*Korean J. Chem. Eng.*, **18**(1), 33-39 (2001)

# Morphology Evolution in PS/LDPE Blends in a Twin Screw Extruder: Effects of Compatibilizer

**Do Young Moon*, Moo Hyun Kwon and O Ok Park†**

*Chemical Division R&D Center, Cheil Industries Inc.,
322-2 Gochen-dong, Euiwang-si, Kyonki-do 437-010, Korea
Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,
373-1 Kusong-dong, Yusong-gu, Taejon 305-701, Korea
(*Received 17 April 2000 • accepted 16 October 2000*)

**Abstract**−In order to understand the mixing in polymer extrusion, the morphology of PS/LDPE blends compatibilized with SEBS was simulated based on the Lee and Park model. Experiments were performed in a co-rotating twin screw extruder and a Haake mixer, and the morphology of the compatibilized blends of various compositions was compared with the non-compatibilized ones. The size of the dispersed phase of the compatibilized blend was smaller than the non-compatibilized one, and the blend of the PE matrix had a smaller size in the dispersed phase than the non-compatibilized one. Simulation results were agreed well with experiments, and the Lee and Park model could be applied in the extrusion analysis of compatibilized polymer blends.

Key words: Morphology, PS/LDPE Blend, Compatibilizer, SEBS, Extruder, Lee and Park Model

## INTRODUCTION

Many existing polymer blends and composites have been further developed instead of making new polymers because of the ability to obtain the desired material properties more easily and more economically [Kim and Chun, 1999; Lyu et al., 1999]. It is well known that the morphology of the polymer blend, that is, the size of the dispersed phase, and interfacial state have influence on properties of the polymer blend, especially impact strength. However, most polymer blend pairs are so immiscible thermodynamically that they do not have good morphology-giving properties. There have been many studies to improve the morphology of polymer blends by using block copolymers or graft copolymers as compatibilizers [Chen and White, 1993; Kim and Chun, 1999]. It is necessary to look into the effects of the compatibilizer on the blend morphology. The effects of shear rate, thermal history, rheological properties, and blend composition are also important when the blend morphology is considered in the real process such as extruder operation.

Fayt et al. found that the molecular structure of the compatibilizer is a key factor for polymer blends to be compatible [Fayt et al., 1989]. Block copolymer SEBS (Styrene-Ethylene/Butylene-Styrene) is well known as a good compatibilizer for olefin and polystyrene polymers. Yang et al. studied the operating condition of the Haake Mixer for the PS/LDPE/SEBS blend system [Yang and Bigio, 1995]. They showed that the size of the dispersed phase decreased as the amount of SEBS was increased up to some extent. Potluri et al. reported that SEBS acted more effectively as a compatibilizer when the viscosity of the blend matrix was lower [Potluri et al., 1995].

To predict the evolution of polymer blend morphology in real polymer processes, it is necessary to understand the behavior of blend interface. Doi and Otta proposed a new theory describing the relationship between overall morphology and rheological properties [Doi and Otta, 1991]. Lee and Park modified the theory, considering the relaxation mechanism of blend interface and the effect of the viscosity ratio [Lee and Park, 1994]. On the other hand, the twin screw extruder has been playing an important role in the field of polymer blend processing. An understanding of polymer mixing in the extruder is essential for obtaining polymer blends of high quality. The purpose of this study, as a continuation of a previous one [Moon and Park, 1998], is to simulate the morphological behavior of PS/LDPE blend compatibilized with SEBS in the co-rotating twin screw extruder using the Lee and Park theory. Experimental results were also compared with the simulation.

## THEORETICAL MODEL AND SIMULATION

A prediction of the morphological evolution of polymer blends requires an understanding of the behavior of blend interface in the given flow field. Doi and Otta [Doi and Otta, 1991] focused on the interface between two phases and proposed an interesting model to describe the relationship between overall morphology and rheological properties. They defined interfacial area per unit volume, Q, and its anisotropy for a given flow field, $q_{ij}$, as follows.

$$Q=\frac{1}{V}\int dS, \tag{1}$$

$$q_{ij}=\frac{1}{V}\int dS\left(n_i n_j-\frac{1}{3}\delta_{ij}\right). \tag{2}$$

Here, $n_i$ is the unit normal vector to the interfaces, $\delta_{ij}$, the Kronecker $\delta$, V, the total volume, and dS, the differential area of interface. Lee and Park [Lee and Park, 1994] modified the Doi theory. They considered the effects of the viscosity ratio and the relaxation

