

# EXPERIMENTAL AND SIMULATED MEASUREMENT OF IN-LINE RHEOLOGICAL BEHAVIOR OF CELLULOSE DIACETATE IN EXTRUSION PROCESSING

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The in-line rheological properties of cellulose diacetate (CDA) in extrusion processing have been measured by a slit rheometer and simulated by Polyflow software under different process conditions. The Power model was applied for numerical simulation, and the results indicated that Polyflow is feasible to simulate the flow of the CDA solution. The distributions of velocity, pressure, shear rate and shear viscosity in the slit were simulated using Polyflow. Both the increasing temperature and solvent content improved the fluidity of the CDA solution, which reduced the shear viscosity. An increasing screw speed was helpful to improve the output of production, but it deteriorated the quality according to the numerical simulation. Because of the evaporation of solvents, the values of shear viscosity calculated by experiment were higher than those obtained from Polyflow. The experiment and numerical simulation of the in-line rheological behavior of the CDA solution have guiding significance for optimizing the process conditions of CDA.

**Keywords:** CDA, in-line rheological behavior, slit rheometer, numerical simulation

## INTRODUCTION

Cellulose acetate (CA) plays an important role in the field of regenerated fibers, and it can be produced from a few kinds of cheap and renewable materials, such as wood, cotton and recycled paper. Due to its advantages, such as non-toxicity, strong hygroscopicity and high filter efficiency,<sup>1-4</sup> CA is widely used for various applications, for instance, in films, separation membranes, textiles, cigarette filters and coating.<sup>5-8</sup>

The molecular formula of CA is  $[C_6H_7O_2(OCOCH_3)_x(OH)_{3-x}]_n$ ,  $n=200-400$ , and  $x$  is the substitution degree of -OH. Depending on the different degrees of  $x$ , CA contains cellulose monoacetate (CMA), cellulose diacetate (CDA) and cellulose triacetate (CTA). Among them, CDA is the most widely applied. Due to the high viscosity and the melt processing temperature close to the degradation temperature,<sup>9</sup> the applications of CDA are limited under extrusion processing conditions. The main method to deal with this issue is the addition of plasticizers, such as phthalate, triethyl citrate, glycerol derivatives, phosphate and ionic liquids.<sup>10-14</sup> The solubility parameter of ethanol, acetone and CDA is  $12.9 \text{ (cal}\cdot\text{cm}^{-3})^{1/2}$ ,  $9.8 \text{ (cal}\cdot\text{cm}^{-3})^{1/2}$  and  $10.9 \text{ (cal}\cdot\text{cm}^{-3})^{1/2}$ , respectively. Therefore, both ethanol and acetone, selected for extrusion processing, are outstanding solvents and plasticizers for CDA on the basis of a similar dissolving principle.

In extrusion processing, the rheological behaviors of the CDA solution are important properties for the quality of products. The out-line rheometers, such as rotational viscometer and capillary rheometer, are common methods to measure the rheological properties.<sup>15,16</sup> Rudaz and Budtova<sup>17</sup> studied the rheological properties of CA solutions dissolved in 1-ethyl-3-methylimidazolium acetate (EMIMAc) by a Bohlin Gemini rheometer. As rheological properties are key factors for the generation of high quality foamed products, Stefan Zepnik and his co-workers reported the influence of external plasticization on the rheological properties of CA via a rotational rheometer and a capillary viscometer.<sup>18,19</sup> Since the out-line rheometers cannot characterize the rheological properties in real time during extrusion processing, a slit rheometer was adopted to measure the in-line rheological behavior of polymers.<sup>20-24</sup> Xue and Tzoganakis<sup>20</sup> reported on determining the rheological properties of a PS/Supercritical CO<sub>2</sub> solution with the method of an extrusion slit die. Xie and his co-workers<sup>21,22</sup> studied the rheological properties of starches with different amylose/amylopectin ratios by a slit rheometer.

Polyflow, professional computational fluid dynamic (CFD) software for extrusion processing based on the finite element method, is widely used for numerical simulation nowadays.<sup>25-27</sup> With the help of Polyflow, the work efficiency will be improved, and the cost of the equipment can be substantially decreased. Through simulating the flow of the CDA solution under different process conditions, the best process condition can be obtained, which will improve the product quality and the production efficiency.

