A Study of Droplet Coalescence In Immiscible PS/LDPE Blends Under Annealing Conditions

Chatchai Kunyawut
Department of Chemical Engineering, Faculty of Engineering,
Rajamangala University of Technology Thanyaburi,
Pathum Thani, 12110, Thailand. Email: kchat@rmut.ac.th
Tel: 02-549-4602-3 Fax: 02-577-5026

Abstract

A change of phase morphology under annealing conditions of immiscible PS/LDPE blends in the absence and presence of polystyrene-block-poly(ethylene-butylene)-block-polystyrene (SEBS) triblock copolymers with different molecular weights has been investigated. The blends were prepared by means of melt mixing using a mini twin-screw extruder. The morphology of the blends was obtained from their fractured surfaces using SEM. Clear evidence of droplet-type morphology was found in both the uncompatibilized and SEBS-compatibilized PS/LDPE blend samples. Granules of the investigated blend were annealed in a chamber under air atmosphere. The annealing temperature used was the same as the melt mixing temperature. Coalescence of dispersed droplets is observed in both the uncompatibilized and SEBS-compatibilized blends under quiescent conditions. A significant increase in dispersed size diameter is observed after a few minutes of annealing. The coalescence of the LDPE particles during annealing mainly arose from coalescence of the smaller particles. The high molecular weight SEBS is shown to be more effective at coalescence retardation than the low molecular weight one. The ability to retard coalescence is found to increase with an increase in concentration of the SEBS. However, a significant increase in the LDPE particle size during annealing under quiescent conditions indicates that the interface of the immiscible blends studied is highly mobile. The SEBSs were shown to have only low ability to suppress coalescence. This is expected to be because of the lower anchoring degree of the blocks of the copolymers within the corresponding homopolymer phases.

Keywords: Annealing, droplet coalescence, immiscible polymer blends, SEBS

1. Introduction

In the processing of multi-phase polymer blends, two steps are generally involved: the first step is the melt blending of two or more polymers using a mixer (i.e. a batch mixer, single- and twin-screw extruders) and the second step is the shaping and solid fabrication of the melt-blended stream using fabricating equipment (e.g. an injection moulding machine). The first step is normally called '*compounding*' and the second step '*fabrication*'. During the melt-blending step, the morphology development is a result of the competitive processes of breakup and coalescence of the dispersed particles [1, 2]. In general, a distribution of dispersed phase is created by breakup [3], so that coalescence of the small ones may occur during steady shear. Moreover, in industrial practice, the flow field within a mixer is inhomogeneous; therefore small droplets are produced in regions of high deformation rates, and coalescence can occur in the regions of more gentle flow within the mixer [4]. During the fabrication step, the change of the phase morphology is dominated by coalescence if the intensity of shear stress applied is not strong enough for generating the breakup of the dispersed phase droplets. In this case, coalescence is *flow-driven*. Annealing leads to *static-coalescence*, a mechanism that reduces interfacial area through particle-particle fusion.

Several researchers studied coalescence in polymer blends [5-11]. These researchers reported that coalescence occurred during and after mixing. Coalescence after mixing is an important area because manufactured polymer products are often annealed, and coalescence may occur during annealing [12]. The coalescence, which was observed during annealing of uncompatibilized immiscible blends shows that polymers have a high interfacial mobility. This indicates that the interface is not rigid as one might expect for highly viscous fluids.

In a quiescent melt, Ostwald ripening [13, 14] is described to take place in blends where the diffusion coefficient of the dispersed component in the matrix phase is sufficiently high. The process involves diffusion of smaller drops to the larger ones. Brownian motion has been proposed to play a major role for the approach of particles and the drainage of the matrix film [15]. However, from the point of view of molecular dynamics, it is difficult to accept this proposition. The particle diffusion coefficient $Ð$ is given by $Ð = k_B T / (\pi \eta_m d)$; therefore, at a given temperature T, the rate of diffusion is inversely proportional to drop diameter d and matrix viscosity η_m. Owing to the high viscosity of most polymers, the diffusion coefficient will be very small. Jang *et al.* [5] have shown that drops of polymer blend are too large for the Brownian motion to have a significant effect on coalescence. Another approach is that viscous flow (interfacially driven coalescence, reshaping agglomeration) leads to the reduction of the interfacial area [16]. In the case of irregularly shaped droplets, as they are normally obtained from melt processing, the droplets will return to a spherical shape when the system is re-melted. At high concentrations of the dispersed phase, this would lead to the contact and coalescence of neighboring drops. Coalescence in molten polymer blends without compatibilizer during annealing has been reported by several researchers [12, 17-23].

Apart from enhancing the finer dispersion of the dispersed phase during melt processing, block copolymers have been expected to be able to stabilize the phase morphology. When present on the dispersed drop, the block copolymers may immobilize the interface and thus retard film drainage and prevent coalescence. However, if the block copolymers are present in the matrix phase, the ability to immobilize the interface is generally less effective since they cannot reach the interface easily, owing to their high viscosity compared with those of the blend components. Several researchers have shown in many immiscible blend systems, in the presence of diblock copolymers, that coalescence of the dispersed droplets is suppressed [16, 19-21, 23]. According to the work of Kunyawut and Higgins [24], the poly(styrene-*block*-(ethylene-butylene)-*block*-styrene) triblock copolymers (SEBS) with varying molecular weights have been shown to be potential compatibilizers. However, over the years, few studies on their ability to suppress coalescence in immiscible polymer blends have been published. Lepers *et al.* [25] studied the coalescence suppression in PP/PET blends. The triblock copolymer used was a SEBS grafted with maleic anhydride (MA). The effect of the level %MA on suppression ability of SEBS was mainly investigated. It was shown that a 2% maleic anhydride level provided the highest coalescence suppression. For all blends studied, the concentration of the SEBS-g-MA used was the same.

The objective of this study is to investigate a change of phase morphology under annealing conditions of uncompatibilized and SEBS-compatibilized PS/LDPE blends.

2. Materials and Method

2.1 Materials

The PS used was provided by BP Chemical Company (M_w = 2.50×10^5, polydispersity (M_w/M_n) = 2.2). The LDPE (Stamylan LD2100 TN00) is a commercial product of DSM, The Netherlands (M_w = 1.21×10^5, polydispersity = 12.3). The molecular weights of the homopolymers were determined using a GPC technique performed by RAPRA Technology Ltd. UK. All homopolymers were obtained in pellet form. The SEBS copolymers used are commercial products of Shell Development Company: Kraton G1651 and Kraton G1652. The number average molecular weight (M_n) values of the SEBS were obtained from the supplier and are shown in Table 1.

