Drag Reduction on a Polymer Gel Surface*

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We investigated the hydrogel of poly (vinyl alcohol) (PVA) which possesses elastic behavior similar to the blood vessel. In this study, drag reduction on the polymer hydrogel tube surface was experimentally investigated at steady flow condition. A transparent PVA hydrogel tube was prepared from the solution of PVA, dimethyl sulfoxide (DMSO) and water by repetitive cooling method and the surface of the hydrogel tube was modified with poly (acrylic-acid) (PAA). Monodisperse polystyrene particles (7.21 μm in diameter) were used as a tracer of fluid flow and the flow was observed by CCD camera under a microscope. The wall shear stress (WSS) was determined from near-wall velocity gradient obtained by particle-tracking (PT) method and drag reduction was calculated from the WSS. Microscopic investigations have shown that the drag reduction on the hydrogel surface depends on the chemical nature of the hydrogel surface, which was varied with changing pH of flow liquid. Maximum drag reduction was obtained with water (flow), when the PAA of modified surface is in the dissociated condition.

Key Words: Poly (Vinyl Alcohol), Poly (Acrylic Acid), Hydrogel Tube, Particle Tracking Method, Velocity Profile, Drag Reduction, pH Dependence, Ionic Strength

1. Introduction

Friction drag reduction is one of the most important engineering and biomedical problems. Although a number of experimental and theoretical investigations have been carried out, researches on drag reduction is still in progress. Usual methods employed for reducing friction drag utilize some additives like long chain polymer⁽¹⁾, surfactants⁽²⁾, and long fibers⁽³⁾. Recent studies^{(4),(5)} show that near wall streamwise vortices are responsible for high skin-friction drag in turbulent boundary layers. Some attempts have been made to reduce the skin friction drag by controlling the interactions between these vortices and the wall. Neural networks have been used to obtain direct numerical simulations of turbulent channel flow at low Reynolds number and observed about 20% drag reduction⁽⁶⁾. The ribbed surfaces aligned in the streamwise direction reduced turbulent skin friction have been established beyond any reasonable

doubt⁽⁷⁾⁻⁽⁹⁾. Fukuhara et al., have investigated that the coefficient of friction of the flexible tube was lower than that of the rigid tube⁽¹⁰⁾. Watanabe et. al., have investigated the drag reduction phenomenon and slip of Newtonian fluid in a square and rectangular ducts with highly water-repellent walls^{(11),(12)}. They reported that the principle cause of drag reduction is fluid slip on the wall.

Several studies have suggested that the variation of microsurface geometry which changes the near-wall structure of the flow were effective in reducing drag. To our knowledge, drag reduction on biomedical materials has not yet been investigated directly by observing the surface microscopically. Understanding the drag reduction phenomenon it is necessary to measure the flow characteristics near the wall. For this purpose, we observed the flow on the hydrogel surface in micron scale accuracy at low Reynolds number.

Hydrophilic gels have attracted considerable attention as candidates for good bio-compatible materials, because the interface between the water-swollen gel and blood or tissues may have a very low free energy leading to very low adverse interaction

* Received 26th February, 1999

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of the gel surface with aqueous biological environment^{(13)–(15)}. A large number of investigations have been undertaken to develop biomedical materials which do not elicit thrombus formation when exposed to the blood flow. Recently many studies showed that PVA is antithrombotic and one of the most promising materials for the inner surface of small vascular prostheses^{(16)–(18)}. PVA hydrogel tubes could be prepared to have the similar mechanical properties to those of an artery through fixing various strain in the structure of the hydrogel tube such as elongation and twisting^{(19),(20)}. These properties of the gel tube were based on the excellent shape memory of the PVA gel⁽²¹⁾.

In this work, an intact and modified PVA hydrogel tubes were prepared and drag reduction on the hydrogel surface was experimentally investigated at steady flow condition. The PVA hydrogel surface was modified with PAA. The wall shear stress (WSS) was determined from near-wall velocity gradient obtained by a particle-tracking method and drag reduction was calculated from the wall shear stress. Microscopic investigations have shown that the drag reduction on the hydrogel surface depends on the chemical nature of the hydrogel surface, which was changed with varying pH of a flow liquid. Maximum drag reduction was obtained with water flow, when the grafted PAA held dissociated condition.

