The 8th TSME International Conference on Mechanical Engineering
12-15 December 2017
Bangkok, Thailand

TSF0004

Adhesive effect of polymer solutions in filament stretching flow

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Abstract. We carried out the experiments on the elongational flow of the polymer solution using the filament stretching method and examined the adhesive effect between a liquid and a solid occurring in the extensional deformation. The test fluid used was the aqueous solution of 1.0wt% PAA. In the evaluation of adhesive effect, we confirmed that the adhesive force was larger than the extensional force acting on fluid in the flowing. Besides, it was found that the relationship between the adhesive force and the strain occurring in the flowing was similar to the time change in extensional force. Especially, since the adhesive force of the PAA solution at the high stretch rate was sustained at a constant value for a long time, it was suggested that the force balance in the PAA solution was kept during elongational deformation.

1. Introduction

Aqueous solutions of polymers produced by dissolving polymeric material in water are composed by macromolecules called polymer chains [1]. The structure of polymer solution depends on the concentration and kinds of polymer material. Especially, in the case of thick concentration, it is known that the inside structure of fluid is in a state where polymer chains are entangled, and that the flow behavior shows viscoelastic characteristics [2]. This viscoelastic behavior is related to the structural change in polymers due to the deformation and is of interests in the rheological point of view. Although the studies on the rheological behavior of polymer solutions have been performed by many researchers, experimentally and numerically, there are many unclear points, yet. One of them is the stretching flow property of polymer solutions. Since the stretching flow is closely related to the extension and contraction of polymer chains, the examination of stretching property is of important in order to discuss the relationship between the macroscopic deformation of fluid and the microscopic change in polymer structure. At the present time, several methods are proposed for the examination of the stretching property of polymer solution. Especially, since the filament stretching method [3-5] can examine the stretching property of fluids under a constant stretch rate, it is widely used as the most available methods in comparison with other methods. In the filament stretching method, we can provide the elongational deformation to the test fluid by inserting test fluid between two cylinders and moving each cylinder in vertical direction. Accordingly, the fluid inserted between two cylinders forms a liquid filament accompanying with the movement of cylinders, and the stretching filament becomes shear-free flow. The evaluation of stretching property in the filament stretching rheometer is carried out using the profile of liquid filament and the elongational force acting on the upper cylinder.

However, it is predicted that the profile of liquid filament is affected by the adhesive condition between the cylinder and liquid, and that the effect of surface tension at the cylinder circumference is included in the measured elongational force. These details are unclear, yet. Then, we focused on the flow in the neighborhood of the upper cylinder during the elongational deformation and tried to examine the adhesive effect between the cylinder and liquid, and the effect of surface tension.

2. Experimental

2.1. Filament stretching rheometer

Figure 1 shows the schematic description of a filament stretching extensional rheometer. Firstly, we insert a test fluid in the gap (2 mm) between two cylinders (ϕ 6 mm) (figure 1(a)) and form the liquid column. At this time, the circumference of liquid column has a free surface and the column geometry is balanced by the surface force acting on the interface between a solid and a liquid. Next, when these two cylinders are moved to upwards and downwards at the same time, the liquid filament is formed between two cylinders (figure 1(b)), and the diameter of filament decreases with increasing the distance between two cylinders. Although the moving mechanism of cylinder was not shown in figure 1, we used the linear moving system to control the movement of cylinder at a constant stretch rate.

The concrete movement of cylinder is shown in equation (1) and figure 2 represents the trajectory of moving cylinder using the optical displacement sensor.

$$L(t) = L_0 e^{\varepsilon t} \tag{1}$$

where ε is the stretch rate and L_0 is the half of initial gap (1 mm) between two cylinders.

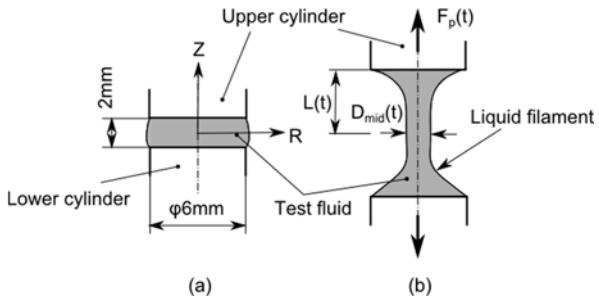

Figure 1. Schematic view of filament stretching extensional rheometer : (a) the initial state, (b) an elongatinal deformation.

