POLYMER/POLYMER INTERFACIAL SLIP BETWEEN POLYPROPYLENE/POLYSTYRENE MELTS IN MULTI-LAYER FLOW

Ryohei Komuro, Sathish K. Sukumaran, Masataka Sugimoto, Kiyohito Koyama*

Graduate School of Science and Engineering, Yamagata University, Japan – koyama@yz.yamagata-u.ac.jp

Abstract - At the interface between two immiscible polymers, chemically different chains are likely to be weakly entangled leading to poor interfacial adhesion. Early observations of unusally high flow rates under coextrusion suggested the existence of liquid-liquid interfacial slip. To understand the behavior at the interface, we investigated interfacial slip using Polypropylene(PP)/Polystyrene(PS) with matched shear viscosity and moduli in co-extrusion process. As seen from this study, We found that the interfacial slip velocity of PP/PS/PP and PS/PP/PS could be evaluated by eq.(2), and the interfacial slip velocity depended on the interfacial shear stress. Furthermore, we demonstrated the existence of polymer/polymer interfacial slip in co-extrusion process by the visualization technique.

Keywords: polymer-polymer interfacial slip, multi-layers, coextrusion

Introduction

In multi-layer film processing, two or more materials are extruded through a single die. Especially, in case of the immiscible polymer systems, the interface has low entanglement densities and weak interactions. Therefore, the interface between polymer-polymer cannot sustain high shear stress. So, it is thought that the interfacial slip is believed to occur under this situation.

Past studies about the slip at polymer/polymer interface, some scientists have investigated via rheological measurements and/or the optical observation [1-8]. When two or more polymers are coextruded, at the interface between two immiscible polymers liquid, the chemically different chains are likely to be weakly entangled leading to poor interfacial adhesion. Hence when two immiscible polymers are coextruded, one might expect slip at the liquid/liquid interface. Han et al. [1] found that the pressure gradient in multi-layer flow was decreased as compared with the individual component at same flow rate. These result suggested the existence of polymer/polymer melts interfacial slip during multi-layer flow. Recently, Lee et al. [2] and Park et al. [3] estimated the interfacial slip velocity using the rotational plate rheometer and the sliding plate rheometer. However, the polymer/polymer interfacial slip in co-extrusion has not been well understood. Because, the method to estimate the polymer/polymer interfacial slip in co-extrusion has not been well established.

Recently, we succeeded to estimate the Polypropylene(PP)/Polystyrene(PS) interfacial slip verocity with matched shear viscosity and moduli in two-phase concentric flow [9]. In this study, we investigated PP/PS interfacial slip in two-layer and three-layer flow using the slit die. Then, we compared with our earlier results from capillary rheometry[9]. Moreover, we investigated the flow velocity distribution by the visualization technique to confirm the existence of. polymer/polymer interfacial slip. Because If interfacial slip occurs at the interface of the multilayer structure, it will be reflected directly by the existence of velocity discontinuity at the interface.

Experimental

Materials

In order to avoid the effect of viscoelastic ratio on the interfacial slip behavior, we used isotactic-PP and atactic-PS having the quite similar viscoelastic properties over a wide range of shear rates as shown in Fig.1. The materials chosen for the experimental study were PP (Mw=345,000 g/mol, Mw/Mn=5.02) and PS (Mw=312,000 g/mol, Mw/Mn=2.66). PP was kindly supplied by JAPAN POLYPROPYLENE Co.. PS was kindly supplied by PS JAPAN Co..