Despite the huge potential of CDA displayed in the field of polymers, the in-line rheology investigation has been quite scarce in the past few decades. In this work, we researched the rheological behavior of a CDA solution with an in-line rheometer, and determined the distributions of velocity, pressure, shear rate and shear viscosity with the assistance of Polyflow software. On the basis of the results obtained from the experiment and numerical simulation, it is possible to optimize the process conditions of extrusion by considering both the quality and output of the product.

## EXPERIMENTAL

### Materials

CDA was supplied by Xi'an North Hui'an Chemical Industries Co., LTD. Ethanol (AR, Nanjing Chemical Reagent Co., LTD) and acetone (AR, Sinopharm Chemical Reagent Co., LTD) were used as received.

### Kneading processing

In this process, CDA (the mass is  $m$ ) was preliminarily dissolved in the mixed solvents of ethanol and acetone (the volume is  $V$ ), by the means of a kneading machine (Jiangsu Guomao Reducer Group Co., LTD); the bath temperature was 30 °C. The volume of ethanol was equal to that of acetone. The value ratio of  $m$  and  $V$  was 1:1.1. Half of the solvent mixture was poured into the kneading machine firstly, and the rest of the mixture was poured into the container after 3 minutes. The CDA solution was removed from the kneading machine after 20 minutes.

### Extrusion processing

The CDA solution was fed into a single screw extruder ( $D=30$  mm,  $L/D=30$ , Jiangsu Cenmen Equipment Co., LTD) at different temperatures and screw speeds. The mass flow rate of the CDA solution was recorded by an analytical scale (Sartorius AG ALC-110.4, with sensitivity of 0.0001 g), and the pressure values were measured by a slit rheometer (Jiangsu Cenmen Equipment Co., LTD).

The schematic diagram of the slit rheometer is given in Figure 1. The length, width and height of the slit are 0.275 m, 0.020 m and 0.002 m, respectively. While the value of width/height is 10, the boundary effect of the slit decreases to less than 5%, which will reduce the experiment measurement errors. The CDA solution flows along the direction of the arrow. There are three pressure transducers located at the points of 0.050 m ( $P_1$ ), 0.180 m ( $P_2$ ) and 0.245 m ( $P_3$ ) away from the inlet of the slit. The data of  $P_1$  and  $P_2$  were applied to calculate the flow of the CDA solution. A temperature transducer was located at the point of 0.115 m away from the inlet of the slit to measure the temperature of the CDA solution during extrusion processing.

With the volume flow rate and the pressure values, the viscosity of the CDA solution can be determined by the equations below.<sup>28</sup>

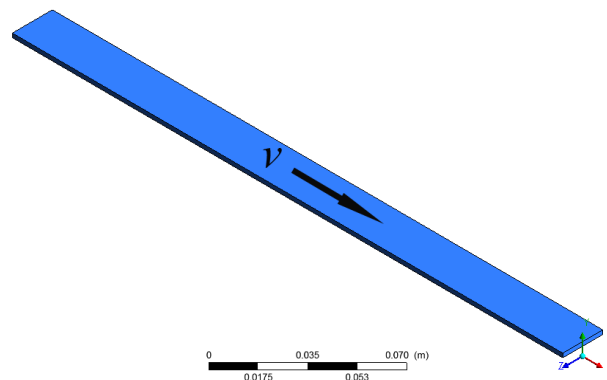


Figure 1: Flow passage of the slit rheometer

The shear stress of the wall of the slit rheometer ( $\tau_w$ ) can be measured by the relation:

$$\tau_w = \frac{H\Delta P}{2L} \quad (1)$$

where  $\Delta P$  is the differential pressure value between pressure transducers.  $H$  and  $L$  are the height of the slit rheometer and the distance between the pressure transducers, respectively.

