

# Morphological development with time for immiscible polymer blends with an *in situ* compatibilizer under controlled shear conditions

H. K. Jeon and Jin Kon Kim\*

Department of Chemical Engineering, Polymer Research Institute, Pohang University of Science and Technology, Pohang, Kyungbuk 790-784, Korea

(Received 18 July 1997; revised 25 September 1997; accepted 15 October 1997)

We have studied morphological development with time under controlled shear condition for 75/25 wt/wt poly(butylene terephthalate) (PBT) and polystyrene (PS) blend having various amounts of poly(styrene-*ran*-glycidyl methacrylate) (PS-GMA) as an *in situ* compatibilizer prepared by solution blending method. The morphology of the blend without PS-GMA develops via a coarsening process during an annealing at higher temperatures. However, the dispersed domain size of the blend with PS-GMA increases slowly at an early stage of annealing, and then levels off. This is due to the *in situ* formation of graft copolymers at the interface. As the initial amount of PS-GMA in the blend increases, enough of the copolymers for the dispersed domain size in the blend to be levelled off are formed at shorter times. An oscillatory shearing with the frequency range 0.5–10 rad s<sup>-1</sup> can induce the coalescence of the dispersed domain in the blend without PS-GMA. However, for the blend with PS-GMA the shear-induced coalescence of the dispersed domain is successfully suppressed by the graft copolymers formed *in situ* at the interface. The time evolutions of shear storage modulus ( $G'$ ) and complex viscosity ( $\eta^*$ ) for blends with PS-GMA are strongly affected by the blend morphology which in turn depends on the initial amount of PS-GMA in the blend. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: morphological development; controlled shearing; reactive compatibilization)

## INTRODUCTION

Blending of two or more polymers has been an effective and powerful technique to obtain a new polymeric material with desirable mechanical properties<sup>1,2</sup>. However, most polymer blends are thermodynamically incompatible because of the positive enthalpy change of mixing and the lower entropy change of mixing resulting from the high molecular weight of polymers. Incompatible polymer blends exhibit coarse morphology, and thus poor mechanical properties. Therefore, compatibilization techniques have been widely used in order to improve the poor properties of immiscible polymer blends.

Compatibilization techniques can be separated into two categories: physical compatibilization utilizing a pre-made copolymer as a compatibilizer<sup>3–8</sup> and chemical compatibilization with an *in situ* reactive compatibilizer<sup>9–17</sup>. In physical compatibilization, the morphology of a polymer blend is controlled with a copolymer concentration in the blend. It has been found that the molecular weight (MW) of a copolymer, the copolymer's structure and composition, and the interfacial concentration of the copolymer across the interface are the key parameters influencing on the interfacial properties, and thus the blend morphology. However, there are some limits to using a pre-made copolymer as a compatibilizer<sup>18–22</sup>. As the MW of a copolymer increases, less of the copolymer reaches the interface and the remainder stays in the bulk phase owing to the higher possibility of micelle formation of the copolymer.

Another difficulty in physical compatibilization is that a copolymer cannot reach the interface easily owing to its high viscosity and the rather short processing time since polymer blends are usually prepared by an extruder or a compounding machine.

Recently, chemical compatibilization has been widely used<sup>9–17</sup>. The morphology of incompatible polymer blends with an *in situ* compatibilizer becomes very fine, since copolymers formed by the reaction between functional groups existing in constituent components in the blend can reduce the interfacial tension between the dispersed phase and the matrix. This finer morphology can persist even at higher shear stresses.

The final morphology of a polymer blend with an *in situ* reactive compatibilizer depends upon various parameters, e.g. blend composition, interfacial tension between the matrix and the dispersed phase, processing temperature, flow type and rate, viscosity or elasticity of blend components, and the molecular weight and the amount of the *in situ* formed copolymer. Among these parameters, the last two, affecting the interfacial properties of a blend, become very important parameters in deciding the final morphology.

It has been reported that, even if the amount of the *in situ* formed copolymers in total blend becomes as much as 10 wt.%, the dispersed domain size decreases merely from 4 to 2  $\mu\text{m}$ <sup>23</sup>. However, a few studies on interfacial reaction kinetics have shown that only about 2% of *in situ* formed copolymers in a blend are enough to stabilize the blend morphology<sup>15,17</sup>. These results suggest that not all of the *in*

\* To whom correspondence should be addressed.

*in situ* formed copolymers can be guaranteed to be located at the interface when a commonly used melt blending method is employed.

Very recently we<sup>24</sup> found that the interfacial areal density ( $\Sigma$ ) of *in situ* formed poly(butylene terephthalate-*graft*-styrene) (PBT-*g*-PS) was approximately 0.1 chains nm<sup>-2</sup> regardless of initial content of PS-GMA in 75/25 wt/wt PBT/PS blend. This blend was prepared by solution blending and precipitation followed by oscillatory shearing at  $\omega = 1.0 \text{ rad s}^{-1}$ . A solution blending and precipitation method can allow one to prepare an immiscible polymer blend with fine morphology since it is kinetically frozen during the precipitation, and thus phase separation is largely suppressed. For a sample prepared by solution blending, most *in situ* formed copolymers are located at the interface when the reaction occurs, because an *in situ* compatibilizer exists in one constituent component miscible with it. However, for a melt-blended sample, at least some of the *in situ* formed graft copolymers are located in the matrix phase as micelles, and thus the interfacial activity is not good as that of the solution-blended sample<sup>24</sup>.

