Korea-Australia Rheology Journal
Vol. 20, No. 2, June 2008 pp. 89-94

Conformation of single polymer molecule in a slot coating flow

Jeong Yong Lee[1], Bo Kyung Ryu[1], Joo Sung Lee[2], Hyun Wook Jung[1,*] and Jae Chun Hyun[1]
[1]Department of Chemical and Biological Engineering, Applied Rheology Center, Korea University, Seoul 136-713, Korea
[2]Information Technology and Electronic Materials R&D, LG Chem/Research Park, Daejeon 305-380, Korea
(Received April 9, 2008; final revision received May 29, 2008)

Abstract

To satisfy good mechanical and optical properties of polymer-coated film products, it will be indispensable to elucidate the molecular orientation of polymer chains within coating liquids in coating flows. Using hybridized numerical method between computational fluid dynamics (CFD) and Brownian dynamics (BD) simulations can provide the useful information for the better quality control of coated films. Flexible polymer chains, *e.g.*, λ-DNA molecules here, change their conformation according to the flow strength and the flow type. The molecular conformation within the coated film on the web or substrate is quite different, because the polymer chains experience the complicated flow strength and flow types in flow field. Especially in the slot coating flow, these chains are more extended by the extension-like flow field generated in the free surface curvature just beyond the downstream die region. Also, the polymer chain extension beneath the free surface can be affected by the die geometry, *e.g.*, the coating gap, changing flow field.

Keywords **:** Brownian dynamics, computational fluid dynamics, slot coating, conformation, flow strength, flow type parameter, single polymer chain

1. Introduction

Slot coating process (Fig. 1), as one of pre-metered coatings, plays an indispensable role in manufacturing IT products such as flat panel displays, secondary batteries, *etc.* The final goal of this coating process, as in other coating processes, is to deposit thin uniform coating liquid layer on the web or the substrate with good physical properties. Dynamics of this process has been exploited by many experimenters and accounted for theoretically by analysts with the aid of appropriate approximations (Ruschak, 1976; Higgins and Scriven, 1980; Sartor, 1990; Gates, 1999; Chu *et al.*, 2006; Chang *et al.*, 2007). One of recent interesting issues is to incorporate polymeric coating liquids with non-Newtonian characteristic nature in this system. The establishment of operating coating windows to secure the uniformity of coated layer is of course an essential requirement in coating processes. Keeping pace with this issue, the conformation of polymer molecules in coatings is also being highlighted for their enhanced optical properties. Therefore, it will be important to scrutinize the molecular orientation of polymer chains in coating liquids for the better quality control of coating products.

To shed light on the fundamental behavior of the polymer molecules in coating flows, this paper investigated the conformation of a single polymer chain in the slot coating flow which can be regarded as a kind of microfluidic channels, by combining Brownian dynamics (BD) with the conventional computational flow dynamics (CFD) simulations. Especially, we focused on the λ-DNA as an example of flexible polymers in this study, because its dynamic behavior has been considerably unraveled from experimental and theoretical reports during a decade. Recent development in direct visualization methods (Smith and Chu, 1998; Smith *et al.*, 1999), coupled with Brownian dynamics simulations (Larson, 2005; Shaqfeh, 2005), has allowed the dynamics of single DNA molecules in flow fields to be studied with unprecedented details. Also, Duggal and Pasquali (2004) reported the flow visualization of λ-DNA in a micro roll coating equipment using a fluorescence microscope and its conformation under various flow conditions. These ingenious studies about the orientation of flexible polymer chains help us to understand the relationship between process conditions, molecular structures, and properties. Based on this background, we have tried to analyze the conformation of polymer chains in a slot coating process.

2. Brownian dynamics and slot coating simulation

Coating bead flow in slot coating has been predicted by two-dimensional model incorporated with Newtonian liquids using the commercial CFD package Flow-3D under