The shear rate of the wall of the slit rheometer ( $\dot{\gamma}$ ) is calculated by the equation:

$$\dot{\gamma} = \frac{6Q}{wH^2} \left( \frac{2+b}{3} \right) \quad (2)$$

where  $Q$  is the volume flow rate of the CDA solution, and  $w$  is the width of the slit rheometer.  $\frac{2+b}{3}$  is the Rabinowitsch correction factor, which compensates the loss of shear rate between Newtonian fluid and shear-thinning fluid. The constant  $b$  can be calculated by the shear rate and shear stress:

$$b = \frac{d \left[ \lg(6Q/wH^2) \right]}{d \left[ \lg(\tau_w) \right]} \quad (3)$$

The shear viscosity  $\eta$  is calculated by the following equation:

$$\eta = \frac{\tau_w}{\dot{\gamma}} \quad (4)$$

## NUMERICAL SIMULATION

### Governing equation

In order to decrease the calculated amount, the following assumptions were made: the solution is a steady laminar flow, which is incompressible; the flow does not exhibit slip at the wall of the slit; because of high viscosity, the effects of inertia and gravity are ignored; the CDA solution is an isothermal fluid. Actually, the temperature recorded by the temperature transducer pointed out that the temperature of the CDA solution was close to the processing temperature.

With the assumptions above, the governing equations of the fluid are shown below:

Continuity equation:

$$\nabla V = 0 \quad (5)$$

Momentum equation:

$$\rho dV/dt = -\nabla p + \nabla \tau \quad (6)$$

Mass equation:

$$\rho C_v dT/dt = -\nabla q + \tau/\nabla V \quad (7)$$

where  $V$  is the velocity vector,  $\rho$  is the density of the CDA solution,  $\tau$  is the stress tensor,  $p$  is the pressure,  $T$  is the temperature,  $C_v$  is the constant-volume specific heat,  $q$  is the thermal flux vector, and  $\nabla$  is the differential operator.

### Constitutive equation

There are several kinds of models to deal with the flow of polymers in Polyflow, such as Power law, Bird-Carreau law, Cross law, Bingham law and Herschel-Bulkley law. However, as the structure of CDA is complex, it is difficult to select a completely suitable model to describe the flow of the CDA solution accurately. Considering the property of a pseudoplastic fluid, the Power model is the ideal model to describe the relationship between shear viscosity and shear rate in a CDA solution:

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

where  $K$  is the coefficient of viscosity,  $\lambda$  is the relaxation time, and  $n$  is the non-Newtonian index.

### Boundary conditions

The values of normal force and tangential force in the outlet are zero, and the values of normal and tangential velocity of the solution along the wall are also zero. The density of the CDA solution is  $1149 \text{ kg/m}^3$ ,  $Q$  ( $\text{m}^3/\text{s}$ ) is the

volume flow rate and  $\lambda = 2.31$  s.

## RESULTS AND DISCUSSION

### Flow curve

The flow curve of the CDA solution was calculated by Eqs. 1, 2, 3 and 4 with the data obtained from the slit rheometer.

In Figure 2, the inset figure shows the relationship between shear viscosity and shear rate at 45 °C, and the main figure presents the relationship between  $\eta$  and  $\dot{\gamma}$ , while the scales of coordinates are set in a base-10 logarithm. There is a significant linear correlation between  $\lg \eta$  and  $\lg \dot{\gamma}$ , which indicates that the flow curve of the CDA solution matches the Power model as following the equation:

$$\eta = 41880 \times (\dot{\gamma})^{-0.8831} \quad (9)$$

The non-Newtonian index ( $n$ ) is 0.1169 ( $<1$ ). The increasing shear rate causes the decrease of molecular chain entanglement, which reduces the interactions among molecular chains and the shear viscosity of the CDA solution. The phenomenon of shear viscosity decreasing with increasing shear rate is called “shear thinning”, and it demonstrates that the CDA solution is a non-Newtonian pseudoplastic fluid.

### Numerical simulation

The flow was simulated by Polyflow software under different process conditions. The numerical simulation of the slit symmetry plane is shown in Figure 3 at 45 °C and 10 rpm. A, B, C, D, E and F are the distributions of velocity X, velocity Y, velocity Z, pressure, shear rate and shear viscosity in the horizontal cross of the slit, respectively.