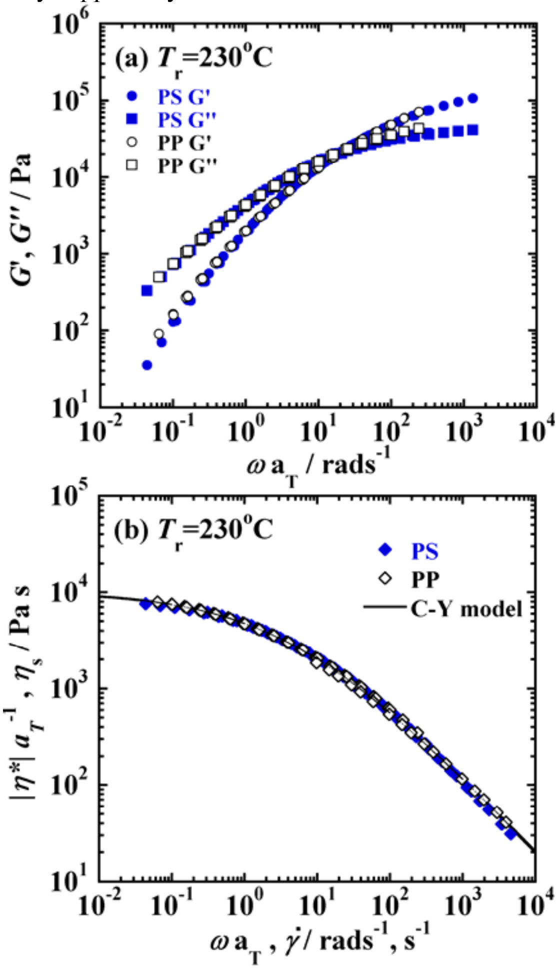

Fig.1 (a) *G', G''*, and (b)$|\eta^*|$ as function of ω at 230 °C.

Rheological measurements

The dynamic small angle oscillatory shear measurements were performed using a rotational plate rheometer (TA instruments, ARES) under a nitrogen atmosphere at 190-250°C. The geometry of jig is parallel-parallel plate with diameter of 25mm. The gap was set to be 1mm. Circular disks of each sample were prepared by compression molding at 230°C. Fig.1 shows the master curve of (a) storage modulus *G'* and loss modulus *G''* and (b) the complex viscosity $|\eta^*|$ and the steady shear viscosity η_s of PP and PS at the reference temperature Tr=230 °C.

The steady shear viscosity η_s at the higher shear rate range $\left(\dot{\gamma} > 10s^{-1}\right)$ was measured using a capillary rheometer (Toyo Seiki Seisaku-sho Co, Capilograph). The wall shear stress σ_w and the wall shear strain rate $\dot{\gamma}_w$ were corrected using the Bagley correction and the Rabinowitsch correction using three types of capillary dies having *D*=1mm, *L*=5, 10, 20mm, respectively. From Fig. 1(b), it is found that the data of $|\eta^*|$ and η_s were in good agreement with Cox-Merz rule [10].

The Carreau-Yasuda equation is found to fit the shear viscosity versus shear rate data quite well [11]:

$$\eta = \eta_0 \left\{1 + \left(\lambda\dot{\gamma}\right)^{\alpha}\right\}^{(n-1)/\alpha}\Big|_{\omega=\dot{\gamma}} \quad (1)$$

where η_0, λ, n, and α are the zero-shear viscosity, time constant, power-law exponent, and dimensionless parameter, respectively. The solid lines in Fig.1 are the Carreau-Yasuda prediction for PP and PS.

Co-extrusion measurements

The polymer/polymer interfacial slip measurements in the multi-layer flow were performed using the two twin-screw extruder (TECHNOVEL Co, ULT nano) and the slit die (width/height=10/0.5mm). This slit die contain the glass window at the bottom of die. In order to investigate the velocity profile for height direction, we used the confocal scanning laser microscope (Yokogawa Electric Co., CSU-22). The scanning data was imported by high speed camera (RED LAKE Inc., Motion Pro HS-4), Ar-laser (MELLES GRIOT Inc., 543-BS-A02). Fluorescence particle 0.05wt% (average diameter is 3μm) were premixed with PP and PS. Then, the velocity profile for height direction was evaluated to scan the velocity of fluorescence particle.

Polymer/polymer interfacial slip velocity in three-layer flow

In case of three-layer flow, if we assumed that *h, w, Q,* $Q_{\text{no-slip}}$, *a,b*, and $V_{\text{s-i}}$ were the height of slit die, the width of slit die, the total volumetric flow rate, the total volumetric flow rate in case of no-slip boundary condition, the interfacial slip velocity, $V_{\text{s-i}}$ is as following equation:

$$V_{s-i} = \left(Q - Q_{\text{no-slip}}\right)/\left(b - a\right)W \quad (2)$$

$Q_{\text{no-slip}}$ was evaluated using eq.(1). Since the wall slip does not occur within our experimental condition, $V_{\text{s-i}}$ was estimated by eq.(2).