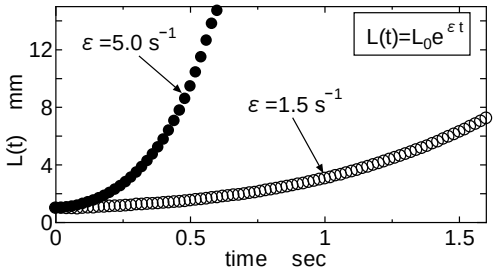

Figure2. Displacement curves of upper cylinder at a constant stretch rate.

The measurement factors in this experiment are the stretching force acting on the fluid and the fluid diameter at the midpoint of filament. These factors were measured by using the load cell set at the upper cylinder and the laser sensor fixed at the midpoint of the gap between two cylinders, respectively. The whole geometry of filament was taken by the video camera.

2.2. Test fluids

We used the aqueous solution of 1.0wt% polyacrylamide (PAA) as test fluid. Besides, for the sake of comparison with the PAA solution, we used glycerin as the Newtonian fluid. Figure 3 shows the steady shear viscosities for the test fluids. The measurement of shear viscosity was carried out by using the rotational rheometer of cone and plate type. With regarding to the aqueous solution of PAA, we confirmed that the decrement of shear viscosity which means a non-Newtonian fluid appeared with

the increment of shear rate. In general, such decrement of shear viscosity is called the shear thinning property. On the other hands, since the glycerin is the Newtonian fluid, its viscosity keeps a constant value over the wide range of shear rate shown in figure 3.

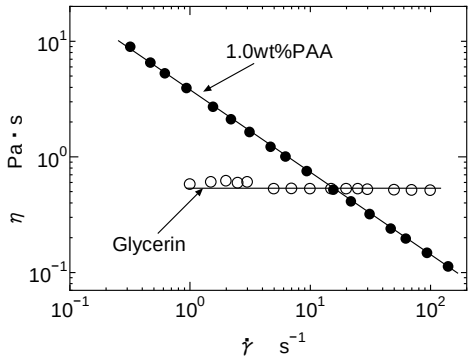

Figure 3. Steady shear viscosity of test fluids.

3. Results and discussion

3.1. Filament shape

Figure 4 shows the images of liquid filament for both fluids at the stretch rate of $\varepsilon = 2.5\,\mathrm{s}^{-1}$. For both fluids, we found that the liquid filament was formed between of two cylinders under the condition of $\varepsilon = 2.5\,\mathrm{s}^{-1}$. However, comparing between both images about the change in filament diameter to the axial direction, we found that the result of glycerin is more remarkable than that of PAA. Especially, the filament diameter of glycerin at the midpoint of filament becomes quite thin. Besides, in the case of glycerin, the shapes of liquid surface around the upper and lower cylinder show remarkable asymmetry. In general, since it is considered that the inside structure of PAA solution is constructed by the entangled polymer chains, it is predicted that the images of PAA solution shown in figure 4(a) might be appeared as the elongational deformation of polymer chains.

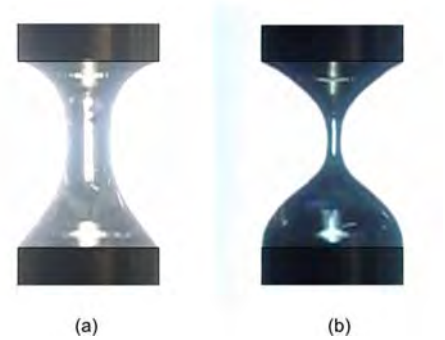

Figure 4. Filament images during the elongational deformation at the stretch rate of $\varepsilon = 2.5\,\mathrm{s}^{-1}$: (a) 1.0wt%PAA, (b) glycerin

Then, in order to examine the time change in the filament shape during elongational flows, we obtained the filament profile by the trace of filament images captured from the video images. Figures 5 and 6 show the time changes in filament shape at the stretch rate of $\varepsilon = 2.5\,\mathrm{s}^{-1}$ and $\varepsilon = 8.0\,\mathrm{s}^{-1}$, respectively. In figure 5, until 0.5sec after the start of flow, the difference of filament profile between

both fluids is not confirmed. However, at 0.68 second after that, the filament diameter of glycerin at the midpoint of filament decreases rapidly despite a short time. Accompanying with the decrement of filament diameter, although the liquid surface under the upper cylinder maintains a concave shape, the surface around the lower cylinder begins to swell and shifts to a convex one. In the results of figure 6, the same behavior as that of figure 5 is confirmed. Also, in figure 6, we can find the filament length of PAA solution at the stretch rate of $\varepsilon = 8.0\,\mathrm{s}^{-1}$ become very long in comparison with that of glycerin. However, in this case, since the concave shape under the upper cylinder have a large curvilinear radius, the contact condition between liquid and cylinder might be varied.