With Polyflow, the flow of the CDA solution in the die can be presented during extrusion processing, which is impossible to achieve experimentally. The velocity X along the center axis is close to  $4.40 \times 10^{-3}$  m/s, the velocity Y is  $4.32 \times 10^{-5}$  m/s and the velocity Z is  $3.16 \times 10^{-5}$  m/s. Therefore, the flow runs along the X direction. The pressure at the inlet is 12.20 MPa, and it decreases smoothly to a value close to the atmospheric pressure. The distributions of shear rate and shear viscosity seem to be uniform. The value of shear rate obtained from numerical simulation is  $4.37$  s $^{-1}$ , while  $4.51$  s $^{-1}$  was obtained from the experiment. The shear viscosity simulated by Polyflow is  $1.03 \times 10^4$  Pa·s, while the value reached experimentally is  $1.11 \times 10^4$  Pa·s. The values of Polyflow simulation are quite close to the ones obtained experimentally, which means that Polyflow software is suitable to simulate the CDA flow and the Power model is appropriate for simulation.

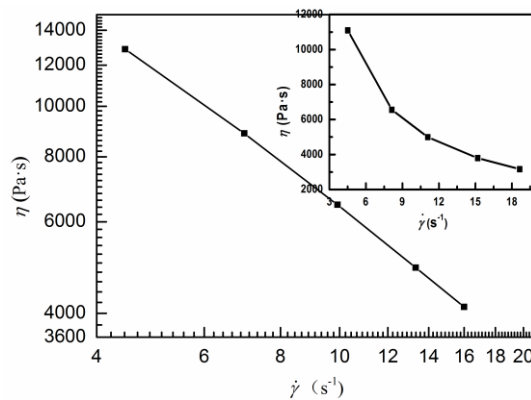


Figure 2: Flow curve of CDA solution at 45 °C

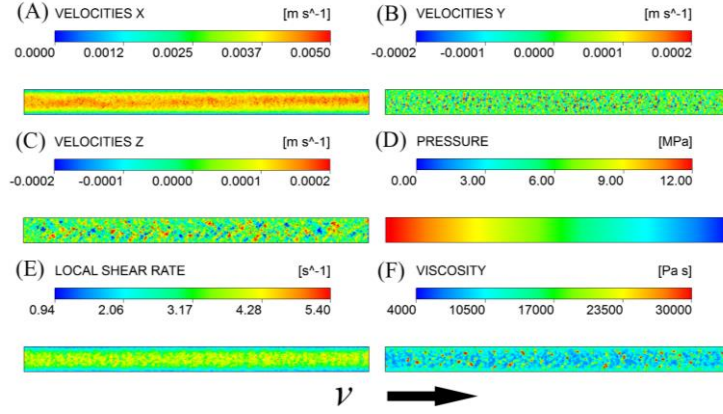


Figure 3: Distributions of CDA flow in the slit simulated by Polyflow (a, velocity X; b, velocity Y; c, velocity Z; d, pressure; e, shear rate; f, shear viscosity)