2. Experiment

2.1 Preparation of PVA hydrogel tube

The PVA purchased from Kuraray Co., was used whose $MW=75\,000$. PVA was used after complete saponification and purification in our laboratory. PAA ($MW=450\,000$) was purchased from Aldrich Chemical Co., and used as obtained.

Homogeneous PVA solution with concentration of 10 wt.% was prepared by heating the mixture of PVA powder, water, and DMSO (water/DMSO=20/80 by weight) for 6 hours in a water bath at 90°C. The solution was cast in a cell of polymethyl methacrylate (PMMA). To prepare the inner hole in the hydrogel tube, we have used a PMMA rod. The polymer solution was changed into hydrogel by a repetitive cooling method. The cooling cycle was comprised of cooling at -22°C for 23 hours and standing at ambient temperature for 1 hour. After completing the six cooling cycles, the PMMA rod was withdrawn from the gel. The gel tube was immersed into water to exchange the DMSO in the gel with water. The hydrogel tube was transparent and easy for the inner surface observation. The inner surface of the PVA hydrogel tube was chemically modified with PAA in a water bath at 30°C for 96 hours in the presence of

hydrochloric acid. The hydrogel tube was filled with the PAA, and the PAA was attached on the PVA hydrogel surface through ester linkage. The modified hydrogel tube was rinsed thoroughly in flowing water to remove unreacted PAA. The inner hole dimension of the tube with square cross-section was 1.85 mm and the length of the tube was 100 mm. A partial illustration of the PVA hydrogel tube is shown in Fig. 1.

2.2 Working fluid

For the flow visualization experiment various particles are available, polystyrene is particularly useful in water, as their density (1.05 g/cm^3) is almost the same as that of water. The working fluids were distilled water and pH buffers with 0.005 percent neutrally buoyant $7.21\text{ }\mu\text{m}$ diameter monodisperse polystyrene particles as a tracer of fluid flow. Throughout these experiments, ionic strength of all buffers was 0.35. The fluid temperature was kept at 22°C .

2.3 Flow system description

The schematic illustration of the experimental apparatus used for this work is shown in Fig. 2. PVA hydrogel tube (1) was placed inside a sample cell (2) which was filled with the working fluid to prevent the gel tube from drying. The sample cell was placed in a water bath (3) made of PMMA. The water of the water bath was circulated by using a roller pump (16) (RP mv9, Furue Science Co. Ltd.) from the thermostat water bath (18) to keep the constant temperature. The gel tube in the PMMA bath was then placed on a stage (4) of a microscope. The stage was movable vertically and horizontally, and the position was controlled (in micron scale) electronically by computer. The constant head upper reservoir (5) supplied the flow through a 75 cm long inlet (6) and 25 cm long outlet (7) silicon tubes. The diameter of the inlet and outlet tubes was matched to that of the hydrogel tube. The upper reservoir constant head was controlled by using a micro tube

Fig. 1 Partial illustration of PVA hydrogel tube

Fig. 2 Schematic illustration of the experimental apparatus

pump (15) (Tokyo Rikakikai Co. Ltd.). After filling the gel tube and the entry flow system with the working fluid, the desired flow rates in the gel tube were established by adjusting the height of the upper reservoir. To get the sharp microscopic image, the hydrogel tube was irradiated by a light (8) from the below. The fluid was subjected to steady flow through the transparent hydrogel tube and the flow patterns were observed with a CCD camera (9) (Model Dxc-108, Sony) under a microscope (10) (OLYMPUS BH2-UMA). The CCD camera equipped with a high speed electronic shutter (up to $10\,000\text{ s}^{-1}$) enables us to obtain a clear picture of moving particles. The picture was directly shown on the monitor screen (13) and the image was recorded by a video recorder (12) (Stereo Video Cassette Recorder EDV-9000, Beta, Sony) at a rate of 30 pictures per second. The mean volumetric flow rate was determined using the measured fluid density and the mass of fluid (14) expelled in a given time during video recording of the flow patterns. The particle flow rates were estimated by analyzing the video images of the flowing particles using a personal computer.

