SLIP AT THE INTERFACE BETWEEN IMMISCIBLE POLYMER MELTS: EFFECT OF VISCOSITY RATIO

S. K. Sukumaran*, R. Komuro, M. Sugimoto, K. Koyama

Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata, 992-8510 Japan
E-mail of corresponding author: sa.k.sukumaran@gmail.com

ABSTRACT

Slip at the interface between polymer melts remains poorly understood. Studies that use only rheological data to deduce the slip velocity usually involve applying a shear deformation to a stack of parallel multilayers. In order to understand slip in the context of polymer extrusion, we have investigated slip at the interface between two immiscible polymer melts undergoing pressure driven flow through a capillary die. To enable the measurement of slip velocity at a polymer/polymer interface during capillary flow, we have adapted the Mooney method, a method usually used to study wall slip. Using the method, one can measure the dependence of the interfacial slip velocity on the interfacial shear stress for cylindrical core-sheath samples of Polypropylene and Polystyrene. We use this method to investigate the effect of varying the shear-rate dependent viscosity of the two polymers on slip at the polymer/polymer interface. We vary the viscosity either by varying the molecular weight of the polymer(s) or by varying the temperature at which the experiment is performed. Our results indicate that polymer/polymer interfacial slip is not sensitive to variations in the molecular weight of the polymers. Increasing the temperature led to an increase in the interfacial slip velocity at a given interfacial stress. A possible reason for this behaviour is discussed.

1. INTRODUCTION

Polymer coextrusion is widely used for developing products for use in a range of industries. An important advantage of polymer coextrusion is that not only the various physical properties of the final product but also its cost can be easily varied to satisfy the needs of the desired application. The variation in the properties can be accomplished by varying the polymers used, the number of layers in the final product, the thickness of the layers etc.

Parallel multilayered products are typically manufactured using either a feedblock, or a distribution block along with single manifold or multi-mainfold dies. Owing to the complexity resulting from both the shape of the extrusion die and the actual flow behaviour, the principal technique for investigating multilayer flow in industry and academia is through viscoelastic flow simulations. In order to investigate flow phenomena using computer simulations, it is necessary to utilize boundary conditions appropriate to the particular flow under consideration. Most simulations of flow phenomena, including those for non-Newtonian fluids, assume that the velocity is continuous at all phase boundaries. Thus, in addition to the relevant constitutive equation, simulations of multilayer coextrusion usually use the "no-slip" boundary condition at a polymer/polymer interface.

Naturally, polymers used for manufacturing multilayers are mutually immiscible. Therefore, one can expect the the density of entanglements at the interface to be low. If interfacial entanglements are the main source of adhesion between the different polymer layers, high shear stresses cannot be sustained by the polymer/polymer interface and slip can occur at the interface. Early experiments [1,2] on multilayer flow indicated that the pressure gradient necessary to extrude a multilayer at a particular flow rate was significantly lower than the pressure gradient necessary to extrude a single layer of either polymer at the same flow rate. In order to explain this, Han and Chin [3]

postulated the existence of slip at the interface between immiscible polymers.

Several researchers have investigated polymer/polymer interfacial slip either using rheological [4-7] or flow visualization [8-9] techniques. Flow visualization techniques are conceptually straightforward and rely on few assumptions. However, such experiments need equipment that is transparent to the kind of light used to probe the suspended particles. Rheological techniques do not need such special equipment. Typically, these experiments use the quantitative deviation in the flow properties due to slip, when compared to the corresponding values assuming the no-slip boundary condition, to estimate the slip velocity. Therefore, such measurements critically depend on obtaining good estimates for the flow properties (such as the viscosity) under the no-slip condition. This restriction has limited most of the available studies to multilayers where parallel layers are stacked on top of each other. In this parallel geometry, the mixing rule for the viscosity can be easily derived. Any deviation from the derived value of the viscosity can be used to estimate the slip velocity at the polymer/polymer interface. If however, the parallel arrangement of the layers were to be modified by the flow, the mixing rules could cease to be valid and the accuracy of the determined the slip velocity is not guaranteed. More importantly, obtaining estimates for the flow properties (such as the viscosity) for multiphase flow in arbitrary geometries is not straightforward [5,7]. Currently proposed mixing rules are either empirical or rely on approximations whose range of validity is not always clear [5,7]. Due to this limitation of the deviation from no-slip method, interfacial slip velocity measurements for other important flows, such as coextrusion through a capillary die are few. One way to approach this problem would be to devise a method that does not rely on the estimates for the flow viscosity of the multiphase sample under the assumption of no-slip.