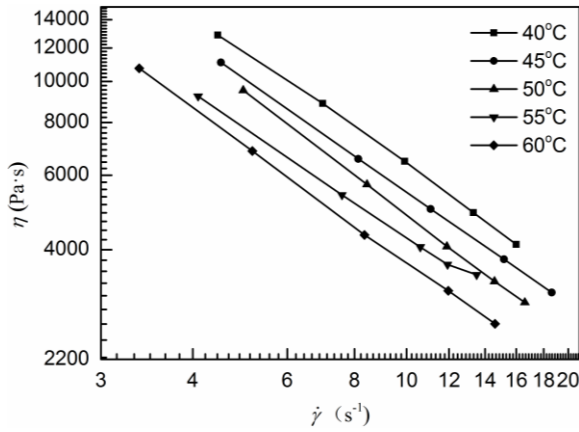


Figure 4: Flow curve of CDA solution at different processing temperatures

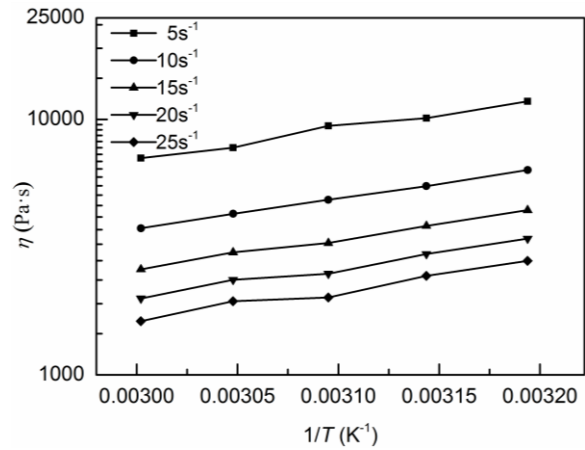


Figure 5: Relationship between  $\eta$  and  $1/T$  at different shear rates

### Effect of temperature on rheological behavior

Processing temperature has an important influence on the rheological behavior in extrusion. Figure 4 shows the relationship between  $\eta$  and  $\dot{\gamma}$  at different processing temperatures. It is obvious that  $\lg \eta$  and  $\lg \dot{\gamma}$  meet the linear correlation, as Figure 2 indicates. The increasing temperature improves the thermal motion of CDA molecular chains and the free volume of the CDA solution, which makes shear viscosity decrease.

Despite complex functional relationships between shear viscosity and temperature, the Arrhenius equation is used to describe the relationships within limits in general.

$$\eta = A \exp\left(\frac{E_{\eta}}{RT}\right) \quad (10)$$

where  $A$  is constant,  $E_{\eta}$  is flow activation energy,  $T$  is the absolute temperature, and  $R$  is the gas constant ( $8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ). Within limits, increasing processing temperature decreases the shear viscosity.

Figure 5 shows the relationship between  $\eta$  and  $1/T$  at different shear rates. The relationship between  $\lg \eta$  and  $1/T$  meets the linear relation as what Arrhenius equation describes, particularly when the shear rate is  $10 \text{ s}^{-1}$  or  $15 \text{ s}^{-1}$ . We also find that the effect of temperature on viscosity at a low shear rate is more remarkable than that at a high shear rate.

The flow curves of the CDA solution at different temperatures have been simulated by Polyflow. In Figure 6, the solid lines stand for the results calculated experimentally, while the dotted lines represent the results obtained from Polyflow. The flow curves of simulated and experimental data match well. By

comparison, because of the evaporation of the solvents during extrusion processing, the values of shear viscosity calculated experimentally are higher than those provided by Polyflow. The effect of temperature on the flow seems to be similar in both experimental and simulated data.

The distribution of pressure along the slit was simulated at different processing temperatures and 10 rpm, as shown in Figure 7. It is apparent that the dropping rate of pressure is maintained at a certain value. The increasing processing temperature improves the flow, which is beneficial for reducing the pressure in the slit. The initial pressure at the inlet is 14.10 MPa at 40 °C and 8.08 MPa at 60 °C, and the initial pressure reduces to about 42.70%, while the temperature is increased by 20 °C, which means that the increasing temperature has a significant effect on the rheological behavior of the CDA solution.

### Effect of screw speed on rheological behavior

Increasing the screw speed is a suitable method to improve the production output, but it has a negative influence on the quality of the product and enhances the cost of the process.

As Figure 8 shows, the curves of velocity along the slit with different screw speeds are simulated at 45 °C. The velocity increases with screw speed. On the other hand, the increasing screw speed makes the flow of the CDA solution unstable, and the curve of 30 rpm seems to be more undulatory than the curve of 10 rpm, which indicates that the increasing screw speed has a harmful influence on the quality of the product. In the actual processing, the higher screw speed increases the output of products, but it degrades the product quality, and it is difficult to figure out the optimal screw speed to meet both the output and the quality of the products. Thus, the velocity along the slit simulated by Polyflow can be used to predict the quality at different screw speeds.

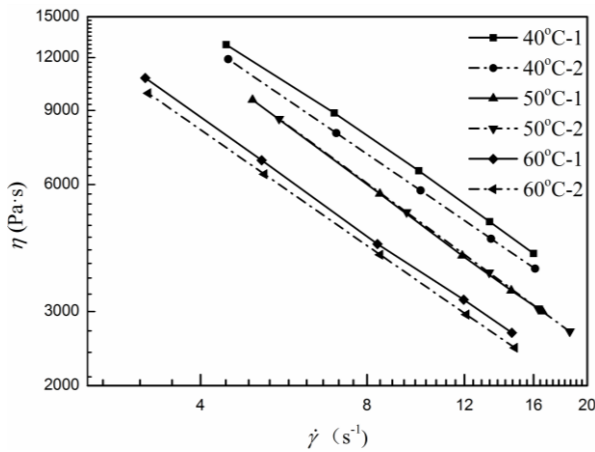


Figure 6: Flow curves of CDA solution obtained experimentally and by Polyflow simulation

