Rheological Properties and Phase Inversion of Polypropylene – Poly(styrene-co-acrylonitrile) Blends

M. S. Han, H. S. Paik, J. H. Park, J. C. Hyun, and W. N. Kim
Department of Chemical Engineering,
Applied Rheology Center, Korea University

Introduction

The influence of composition and viscosity ratio on the morphology of immiscible blends has been widely studied [1,2], while in the co-continuity region only a few attempts at studying the morphology have been addressed [3-5]. For the PS/PE, PMMA/PE, PMMA/PS, and PC/PS blends, Mekhilef and Verhoogt [5] have studied phase inversion of the blends. In their study, they have used shear viscosity ratio in the several semi-empirical phase inversion models. However, morphology of the extruded blend may be affected by extensional stresses encountered in a converging part of die. Thus, the extension viscosity ratio is more important than the shear or complex viscosity ratio [6]. In the present work, we demonstrate the measurement of extension viscosity and shear viscosity of the PP/SAN blends using Advanced Rheometric Expansion System (ARES), capillary rheometer, and extension rheometer to predict the composition of phase inversion of the blends. The obtained results of phase inversion were compared with the results obtained from the morphological studies of the polypropylene (PP)/poly(styrene-co-acrylonitrile) (SAN) blends.

Experimental

Blend Preparations

Blends with weight fraction of PP from 0.1 to 0.9 in increment of 0.1 were prepared using a 20 mm diameter laboratory scale screw extruder, with a 24:1 length to diameter screw. To determine the extension rate from entrance flow at extruded condition, the extrusion die had a conical entrance with an angle of 48° and radius of 1mm was used.

Capillary measurement

High shear rate viscosity has been determined by Gottfert capillary rheometer (Model Rheotester 1501). Three 1mm diameter capillaries with length to diameter L/D ratio of 10, 20, and 30 have been used. The Rabinowitsch and Bagley correction have been made to obtain the true shear rate of the samples.

Extension viscosity measurement

Measurement of the uniaxial extension viscosity at constant strain rate was carried out using Meissner type extensional rheometer at 190 °C. Stress growth curves were recorded in uniaxial extension rates from 0.01 to 5 s^{-1} and for accumulated strain ($\varepsilon = \dot{\varepsilon} \cdot t$) up to 4 strain unit (s.u.).

Results and discussion

Composition of phase inversion from shear viscosity measurement

The composition of phase inversion at which co-continuity is observed is related to the rheology of the pure materials through semi-empirical models. Utracki phase inversion model is defined as follows:

$$\lambda = \frac{\eta(\dot{\gamma})_1}{\eta(\dot{\gamma})_2} = \left(\frac{(\phi_m - \phi_2)}{(\phi_m - \phi_1)} \right)^{[\eta]\phi_m} \quad (1)$$

where λ is a shear viscosity ratio of the component, $\eta(\dot{\gamma})_i$ is the viscosity of polymer i at the shear rate of blending, $[\eta]$ is the intrinsic viscosity, ϕ_m is the maximum packing volume fraction, and ϕ_i is the volume fraction for phase inversion. To obtain the volume fraction of phase inversion for the PP/SAN blends, shear viscosity ratio and Eq. (1) can be used. From the shear viscosity measurements, the shear viscosity of the PP and SAN was 1.96×10^2 and 8.01×10^2 Pa·s at the shear rate of 180 s^{-1}, respectively, and shear viscosity ratio (λ) of the PP and SAN is 0.25. From Eq. (1) and shear viscosity ratio of the PP and SAN, the weight fraction of phase inversion for the PP in the PP/SAN blends has been calculated and found to be 0.32. Also, from the shear viscosity ratio in the Miles and Zurek [7] and the Metelkin and Blekht [8] models, the weight fraction of phase inversion for the PP in the PP/SAN blends have been calculated and found to be 0.17 and 0.06, respectively, and shown in Table 1.

Composition of phase inversion from extension viscosity measurement

At the extruder die, the exerted strain and extension rate of PP and SAN can be determined from Entry Flow Method [9]. From the Entry Flow Method, the radii ratio (α) of the barrel and capillary and the strain were found to be 3.5 and 2.36, respectively, in this study. Also, the extension rate of blending condition was calculated and found to be 1.64 s^{-1}. Figures 1 (a) and (b) show the extension viscosity growth curves of the PP and SAN, respectively, as measured from extension rheometer. No steady state extension viscosity could be measured for the PP and SAN up to 4 s.u. which is the sample breaking point in Fig. 1. Therefore, extension viscosity of the PP and SAN with the extension rate obtained from the integration of the data up to exerted stain unit ($\varepsilon_{entr} = 2.36$) in Fig. 1, and this work was done numerically. From Fig. 1, the extension viscosity of the PP and SAN with the extension rate can be obtained, and the extension viscosity at 1.64 s^{-1} which is extruded condition of the blends for the PP and SAN was estimated and found to be 2.0×10^4 and 2.8×10^4 Pa·s, respectively. Also, extension viscosity ratio (λ_e) of the PP and SAN is 0.70 at the 1.64 s^{-1}. By using the extension viscosity ratio in Eq. (1), the weight fraction of phase inversion for the PP in the PP/SAN blend has been calculated and found to be 0.41.

The morphology of PP/SAN blends was studied using scanning electron microscopy.

