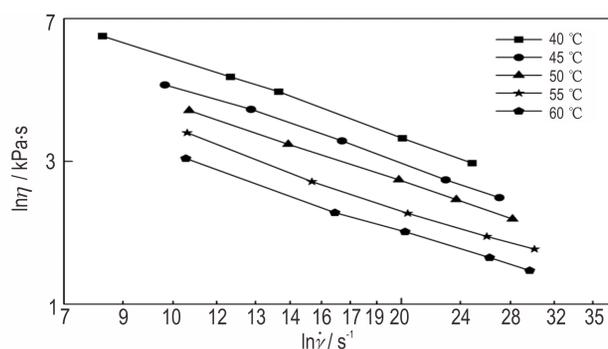
Fig.4   Rheological curves of $CA/CaCO_3/SC$-CO_2 solutions at different temperatures

The viscosity of the $CA/CaCO_3/SC$-CO_2 solutions at different temperatures are shown in Table 3

Table 3   Viscosity of $CA/CaCO_3/SC$-CO_2 solutions at different temperatures

screw speed / $r\cdot mim^{-1}$	viscoity / kPa·s				
	40 ℃	45 ℃	50 ℃	55 ℃	60 ℃
6	6.53	4.64	3.88	3.32	2.77
8	4.91	3.91	3.06	2.36	1.90
10	4.43	3.14	2.39	1.89	1.66
12	3.19	2.39	2.08	1.61	1.39
14	2.68	2.11	1.81	1.47	1.27

（Based on Fig.4）. From 40 ℃ to 45 ℃, the viscosity of the $CA/CaCO_3/SC\text{-}CO_2$ solution decreases by 28.94% at 6 r·min⁻¹, and decreases by 21.27% at 14 r·min⁻¹, while the smaller decreases in viscosity levels of 16.57% and 13.61% observed from 55 ℃ to 60 ℃. These results indicate that the viscosity of the $CA/CaCO_3/SC\text{-}CO_2$ solution decreases more at lower speeds with the increase of temperature. Since the total time required for $SC\text{-}CO_2$ and $CA/CaCO_3$ solutions to be completely mixed decreases as the screw speed increases, a small amount of $SC\text{-}CO_2$ is dissolved in the $CA/CaCO_3$ solution, which reduces the plasticizing effect of the $SC\text{-}CO_2$ component.

Besides, the viscosity of the $CA/CaCO_3/SC\text{-}CO_2$ solution from 40 ℃ to 60 ℃ decrease by 29.12%, 23.89%, 20.92% and 12.17%, respectively, at 10 r·min⁻¹（same conditions as before）. As the temperature increases, the effect of $SC\text{-}CO_2$ on the reduction in the viscosity of the $CA/CaCO_3$ solution becomes weaker. Due to the enhanced diffusion capacity of $SC\text{-}CO_2$ at higher temperatures, the dissolution in the $CA/CaCO_3$ solution is reduced, which results in a more uneven distribution of $SC\text{-}CO_2$, and the interaction between $SC\text{-}CO_2$ and $CA/CaCO_3$ phases is reduced. The viscosity of $CA/CaCO_3/SC\text{-}CO_2$ solution decreases obviously when the temperature rises from 40 ℃ to 55 ℃, but the viscosity changes unobvious when the temperature is in the range of 55 ℃ to 65 ℃. Therefore, the processing temperature is unsuitable to exceed 55 ℃ for $CA/CaCO_3$ extrusion assisted with $SC\text{-}CO_2$. Therefore, these results indicate that for the safe manufacture of CA/RDX-based propellants using extrusion processes, precise temperature and screw speed control may be required.

The relationship between fluid viscosity and temperature can be expressed by the Arrhenius relationship[25] in a certain temperature ranges using Equation（11）:

$$\eta = A\exp(E_\eta/RT) \tag{11}$$

Taking the logarithm of this formula, Equation （12）can be derived:

$$\ln\eta = \ln A + E_\eta/RT \tag{12}$$

where A is the viscosity constant; R is the gas con-

stant, 8.314 J·mol⁻¹·k⁻¹; T is the absolute temperature, K; and E_η is the viscous activation energy, kJ·mol⁻¹.