*Corresponding author: hwjung@grtrkr.korea.ac.kr

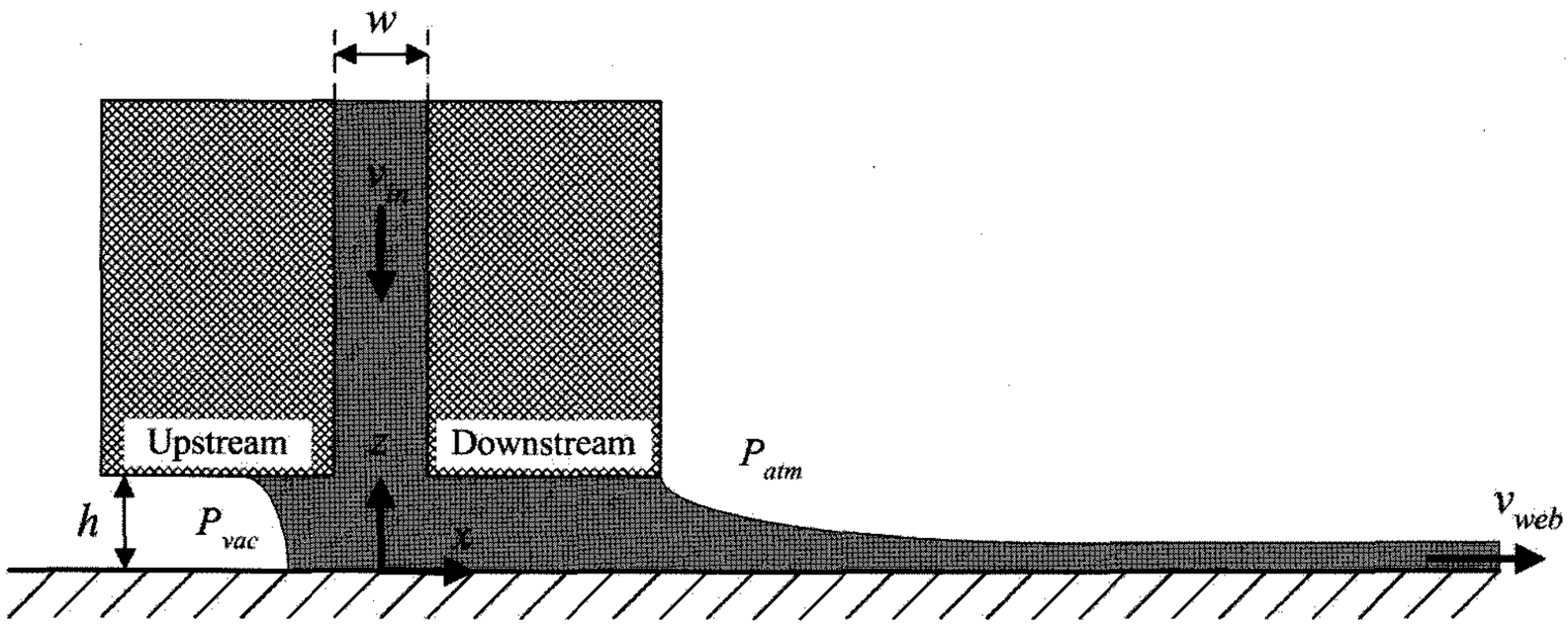