2.2 Methods

Blends were prepared using a co-rotating twin-screw extruder (PRISM Co., UK). The barrel length and diameter are 224 mm and 16 mm, respectively. The diameter of the capillary die is 1 mm. The concentrations of the LDPE used were 10, 20 and 30 wt%. The blend components were dry mixed before feeding into the hopper of the extruder. At the desired screw speed (60 rpm), the temperature of the barrel wall inside the extruder (the feed and mixing zone and at the die) was maintained constant at 180 ± 5°C using 3 automatic temperature controllers.

Table 1. Molecular characteristics of SEBS.

SEBS	Total M_n	Mid-Block M_n	End-Block M_n	PS (%)
G1651	2.40×10^5	1.60×10^5	3.90×10^4	33
G1652	5.50×10^4	3.90×10^4	8.00×10^3	29

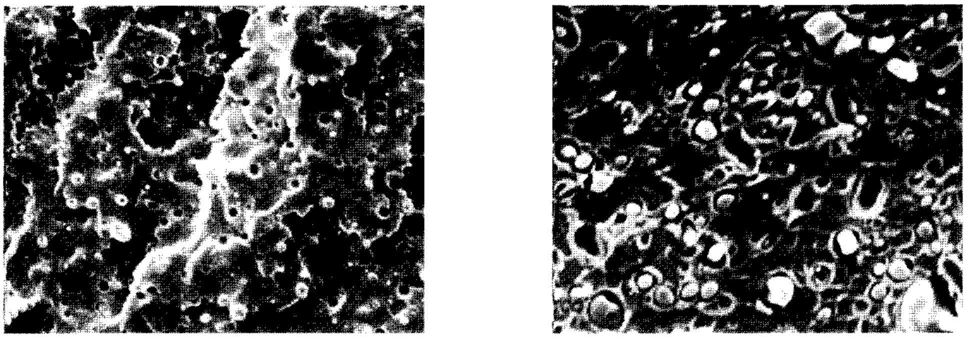
The SEBS triblock copolymers (G1651 and G1652) which were varied from 5 to 15 wt% with respect to LDPE content, were added into the blend having 30 wt% LPDE. The uncompatibilized and compatibilized PS/LDPE blend samples were prepared at only a temperature of 180°C and screw speed of 60 rpm in order to minimize the number of variables and processing conditions. After extruding, the strands were cooled in air to room temperature. The cooling time was about 10 min. The extruded strands of about 10 cm in length were immersed in liquid nitrogen for 5 min and then kept in plastic bags. They were stored in a dry place until required for morphological investigation. The rest of the strands were cut into small pellets using a pelletizer (PRISM Co., UK). In order to minimize any possible contamination arising from the blend components remaining in the extruder, all parts of the extruder, which were in contact with the material (the barrel, the screw and the die), were cleaned after every single preparation.

For the study of stability of the blend morphology against coalescence under quiescent conditions, granules of the blend investigated were annealed in a measuring chamber of a Parr Physica USD200 rheometer (Physica Messtechnik GmbH: Stuttgart, Germany) at 180 ± 2°C under air atmosphere. The annealing times used were 5, 10 and 30 min. Upon removal from the USD measuring chamber, the annealed granules were immediately quenched in liquid nitrogen for 10 min in order to freeze-in the existing morphology. They were stored at room temperature in a dry place until required for morphological investigation.

The morphology of the blends was obtained from their fractured surfaces using SEM (JEOL model JSM-5300, Japan Electric and Optic Laboratories, Co. Ltd., Tokyo). The PS can be identified as the matrix phase while the dispersed phase is LDPE. The two phases are distinct for each composition at which the LDPE droplets were dispersed in the PS. The LDPE phase was identified by polarized light microscopy of a thin section of a strand of the blend samples [26]. White spot areas observed are the LDPE due to its semi-crystalline property while the large dark area is the PS. Note that when the droplets of the LDPE locate close to or touch each other, their spherulitic textures are superimposed and this leads to difficulty in determining their size. Although phase contrast microscopy normally provides better contrast between phases of the PS and the LDPE, this technique was not used to determine size and size distribution owing to the problem of surface roughness of the thin section. To overcome this problem, a solvent extraction technique widely employed for investigation of co-continuous and phase inversion of immiscible blends [12, 19, 27-30], was used. Pellets of blend samples were extracted using warm tetrahydrofuran (THF) in which the PS phase was dissolved while droplets of the LDPE were suspended in THF. A drop of this solution was placed on a glass slide and the solvent was allowed to evaporate at room temperature. The glass slide was stored in an oven at room temperature for several days (normally a couple of weeks) before performing optical microscopy (OM). This would allow the LDPE droplets to return to their original shape and size from swelling. An optical microscope (Optiphot-2, Nikon Co. Ltd.: Japan) set for phase contrast was used to determine an average phase size and size distribution of the minor phase. A video camera coupled with image frame grabber installed in a computer was mounted onto the microscope. The image analysis was performed using Image-Pro, a commercial image analysis software. The blend morphology was

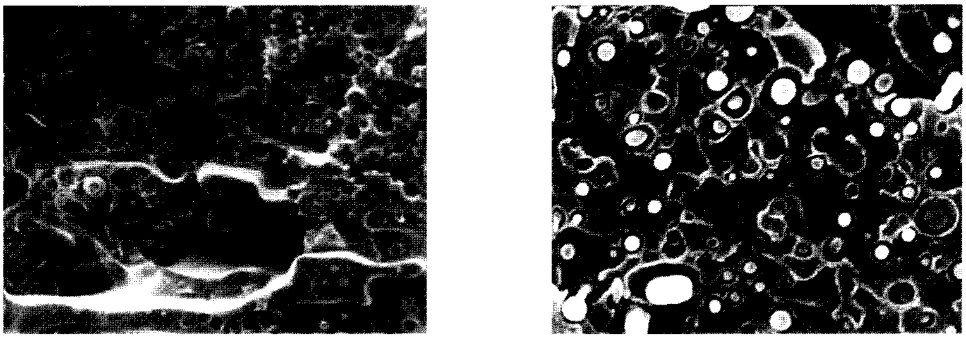
Uncompatibilized PS/LDPE blends

SEBS compatibilized PS/LDPE blends
(PS/LDPE = 70/30 wt%)