According to Equations（11）and（12）, Fig.5 is obtained within a certain temperature range. Fig.5 reveals the relationship between the logarithm of the viscosity of the $CA/CaCO_3/SC\text{-}CO_2$ solution and the reciprocal of temperature, with $\ln\eta$ exhibiting a degree of linear relationship with $1000/T$. The viscous activation energy of the $CA/CaCO_3/SC\text{-}CO_2$ solution at a shear rate of 4 s⁻¹ to 20 s⁻¹ are calculated as 37.87, 35.85, 34.67, 33.83 kJ·mol⁻¹ and 33.18 kJ·mol⁻¹ obtained from the slope of the linear fit, respectively. These values represent the sensitivity of the polymer fluid to the processing temperature, showing that they decrease with increasing shear rate. Therefore, the shear viscosity of the $CA/CaCO_3/SC\text{-}CO_2$ solution at higher shear rates is less sensitive to temperature fluctuation than that at lower shear rates.
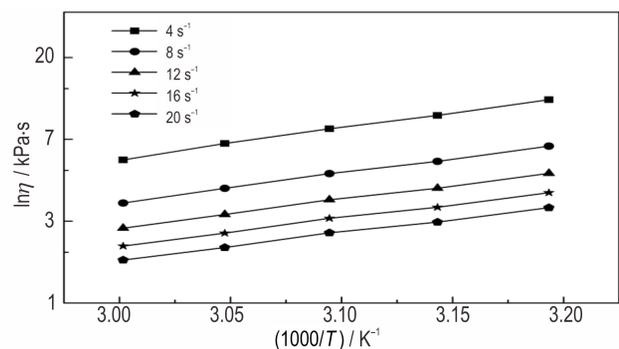
Fig.5 Effects of temperature on the rheological behaviors of $CA/CaCO_3/SC\text{-}CO_2$ solutions

4.3 Dispersive Mixing Properties of CA/CaCO₃ Solution in the Presence of SC-CO₂

The dispersion mixing properties have a significant influence on the viscosity distribution during extrusion processes, which is closely related to the rheological behavior of the material being extruded. Particle-tracking technology can be used to simulate the probability and density of the probability functions corresponding to the maximum shear stress level of the dispersion mixing process. In this type of experiment, the greater the proportion of tracer particles

that experience high shear levels，the higher the dispersion level.

Based on the above experimental results，Polyflow was used to numerically calculate the flow of the $CA/CaCO_3$ and $CA/CaCO_3/SC-CO_2$ solutions in the screw channel. Fig.6 shows the flow field distribution of the viscosity of the $CA/CaCO_3$ and $CA/CaCO_3/SC-CO_2$ solutions at 50 ℃ and 10 $r\cdot min^{-1}$（the selection of conditions corresponds to the viscosity measurement experiment）. Compared with $CA/CaCO_3$ solution，the maximum viscosity of $CA/CaCO_3/SC-CO_2$ solution is reduced by 48.03%，and $SC-CO_2$ has a great effect on increasing the viscosity distribution of $CA/CaCO_3$ solution，which is consistent with the above experimental results. Fig.7 and Fig.8 show the curves of probability and probability density functions of $CA/CaCO_3$ and $CA/CaCO_3/SC-CO_2$ solutions at 50 ℃ and 10 $r\cdot min^{-1}$ under maximum shear stress，respectively. Fig.7 reveals that the maximum shear stress value of the $CA/CaCO_3/SC-CO_2$ solution is lower than that of the $CA/CaCO_3$ solution，because the injection of $SC-CO_2$ reduces the shear stress of the $CA/CaCO_3$ solution during extrusion. Fig.8 reveals that the maximum probability density of the $CA/CaCO_3$ and $CA/CaCO_3/SC-CO_2$ solutions are 0.63 and 0.76 under maximum shear stress，respectively. The results show that the maximum probability density of the $CA/CaCO_3/SC-CO_2$ solution under maximum shear stress is 20.63% higher than that of the corresponding $CA/CaCO_3$ solution. Because the plasticizing effect of $SC-CO_2$ improves the thermal movement of the CA molecular chains and the free volume of the CA solution，thereby promoting a more effective mixing of the $CaCO_3$ and CA components. Therefore，$CaCO_3$ particles can be better dispersed in the CA matrix，leading to more uniformly dispersed phase system. These results clearly demonstrate that the addition of $SC-CO_2$ can improve the overall dispersion mixing properties of the $CA/CaCO_3$ solution，which provide theoretical fundamentals and important reference value for the research of continuous and safe extrusion of high solid content propellant.