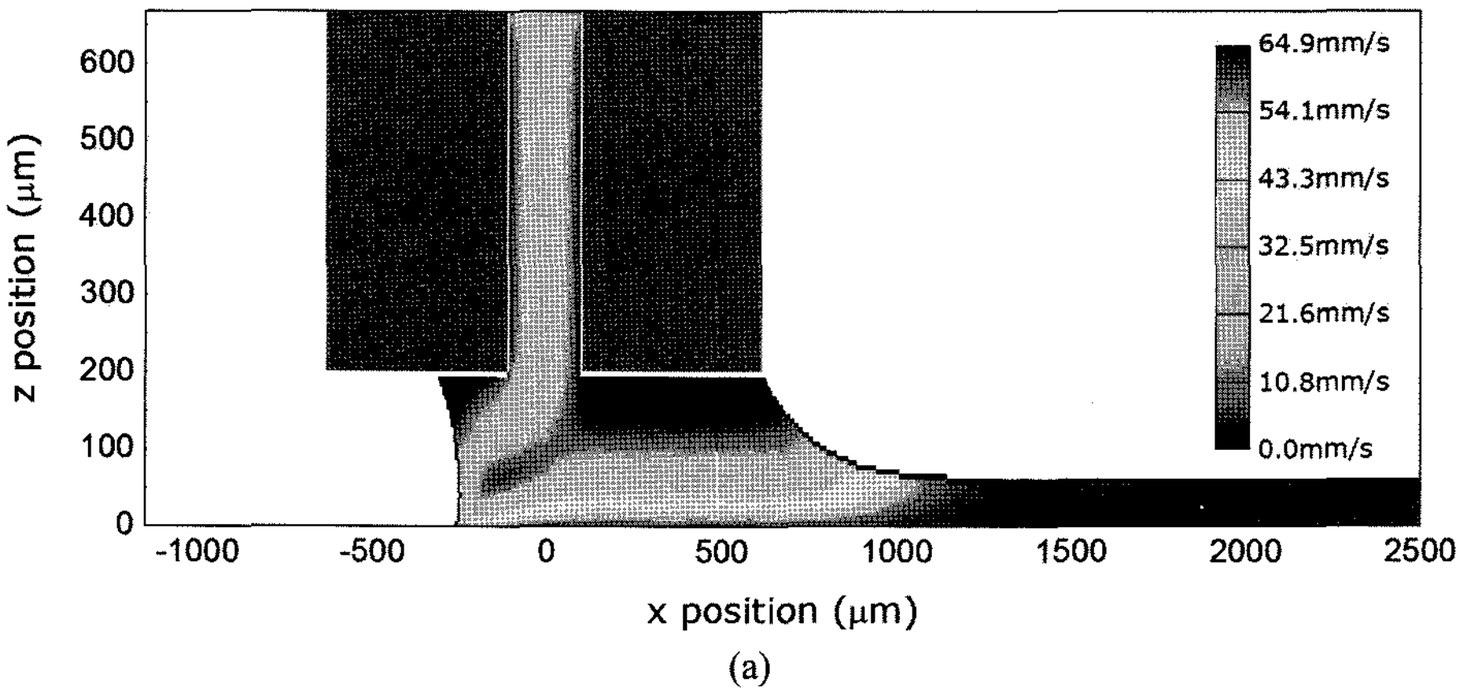
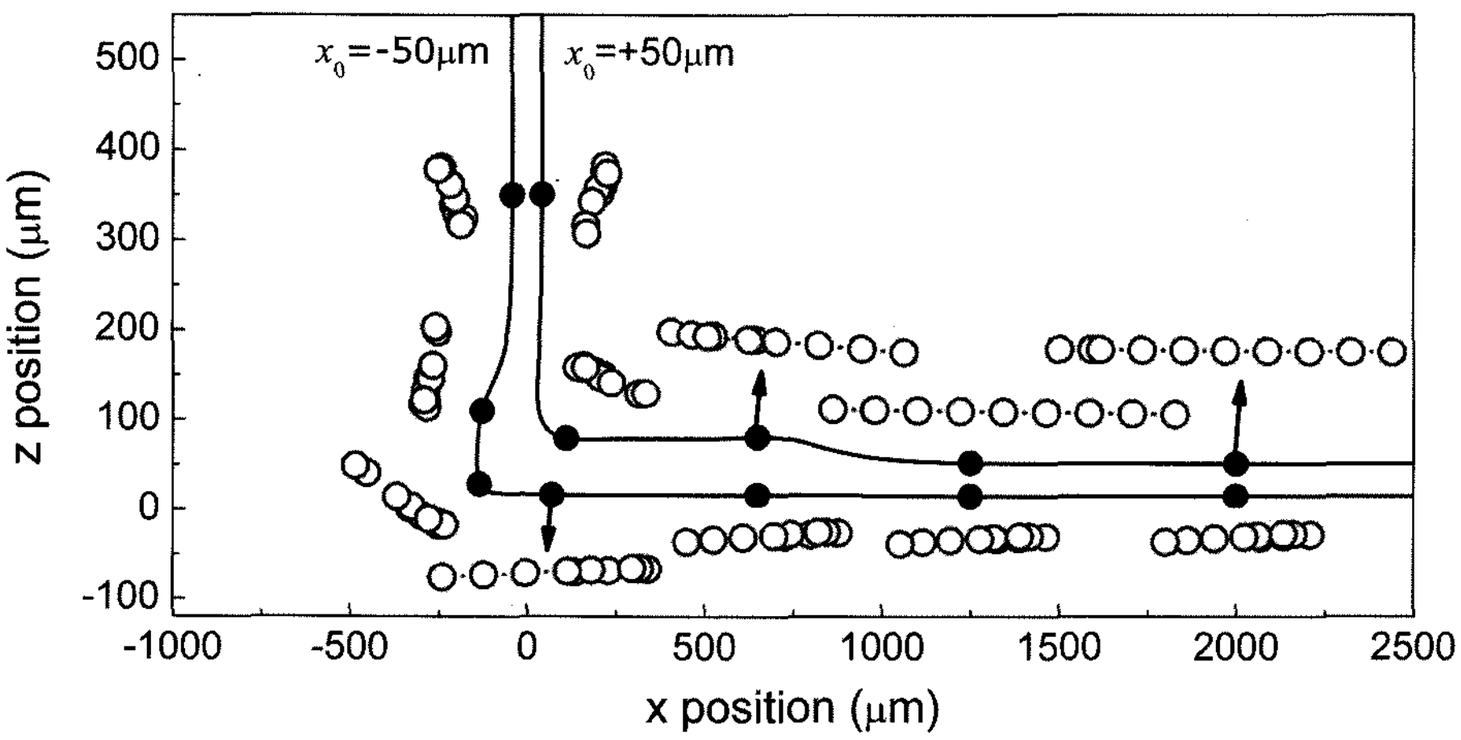