Figure 2 (a) and (b) shows micrographs of the cryogenically fractured cross-section surfaces for the 50/50 and 45/55 PP/SAN blends, respectively. In Fig. 2(a) and (b), the PP and SAN show the co-continuous morphology at the composition of 50/50 and 45/55 PP/SAN blends. Since co-continuity is observed within a range of composition rather than at a single point, the results from morphological studies in this study are consistent with the results from that of other researchers.

From the shear and extension viscosity measurements, when the shear viscosity ratio was replaced by the extension viscosity ratio in the Utracki model, the composition of phase inversion in the PP/SAN blend shows much close value to the result obtained from the morphological studies. Also, difference of phase inversion composition of PP/SAN blends between the morphological studies and the Utracki model in which extension viscosity ratio used might be come from the interfacial tension effect on the formation of the morphology of the blends. Therefore, in order to more precisely prediction of phase inversion composition for the PP/SAN blends, it is suggested that the interfacial tension effect on the PP/SAN blends was considered in phase inversion models.

Acknowledgment

This study was supported by research grants from the KOSEF through Applied Rheology Center at Korea University, Korea.

References

1. Favis BD and Chalifoux JP, *Polymer,* **29**, 1761 (1988).
2. Favis BD and Therrien D, *Polymer*, **32**, 1474 (1991).
3. He J, Bu W, and Zeng J, *Polymer*, **38**, 6347 (1997).
4. Astruc M and Navard P, *J. Rheol.*, **44**, 693 (2000).
5. Mekhilef N and Verhoogt H, *Polymer*, **37**, 4069 (1996).
6. Utracki LA, *J. Rheol.*, **35**, 1615 (1991).
7. Miles IS and Zurek A, *Polym. Eng. Sci.*, **28**, 796 (1988).
8. Metelkin VI and Blekht VS, *Colloid J. USSR,* **46**, 425 (1984).
9. Gotsis AD and Odriozola A, *Rheol. Acta*, **37**, 430 (1998).

Table 1. The weight fraction of phase inversion for the PP in the PP/SAN blends calculated from the Utracki, the Miles and Zurek, and the Metelkin and Blekht phase inversion models

Model	Weight fraction PP (shear viscosity ratio: λ=0.25)	Weight fraction PP (extension viscosity ratio: λ_e=0.70)
Utracki	0.32	0.41
Miles and Zurek	0.17	0.37
Metelkin and Blekht	0.06	0.29

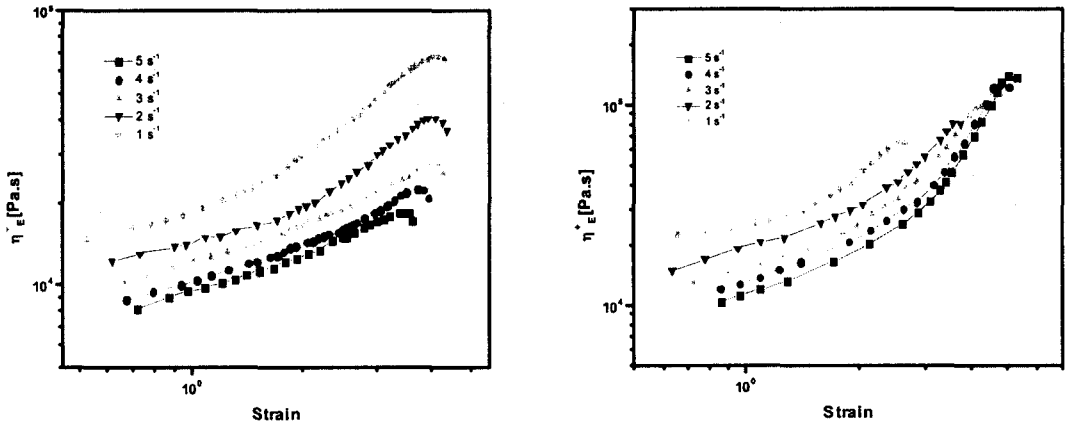

Fig. 1. Uniaxial extension viscosity growth curves at different extension rate as a function of accumulated strain for PP and SAN: (a) PP; (b) SAN.

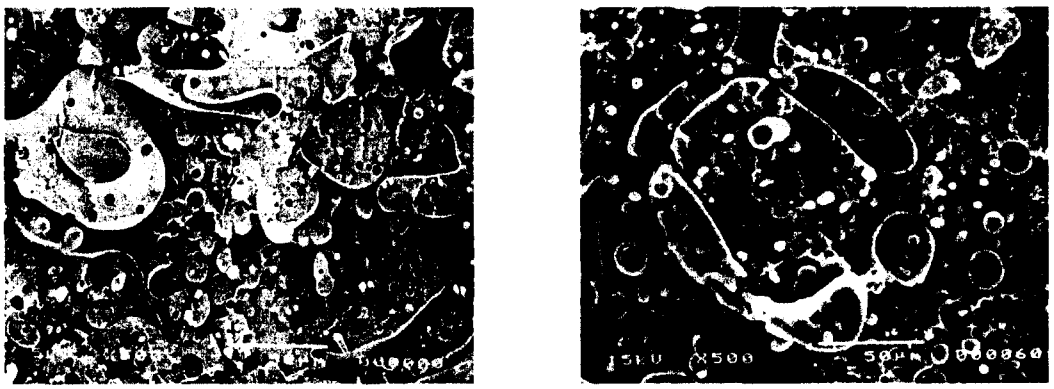

Fig. 2. Scanning electron micrographs obtained from cryogenically fractured cross-section surfaces of PP/SAN blends: (a) 50/50; (b) 45/55.