Taylor's theory<sup>25,26</sup> has been often employed to explain the change in the dispersed domain size in polymer blends with various amounts of compatibilizer<sup>16</sup>. However, since most polymer blends or alloys have been prepared by an internal mixer or a twin screw extruder, the exact description of flow type and the magnitude of the shear rate (or elongation rate) in an internal mixer or a twin screw extruder is not attainable, and thus the application of Taylor's theory to polymer blends prepared by this method is not quantitatively guaranteed. Note that Taylor's theory requires an assumption of a single Newtonian drop under simple shearing flow or elongational flow.

In a series of papers<sup>8,16,27-31</sup>, Macosko and coworkers proposed a mechanism for morphological development with time from pellet form to final morphology for polymer blends with and without a compatibilizer. They showed that a major reduction in the dispersed domain size with time in polymer blends occurs when the components begin to melt or soften at short processing times (e.g. 1.5 min). Also, by including the elasticity of constituents in the blend in Taylor's theory, they proposed an expression to predict the dispersed domain size and found that experimental results are consistent with predictions<sup>16,32</sup>. It should be mentioned that polymer blends employed by Macosko and coworkers were prepared using an internal mixer and an extruder, in which the exact flow type and the magnitude of shear rate are not quantified.

In this paper, we have studied the morphological development with time under controlled flow conditions for immiscible polymer blend of poly(butylene terephthalate) (PBT) and polystyrene (PS) with various amounts of poly(styrene-*ran*-glycidyl methacrylate) (PS-GMA) as an *in situ* compatibilizer. The reaction between carboxylic acid in PBT and epoxy group in PS-GMA occurs very easily at higher temperatures and the *in situ* formed PBT-*graft*-PS acts as an effective compatibilizer between PBT and PS<sup>24,33-36</sup>. The time evolution of rheological properties of the blend is monitored and this is discussed in terms of blend morphology.

## EXPERIMENTAL

### Materials

The polystyrene (PS) used in this study was a commercial grade (GP-125) from Miwon Petrochemical Co., Korea. Its

number average molecular weight ( $M_n$ ) and the polydispersity ( $M_w/M_n$ ) are 55 000 and 3.6, respectively, which were determined by gel permeation chromatography (g.p.c.) using calibration curves for standard polystyrenes.

The poly(butylene terephthalate) (PBT) was a commercial grade (HV 1010) from LG Chemical Co., Korea. The intrinsic viscosity (IV) was  $1.0 \text{ dl g}^{-1}$  in a mixed solvent of phenol and tetrachloroethane (60/40 volume ratio) at 25°C. With the Mark-Houwink relationship ( $IV = 7.39 \times 10^{-5} M_v^{0.871}$ ) and a polydispersity index of 2.2 measured using g.p.c.,  $M_n$  of PBT was calculated to be 25 000. The amount of carboxylic acid in PBT was determined to be 63 eq per  $10^6 \text{ g}$  using end-group titration method. Thus, there are approximately 1.6 carboxylic acid units per each chain based on  $M_n$ .

The poly(styrene-*ran*-glycidyl methacrylate) (PS-GMA) employed in this study was kindly donated from LG Chemical Co., Korea, which was prepared by suspension polymerization<sup>33</sup>. The  $M_n$  and polydispersity index of PS-GMA are 46 000 and 2.5, respectively. The amount of GMA in PS-GMA is 2.0 wt.% determined from <sup>13</sup>C n.m.r. Thus, about 6.4 epoxy groups are present on each PS-GMA chain<sup>33</sup>.

### Sample preparation

The 75/25 wt/wt PBT/PS blends with various amounts of PS-GMA (0, 5, 10, and 20 wt.% based on neat PS and PS-GMA) were prepared by solution blending followed by precipitating the blend using methanol as a non-solvent. Phenol and *o*-dichlorobenzene (OCB) were used as the solvents of PBT and PS or PS-GMA, respectively.

To prevent any reaction between PBT and PS-GMA during preparation of the polymer solution, 4.5 wt.% of PBT solution in phenol was prepared in one beaker, while 1.5 wt.% of PS and PS-GMA solution in OCB was prepared in the other. PBT was completely dissolved in phenol at 60°C, and neat PS and PS-GMA in OCB at room temperature. The two solutions were mixed together at  $\approx 40^\circ\text{C}$  for 5 min, and immediately precipitated into powder form using excess methanol.

Powders were repeatedly washed with fresh methanol to remove the residual solvents in the blend, dried at room temperature for 1 day, and further dried at 60°C for 2 weeks in vacuum. Completely dried powders were moulded into a plaque having dimensions 3 cm  $\times$  3 cm  $\times$  1 mm (L  $\times$  W  $\times$  T) using a compression moulder at 230°C for less than 2 min.