---

†To whom correspondence should be addressed.
E-mail: oopark@sorak.kaist.ac.kr

of interface due to interfacial tension α, and obtained the time evolution of Q and $q_{ij}$ given by

$$\frac{d}{dt}q_{ij}=-q_{ik}d_{kj}-q_{jk}d_{ki}+\frac{2}{3}\delta_{ij}d_{lm}d_{lm}-\frac{Q}{3}(d_{ij}+d_{ji})$$

$$+\left(\frac{q_{lm}d_{lm}}{Q}\right)q_{ij}-\lambda\frac{\alpha}{\eta_m}Qq_{ij}-\lambda\nu\frac{\alpha}{\eta_m}\left(\frac{q_{lm}q_{lm}}{Q}\right)q_{ij}, \tag{3}$$

$$\frac{d}{dt}Q=-q_i d_{ij}-\lambda\mu\frac{\alpha}{\eta_m}Q^2-\lambda\mu\frac{\alpha}{\eta_m}q_{ij}q_{ij}. \tag{4}$$

Here, $d_{ij}$ is the velocity gradient tensor. $\eta_m$ and $\eta_i$ are the matrix and dispersed phase viscosity, respectively. The Lee and Park model includes three dimensionless parameters: degree of total relaxation λ, size relaxation μ, and break-up and shape relaxation ν, which represent the characteristics of blend morphology for a given binary blend system. The constitutive equation including the contribution of the viscosity ratio is as follows.

$$\sigma_{ij}=\left(1+\frac{6(\eta_i-\eta_m)}{10(\eta_i+\eta_m)}\phi\right)\eta_m(d_{ij}+d_{ji})-\alpha q_{ij}-P\delta_{ij}, \tag{5}$$

where $\sigma_{ij}$ is a stress tensor, ϕ is the volume fraction of dispersed phase, and P is the pressure.

In general, interfacial tension of polymer blends could be reduced using compatibilizers, but it is not easy to estimate the interfacial tension of compatibilized blends. In the Lee and Park model, interfacial tension α always exists with the parameter λ. Thus, in the real application of the model, term αλ may be used instead of α. Parameter λ can be obtained from the oscillatory dynamic experiment at the small amplitude, and μ from size data of the dispersed phase in mixing experiments using the Haake mixer. ν is practically fixed in our previous theoretical work. For the viscosity of polymer blends, the power law model is used.

$$\eta=K\dot{\gamma}^{1-n}, \tag{6}$$

where K is the consistency factor and n is the power law index. The flow in each element of the extruder was assumed to be simple shear flow, and the average residence time $t_r$ is given by

$$t_r=V_F/F, \tag{7}$$

where $V_F$ is the free volume of the extruder channel and F is the volumetric flow rate. In the case of the partially filled element, the average residence time $t_s$ is given by

$$t_s=\zeta t_r,$$

where ζ is the degree of fill. The average shear rate, $\gamma_s$, of the partially filled region is related to the average maximum shear rate at the fully filled condition, $\gamma_m$, as follows.

$$\dot{\gamma}=\zeta\dot{\gamma}_m.$$

Because we calculate the average shear rate and residence time at each screw element, the twin screw extruder can be regarded as the series of simple shear flows with its own shear rate and residence time. Two terms Q and $q_{ij}$ are calculated sequentially from the first element the initial morphology (for example, $Q_o=10$ μm and $q_{ijo}=0$) is given. Below, we summarized the simulation scheme for prediction of morphology evolution with some assumptions.

(1) The screw characteristic curves (‘Flow rate F vs. Pressure gradient dP/dx’) at each element are calculated using the program package ‘Twin Screw Extrusion Analysis Package’ developed by PPI (Polymer Processing Institute). The power law model and isothermal conditions are assumed. More details of the calculation scheme are shown in the previous work [Moon and Park, 1998].

(2) From the screw characteristic curve, pressure distribution is calculated in the reverse direction beginning at the die region.

(3) When the pressure dropped to 0, it is assumed that starvation occurred. Degree of fill ζ is defined as the ratio of filled area $A_f$ to total channel area $A_s$. For a Newtonian fluid, it is the ratio of flow rate F to maximum flow rate $F_{max}$.

$$\zeta=A_f/A_s=F/F_{max}. \tag{8}$$

(4) The velocity profile is obtained from the pressure distribution and degree of fill. Each element is assumed to be a rectangular channel, and the calculation begins from the first molten state (usually the first kneading block).

(5) Average shear rate and residence time are calculated from the velocity profile.

(6) Interfacial area density Q and its anisotropy $q_{ij}$ in each element are calculated.

(7) Finally, from the two morphology terms above, the evolution of the blend morphology is predicted.

In the previous description, we assumed that the extruder is operated in the isothermal condition and that the rheological characteristics of the binary blend can be described by the interfacial tension, power law indices, and the parameters of the Lee and Park model. Because we could not find the proper model that considers both the melting and solid conveying zone of the extruder yet, only the melt zone is considered.