a.   without $SC-CO_2$
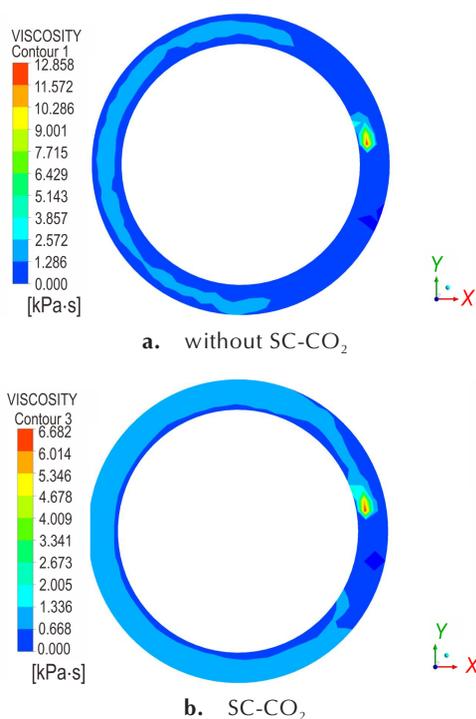
b. $SC-CO_2$

Fig. 6   Viscosity nephograms of $CA/CaCO_3$ and $CA/CaCO_3/$ $SC-CO_2$ solutions at 50 ℃ and 10 $r\cdot min^{-1}$
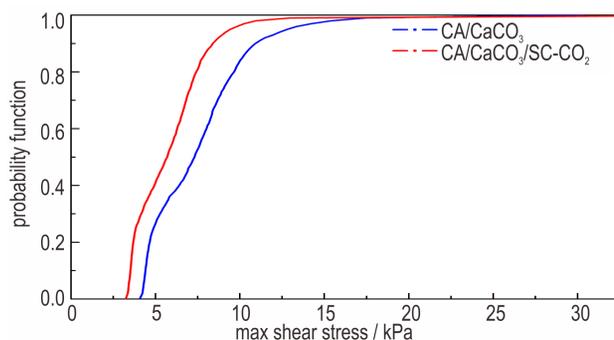
Fig.7   Probability functions of $CA/CaCO_3$ and $CA/CaCO_3/$ $SC-CO_2$ solutions at 50 ℃ and 10 $r\cdot min^{-1}$
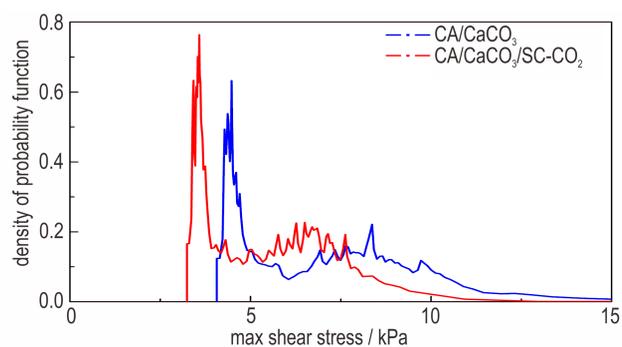
Fig.8   Density of probability functions of $CA/CaCO_3$ and $CA/$ $CaCO_3/SC-CO_2$ solutions at 50 ℃ and 10 $r\cdot min^{-1}$

4.4 Effect of Temperature on Dispersive Mixing Properties

Using Polyflow's particle-tracking technology, the effect of processing temperature on the flow of CA/CaCO$_3$/SC-CO$_2$ solution was numerically simulated. Fig.9 shows the viscosity flow field distribution of the CA/CaCO$_3$/SC-CO$_2$ solution at different temperatures and 10 r·min^{-1}, indicating that the viscosity decreases and the viscosity distribution uniformity gradually increases with increasing temperatures. From 40 ℃ to 60 ℃, the maximum viscosity of the CA/CaCO$_3$/SC-CO$_2$ solution decrease by 37.56%, 40.36%, 17.69% and 37.27%, respectively. In spite of the maximum viscosity decreases by 37.27% from 55 ℃ to 60 ℃, as the temperature approach 60 ℃, the decrease coincided with a more uneven viscosity distribution. This may be due to the too low viscosity and pressure of the CA/CaCO$_3$ solution at higher temperature, so a part of the SC-CO$_2$ fluid will convert the CO$_2$ gas and form a gas flow in the CA/CaCO$_3$ solution, resulting in instability during extrusion process. As a result, the uniformity of the viscosity distribution is weak.