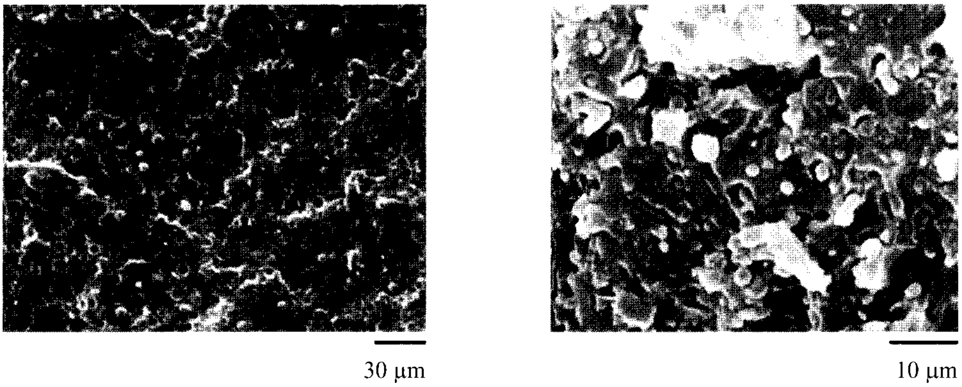
10 wt% LDPE

5 wt% SEBS(G1651)



20 wt% LDPE

10 wt% SEBS(G1651)



30 wt% LDPE

5 wt% SEBS(G1652)

Figure 1 A representative series of SEM Micrographs of uncompatibilized and compatibilized PS/LDPE (with SEBS triblock copolymers) blends prepared at 180°C/60 rpm.

characterized by its size distribution function, $f(d)$, or by the corresponding cumulative distribution, $F(d)$, where d is the droplet diameter.

Once $f(d)$ is known, average quantities can be computed. In particular, use will be made of the number-average and volume-average diameters, d_n and d_v, defined as:

$$d_n = \sum_i f(d_i) d_i = \frac{\sum_i n_i d_i}{\sum_i n_i} \qquad (1)$$

$$d_v = \frac{\sum_i f(d_i) V_i d_i}{\sum_i f(d_i) V_i} = \frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3} \qquad (2)$$

Considering equations (1) and (2), d_i is the diameter of a generic drop and n_i is the total number of the droplets of diameter d_i. In each blend, a number of the order of 800 droplets were analyzed. The measurements of particle size diameter were repeated 3 times on several samples and it was found that d_n and d_v were reproducible to ± 15%.

3. Results and discussion

Figure 1 shows a representative series of SEM micrographs of cryogenic fracture surfaces of uncompatibilized and SEBS compatibilized PS/LDPE blends obtained from the same processing conditions. It can be clearly seen in Figure 1 that both the uncompatibilized and SEBS compatibilized PS/LDPE blend samples exhibit only the droplet-type dispersion morphology. Hemispherical embeddings and hollows representing removed particles are clearly visible on the fracture surface. The SEBS copolymers have the effect of reducing the interfacial tension between the PS and LDPE homopolymers, as indicated by the smaller dispersed phase dimensions when small amounts of the SEBS copolymers were added to the blends. By producing lower dispersed phase size dimensions and more uniform size distribution, the SEBS(G1652) has been shown to be a more effective compatibilizer than the SEBS(G1651) at the same concentration used (see Figures 2 and 3). This may be explained by the fact that there is more of the low molecular weight SEBS at the interface than the high molecular weight one. The high molecular weight SEBSs forms micelles more readily in the matrix phase than the small molecular weight ones [31] and together with the higher viscosity, one can expect that much of the high molecular weight SEBS does not reach the interface [32]. A superior compatibilizing efficiency of the SEBS(G1652) over the SEBS(G1651) has also been found in the PS/EBR blend systems reported by Cigana *et al.* [32] and Hong and Jo [33].

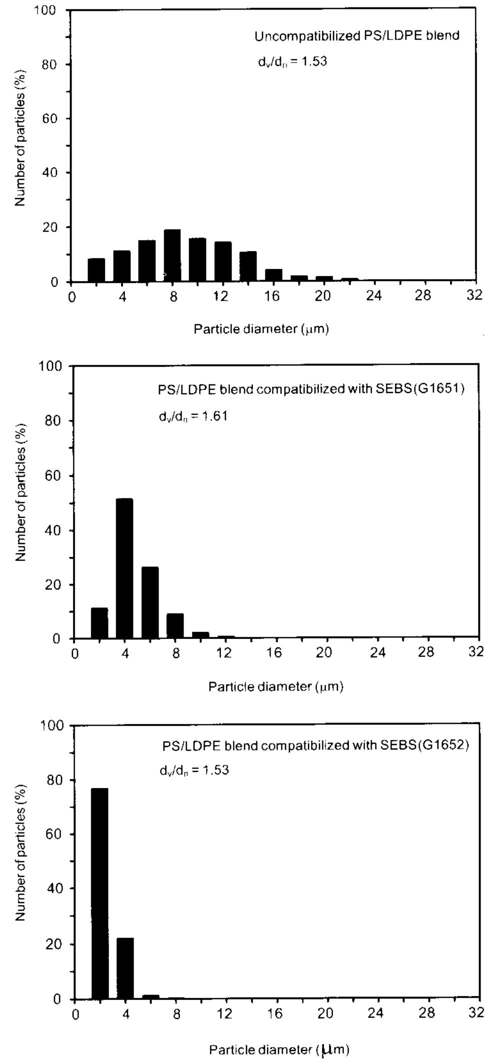


Figure 2 Frequency-distribution of PS/LDPE (70/30 wt%) blends uncompatibilized and compatibilized with SEBS (5 wt% with respect to LDPE content).

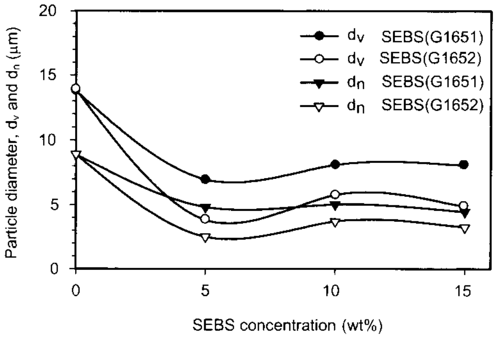


Figure 3 Emulsification curves of PS/LDPE (70/30 wt%) blends compatibilized with SEBS(G1651) and SEBS(G1652) (5, 10, and 15 wt% with respect to LDPE content).