## EXPERIMENT

The polymer blend system used in this study is polystyrene (PS; HF2660) from Cheil Industries, Inc. and low density polyethylene (LDPE; LD210H) from Samsung General Chemicals Co. SEBS, commercialized by Shell Chemical as ‘Kraton G’, was used as a compatibilizer. Six compositions of blend were examined; by weight, PS 10%, 20%, 30%, and LDPE 10%, 20%, and 30%. To make the blend compatibilized, SEBS was added. Blends were prepared using the internal mixer (Haake Rheomix 90) and co-rotating twin screw extruder (SM Engineering TEK45). Their dynamic and shear viscosities were measured using the cone and plate rheometer (Physica MC120) and capillary viscometer (Rosand) at 200 °C.

Two blends of PS 10% and LDPE 10% were examined to estimate the effect of SEBS on the viscosity. The effect of a small amount of SEBS on the blend viscosity is negligible. The blend morphology was observed using SEM (Joel 800A). In mixing experiments by Haake mixer, each blend sample was kept 10 minutes and quenched in liquid nitrogen. PS 10% blend having LDPE matrix was treated with chloroform to remove the PS phase, while LDPE 10% blend was viewed without chemical treatment. Average particle size was obtained from image analysis of SEM pictures. Extrusion experiments to find out the effect of the screw configuration were also performed for two different screw configura-

**Table 1. Parameters of the Lee and Park model of PS/LDPE blend compatibilized with SEBS and compared with the non-compatibilized one**

| Parameters | Non-Compatibilized | | Compatibilized with SEBS | |
|---|---|---|---|---|
| | LDPE 90% | PS 90% | LDPE 90% | PS 90% |
| $\alpha\lambda$ | 70.5 | 23.5 | 23.5 | 14.1 |
| $\mu$ | 0.02 | 0.2 | 0.02 | 0.08 |
| $\nu$ | 1.5 | 1.5 | 1.5 | 1.5 |

tions.

## RESULTS AND DISCUSSION

Table 1 shows the parameters of the Lee and Park model obtained from the small angle dynamic experiment and the Haake mixer experiment. The parameter values of compatibilized blends are compared to those of non-compatibilized blends. We can estimate the overall morphology characteristics of blends using the Lee and Park parameters because the parameters represent the characteristics of the interfacial relaxation of the binary blend. It can be seen in the table that parameter $\lambda$ of LDPE 90% blend decreases significantly when it is compatibilized.

In the Lee and Park model, parameter $\lambda$ always exists together with the interfacial tension $\alpha$. Therefore, in the case of LDPE 90% blend, the decrease of $\lambda$ has the same effect as decreasing the interfacial tension $\alpha$. Parameter $\mu$ of PS 90% blend compatibilized with SEBS has a lower value compared to the corresponding non-compatibilized blend. Since parameter $\mu$ means the degree of coalescence, the obtained result shows that SEBS holds down the coalescence of PS 90% blend. Elmendorf has reported that the degree of coalescence depends mainly on the matrix viscosity of the blend [Elmendorf, 1986]. Therefore, we think that coalescence of PS 90% blend having low-matrix viscosity would be more restricted compared to LDPE 90% blend. We can confirm this in Fig. 1 which shows SEM pictures of compatibilized and non-compatibilized PS/LDPE blends at three different concentrations of LDPE 10%, 20%, and 30%. From cases of non-compatibilized blend as shown in Fig. 1(a), (b), and (c), we can see that most of the LDPE dispersion phase is pulled out from matrix phase, while the compatibilized blends of Fig. 1(d), (e), and (f) show good interface adhesion between the dispersed and matrix phases. In general, as the content of the dispersion phase increases, the size of the dispersion phase increases due to coalescence. Compared to the case of compatibilized blend, the size of the dispersed phase of non-compatibilized blend increases more rapidly with increasing content of the dispersion phase. Especially for the non-compatibilized case of PS 70% blend, the degree of coalescence is high so that many parts of the dispersed phase appear as the co-continuous phases. But, for compatibilized blend, the degree of coalescence is relatively low. From this, we see that the compatibilizer, SEBS, restrains the coalescence, and this effect is reflected in the value of parameter $\alpha\lambda$ of the Lee and Park model. As previously mentioned, the effect of SEBS on the blend viscosity is negligible. Thus, the blend viscosity is not expected to be influenced by adding a small amount of SEBS during extrusion. Fig. 2 shows viscosity of PS/LDPE blend according to the amount of SEBS (0%, 2%, 4%). We can see that the effect of SEBS on the blend viscosity is negligible. The viscosity of the blend will not be influenced by adding the small amount of SEBS. Fig. 3 shows the diameter of the dispersed phase; that is, the domain size as a function of screw speed (a) and flow rate (b). In cases of PS matrix, the size of the dispersed phase increases with the screw speed as shown in Figure (a). We can say that the compatibilization reduces the influence of the processing condition, such as the screw speed on the