2.4 Determination of particle velocity

To estimate the individual particle velocity in PVA hydrogel tubes, a particle tracking (PT) method has been used. In the PT method, the fluid velocity was inferred from the motion of tracking particles. The tracking particles were considered exactly to follow the motion of the fluid. The particles, which were in good focus and clearly belonged to the same particle, were used. The focusing latitude of the

Fig. 3 Measurement of the velocity of flowing particle by particle tracking method in a modified PVA hydrogel tube with pH 5.6 buffer. A microscopic image was shown which was prepared by overlaying two consecutive video images. Velocity of the flowing particle was estimated by analyzing the image data.

observing lens was $30\text{ }\mu\text{m}$. The data was obtained from an optical section around the median plane of the hydrogel tube. A microscopic image of velocity measurement by the PT method in a modified PVA hydrogel tube with pH 5.6 buffer is shown in Fig. 3. Two consecutive images were overlapped. The time differences of the two consecutive images were recorded. Particle displacement for the time interval was measured from the overlapped image. The velocity of the individual particle was estimated from the particle displacement divided by the time interval of the two consecutive images. From Fig. 3 it is clear that even in modified PVA gel we could observe the surface easily.

2.5 Data analysis

The Reynolds number (Re) for a tube with square cross-section and a wall shear stress (WSS) (τ) are defined as follows:

$$Re = \frac{WU}{v} \quad (1)$$

$$\tau = \mu \left(\frac{du}{dx} \right)_0 \quad (2)$$

Where U is mean velocity (Q/A), A is cross-sectional area, Q is flow rate, W is the length of a side of the square cross-section, v is the kinematic viscosity, μ is the fluid viscosity, and $(du/dx)_0$ is a velocity gradient on the gel surface.

The drag reduction (DR) is calculated by the ratio of the WSS τ_w , for the modified PVA hydrogel surface with suffix m and the intact PVA hydrogel surface with suffix i .

$$DR = \frac{\tau_{wm}}{\tau_{wi}} \quad (3)$$

The most common, however, in the report on drag

reduction is given as the percent drag reduction

$$DR(\%) = \left(1 - \frac{\tau_{wm}}{\tau_{wt}}\right) \times 100 \quad (4)$$

3. Results and Discussion

The PAA grafting on the PVA hydrogel tube surface was detected by a dye-staining method. The dye employed in this experiment was cationic, methylene blue (MB). Fig. 4 shows the video micrographs of tube cross-sections of an intact and a modified PVA hydrogels dyed with MB. After dyeing both hydrogels were immersed in water and found that the modified PVA hydrogel stained the dye and showed blue color in the inner surface of the hydrogel tube, while the intact PVA did not stain the dye. MB is a cation, and can bind electrostatically to anionic species. Modified gel has residual carboxylic acid in a large amount, which can easily be bound ionically with methylene blue. On the contrary, the intact PVA hydrogel does not have such activity, due to the absence of ionic groups in it. The PAA was grafted on the PVA hydrogel surface by ester linkage.

We estimated the individual particle velocity in hydrogel tube by the PT method. Fig. 5 shows representative examples of the velocity profiles in intact and modified PVA hydrogel tubes under the flow of

water and various pH buffers. Each open square in the plot indicates the velocity of a particle. All the velocity profiles were curve fitted with a second-order polynomial (r^2 usually greater than 0.99), and the wall shear stress are calculated from the velocity gradient on the hydrogel tube surface by using Eq. (2). In all cases curve fitting error of the velocity profiles were less than 1% therefore the wall shear stress estimation for the PVA hydrogel tube should be accurate.

We could find slip in Fig. 5, particularly in (b) to (e), and the slip was the largest in modified PVA gel (b) in water. The swelling degree of PAA is largest in water (pH=5.6 without buffer ($I=0$)), suggesting the surface structure of the PAA layer plays a critical roll on the slip. Further detail will not be discussed here, since further investigation is necessary for the clarification of the detail of the slip.