Fig. 1. Schematic diagram of the slot coating process.



(a)



(b)

Fig. 2. (a) Velocity magnitude contour under the operating conditions considered in this study and (b) two different ways for the conformational change of polymer molecules along each streamline in the slot coating flow.

the various operating conditions, as depicted in Fig. 2. Typical operating conditions and material properties are summarized in Table 1. To stabilize the coating bead flow, the bead pressure condition between upstream and downstream menisci has been applied (Gates, 1999). Flow field inside coating bead regime can be represented from the flow type parameter (α) defined as

$$\alpha = \frac{\|\boldsymbol{D}\| - \|\boldsymbol{\Omega}\|}{\|\boldsymbol{D}\| + \|\boldsymbol{\Omega}\|}, \tag{1}$$

where $\|\boldsymbol{D}\|$ and $\|\boldsymbol{\Omega}\|$ are the magnitudes of the deformation and vorticity tensors, respectively. For the 2D flow field,

Table 1. Model parameters in this study

Parameters		Values
Process conditions	Inlet speed, v_{in}	20 mm/s
	Web speed, v_{web}	65 mm/s
	Bead pressure, $\Delta P = P_{atm} - P_{vac}$	100 Pa
	Slit gap, w	200 μm
	Coating gap, h	100~200 μm
Fluid properties	Density, ρ	1,200 kg/m^3
	Surface tension, γ	30 mN/m
	Viscosity, η	0.04 Pa·s
Polymer chain (λ-DNA)	Dimensionless relaxation time, τ_0	15.7
	Number of springs	9
	Kuhn steps per spring	17

these magnitudes are expressed as follows.

$$\|\boldsymbol{D}\| = \sqrt{\frac{1}{2}(\boldsymbol{D}:\boldsymbol{D}^T)} = \sqrt{\left(\frac{\partial v_x}{\partial x}\right)^2 + \frac{\partial v_x}{\partial z}\frac{\partial v_z}{\partial x} + \left(\frac{\partial v_z}{\partial z}\right)^2 + \frac{1}{2}\left(\frac{\partial v_x}{\partial z}\right)^2 + \frac{1}{2}\left(\frac{\partial v_z}{\partial x}\right)^2}, \quad (2)$$

$$\|\boldsymbol{\Omega}\| = \sqrt{\frac{1}{2}(\boldsymbol{\Omega}:\boldsymbol{\Omega}^T)} = \sqrt{\frac{1}{2}\left(\frac{\partial v_x}{\partial z}\right)^2 + \frac{1}{2}\left(\frac{\partial v_z}{\partial x}\right)^2 - \frac{\partial v_x}{\partial z}\frac{\partial v_z}{\partial x}}. \quad (3)$$

This flow type parameter (α) varies from −1 (purely rotational flow), 0 (purely shear flow) to +1 (purely extensional flow). Brownian motion of a single molecule has been predicted by the following stochastic equation, Eq. (4) (Larson, 2005; Shaqfeh, 2005), based on the flow field in the coating bead regime. Albeit the usage of a phantom chain in this study, one may acquire physically meaningful results by effectively circumventing the complexity of hybrid simulations for coating problems. Moreover, it is noted that the microstructural change of polymer molecules does not significantly affect the flow field in the Newtonian system (Suen *et al.*, 2002).

$$d\boldsymbol{Q}_i = \left[\boldsymbol{k}_j \cdot \boldsymbol{Q}_i + \frac{\boldsymbol{F}^S_{i+1} - 2\boldsymbol{F}^S_i + \boldsymbol{F}^S_{i-1}}{4}\right]dt + \sqrt{\frac{1}{2}}(d\boldsymbol{W}_{i+1} - d\boldsymbol{W}_i), \quad (4)$$

where $\boldsymbol{Q}$ denotes the displacement vector, $\boldsymbol{k}$ the flow gradient tensor in flow field, $\boldsymbol{W}$ the Wiener process for the random walk, and $\boldsymbol{F}^S$ is spring force. The components in flow gradient tensor ($\boldsymbol{k}$) were linearly interpolated from the flow field data by CFD simulations. The subscript i represents the individual spring in the polymer chains, and j is the location of polymer chains in the nonhomogeneous flow field. In this coating flow, the Brownian force is weaker than drag and spring forces owing to a quite strong flow field. Also, the effect of excluded volume is not considered in the governing equations, judging that the polymer chain will not collide with moving web or penetrate through boundaries under the typical operating conditions. As the spring model, worm-like chain (Marko and Siggia, 1995) has been adopted in this study. This model, which is good for stiff polymers, is a special case of the freely rotating chain models with very small bond angles.

The velocity components and their gradients in slot coating bead region have been calculated from two-dimensional simulations with unequal rectangular meshes, *e.g.*, 350×67 meshes under 200 μm coating gap condition, guaranteeing the numerical convergence. Typical geometry of slot coating process with the steady velocity magnitude contour is depicted in Fig. 2(a). To effectively characterize the flow field, the magnitude of velocity gradient ($|\nabla v|$) representing a flow strength as well as flow type parameter (α) has been considered (Lee *et al.*, 2007a). Because of the complex flow characteristics, these parameters are defined as the local variable rather than universal one incorporated in simple flows. In coating bead flow region, various flow patterns can be obtained. The polymer chains typically undergo shear flow until the slit die exit. However, extension-like flows have been generated by the moving web condition and the formation of downstream meniscus which is free surface curvature. As an example, the temporal pictures of a single molecule were plotted on Fig. 2(b) with its streamline. Due to the Brownian motion, it may migrate from the streamline, but it hardly stray far away from the streamline if the velocity gradient is high enough as illustrated in Fig. 3. The molecule entered at x_0 = +50 μm from the centerline of the slit (plus sign means the chain locates in the direction of the downstream) was strongly stretched at the downstream, because of the extension-like flow generated by the free surface curvature. Another molecule started at x_0=−50 μm was slightly extended in the upstream region when it was subjected to the moving web, however, it eventually recoiled by the plug flow acting on the downstream region.