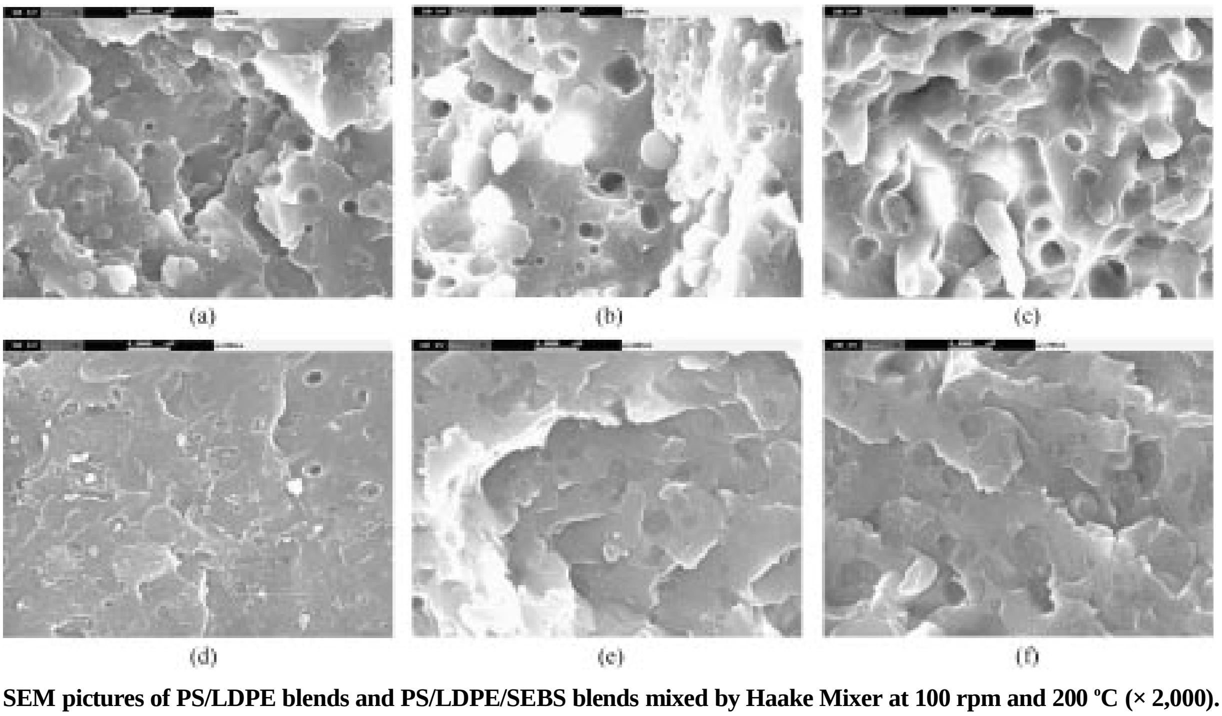

**Fig. 1. SEM pictures of PS/LDPE blends and PS/LDPE/SEBS blends mixed by Haake Mixer at 100 rpm and 200 °C (× 2,000).** (a) PS 90%, (b) PS80%, (c) PS70% (d) PS90%/SEBS, (e) PS80%/SEBS, (f) PS70%/SEBS