Results and Discussion

Fig.2 shows $V_{\text{s-i}}$ as $\sigma_{\text{a-i}}$ for PP/PS (capillary), PS/PP/PS (slit), and PP/PS/PP (slit). From Fig.2, it is found that the interfacial slip velocity of PP/PS/PP and PS/PP/PS were rather close and increase confidence the determined interfacial slip velocities, and the dependence of $V_{\text{s-i}}$ on $\sigma_{\text{a-i}}$ was a power-law. the power-law exponent were approximately 2.2 at an interfacial stress. These results suggested that $V_{\text{s-i}}$ depended on $\sigma_{\text{a-i}}$ although the $V_{\text{s-i}}$ was not affected by the shape of die.

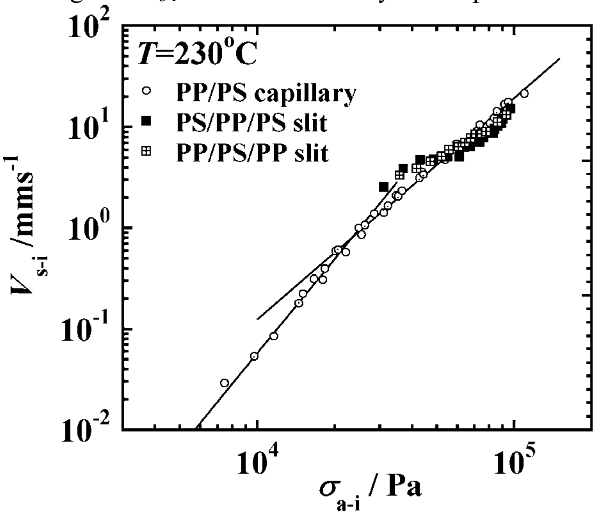

Fig.2 Interfacial slip velocity Vs-i as a function of interfacial shear stress σs-i for ○ PP/PS (capillary), ■PS/PP/PS (slit), and ⊞ PP/PS/PP (slit).

Fig.3 shows the velocity profile for PP, PS, and PS/PP/PS at almost similar pressure gradient. In this study, PP and PS have quite similar viscoelastic properties over a wide range of shear rates as shown in Fig.1. Namely, the velocity profile of PP and PS at same pressure gradient must be same. If the interfacial slip does not occur in PS/PP/PS, the velocity profile of PS/PP/PS would be same with PP and PS (at same pressure gradient). However, As seen from Fig.3, it is found that the velocity profile of PS/PP/PS was discontinued at PP/PS interface although the velocity profile of PP and PS were almost same. We demonstrated that the existence of polymer/polymer interfacial slip in co-extrusion process by the visualization technique

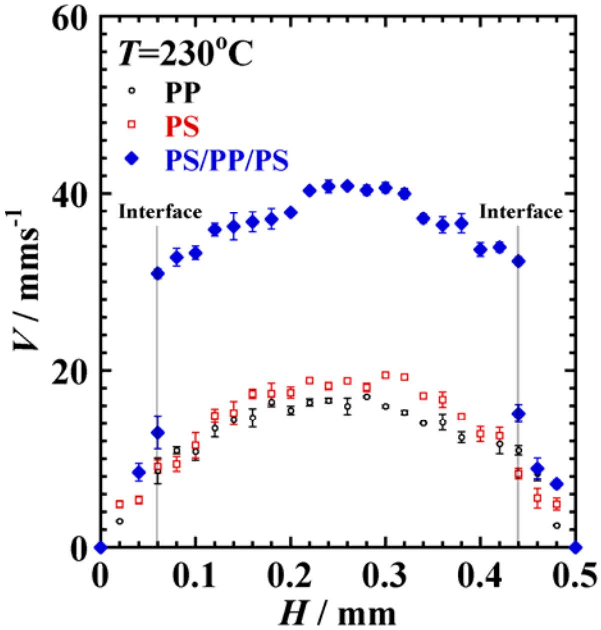

Fig.3 Velocity profile for PP, PS, and PS/PP/PS at constant pressure gradient.

Conclusions

We investigated interfacial slip using PP/PS with matched shear viscosity and moduli in co-extrusion process. As seen from this study, We found that the interfacial slip velocity of PP/PS/PP and PS/PP/PS could be evaluated by eq.(2), and the interfacial slip velocity depended on the interfacial shear stress. Furthermore, we demonstrated the existence of polymer/polymer interfacial slip in co-extrusion process by the visualization technique.

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