Fig. 3 displays flow characteristics around a polymer chain in downstream region, following three different streamlines entered at x_0=−50, 0, and +50 μm from the slit centreline, respectively. Dimensionless mean extension ($<x>/L$) of polymer chains has been correlated with the change of flow characteristics such as $|\nabla v|$ and α. Firstly, the role of flow characteristics will be described. As indicated in Fig. 3(a), the flow type can affect the molecular orientation or conformational change of polymer chains. According to the flow type parameter (α), flow features in coating bead region can be classified into several different cases. The extruded polymer solution mainly experiences the shear flow within the upstream/downstream die lip

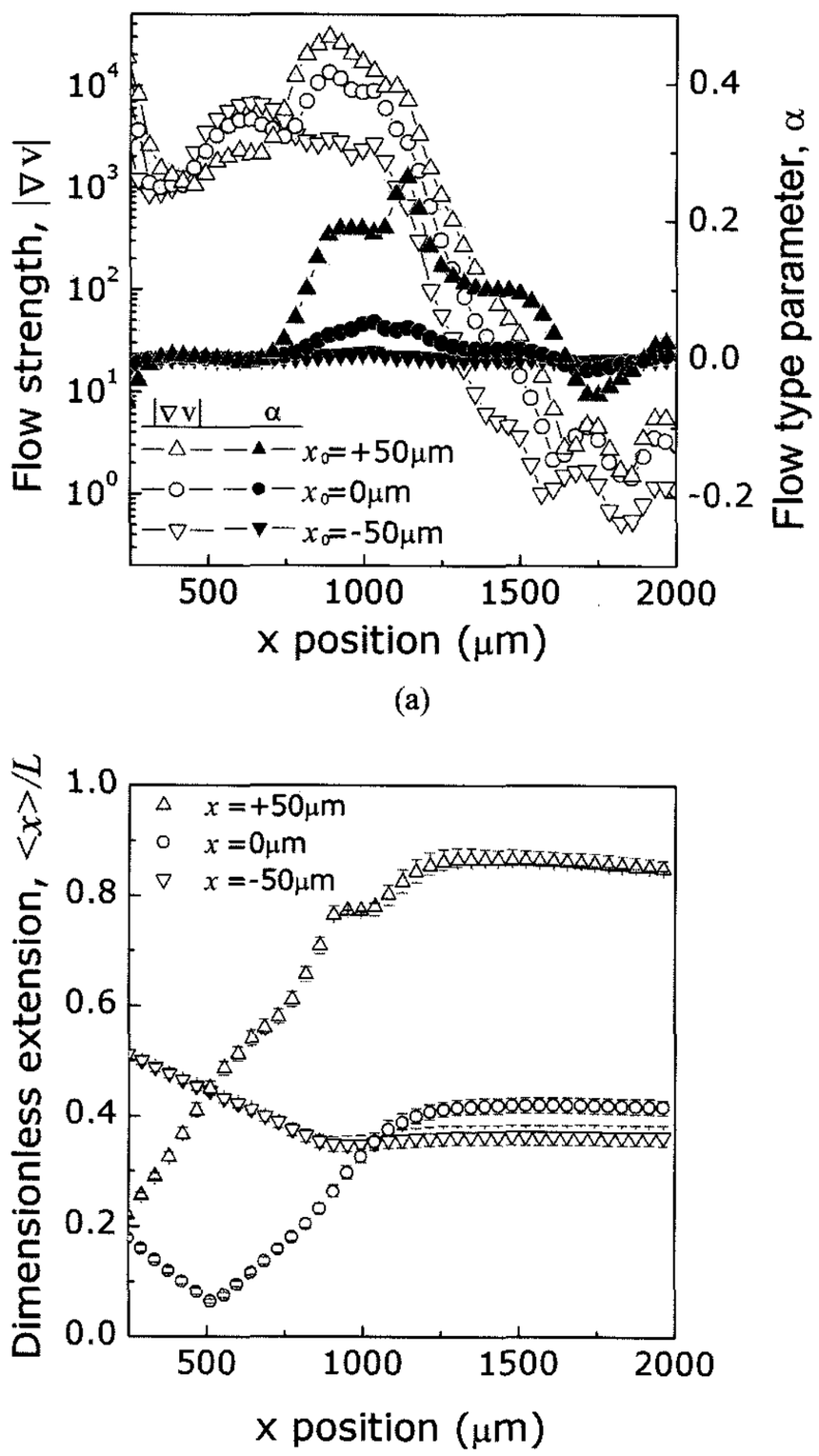


Fig. 3. (a) The changes of flow strength ($|\nabla v|$) and flow type parameter (α) around polymer chains entered at three different positions (*i.e.*, $x_0=-50$, 0, $+50$ μm) and (b) the conformational change embedded in chain extension ($<x>/L$) of each molecule along the flow direction (x) under the same operating conditions in Fig. 2.