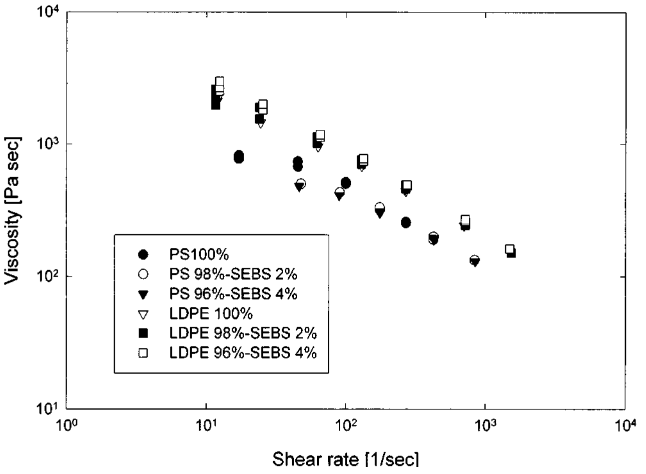

**Fig. 2. Effects of SEBS on shear viscosity of LDPE/SEBS and PS/SEBS blend at 200 °C.**

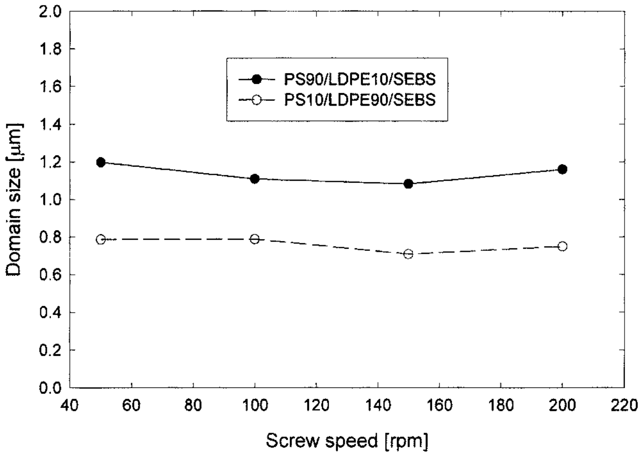

**Fig. 4. Effect of rotor speed on the particle size for PS/LDPE/SEBS blends in the Haake internal mixer at 200 °C.**

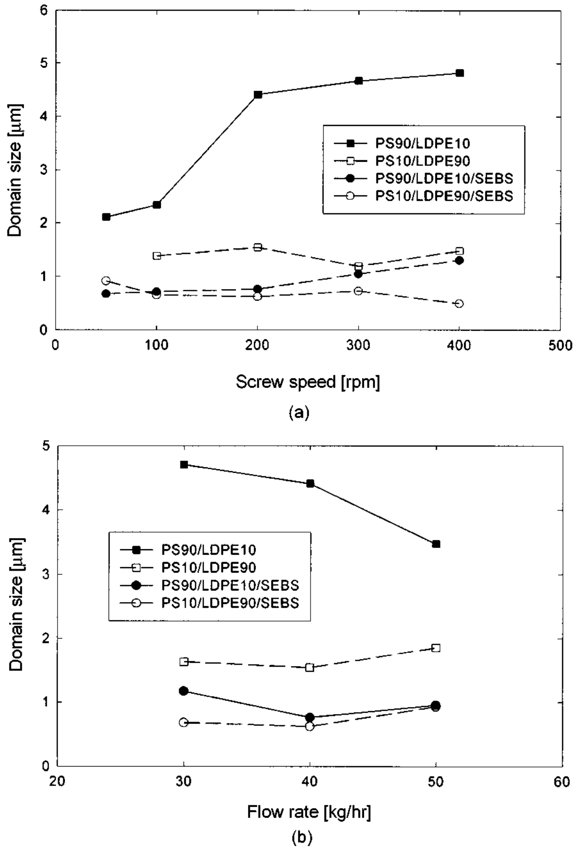

**Fig. 3. Effects of SEBS compatibilizer for PS/LDPE blend on the domain size according to screw speed.**
(a) and flow rate, (b) in twin screw extrusion at 200 °C

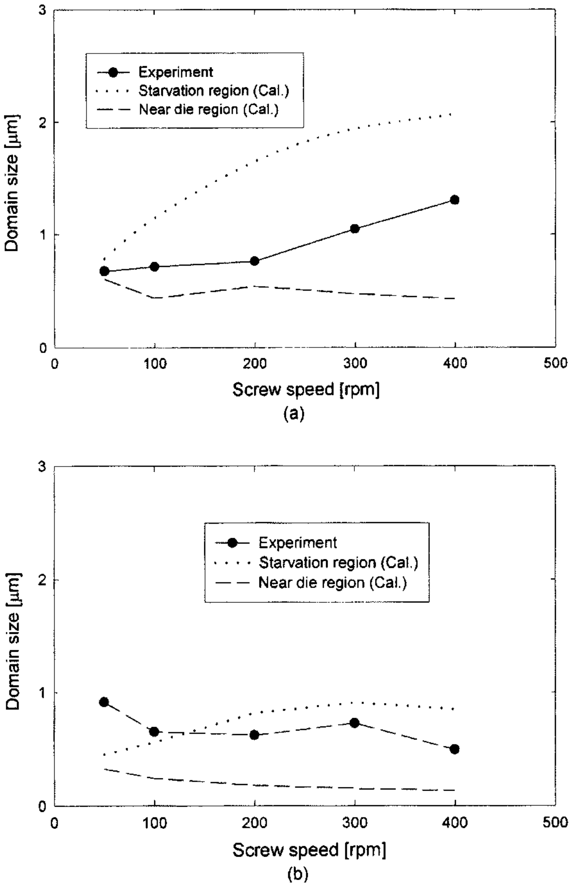

**Fig. 5. Comparison between calculated and experimental domain sizes according to screw speed.**
(a) PS90%/LDPE10%/SEBS, (b) PS10%/LDPE90%/SEBS

domain size. When the matrix viscosity was low, the size variation of the dispersed phase according to the screw speed was more pronounced. This agrees with Potluri's result that the compatibilizer is more effective in the size reduction of the dispersed phase in case of low viscosity matrix. As we previously explained this effect with the Lee & Park model, the compatibilizer stabilizes the interface of the blend by reducing the interfacial tension and is especially effective in reducing the size of the dispersion phase by restraining the coalescence.

Blends of PS matrix have the larger size of dispersed phase than blends of LDPE matrix because PS has the smaller value of viscosity than LDPE. Fig. 4 shows the effect of the rotor speed of the Haake mixer on the size of the dispersed phase for two blends of PS matrix and LDPE matrix, respectively, compatibilized with SEBS.