Recently, we proposed a novel approach to estimate the slip velocity at a polymer/polymer interface undergoing two-phase coaxial flow [10]. The approach uses an adaptation of the Mooney method, which is usually used to study slip of a polymer liquid at a solid wall. Henceforth, we will refer to this new approach as the "modified Mooney method". In our earlier work, we established the validity of the modified Mooney method by comparing the interfacial slip velocity obtained from this method with that obtained using the deviation from no-slip [10]. In order to facilitate the determination of the slip velocity using the deviation from no-slip, we chose samples with identical shear-rate dependent viscosities over a range of shear rates. Therefore, in that work, the modified Mooney method was used only with polymers with almost identical viscosities [10].

The main advantage of the modified Mooney method is that it can be applied to investigate polymer/polymer interfacial slip even when polymers with different viscosities are undergoing capillary flow. Therefore, in this work, we use the modified Mooney method to obtain the dependence of the slip velocity on the interfacial stress for several pairs of isotactic polypropylene (PP) and the atactic polystyrene (PS). By choosing PPs of three different molecular weights, we investigated the effect of varying the molecular weight of the inner layer on the slip velocity. In addition, we also investigated the effect of varying the temperature for one of the polymer pairs.

2. EXPERIMENTS

Three different PPs (differing by their molecular weights and labelled as PP1-3) and one PS (labelled PS3) were chosen. The PPs were kindly supplied by Sumitomo Chemical Corporation and Japan Polypropylene Corporation. The PS was kindly supplied by PS Japan Corporation. The molecular weights of the polymers and the experimental temperature were chosen such that the viscosities of two of the PPs (PP1 and PP2) are larger and that of PP3 is approximately equal to that of PS3 over a range of shear-rates (see Fig. 2(a)). The interfacial slip velocity was evaluated using capillary dies of three different diameters D=1.0, 1.5 and 2.0 mm.

Fig. 1(a) shows an illustration of the cross section of the core-sheath samples used for the coextrusion through the capillary die. The core consists of PP with a thin PS sheath surrounding the PP core. A schematic of the expected flow velocity distribution during two-phase coaxial flow is shown in Fig. 1(b). The slip velocity at the polymer/polymer interface is evaluated using

the modified Mooney method. For details about sample preparation, experimental procedure, extensive discussions regarding the modified Mooney method including its limitations, please refer Komuro et al. [10].
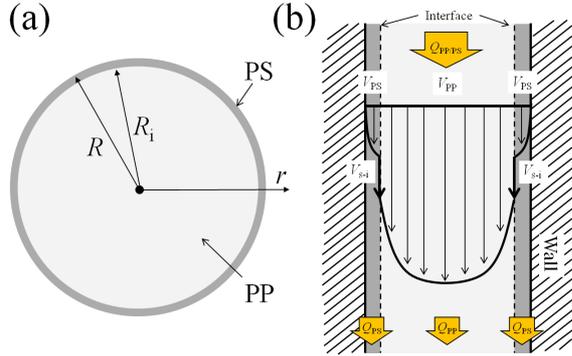
Fig. 1 (a) Cross section of the core-sheath sample with the PP core and PS shell and (b) schematic of the flow velocity distribution during two-phase coaxial flow.