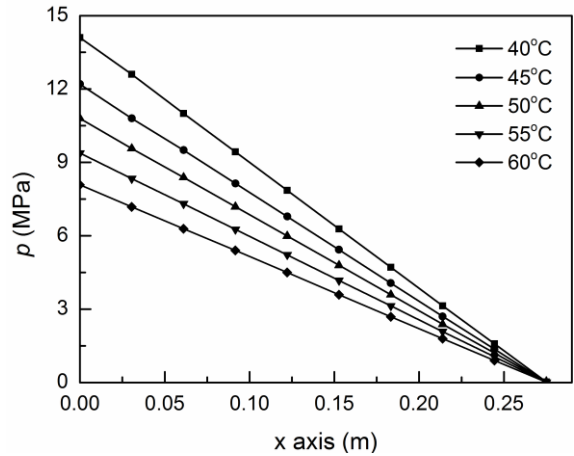


Figure 7: Distribution of pressure along the slit at different processing temperatures

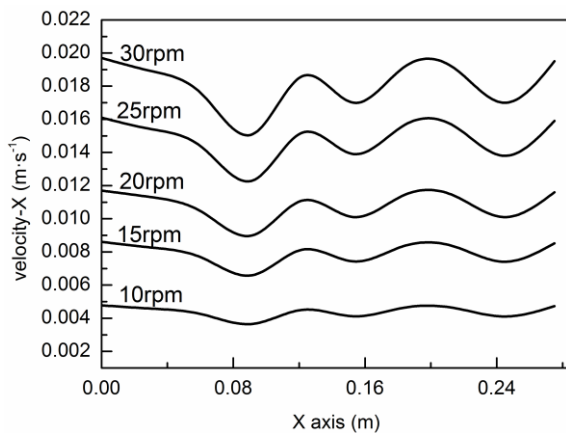


Figure 8: Distribution of velocity X at different screw speeds

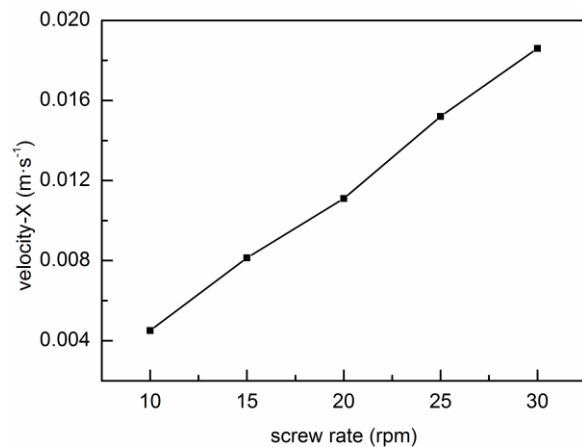


Figure 9: Curve of velocity at different screw speeds

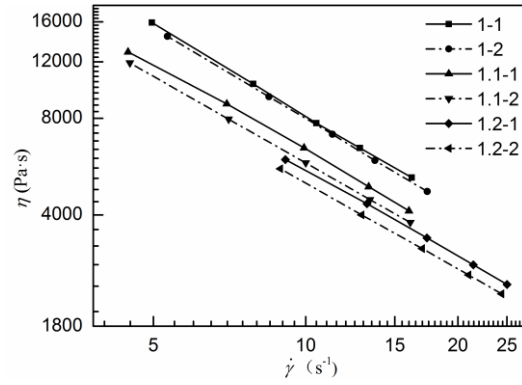


Figure 10: Flow curves with different solvent contents

Table 1

Dropping rate of pressure (MPa/m) at different temperatures and screw speeds

Temperature (°C)	Screw speed (rpm)				
	10	15	20	25	30
40	51.20	53.74	55.92	57.73	58.82
45	44.30	47.46	49.21	51.05	52.29
50	39.22	39.94	40.30	40.67	41.03
55	34.06	37.04	38.85	39.58	40.31
60	29.34	30.61	31.92	32.93	33.51

The values of velocity at the point 0.122 m away from the inlet are simulated at different screw speeds. It is well-known that the volume flow rates and screw speed match the following equation:

$$Q = CN \quad (11)$$

where  $C$  is a constant, and  $N$  is the screw speed.