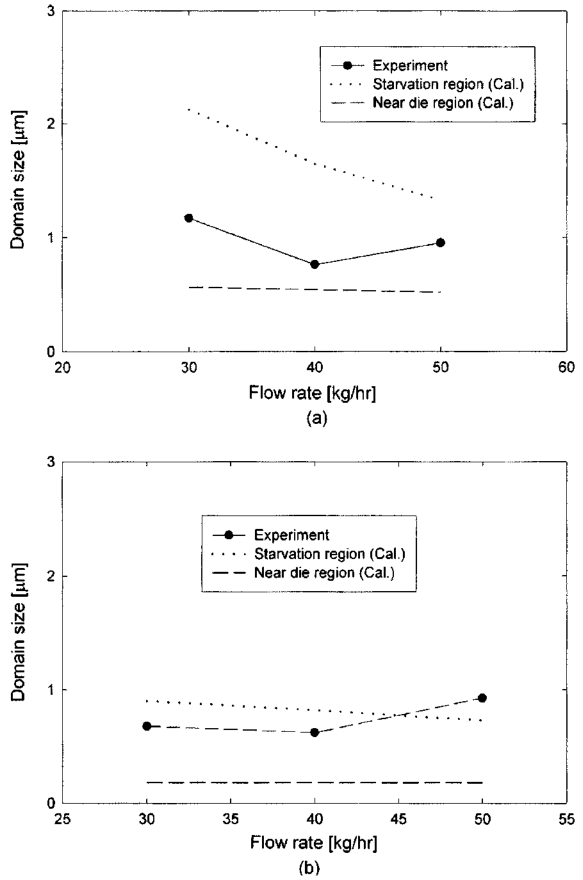

**Fig. 6. Comparison between calculated and experimental domain sizes according to flow rate.**
(a) PS90%/LDPE10%/SEBS, (b) PS10%/LDPE90%/SEBS

In Figs. 5 and 6, the sizes of the dispersed phase, (that is, the domain size) measured in extruder experiments are compared with simulation results. The domain size was calculated from interfacial area density Q. The predicted domain size shows a large difference between the high-shear region near the die exit and the low-shear region at the starvation region. In order to know the final domain size, two limit cases should be examined together. We see in Figs. 5 and 6 that the predicted domain size of the two regions has the same tendency as the experimental results. In both figures, the blend of PS 90% has the larger domain size than the blend of PS 10%, and the predicted values show the same tendency according to the screw speed and flow-rate. These results mean that the parameters of the Lee and Park model represent correctly the characteristics of interface.

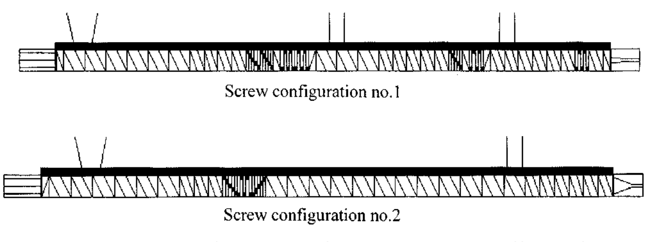

**Fig. 7. Two screw configurations for evaluating the effects of screw configurations.**

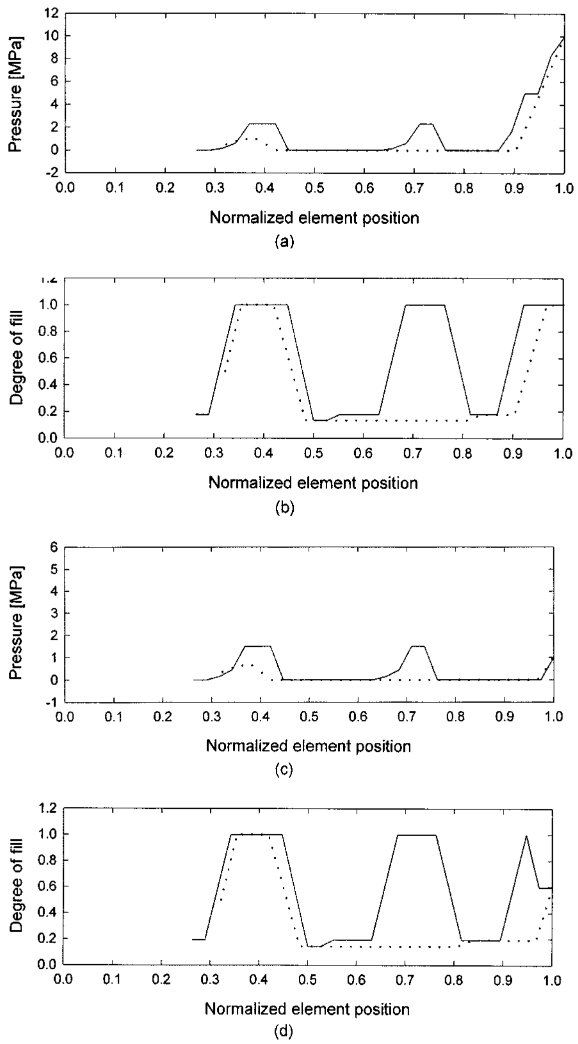

**Fig. 8. Predictions of the effects of screw configurations on the pressure and degree of fill for the TEK45 twin screw extruder.**
(···) Screw configuration no. 1, (—) Screw configuration no. 2. (a), (b): PS10%/LDPE90%/SEBS, (c), (d): PS90%/LDEP10%/SEBS