3. RESULTS AND DISCUSSION

3.1 Effect of molecular weight
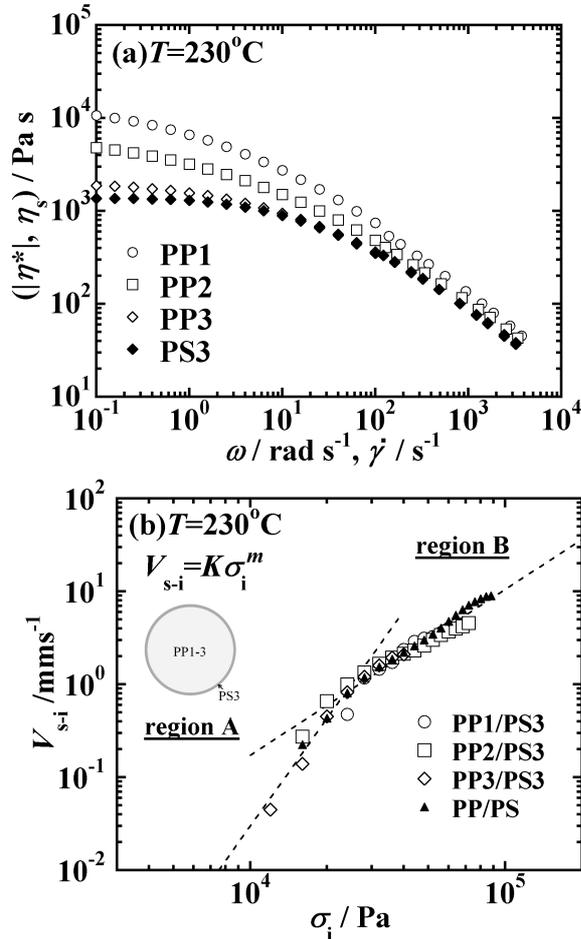
Fig. 2 (a) $|\eta^*|$ and η_s of PP1-PP3 and PS3 at 230ºC. and (b) $V_{s\text{-}i}$ as function of σ_i for PP1-PP3/PS3 at 230ºC.

Fig. 2(b) shows a log-log plot of $V_{s\text{-}i}$ versus σ_i for the three polymer pairs investigated, PP1-PP3/PS3. In agreement with prior results [5,7,9,10], $V_{s\text{-}i}$ exhibits a power-law dependence on σ_i (i.e., $V_{s\text{-}i} = K\sigma_i^m$). The power-law dependence of $V_{s\text{-}i}$ comprises two distinct power-law regimes with different power-law exponents. The transition from the regime with m ≈ 3 to that with m ≈ 2 occurs at a critical interfacial shear stress ≈ 2×10^4 Pa.

Several striking features can be immediately discerned from Fig. 2(b). This can be summarised by noting that the dependence of the $V_{s\text{-}i}$ on σ_i, over the entire range of the investigated σ_i, appears to be almost identical for all three of the polymer pairs studied. This is irrespective of the molecular weight of the PP (PP1-PP3) and the consequent difference in the viscosity ratio of the polymer pairs. These results suggest that the polymer/polymer interfacial slip velocity is not sensitively dependent on the molecular weight of the inner (PP) layer.

In our previous work, we determined the polymer/polymer interfacial slip velocity at the same temperature (230ºC) for another PP/PS pair that also possessed almost identical viscoelastic properties over a range of shear rates [10]. In that case, the molecular weights of both the PP and the PS were larger than that of PP3 and PS3 such that the zero-shear viscosities of both of the polymers were approximately 10 times that of PP3 and PS3. The data for the slip velocity for the higher viscosity pair, referred to as PP/PS, is also shown in Fig. 2(b) [10]. From a comparison of the data for these two pairs, it is clear that the slip velocities for both of the polymer pairs (PP/PS and PP3/PS3) are almost identical although the shear-rate dependent viscosities for each of the pairs is rather different (($\eta_{PP} \approx \eta_{PS}$) > ($\eta_{PP3} \approx \eta_{PS3}$)).

As the slip velocities of all four of the polymer pairs are rather close to each other, we tentatively suggest that the slip velocity is essentially independent of the molecular weight of either of the two polymers. However, it is germane to note that all of the samples used here are rather polydisperse. The polydispersity of the PP samples is about 4 while that of the PS is

about 2. Regrettably, the effect of polydispersity on interfacial slip, especially the depedence of V_{s-i} on σ_i, has hitherto not been elucidated. Therefore, the aforementioned lack of dependence of the slip velocity on the molecular weight is indeed only a tentative suggestion.