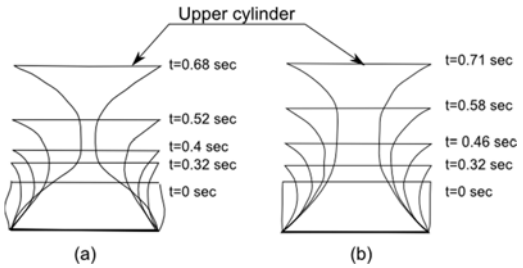

Figure 5. Time changes in filament profile at the stretch rate of 2.5 s^{-1} : (a) Glycerin, (b) 1.0wt%PAA

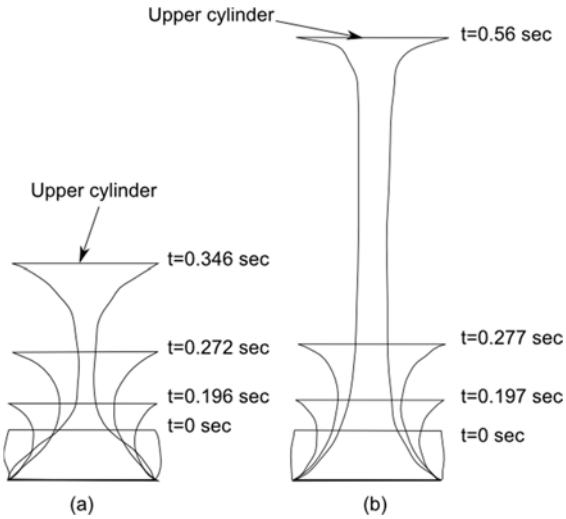

Figure 6. Time changes in filament profile at the stretch rate of 8.0 s^{-1} : (a) Glycerin, (b) 1.0wt%PAA

3.2. Time response in elongational deformation

Figure 7 shows the time responses of filament diameter and extensional force at the stretch rates of 2.5 s^{-1} and 8.0 s^{-1}. However, since the results for the stretch rate of 2.5 s^{-1} varies in the different time scale from those of 8.0 s^{-1}, the results under both conditions cannot express in the same figure. Then, for the sake of comparison between both results at the different stretch rate, we showed the measurements factors using the Hencky strain. The Hencky strain is called the true or logarithmic strain and is used in the situation where the deformation progresses. In this experiment, as shown in figures 5 and 6, since the elongational deformation is progressing with time, the use of the Hencky strain becomes effective to discuss the force balance acting on fluid. The Hencky strain is defined by equation (2).

$$\text{Hencky strain} = \varepsilon\, t \tag{2}$$

In figure 7, we found that the elongational force F_p acting on fluid increases with the progress of elonagational deformation. However, for each force curve, after showing the peak of F_p, the elongational force decreases with increasing the Hencky strain. Especially, with regarding to the peaks of force curve, although there is no difference of the value of peak between both fluids, the value of the Hencky strain at the peak of force curve depends on the magnitude of the stretch rate. In the case of $\varepsilon = 8.0\,\mathrm{s}^{-1}$, since the changes in the filament diameter become gentle for the increase of the Hencky strain, it is considered that the force balance inside the fluid follows the progress of elongational

deformation. On the other hand, in the results of $\varepsilon = 2.5\ \mathrm{s}^{-1}$, we can find that the change in filament diameter is remarkable in comparison with that at $\varepsilon = 8.0\ \mathrm{s}^{-1}$. Consequently, considering the filament profile shown in figures 5 and 6, we predict that the force balance is important in the elongational flow at the low stretch rate. Especially, since the elongational force is measured at the upper cylinder, it is considered that the filament shape in the neighborhood of the upper cylinder is relate to the force balance in the inside of fluid in elongational flow.