regions, *i.e.*, $\alpha\sim0$ (Actually, there exist some rotational flow transitions (negative α) between feed and upstream regions.). After passing through the downstream die region, the liquid forms its free surface depending on its surface tension or capillary number. This curvature produces extensional flow mingled with shear flow, leading to the increase of the flow type parameter, α (Graham, 2003). Even though α could not evolve to purely extensional flow (*i.e.*, $\alpha<0.2$ under the operating conditions involved in this study), it has been confirmed that the conformational changes of the molecules from the coiled state to the stretched state are clearly observed in the nonhomogeneous slot coating flows due to the rather weak extensional flow, as described by Woo and Shaqfeh (2003) in the homogeneous flow field. Eventually, the flow on the moving web will become plug-like, *i.e.*, approach of $|\nabla v|$ and α to zero values, resulting in the recoil of polymer chains. Secondly, the conformation of polymer chain in coating bead region will be further delineated, closely linked with flow characteristics. The initial configuration of the polymer chains are almost same, but the polymer chain started at -50 μm position from the slit centerline is a little longer than other cases at initial stage because it may experience weak extensional flow caused by turning to upstream die region. Thereafter, the chain around the web position far from the free surface will be recoiled due to the shear flow type at this position. Whereas, the polymer chain near the free surface is more strongly extended after passing through the downstream die region because of higher $|\nabla v|$ and α. This extended chain will eventually return to the coiled state after $|\nabla v|$ and α attain to zero. It is also noted that it would be important to control processing time in a slot coating flow for producing the desired oriented coatings. In other words, the detailed explanation for the phase transition of polymer chains in this process can be clarified by considering the relationship between processing time and molecular relaxation time (Lee *et al.*, 2007b).

The effective Weissenberg number ($Wi_{eff}\equiv Wi\sqrt{\alpha}=|\nabla v|\tau_0\sqrt{\alpha}$) can be a useful parameter to characterize the flow pattern and the conformational change of the polymer chains in the mixed flow, as reported in Shaqfeh (2005) and Lee *et al.*, (2007a). Regarding the high Weissenberg number in this slot coating flow case, however, it is found that the change of the flow type parameter plays a key role in elucidating the relationship between mixed flow and chain extension. By tracking molecules entered at $x_0=\pm50$ μm position inside slit die along with its streamline, the conformational changes have been sought according to α (Fig. 4). Along the flow direction, flows within up-