In this study the annealing temperature used was the same as the melt mixing temperature. In order to reduce the volume of work in this study, an annealing time longer than 30 min was not used. It is found that annealing of melts of both the uncompatibilized and compatibilized blends leads to a pronounced coarsening of the morphology (see Figures 4-6). The corresponding quantitative analysis is given in Figure 7. An increase in d_V and d_n was observed with annealing time. However, a significant increases in the value of d_V and d_n was found after 5 min of annealing in most of the blends studied. The increase in the dispersed particle size during a short time of annealing is also reported by Guo *et al.* [34]. For most cases, after 15 and 30 min of annealing, no further significant change in the particle diameters was observed.

3.1 The uncompatibilized blends

For the uncompatibilized blends, as can be obviously seen from Figures 4b, 4f and 4j, an increase in the number of the larger particles after 5 min of annealing is more pronounced in the blend with 10 wt% LDPE. The blend with 10 wt% LDPE has a higher rate of coalescence than those with 20 and 30 wt% LDPE as is confirmed by the data shown in Figure 7a. In general, with little difference in size and size distribution (see Figure 4a, 4e and 4i), coalescence is likely to take place with higher probability in a blend with higher concentration of the dispersed phase. This is due to the higher concentration of the particles dispersed within the same space. Moreover, the interparticle distance of the blend with high concentration of the dispersed phase is also likely to be shorter than that of the blend with a low concentration of the dispersed phase and this leads to shorter times required for droplets to move close to one another. An explanation for higher coalescence observed in the uncompatibilized blend with 10 wt% LDPE may be that coalescence is likely to occur from collision of small particles. In the absence of external forces applied, the large particles which form a large fraction in the blend at higher concentrations are unlikely to move easily toward one another. Another possible reason is that the discrepancy in the results may arise from experimental error, i.e. droplet swelling. As seen obviously in Figure 4d, the number of smaller particles with diameters less than 6 μm after annealing for 30 min is higher than those after annealing for 15 min in the uncompatibilized blend with 10 wt% LDPE. This behavior is not observed in the uncompatibilized blend with 20 and 30 wt% LDPE (see also Figures 4h and 4l).

3.2 The compatibilized blends

According to the work of Kunyawut and Higgins [24], the Charpy impact strength of the PS/LDPE blends having 30 wt% LDPE in the absence and presence of SEBS prepared using the PRISM mini twin screw extruder with a melt temperature of 180 ± 5°C and screw speed of 60 rpm is higher than for those having 10 and 20 wt% LDPE in the absence of the SEBSs. Therefore, in order to minimize the number of variables, the change of the blend morphology under annealing condition was investigated only on the blends having 30 wt% LDPE in the absence and presence of SEBS. The effect of annealing on coalescence in the SEBS compatibilized blends is illustrated in Figures 5 and 6. An increase in the fraction of large particle size in the SEBS(G1651) compatibilized blends with increasing annealing time is found to be inversely dependent on the concentration of the SEBS(G1651) used. The blend compatibilized with 5 wt% of the SEBS(G1651) is shown to annealing for 15 and 30 min. However, these phenomena are less significant in the blend compatibilized with

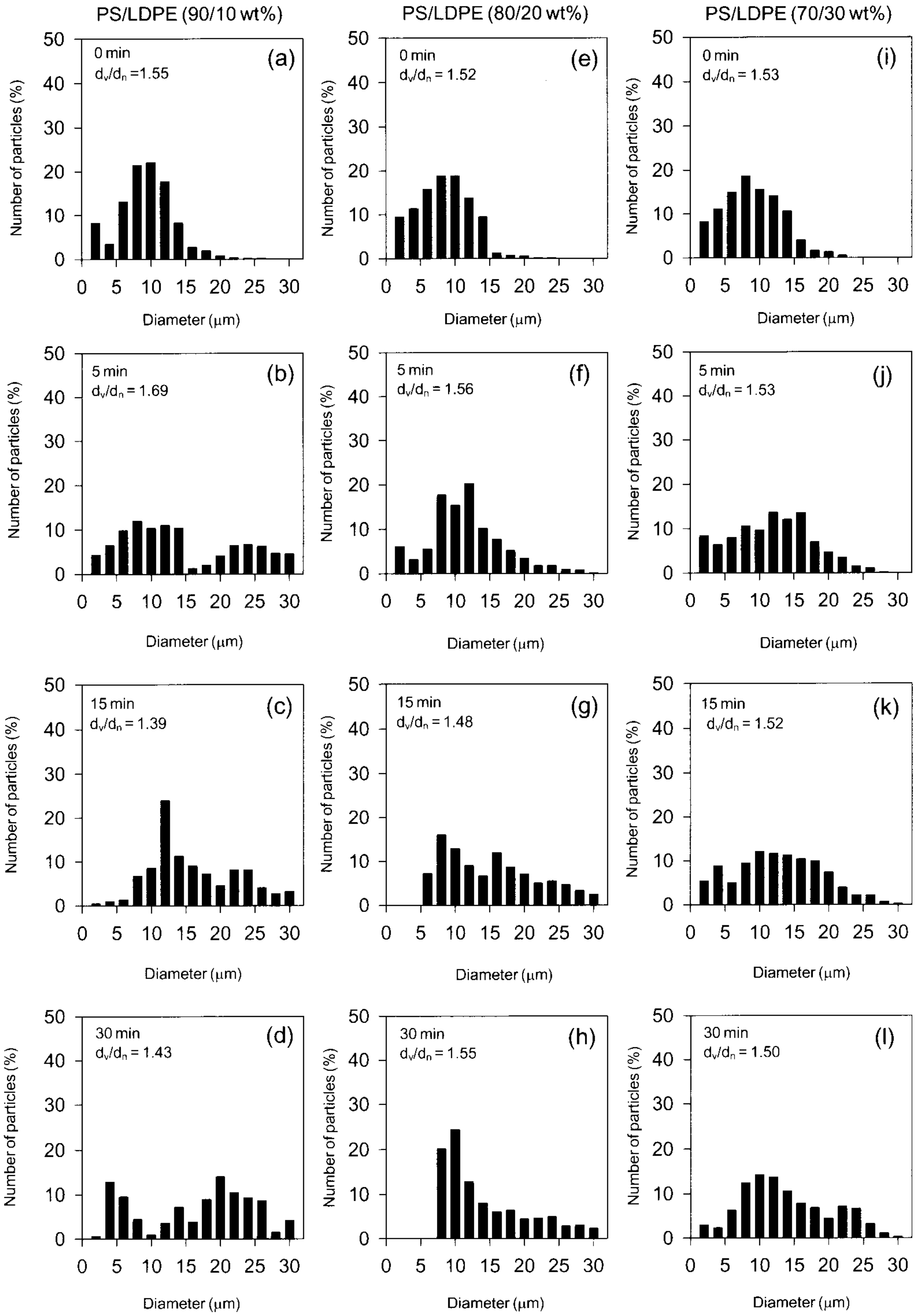


Figure 4 Frequency-distribution histograms at various annealing times of uncompatibilized PS/LDPE blends.