As Figure 9 shows, the relationship between simulated velocity and screw speed also matches a linear relation, and the slope of the line is  $0.0007048 \text{ m}\cdot\text{s}^{-1}\cdot\text{rpm}^{-1}$ . We can estimate the velocity at a certain screw speed via equation 11 without experiment, which will save time and cost.

Table 1 lists the values for the dropping rate of pressure (MPa/m), the ratio between the pressure changes and the length of the slit, at different temperatures and screw speeds. The low temperature and high screw speed will increase the dropping rate of pressure. The low temperature is not beneficial to the flow, and it will increase the viscosity, which causes an increase of the pressure. The higher screw speed will increase the velocity and pressure in the inlet, which will increase the dropping rate of pressure. Therefore, we can simulate the distribution of pressure along the slit under various process conditions to optimize the product and request. Meanwhile, the effect of temperature on the dropping rate of pressure is more obvious than that of the screw speed. For instance, the dropping rate of pressure at  $40^\circ\text{C}$  and 10 rpm is 51.20 MPa/m, while it is 29.34 at  $60^\circ\text{C}$  and 10 rpm, which indicates that the dropping rate decreases by about 42.70% when the temperature increases by only  $20^\circ\text{C}$ . The dropping rate of pressure at  $40^\circ\text{C}$  and 30 rpm is 58.82 MPa, increasing by 14.88% compared with that at 10 rpm, which implies that an increased screw speed has fewer effects on the dropping rate than temperature.

### Effect of solvent content on rheological behavior

We also investigated the effect of solvent content on the rheological behaviors of the CDA solution. While the ratio between the mass of CDA and the volume of solvent mixture is 1.1 in the research above, Figure 10 exhibits the flow curves for the experimental and numerically simulated data for the ratios of 1, 1.1 or 1.2. It demonstrates that the increasing solvent content improves the flow of the CDA solution. Ethanol and acetone are excellent solvents to swell and dissolve CDA, which is utilized as plasticizer for the extrusion processing. However, the more solvent is added in CDA, the worse the product shrinks. Therefore, it is necessary to obtain a suitable ratio for extrusion processing, considering the quality of the product. When the ratio is 1.1 or 1.2, the solvent evaporates from the CDA solution more seriously than at the ratio of 1, which makes the experimental values of shear viscosity higher than the Polyflow

simulated ones.

## CONCLUSION

A slit rheometer and Polyflow software were used to study the in-line rheological properties of a CDA solution in extrusion processing. The results obtained from the numerical simulation correspond with the results from the experiment, which indicates that Polyflow is feasible to simulate the rheological behavior of a CDA solution. A CDA solution is a non-Newtonian pseudoplastic fluid, which has the property of shear thinning. Based on the experimental data, Polyflow was applied to obtain the numerical simulation of the CDA solution in the slit, namely, to measure the distribution of velocity, pressure, shear rate and shear viscosity. The Arrhenius equation was found suitable to describe the relationship between shear viscosity and temperature within the specified temperature range. The increasing temperature improves the rheological behavior, which makes the shear viscosity decrease. The pressure values at the inlet are 14.10 MPa at 40 °C and 8.08 MPa at 60 °C, as obtained from Polyflow. In other words, the pressure decreases by about 42.70%, while the temperature increases by only 20 °C. The velocity obtained from the numerical simulation demonstrates the influence of increasing screw speed on the quality and output of the product. The velocity at a high screw speed is greater than that at a low screw speed, and it improves the output of the product. However, increasing the screw speed makes the flow of the CDA solution unstable, and the velocity at high screw speed seems to be more undulatory than that at low screw speed, which deteriorates the quality of the product. The increasing solvent content improves the flow of the CDA solution owing to the plasticization of the mixed solvent. Because of the evaporation of solvents during extrusion processing, the values of shear viscosity obtained from the experiment are higher than those provided by Polyflow. The process conditions of CDA in extrusion can be optimized according to the in-line measurement data on the rheological behavior of the CDA solution obtained both experimentally and by numerical simulation.

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