3.2 Effect of temperature

Fig. 3 shows V_{s-i} as a function of σ_i for the PP1/PS3 polymer pair at three different temperatures: 230°C, 208°C, and 187°C. At a given σ_i, the slip velocity progressively increases with an increase in the temperature. However, the power-law dependence of V_{s-i} on σ_i and the value of the power-law exponent, do not appear to be affected by the change in temperature.

With an increase in temperature, the viscosity of both of the polymers decreases. However, in subsection 3.1, we found that V_{s-i} was essentially independent of the viscosities of either of the two polymers. Therefore, it appears unlikely that the increase in V_{s-i} with temperature is related to the effect of the temperature on the viscosity.

For wall slip, de Gennes [11] hypothesised that the friction at an interface is related to the monomer viscosity. Adapting that hypothesis and noting that the monomer viscosity decreases with temperature allows us to suggest that, at a given σ_i, the V_{s-i} increases with temperature to compensate for monomer viscosity decrease.
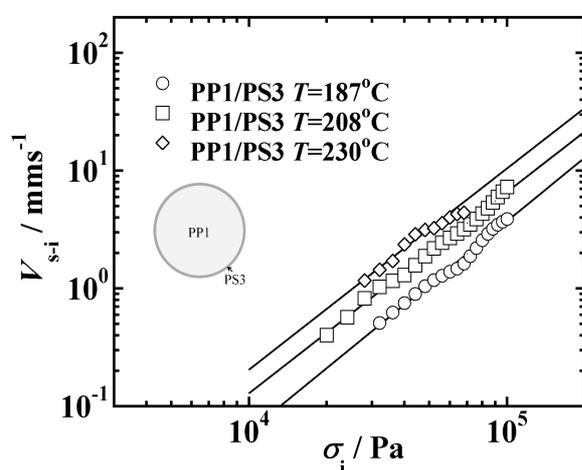
Fig.3 V_{s-i} as function of σ_i for PP1/PS3 at 230°C, 208°C, and 187°C.

4. SUMMARY

Using the recently introduced modified Mooney method, we have measured the slip velocity at the interface between immiscible polymers undergoing capillary flow. The results suggest that the polymer/polymer interfacial slip velocity is not sensitively dependent on the variations in the molecular weight of the two polymers. In addition, we have found that the the interfacial slip velocity increases with an increase in the temperature. Still, the dependence of V_{s-i} on σ_i remains a power-law with almost identical power-law exponents for all of the temperatures investigated. Future work will involve investigating the reasons for the observed (in)dependence on molecular weight and temperature and the light this sheds on the mechanism of polymer/polymer interfacial slip.

5. ACKNOWLEDGMENTS

REFERENCES
1. T. C. Yu, C. D. Han, J. Appl. Polym. Sci., Vol 17, pp. 1203-1225 (1972).
2. C. D. Han, R. Shetty, Polym. Eng. Sci., Vol 16, pp. 697-705 (1976).
3. C. D. Han, H. B. Chin, Polym. Eng. Sci., Vol 19, pp. 1156-1162 (1979).
4. L. Jiang et al., J. Appl. Polym. Sci., Vol 89, pp 1464-1470 (2003).
5. P. C. Lee et al., J. Rheol., Vol 53, pp 893-915 (2009).
6. H. E. Park, P. C. Lee PC, C. W. Macosko CW, J. Rheol., Vol 54, pp 1207-1218 (2010).
7. R. Zhao, C. W. Macosko, J. Rheol., Vol 46, pp 145-167 (2002)
8. Y. C. Lam, L. Jiang, C. Y. Yue, K. C. Tam, L. Li, X. Hu, J. Rheol., Vol 47, pp 795-807 (2003).
9. K. B. Migler et al., J. Rheol., Vol 45, pp 565-581 (2001).
10. R. Komuro et al., Rheo. Acta (2013) (to be published).
11. P.-G. de Gennes, Soft Interfaces, Cambridge University Press, Cambridge, New York, pp. 20-22 (1997).