To examine the effect of screw configuration, two different screw configurations of TEK 45 twin extruder as shown in Fig. 7 were simulated for PS 10% and PS 90% blends compatibilized with SEBS. Two screw configurations of Fig. 7 are different mainly in the number of kneading blocks, which influences the overall mixing intensity. Fig. 8 presents the simulation results on the pressure and the degree of fill obtained for the two blend systems above. We can see that the pressure is highly built up in sections of kneading block and in front of die. In the pressurized region, mixing intensity is high and the degree of fill has the value of ‘1’. Except for the high pressure of PS 10% blend at the die region, the difference between the two blend systems is not so noticeable. Fig. 9 shows the predicted domain size of two screw configurations and two blend systems. We can see that the predicted domain size along the screw axis depends on the mixing intensity, but the final domain size at the die region has practically the same value regardless of the screw configuration. We can confirm this conclusion from Figs. 10 and

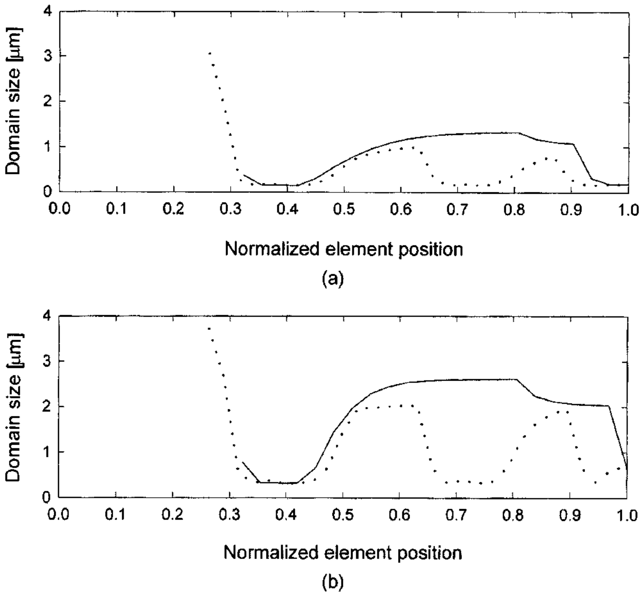

**Fig. 9. Predictions of the effects of screw configurations on domain size for the TEK45 twin extruder.**
(···) Screw configuration no. 1, (—) Screw configuration no. 2. (a) PS10%/LDPE90%/SEBS, (b) PS90%/LDEP10%/SEBS

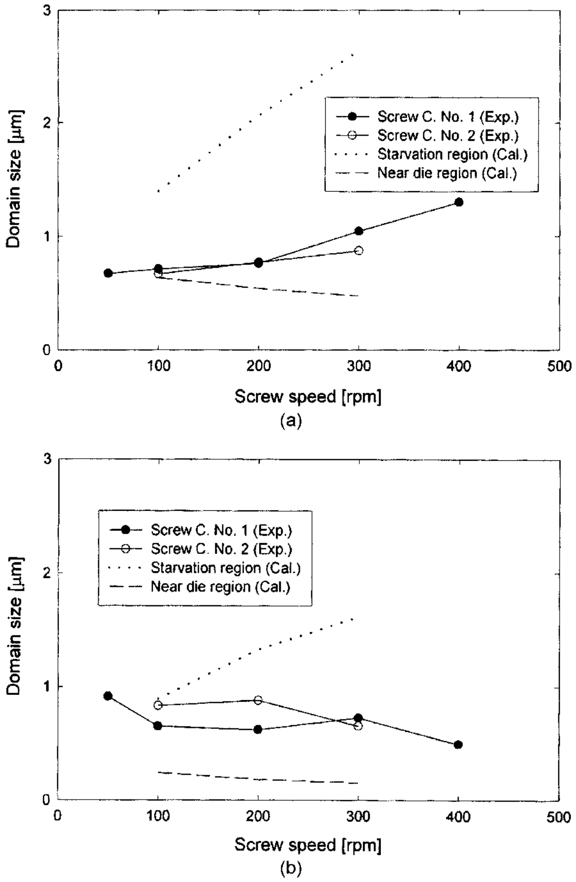

**Fig. 10. Comparison between calculated and experimental domain sizes according to screw speed or different screw configurations.**
(a) PS90%, (b) LDPE90%