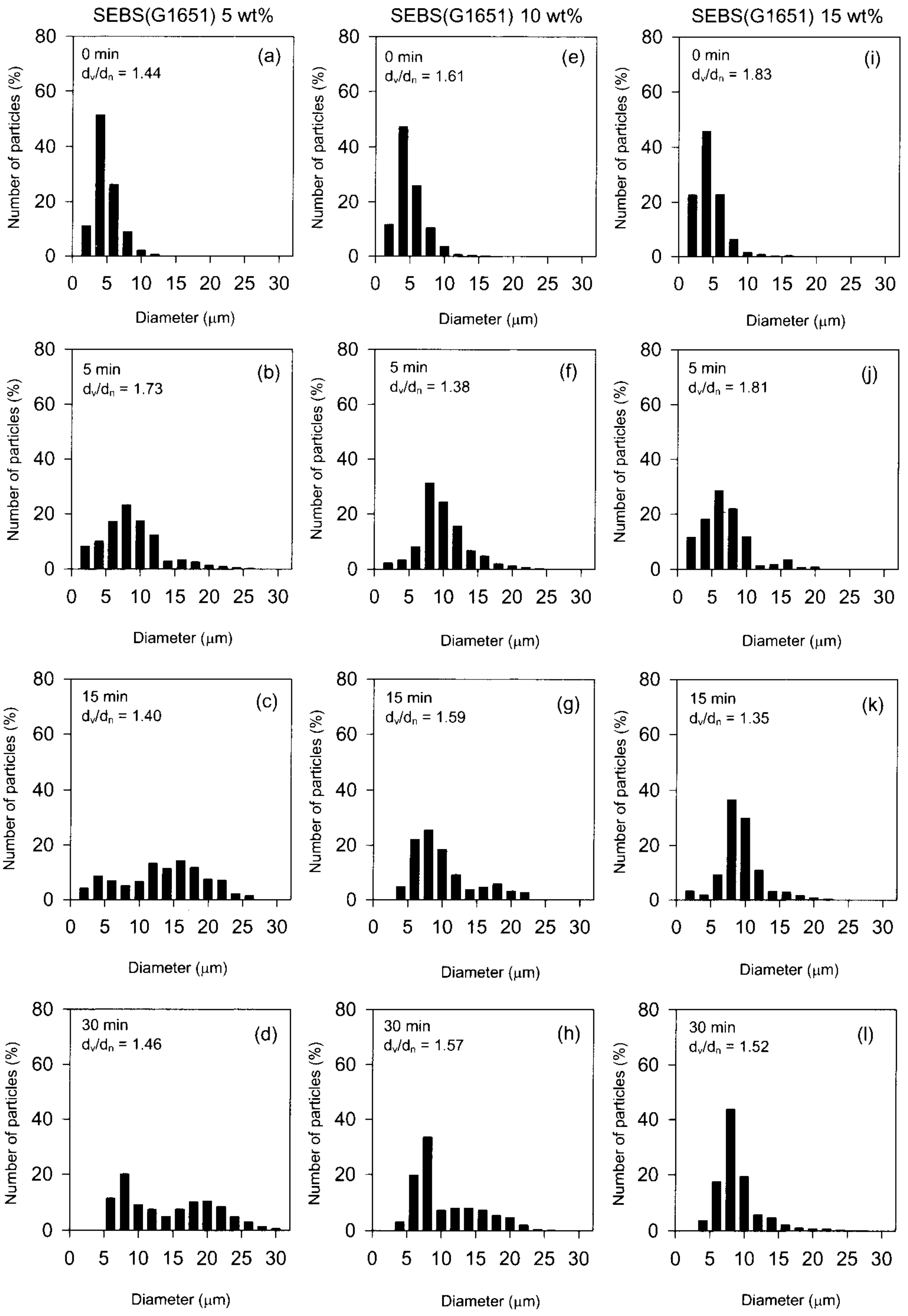


Figure 5 Frequency-distribution histograms at various annealing times for PS/LDPE (70/30 wt%) blends compatibilized with SEBS(G1651) (5, 10 and 15 wt% with respect to LDPE content).