The curves of probability and probability density functions of the CA/CaCO$_3$ and CA/CaCO$_3$/SC-CO$_2$ solutions at 10 r·min^{-1} and different temperatures under maximum shear stress are shown in Fig.10 and Fig.11. Fig.10 indicates that the maximum shear stress of the CA/CaCO$_3$/SC-CO$_2$ solution decreases as the temperature increases. When temperature increases from 40 ℃ to 60 ℃, the maximum probability density are 0.44, 0.49, 0.76, 1.34 and 1.30, increase by 11.36%, 55.10%, 76.32% and −2.99%, respectively (shown as Fig.11). These results confirm that temperature increases is favorable for the dispersive mixing of the CA/CaCO$_3$/SC-CO$_2$ solution during the extrusion process. However, when the temperature achieves 60 ℃, the increase in the maximum probability density of the CA/CaCO$_3$/SC-CO$_2$ solution showed a negative value under maximum shear stress, indicating a less dispersion mixing efficiency of the CA/CaCO$_3$/SC-CO$_2$ solution at this temperature. Due to the higher temperature reduces the strength of the CA/CaCO$_3$ solution,
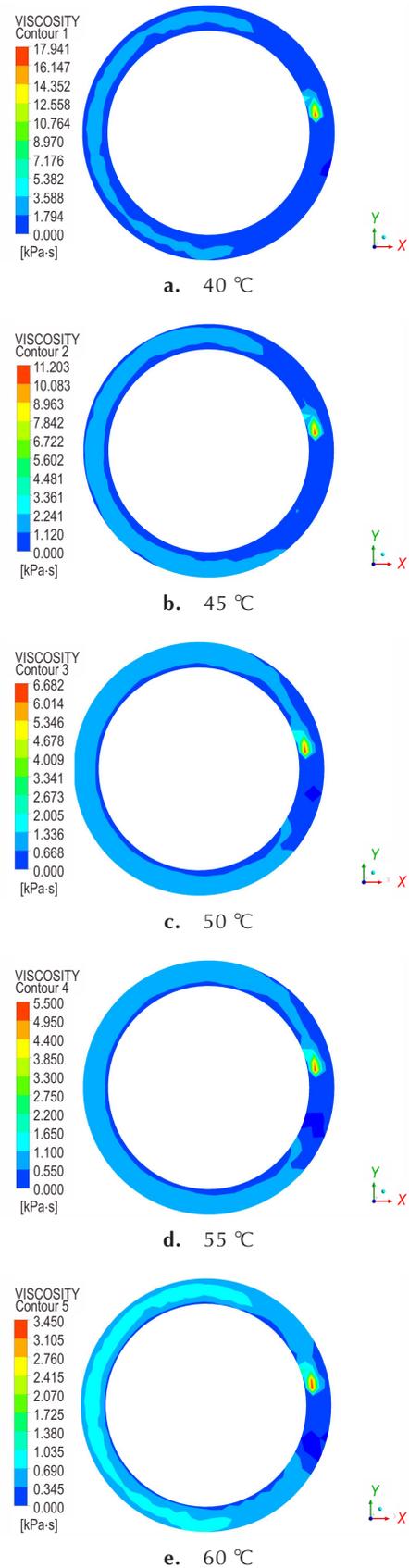
Fig.9 Viscosity nephograms of CA/CaCO$_3$/SC-CO$_2$ solutions at different temperatures
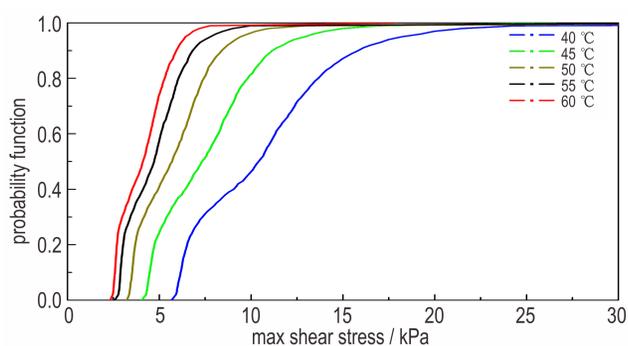
Fig.10 Probability functions of $CA/CaCO_3/SC-CO_2$ solutions at different temperatures
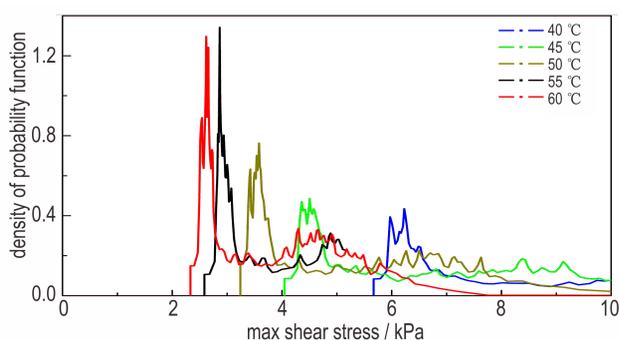
Fig.11 Density of probability functions of $CA/CaCO_3/SC-CO_2$ solutions at different temperatures