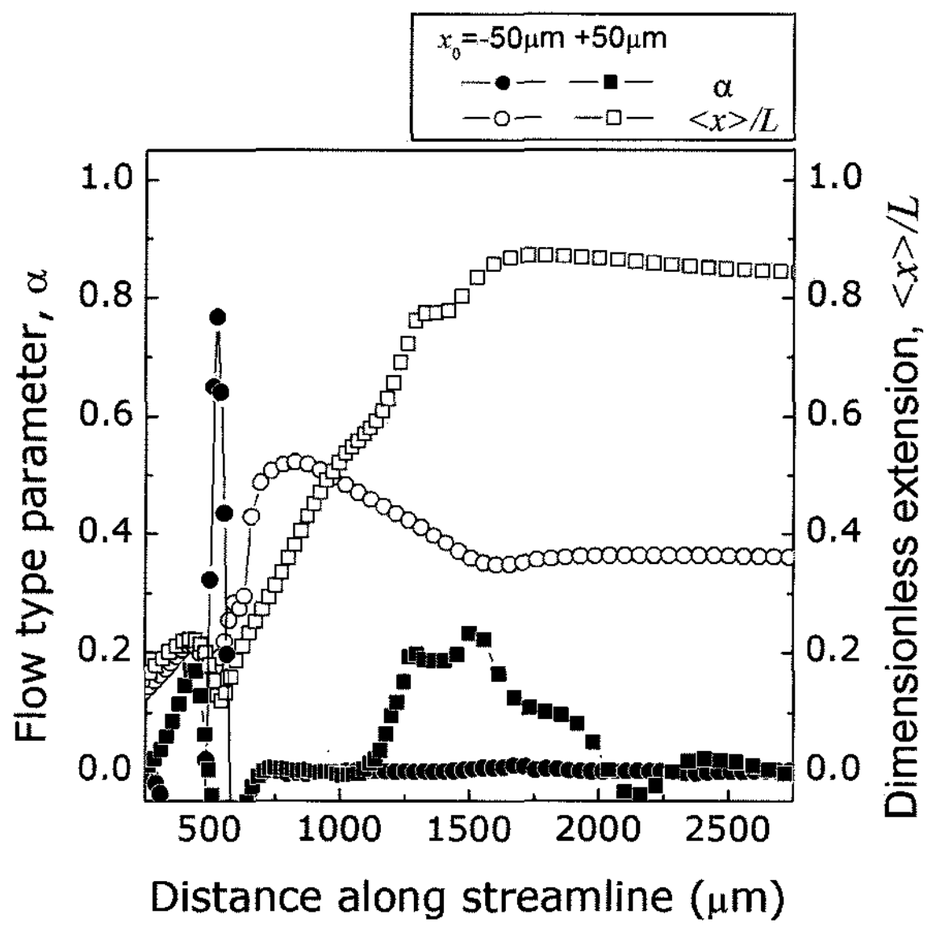
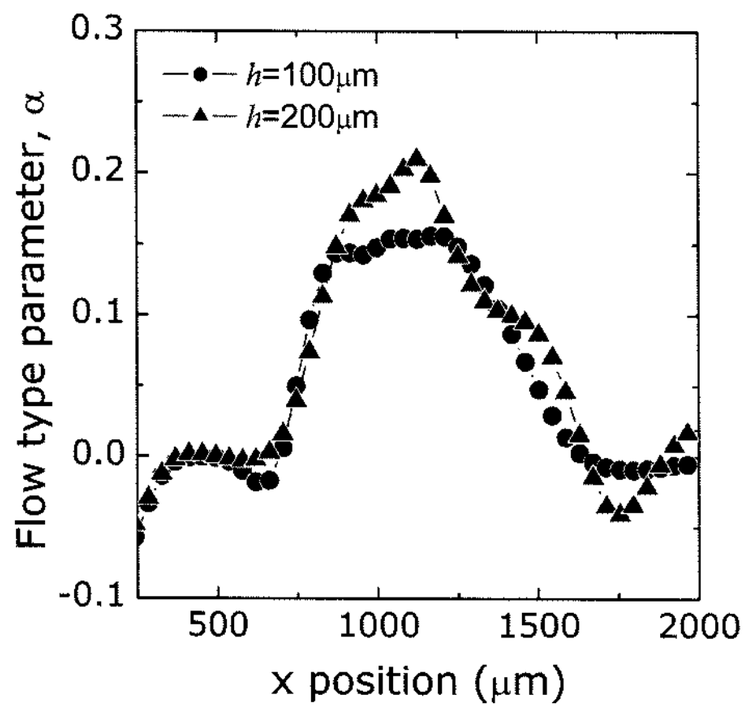


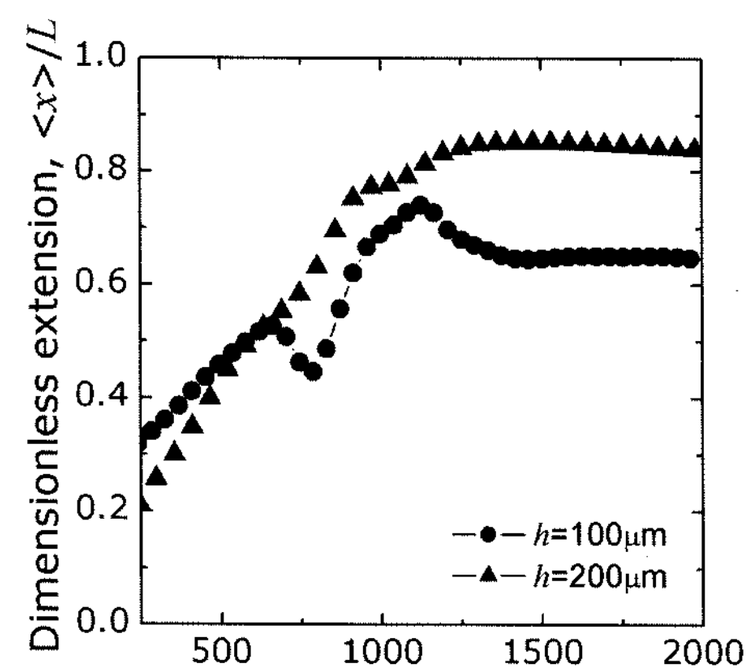
Fig. 4. An example of the molecular extension ($<x>/L$) along the streamline at the position $x_0=-50$ and $+50$ μm from the slit centerline.

stream/downstream die regions show the shear-like behavior and the flow type parameter was almost 0 ($|\alpha|<0.05$). However, α gives a peak by the free surface curvature when the coating liquid just exits the downstream die lip, resulting in the significant extension of polymer molecules. In the case of polymer chain entered at $x_0=-50$ μm, the α value exhibits the sharp peak when the molecule meets the moving web after its turn to the upstream region. Due to the extension-like flow in this region, the polymer chain is suddenly extended. And then, it will be recoiled, as already mentioned in Fig. 3.