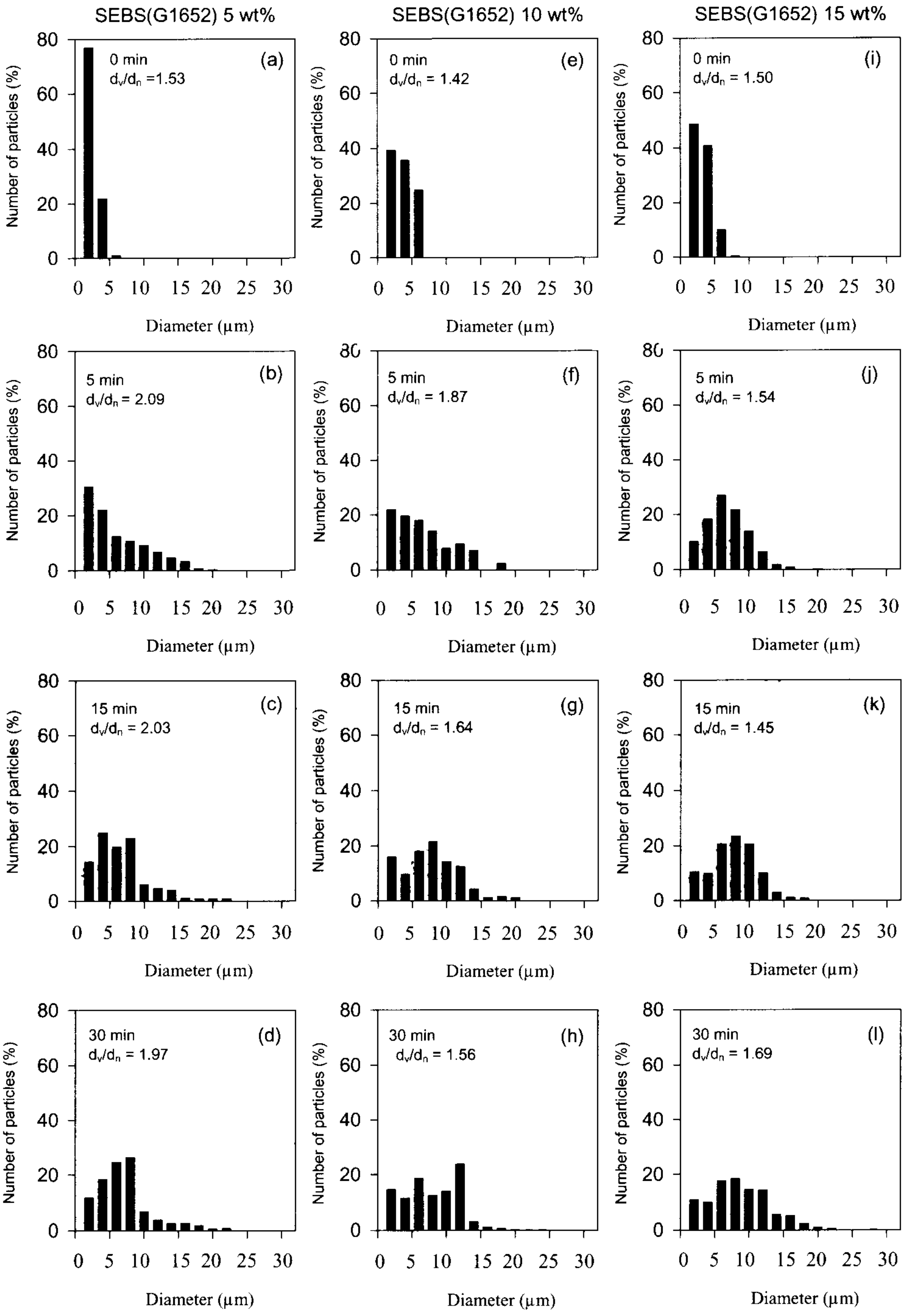


Figure 6 Frequency-distribution histograms at various annealing times for PS/LDPE (70/30 wt%) blends compatibilized with SEBS(G1652) (5, 10, and 15 wt% with respect to LDPE content).

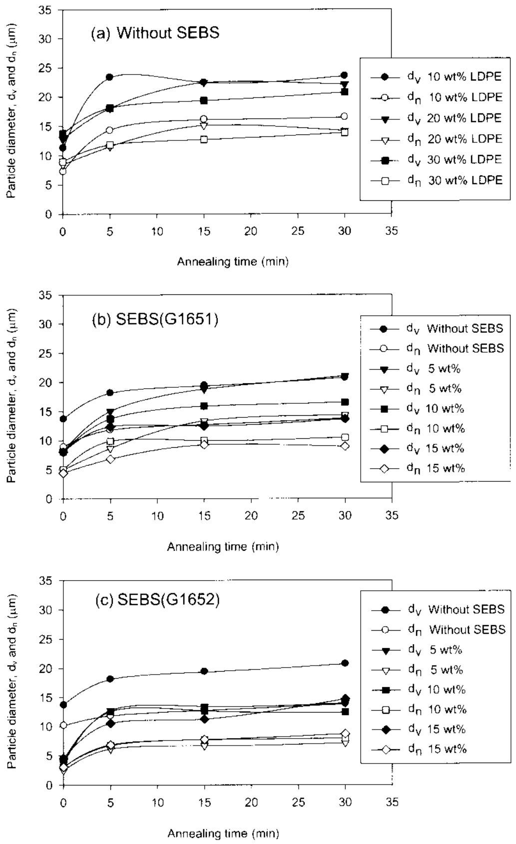


Figure 7 Volume- and Number-average diameters as a function of annealing time for PS/LDPE blends with and without SEBS (5, 10 and 15 wt% with respect to LDPE content).

10 and 15 wt% of the SEBS(G1651). The coarse morphology of the blend compatibilized with the SEBS(G1652) resulting from coalescence was also observed during annealing. The degree of coalescence of the blend compatibilized with the SEBS(G1652) was found to be higher than that of the blends compatibilized with the SEBS(G1651). This was indicated by much change in the size distribution of the blend compatibilized with the SEBS(G1652) after 5 min of annealing (see Figure 6). Moreover, the influence of the concentration of the SEBS(G1652) on the degree of coalescence is less significant as little change in size and size distribution of these blends can be seen in Figures 6 and 7c. The coalescence which occurred in the compatibilized blend with the SEBS(G1651) and the SEBS(G1652) mainly arises from the relatively large fraction of small droplets of the LDPE dispersed in the PS (see Figures 5 and 6). According to the so-called *drainage model*, the small droplets have much more probability to coalesce than the large droplets since the time required for film drainage from a pair of small droplets would be shorter than that of the big ones. This can lead to a high degree of coalescence. The coalescence model proposed by Chesters [35] expressed in equation (3) also indicates that small droplets have a higher probability of coalescence, P_{coal} .

$$P_{coal} \approx \exp\left(-\frac{Kd^{13/6}}{\Gamma^{7/6}} \left[\eta_m \dot{\gamma} \right]^{3/2} \right) \qquad (3)$$

where K is the viscosity of the continuous phase to the viscosity of the dispersed phase, d is the droplet diameter, η_m is the viscosity of the continuous phase, Γ is the interfacial tension, and $\dot{\gamma}$ is the shear rate. Although equation (3) was derived for the case of flow-driven coalescence, its application to the case of static coalescence (annealing) may be possible. One can expect that the coalescence caused by annealing will never take place if there is no movement of the droplets. The movement of the droplets generated by viscous flow is expected. The shear stress term $(\sigma = \eta_m \dot{\gamma})$ expressed in equation (3) will, therefore, never be zero though the size of this parameter would be very small. According to equation (3), the smaller the size of the dispersed phase particles, the higher the coalescence probability. This equation was later modified by Janssen and Mejier [36] for partially mobile interfaces.