To understand the drag reduction phenomenon, we observed the flow on the hydrogel tube surface in micron scale accuracy at low Reynolds number. Fig. 6 shows the Reynolds number dependence of drag reduction in the modified PVA hydrogel tubes conveying water and various pH buffers. Drag

Fig. 4 Micrographs of cross-section of hydrogel tubes. (a) Intact PVA hydrogel (b) Modified PVA hydrogel. Both samples were dyed with methylene blue, and were rinsed in water for three days

Fig. 5 Velocity profiles in an intact and modified PVA hydrogel tubes. (a) intact PVA water, (b) modified PVA water, (c) modified PVA pH 5.6, (d) modified PVA pH 8 and (e) modified PVA pH 3

Fig. 6 Reynolds number vs drag reduction (%) in a modified PVA hydrogel tube at various pH

reduction on the modified hydrogel tube surface highly depended on the flow liquid pH. The maximum drag reduction was obtained in the modified PVA hydrogel tube at water flow. It should be noted that the degrees of dissociation (DD) of PAA at pH 3, 5.6, and 8 are about 5, 95, and 99 percent, respectively. The diffusibility of the modified hydrogel surface increases at dissociated condition and decreases at associated condition. The dissociated surface is slippery and the segment density of the interface is too low to interact with flowing liquid caused a higher drag reduction. On the other hand, at pH 3 the grafted PAA layer on the modified hydrogel surface associated and the surface became tight like an intact PVA and caused low drag reduction. The degree of dissociation of the grafted PAA on the PVA hydrogel surface is almost the same in water as in buffer of pH 5.6, because the pH of water is about 5.6, but the drag reduction was higher in water than pH 5.6 buffer. It is due to the effect of ionic strength of pH buffer on the anionic hydrogel tube surface layer.

At pH 8 the grafted PAA is fully dissociated. Due to the very high degree of swelling, the boundary of the hydrogel surface might be diffuse and very soft. The surface must be smooth enough to indicate large drag reduction value than that in pH 5.6 buffer at low Reynolds number. The increase of Reynolds number (or flow rate), however, the slippery soft surface deformed very easily into a deteriorated rough surface accompanying a sharp drop of drag reduction value. As a result, the drag reduction value at pH 8 became less than that at pH 5.6.

In all cases, the drag reduction decreases with the increase of the Reynolds number. At the dissociated condition the hydrogel tube surface becomes diffused and the grafted PAA layer is elongated and deformed

Fig. 7 Tentative illustration of the cross-sectional view of the grafted PAA chain on the PVA hydrogel surface at low pH (pH=3.0, $I=0.35$) and high pH (pH=8.0, $I=0.35$) and water. I =ionic strength

to align in the flow direction with increasing the velocity and surface became little-bit rougher than lower velocity. At very low Reynolds number maximum drag reduction was obtained because the modified hydrogel surfaces swells out more to form the boundary more diffuse.

The swelling/deswelling behavior in the surface of modified PVA hydrogel tube at different pHs could be explained in terms of the grafted PAA chains which respond to pH and flowing rate. Tentative models of the structure of the grafted PAA chains on the PVA gel surface are schematically illustrated in Fig. 7. In neutral and alkaline solutions the grafted PAA chains dissociate and the surface became hairy, whereas they shrink and associated on the gel surface at acidic pH. In water (pH=ca. 5.6, $I=0$), however, the swelling might be the highest among the measured samples, since the dissociation is not depressed by the shielding effect with buffer. Thus, the graft chains can change the hydrogel surface in response to the flow liquid pH change and the ionic strength. It is assumed that the main part of drag reduction is due to a universal mechanism based on the alignment of the elongated additives in local flow direction. In the modified PVA hydrogel, the dissociated PAA chain easily aligned in the flow direction and this seems the most important contribution to drag reduction at low flowing rate.

4. Conclusion

Drag reduction on the modified PVA hydrogel

tube surface at steady flow condition was experimentally studied by using microscope. The observation and the measurement of the flow in the hydrogel tube in micron scale accuracy were shown to be possible by PT method. Microscopic investigations have revealed that the drag reduction on the modified hydrogel surface depends on the chemical nature of the hydrogel surface, which was varied with flow liquid pH. Maximum drag reduction was obtained with flowing water where the PAA chain of modified hydrogel tube surface is at dissociated condition.

Acknowledgement

This work was supported by Grant-in-Aid for COE Research (10CE2003) by the Ministry of Education, Science, Sports and Culture of Japan.

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