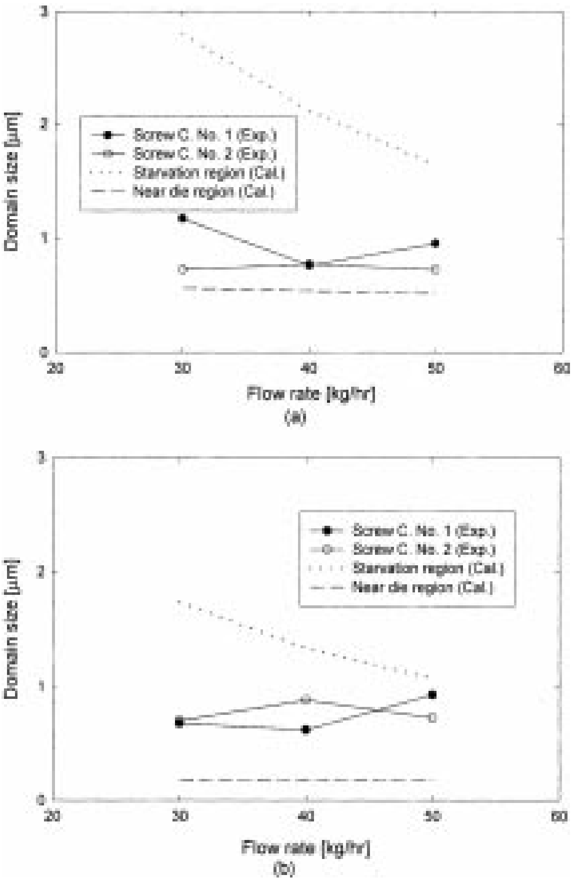

**Fig. 11. Comparison between calculated and experimental domain sizes according to flow rate for different screw configurations.**
(a) PS90%, (b) LDPE90%

11. Experimental results of the domain size according to the screw speed (Fig. 10) and flow rate (Fig. 11) are compared to simulations in two limit cases of near die and starvation regions. This agrees well with the previous work's finding that the final domain size is determined in the initial softening stage of the twin extruder.

## CONCLUSION

The blend morphology of PS/LDPE system compatibilized with SEBS was investigated based on the Lee and Park theory describing the relaxation characteristics of blend interface. From the experimental results obtained using the co-rotating twin screw extruder and the Haake mixer at various operational conditions, we found that the Lee and Park theory model could be applied in performance prediction of twin screw extrusion for the compatibilized blend system. Compatibilized blend showed the smaller domain size than non-compatibilized blend, and PS10%/LDPE90%/SEBS blend had low coalescence tendency compared to PS90%/LDPE0%/SEBS blend which has the high matrix viscosity. Experimental results were compared and agreed well with the simulation. Compatibilized blends also showed less sensitivity to the operating conditions like the screw speed and flow rate than non-compatibilized ones. And from the extrusion results of two different screw configurations, we found that the overall mixing intensity did not affect the final domain size.

## REFERENCES

Chen, C. C. and White, J. L., “Compatibilizing Agents in Polymer Blends: Interfacial Tension, Phase Morphology and Mechanical Properties,” *Polym. Eng. Sci.*, **33**, 923 (1993).

Doi, M. and Otta, T., “Dynamics and Rheology of Complex Interfaces I,” *J. Chem. Phys.*, **1247**, 15 (1991).

Elmendorf, J. J., “A Study on Polymer Blending Microrheology,” *Polym. Eng. Sci.*, **26**, 418 (1986).

Fayt, R., Jerome, R. and Teyssie, P., “Molecular Design of Multicomponent Polymer Systems XIV. Control of the Mechanical Properties of PE-PS Blends by Block Copolymers,” *J. Polym. Sci.*, **27**, 775 (1989).

Kim, S. W. and Chun, Y. H., “Barrier Property by Controlled Laminar Morphology of LLDPE/EVOH Blends,” *Korean J. Chem. Eng.*, **16**, 511 (1999).

Lee, H. M. and Park, O. O., “Rheology and Dynamics of Immiscible Polymer Blends,” *J. Rheol.*, **38**, 1405 (1994).

Lyu, S. G., Park, S. D. and Suh, G. S., “The Synthesis of Vaterite and Physical Properties of PP/$CaCO_3$ Composites,” *Korean J. Chem. Eng.*, **16**, 538 (1999).

Moon, D. Y. and Park, O. O., “Development of a Computational Model to Predict Blend Morphology in a Twin-Screw Extruder,” *Adv. in Polym. Tech.*, **17**, 203 (1998).

Potluri, R., Gogos, C. G., Libera, M. R. and Dagli, S. S., *SPE ANTEC papers*, 3172 (1995).

Yang, L. Y. and Bigio, D., “Melt Blending of LLDPE and PS in Haake Internal Mixer I. Compatibilization and Morphology Development,” *J. Appl. Polym. Sci.*, **58**, 117 (1995).