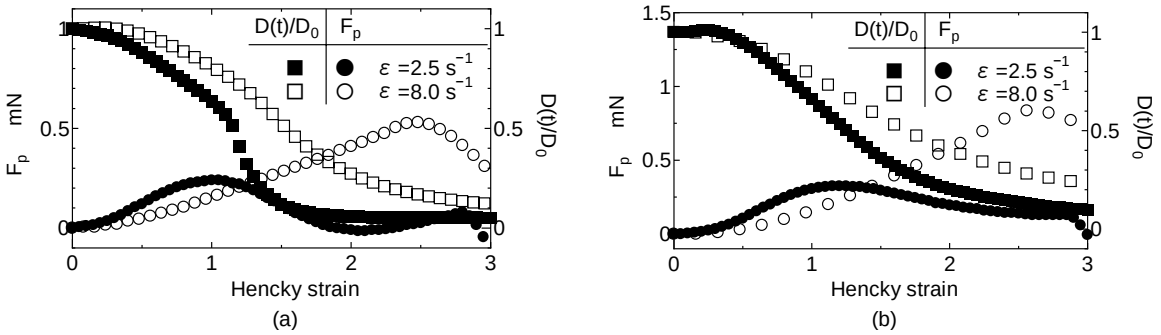

Figure 7. Changes in the extensional force and the filament diameter during the elongational flow at a constant stretching rate : (a) glycerin, (b) 1.0wt%PAA

3.3. Filament shape

Szabo [6] carried out the analysis of force balance in fluid subjected to the elongational deformation in the filament stretching rheometer. According to his analysis, the stretching force occurring at the upper cylinder is expressed by the following equation.

$$F_p = \pi R_p^2 \Delta P - \frac{2\pi\sigma R_p}{\sqrt{1+\left(R_p'\right)^2}} - \int_{S_p} \tau_{zz} dS \tag{3}$$

where the first term in the right side in equation (3) means the effect of Laplace pressure around the cylinder. Besides, the second term is the surface force at the circumference of upper cylinder, and the third term represents the internal force of fluid acting on the cylinder. Also, the third term can be regarded as the adhesive force between the cylinder surface and the test fluid. Accordingly, we evaluated the adhesive effect in the elongational deformation from the stretching force and the filament profile. In equation (3), ΔP is given in equation (4). Besides, in equations (3) and (4), σ is the surface tension of test fluids and R_p the radius of cylinder, $R_p' = dR_p / dz$. ρ in equation (4) is the density of test fluids.

$$\Delta P = \rho g z + \frac{\sigma}{R_p R_p'} \frac{d}{dz}\left(\frac{R_p}{\sqrt{1+\left(R_p'\right)^2}} \right) \tag{4}$$

Figure 8 shows the adhesive force calculated from the filament profile and the time change in stretching force. From figures 7 and 8, we confirmed that the Hencky strain which shows the peak of adhesive force is almost consistent with that of the stretching force. Besides, the decrement of adhesive force after passing the peak is similar to the behaviors of stretching force. Especially, the decrement of adhesive force for glycerin becomes remarkable at both the stretch rate. However, the

adhesive force of the PAA solution at the stretch rate of 8.0 s^{-1} maintains a high value up to the region of high strain. In the whole region of the strain, we found that the adhesive force was larger value than the stretching force. Therefore, it is deduced that the adhesive effect occurring at the surface of cylinder dominates the elongational deformation. In other words, it be might be said that the effect of surface force around the cylinder is significant with regarding to the evaluation of stretching force. Especially, in the case of PAA solution, since the liquid filament is greatly stretched due to the magnitude of stretch rate, it might be suggested that the adhesive effect between a liquid and a solid is sustained for a long time. Although this consideration seems to be closely related to the elongational deformation of polymer chains, the details was not clarified at this time because of small data. Therefore, we need to examine those by many data furthermore.

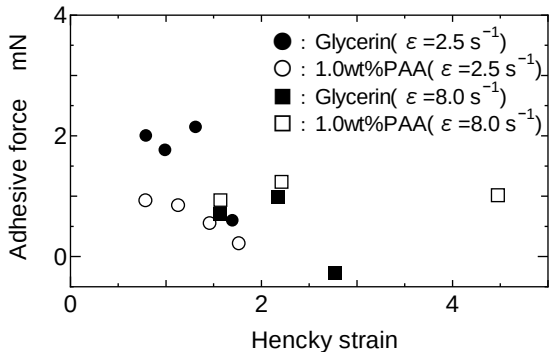

Fig.8 Evaluation of adhesive force during the elongational deformation.

4. Conclusion

We carried out the experiments on the elongational flow of the polymer solution using the filament stretching method and examined the adhesive effect which affected the extensional deformation of fluid. As the polymer solution, the aqueous solution of 1.0wt% PAA was used. As the results, we confirmed that the adhesive force was larger than the extensional force acting on fluid in the elongational flow. Besides, it was found that the relationship between the adhesive force and the strain occurring in fluids was similar to the change in extensional force. Especially, the adhesive force of the PAA solution at the high stretch rate was sustained at a constant value for a long time. Consequently, it was suggested that the force balance in the PAA solution in the flowing was kept during elongational deformation.

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