$SC-CO_2$ cannot be completely absorbed by the CA/ $CaCO_3$ solution, which causes the $CA/CaCO_3/$ $SC-CO_2$ mixture to crack and phase separate. Therefore, the dispersion property of $CaCO_3$ in the CA matrix becomes poor.

Therefore, in combination with the above results, the maximum viscosity and viscosity distribution do not change significantly from 50 ℃ to 55 ℃, and 50 ℃ represents the optimal processing temperature for $CA/CaCO_3$ extrusion assisted with $SC-CO_2$. The results obtained from the numerical simulation correlate well with the experimental data, thus Polyflow can be used to predict the performance of such extrusion process.

5　Conclusions

The slit die rheometer and Polyflow modeling have been used to investigate the effect of $SC-CO_2$ on the rheological behavior and dispersive mixing properties of high solid content propellant substitutes in extrusion process. The following conclusions have

been reached：

（1）During screw extrusion process, $CA/CaCO_3$ and $CA/CaCO_3/SC-CO_2$ solutions behave as non-Newtonian pseudoplastic fluids. With the presence of $SC-CO_2$, the viscosity coefficient of the $CA/$ $CaCO_3$ solution is reduced by 26.00% at 50℃. This is consistent with the role of $SC-CO_2$ in reducing the viscosity and pressure of the $CA/CaCO_3$ solution system, resulting in an increase in its overall volumetric flow rate of extrusion.

（2）Increasing the extrusion temperature causes the viscosity of the $CA/CaCO_3/SC-CO_2$ solution to decrease, and the beneficial effect of $SC-CO_2$ on the reduced viscosity levels at higher temperatures. The viscosity of the $CA/CaCO_3/SC-CO_2$ solution at lower shear rates is more sensitive to temperature than for high shear rates.

（3）The overall dispersion mixing properties of the $CA/CaCO_3$ solution in the extrusion process is significantly improved with the presence of $SC-CO_2$. Although the maximum viscosity of the $CA/CaCO_3/$ $SC-CO_2$ solution decreases by 37.27% from 55 ℃ to 60 ℃, the maximum probability density under the maximum shear stress decreases 2.99%. This results in a more uneven viscosity distribution and reduced dispersion mixing properties, 50 ℃ was found to be the optimal processing temperature.

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SC-CO₂辅助高固含量发射药代料挤出加工的流变行为

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摘 要： 为了改善高固含量发射药挤出加工时流变性能，采用超临界二氧化碳($SC\text{-}CO_2$)作为增塑剂辅助高固含量发射药代料醋酸纤维素/碳酸钙($CA/CaCO_3$)挤出加工，通过狭缝流变仪和幂律方程研究了 $CA/CaCO_3$ 和 $CA/CaCO_3/SC\text{-}CO_2$ 溶液的在线流变行为，使用Polyflow软件模拟了 $CA/CaCO_3/SC\text{-}CO_2$ 溶液的分散混合性能。结果表明，温度为 50 ℃时，$SC\text{-}CO_2$ 使 $CA/CaCO_3$ 溶液的稠度系数降低了 26.00%，非牛顿指数增加了 16.67%，降低了 $CA/CaCO_3$ 溶液在挤出过程的粘度和压力；随着加工温度的升高，$CA/CaCO_3/SC\text{-}CO_2$ 溶液的粘度降低；在低剪切速率下，$CA/CaCO_3/SC\text{-}CO_2$ 溶液的剪切粘度对温度的敏感性较高；根据模拟结果，温度为 50 ℃时，$CA/CaCO_3/SC\text{-}CO_2$ 溶液经受最大剪切应力的最大概率密度比 $CA/CaCO_3$ 溶液增加了 20.63%，$SC\text{-}CO_2$ 的注入有利于 $CA/CaCO_3$ 溶液分散混合性能的提高。

关键词： 高固含量发射药；超临界二氧化碳($SC\text{-}CO_2$)；流变行为；分散混合性能