Although stability of the morphology against droplet coalescence during annealing has been reported in many compatibilized blend systems [19, 21, 34], the results observed in this study showed that coalescence did occur in the SEBS compatibilized blends. An explanation may be that the degree of anchoring by segments of blocks of both the SEBS(G1651) and SEBS(G1652) corresponding to the PS and LDPE is not high enough to prevent the block copolymer segments from being pushed out of the interface by an approaching particle during a long annealing time. Furthermore, according to the work of Kunyawut [37], the high molecular weight SEBS(G1651) is shown to be less effective than the low molecular weight one because its critical micelle concentration is very low. So even if diffusion is promoted by the mixing flow field, the long chain SEBS(G1651) gets stuck in micelles. Therefore, in order to have much of the SEBS at the interface, a higher amount is needed in the blend. As seen in Figure 7b, the ability to reduce coalescence to the same level as the SEBS(G1652) was found when 15 wt% of the SEBS(G1651) was used. However, the amount of the high molecular weight SEBS used must not be too high so as to avoid the effect of micelle formation and an increase in viscosity of the matrix phase (Kunyawut, 2001). Another possibility is that the melt processing conditions used do not provide a high enough degree of dispersive mixing to allow the SEBS to reach the interface at any reasonable concentration, i.e. the mixing temperature used was relatively low compared with the order-disorder transition temperature T_{ODT} of the SEBS Kraton G series, i.e. T_{ODT} of SEBS(G1650) ($M_n = 1.00 \times 10^5$) is about 350°C [38]. Note that in the ordered state, an A-B block copolymer forms microdomains with a long-range order having a spatial periodicity of the size of the polymer coil, as characterized by the radius of gyration of the block copolymer. The block copolymer can also form a homogeneous structure in which the segments A and B are molecularly mixed in the disordered state. The temperature at which the transition from the ordered to disordered state takes place is called the order-disorder transition temperature [39].

4. Conclusion

A change of phase morphology under quiescent (annealing) conditions of the PS/LDPE blend in the absence and presence of SEBS triblock copolymers has been investigated. Coalescence of dispersed droplets is observed in both the uncompatibilized and SEBS-compatibilized blends under quiescent conditions. A significant increase in dispersed size diameter is observed after a few minutes of annealing. The coalescence during annealing mainly arose from coalescence of the smaller particles. The high molecular weight SEBS is shown to be more effective at coalescence retardation than the low molecular weight one. This is expected from the higher degree of resistance to chain-push-out of the high molecular weight SEBS when the droplets move towards one another. The ability to retard coalescence is found to increase with an increase in concentration of the SEBS. However, a significant increase in the LDPE particle size during annealing under quiescent conditions indicates that the interface of the immiscible blends studied is highly mobile. The SEBS triblock copolymers were shown to have only low ability to suppress coalescence. This is expected to be because of the lower anchoring degree of the blocks of the copolymers within the corresponding homopolymer phases.

5. Acknowledgement

The author would like to acknowledge and thank sincerely Professor Julia S. Higgins, Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, University of London, UK, for fruitful comments and discussion.

6. References

[1] Plochocki, A.P., Dagli, S.S. and Andrews, R.D., The Interface in Binary Mixers of Polymers Containing a Corresponding Block Copolymer: Effects of Industrial Mixing Processes and of Coalescence, Polymer Engineering and Science, Vol. 30, No. 12, pp. 741-752, 1990.

[2] Utracki, L.A. and Shi, Z.H., Development of Polymer Blend Morphology during Compounding in Twin-screw Extruder. Part I: Droplet Dispersion and Coalescence: A Peview, Polymer Engineering and Science, Vol. 32, No. 24, pp. 1824-1833, 1992.

[3] Janssen, J.M.H. and Meijer, H.E.H., Droplet Break up Mechanisms: Stepwise Equilibrium Versus Transient Dispersion, Journal of Rheology, Vol. 37, No. 4, pp.579-608, 1993.

[4] Milner, S.T. and Xi, H., How Copolymer Promote Mixing of Immiscible Homopolymers, Journal of Rheology, Vol. 40, No. 4, pp. 663-687, 1996.

[5] Jang, B.Z., Uhlmann, D.R. and Van Den Sande, J.V., The Post Dispersion Coalescence Phenomenon in Polymer-Polymer Blends, Rubber Chemistry and Technology, Vol. 57, No. 2, pp. 291-306, 1984.

[6] Endo, S., Min, K., White, K.L. and Kyu, T., Polyethylene-polycarbonate

Blends: Interface Modification, Phase Morphology and Measurement of Orientation Development during Cast Film and Tubular Extrusion by Infrared Dichroism, Polymer Engineering and Science, Vol. 26, No. 1, pp. 45-53, 1986.

[7] Fayt, R., Jerome, R., and Teyssie, P.H., Molecular Design of Multi-component Polymer Systems. XIV. Control of the Mechanical Properties of Polyethylene-Polystyrene Blends by Block Copolymers, Journal of Polymer Science Part B: Polymer Physics, Vol. 27, No. 4, pp. 775-793, 1989.

[8] Favis, B.D. and Chalifoux, J.P., Influence of Composition on the Morphology of Polypropylene/Polycarbonate Blends, Polymer, Vol. 29, No. 29, pp. 1761-1767, 1988.

[9] Favis, B.D., The Effect of Processing Parameters on the Morphology of an Immiscible Binary Blend, Journal of Applied Polymer Science, Vol. 29, pp. 285-300, 1990.

[10] Yoshida, M., Ma, J.J., White, J.L. and Quirk, R.P., Polyester-polystyrene Block Copolymers and Their Influence on Phase Morphology and Mechanical Properties in Polymer Blends, Polymer Engineering and Science, Vol. 30, No. 1, pp. 30-43, 1990.

[11] Datta, S. and Lohse, D.J., Graft Copolymer Compatibilizers for Blends of Isotactic Polypropylene and Ethene-propene Copolymer. 2. Functional Polymers Approach, Macromolecule, Vol. 26, No. 8, pp. 2064-2076, 1993.

[12] Sundararaj, U. and Macosko, C.W., Drop Break-up and Coalescence in Polymer Blends : The Effects of Concentration and Compatibilization, Macromolecules, Vol. 28, No. 5, pp. 2647-2657, 1995.

[13] Crist, B. and Nesarikar, A.R., Coarsening in Polyethylene-copolymer Blends, Macromolecules, Vol. 28, No. 4, pp.890-896, 1995.

[14] Mirabella, F.M., Jr. and Barley, J.S., Ostwald Ripening in Immiscible Polyolefin blends, Journal of Polymer Science Part B: Polymer Physics, Vol. 33, pp. 2281-2287, 1995.