By chasing a polymer chain started at $x_0=+50$ μm, the chain extension has been compared under different coating gap conditions (Fig. 5). Reducing coating gap (h) leads to the decrease of the free surface curvature and thus the flow type parameter (α). When the coating gap reduces to 100 μm, the chain extension near the free surface decreases as in the case of α and extensional component in the flow field becomes weak (Fig. 5(a)). As portrayed in Fig. 5(b), all molecules start to extend, and show similar chain extension until the downstream die lip ($x=700$ μm), however, their chain extensions are totally different due to the different contribution of extension-like flow near free surface curvatures.



(a)



(b)

Fig. 5. The effect of coating gap on the flow field near the free surface and molecular conformation. (a) The change of flow type parameter (α) around polymer chains entered at $x_0=+50$ μm and (b) chain extension ($<x>/L$) at each position.

It has been found that a small change of flow type from pure shear to extensional flow can remarkably extend flexible polymer chains, and their conformation may be controlled by further drying step. The hybridization method between computational fluid dynamics and Brownian dynamics simulations used in this study can be a useful tool to qualitatively estimate conformations of polymeric molecules in coated films.

3. Conclusion

The conformational change of flexible polymer chains, *i.e.*, λ-DNA, in a slot coating flow has been investigated using hybridized numerical method of computational fluid dynamics with Brownian dynamics simulations. It is noted that even though the conformational change of λ-DNA has been illustrated in the slot coating flow in this paper, the same methodology can be further applied to other general polymer solutions. Chain extension of a flexible polymer varies with the flow strength, $|\nabla v|$, and flow type parameter, α. Chains are significantly extended just after passing through the downstream die lip region due to the extensional flow created by the free surface curvature. Also, it has been found that by altering the flow type in coating bead flow region, *e.g.*, the change of coating gap, the chain extension near the free surface can be controlled. Especially, molecules with high $|\nabla v|$ and a near the free surface position are more extended than those near the moving web position which are only affected by the weak extensional flow in upstream die region.

Acknowledgements

This study was supported by research grants from the Seoul R&BD program and the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC). Also, the support of the KOSEF (R01-2008-000-11701-0) is gratefully acknowledged.

References

Chang, Y.-R., H.-M. Chang, C.-F. Lin, T.-J. Liu and P.-Y. Wu, 2007, Three minimum wet thickness regions of slot die coating, *J. Colloid Interf. Sci.* **308**, 222-230.

Chu, W.-B., J.-W. Yang, Y.-C. Wang, T.-J. Liu, C. Tiu and J. Guo, 2006, The effect of inorganic particles on slot die coating of poly(vinyl alcohol) solutions, *J. Colloid Interf. Sci.* **297**, 215-225.

Duggal, R. and M. Pasquali, 2004, Visualization of individual DNA molecules in a small-scale coating flow, *J. Rheol.* **48**, 745-764.

Gates, I. A., *Slot Coating Flows: Feasibility, Quality*, Ph.D. Thesis, University of Minnesota, 1999.

Graham, M. D., 2003, Interfacial hoop stress and instability of viscoelastic free surface flows, *Phys. Fluids* **15**, 1702-1710.

Higgins, B. G. and L. E. Scriven, 1980, Capillary-pressure and viscous pressure-drop set bounds on coating bead operability, *Chem. Eng. Sci.* **35**, 673-682.

Larson, R. G., 2005, The rheology of dilute solutions of flexible polymers: Progress and problems, *J. Rheol.* **49**, 1-70.

Lee, J. S., E. S. G. Shaqfeh and S. J. Muller, 2007a, Dynamics of DNA tumbling in shear to rotational mixed flows: Pathways and periods, *Phys. Rev. E* **75**, 040802-1-040802-4.

Lee, J. Y., B. K. Ryu, J. S. Lee, H. W. Jung and J. C. Hyun, 2007b, Conformation of single polymer molecule in a slot coating flow, 7th European Coating Symposium, Paris, France.

Marko, J. F. and E. D. Siggia, 1995, Stretching DNA, *Macromol.* **28**, 8759-8770.

Ruschak, K. J., 1976, Limiting flow in a pre-metered coating device, *Chem. Eng. Sci.* **31**, 1057-1060.

Sartor, L., *Slot Coating: Fluid Mechanics and Die Design*, Ph.D. Thesis, University of Minnesota, 1990.

Shaqfeh, E. S. G., 2005, The dynamics of single-molecule DNA in flow, *J. Non-Newtonian Fluid Mech.* **130**, 1-28.

Smith, D. E. and S. Chu, 1998, Response of flexible polymers to a sudden elongational flow, *Science* **281**, 1335-1340.

Smith, D. E., H. P. Babcock and S. Chu, 1999, Single-polymer dynamics in steady shear flow, *Science* **283**, 1724-1727.

Suen, J. K. C., Y. L. Joo and R. C. Armstrong, 2002, Molecular orientation effects in viscoelasticity, *Ann. Rev. Fluid Mech.* **34**, 417-444.

Woo, N. J. and E. S. G. Shaqfeh, 2003, The configurational phase transitions of flexible polymers in planar mixed flows near simple shear, *J. Chem. Phys.* **119**, 2908-2914.