[15] Fortelný, I. and Ková, J., Theory of Coalescence in Immiscible Polymer Blends, Polymer Composite, Vol. 9, No. 2, pp. 119-124, 1988.

[16] Søndergaard, K. and Lyngaae-Jørgensen, J., Chapter 12: Influence of Interface Modification on Coalescence in Polymer Blends in Flow-induced Structure in Polymers, Nakatani, A.I. and Dadmun, M.D., eds., American Chemical Society, Washington, D.C., 1995.

[17] Gonzáles-Núnez, R., De Kee, D. and Favis, B.D., The Influence of Coalescence on the Morphology of the Minor Phase in Melt-draw Polyamide-6/HDPE blends, Polymer, Vol. 37, No. 21, pp. 4689-4693, 1996.

[18] Yang, K. and Han, C.D., Effects of Shear flow and Annealing on the Morphology of Rapidly Precipitated Immiscible Blends of Polystyrene and Polyisoprene, Polymer, Vol. 37, pp. 5795-5805, 1996.

[19] Mekhilef, N., Favis, B.D. and Carreau, P.J., Morphological Stability, Interfacial Tension, and Dual-phase Continuity in Polystyrene-polyethylene Blends, Journal of Polymer Science Part B: Polymer Physics, Vol. 35, pp. 293-308, 1997.

[20] Pöetschke, P., Wallheinke, K., Fritsche, H., and Stutz, H., Morphology and Properties of Blends with Different Thermoplastic Polyurethanes and Polyolefins, Journal of Applied Polymer Science, Vol. 65, pp. 749-762, 1997.

[21] Wallheinke, K., Pöetschke, P. and Stutz, H., Influence of compatibilizer Addition on Particle size and Coalescence in TPU/PP blends, Journal of Applied Polymer Science, Vol. 65, pp. 2217-2226, 1997.

[22] Wallheinke, K., Pöetschke, P., Macosko, C.W. and Stutz, H., Coalescence in Blends of Thermoplastic Polyurethane with Polyolefins, Polymer Engineering and Science, Vol. 39, No. 6, pp. 1022-1034, 1999.

[23] Kim, Y. H., Kikuchi, M., Akiyama, S., Sho, K. and Izawa, S., Morphology and Coarsening Behavior in Polycarbonate/ nylon6-co-12 blends with and without Compatibilizer, Polymer, Vol. 40, pp. 5273-5278, 1999.

[24] Kunyawut, C. and Higgins, J.S., The Impact Properties of Bulk Compatibilized PS/LDPE blends, Journal of Engineering. RIT, Vol. 3, No. 5, pp. 55-65, 2005.

[25] Lepers, J. -C., Favis, B.D. and Lacrox, C., The influence of Partial Emulsification on Coalescence Suppression and Interfacial Tension Reduction in PP/PET Blends, Journal of Polymer Science Part B : Polymer Physics, Vol. 37, pp. 939-951, 1999.

[26] Sawyer, L.C. and Grubb, D.T., Polymer Microscopy, Chapman and Hall, 1987.

[27] Bourry, D. and Favis, B.D., Cocontinuity and Phase Inversions in HDPE/PS blends : Influence of Interfacial Modification and Elasticity, Journal of Polymer Science Part B: Polymer Physics, Vol.36, pp. 1889-1899, 1998.

[28] Lyngaae-Jorgensen, J. and Utracki, L.A., Dual Phase Continuity in Polymer Blends, Makromolekular Chemie, Macromol. Symp., Vol. 48/49, pp. 189-209, 1991.

[29] Willemse, R.C., Posthuma de Boer, A., van Dam, J. and Gotsis, A.D., Co-continuous Morphologies in Polymer Blends: A New Model, Polymer, Vol. 39, No. 24, pp. 5879-5887, 1998.

[30] Willemse, R.C., Co-continuous Morphologies in Polymer Blends : Stability, Polymer, Vol. 40, pp. 2175-2178, 1999.

[31] Char, K., Brown, H.R. and Deline, V.R., Effects of a Diblock Copolymer on Adhesion between Immiscible Polymers. 2. PS-PMMA copolymer between PPO and PMMA, Macromolecules, Vol. 26, No.16, pp. 4164-4171, 1993.

[32] Cigana, P., Favis, B.D., Albert, C. and Vu-Khanh, T., Morphology-interface-Property Relationships in Polystyrene/ Ethylene-propylene Rubber Blends. 1. Influence of Triblock Copolymer Interfacial Modifiers, Macromolecules, Vol. 30, No. 14, pp. 4163-4169, 1997.

[33] Hong, B.K. and Jo, W.H., Effect of Molecular Weight of SEBS Triblock Copolymer on the Morphology, Impact Strength, and Rheological Property of Syndiotactic Polystyrene/ethylene-Propylene Rubber Blends, Polymer, Vol. 41, pp. 2069-2079, 2000.

[34] Guo, H. F., Packirisamy, S., Mani, R.S., Aronson, C.L., Gvozdic, N.V. and Meier, D.J., Compatibilizing Effect of Block Copolymers in Low-density Polyethylene/ Polystyrene Blends, Polymer, Vol. 39, No. 12, pp. 2495-2505, 1998.

[35] Chesters, A.K., The Modelling of Coalescence Process in Fluid-liquid Dispersion : A Review of Current Understanding, Chemical Engineering Research and Design, Vol. 69, pp. 259-270, 1991.

[36] Janssen, J.M.H. and Meijer, H.E.H., Dynamics of liquid-liquid Mixing : A 2-zone Model, Polymer Engineering and Science, Vol. 35, No. 22, pp. 1766-1780, 1995.

[37] Kunyawut, C., Effect of Processing Conditions on the Morphology and Mechanical Properties of Immiscible Polymer Blends, [Ph.D. thesis], Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, University of London, UK, 2001.

[38] Chun, S.B. and Han, C.D., The Role of the Order-disorder Transition Temperature of Block Copolymer in the Compatibilization of two Immiscible Homopolymers, Macromolecules, Vol. 32, pp. 4030-4042, 1999.

[39] Hashimoto, T., Research on Thermoplastic Elastomers: Section 3: Order-disorder Transition in Block Copolymers in Thermoplastic Elastomers: A Comprehensive and Review, Legge, N.R., Holden, G. and Schroeder, H.E., eds., Hanser Publishers, New York, 1987.