### Rheological properties

Rheological properties of each blend were measured using a Rheometrics Dynamic Spectrometer (RDS-II) with a 25 mm cone and plate fixture under an oscillatory shear mode at 245°C. To minimize the reaction between PBT and PS-GMA and morphological development during sample loading, the specimen was loaded as fast as possible. The specimen temperature inside the RDS-II was equilibrated within 2 min. Time evolution of storage modulus ( $G'$ ) and complex viscosity ( $\eta^*$ ) at three different frequencies ( $\omega$ ) of 0.5, 1 and 10 rad s<sup>-1</sup> was monitored over 1 h. The strain was 15% and was found to be in a linear viscoelastic region. After oscillatory shearing for a given time, molten polymer blend inside the RDS-II was successfully removed from the rheometer by quenching to room temperature within 1 min using nitrogen gas. It should be mentioned that, during the cooling process, the torque in the rheometer must be carefully checked in order to avoid any damage to the torque transducer.

### Morphology

A scanning electron microscope (Hitachi S 570) was used to observe the morphology of a specimen fractured at liquid nitrogen atmosphere. In order to improve phase contrast between two phases, the PS phase in the fractured specimen was further etched out using tetrahydrofuran for 5 min, and then coated with a thin layer of gold. The number average dispersed domain size ( $D_n$ ) was obtained using a Quantimet 570 image analyser (Cambridge Instrument). The cross-sectional area ( $A_i$ ) of each particle on the micrograph was measured, and then converted to the diameter ( $D_i$ ) of a circle having the same cross-sectional area.

$$D_i = 2(A_i/\pi)^{1/2} \quad (1)$$

## RESULTS AND DISCUSSION

### Morphological development without shear

Figure 1 shows scanning electron micrographs for 75/25 wt/wt PBT/PS blends with various amounts of PS-GMA which were fractured at liquid nitrogen atmosphere. Each specimen for scanning electron microscopy (SEM) was prepared by compression moulding using powders obtained from a solution blending and precipitation method. It can be seen in Figure 1 that more finely dispersed domains with irregular shapes are observed and the dispersed domain size with less than  $0.2 \mu\text{m}$  does not vary with the added amounts of PS-GMA in the blend. This results from a kinetically frozen structure when each blend was prepared by the precipitation of the solution into a non-solvent. We also obtained a thin film of  $0.1 \text{ mm}$  thickness by a compression moulding of powders at  $80^\circ\text{C}$ . When we observed the fracture surface of this thin film, we found that scanning electron micrographs are essentially the same as those in Figure 1. This indicates that, although compression moulding was done at  $230^\circ\text{C}$  and the melting temperature of PBT is approximately  $230^\circ\text{C}$ , we consider that the time

(less than 2 min) and the temperature employed in the compression moulding were too short and too low for the reaction between PBT and PS-GMA to occur. This results from the fact that during compression moulding for 2 min the actual temperature of two metal plates contacted directly to the blend powders was about  $220\text{--}225^\circ\text{C}$ , which is less than the setting temperature of  $230^\circ\text{C}$ , since the blend powders were placed between two metal plates at  $25^\circ\text{C}$ , and pressed immediately after the plates were inserted into the compression moulder. Moreover, the shear modulus ( $G'$ ) of PBT at temperatures from  $190^\circ\text{C}$  to  $225^\circ\text{C}$  was  $10^7 \text{ Pa}$  which is the typical value of a semi-crystalline polymer at a rubbery state. Even at  $230^\circ\text{C}$ , very close to the  $T_m$  of PBT, the loaded rectangular bar does not break (or flow) within 2 min although  $G'$  decreased to  $10^6 \text{ Pa}$ . Note that the  $G'$  was measured in a torsional rectangular mode at a frequency  $\omega$  of  $0.1 \text{ rad s}^{-1}$  and a strain amplitude  $\gamma_0$  of 1%. Thus, PBT exhibits too high a viscosity to react with PS-GMA at temperatures lower than  $230^\circ\text{C}$ . However, it is observed that the loaded rectangular bar is broken and flows easily at  $240^\circ\text{C}$ , suggesting the critical temperature for the reaction between PBT and PS-GMA was estimated to be approximately  $235^\circ\text{C}$ . The morphology shown in Figure 1 is taken as the initial structure for each blend. Therefore, we consider that solution blending is an effective way to ensure initial finer morphology of a blend even when different amounts of an *in situ* compatibilizer are added to the blend.

The morphological development of the blends without PS-GMA and with 20 wt.% PS-GMA with annealing time is given in Figures 2 and 3, respectively. According to Figure 1a and Figure 2, it took only 30 s for a dispersed domain with the finer and irregular shape found in the initial morphology to develop into a dispersed domain with larger ( $0.39 \mu\text{m}$ ) spherical particles. This is attributed to the fact that, once a blend with kinetically frozen morphology was exposed at higher temperature, a phase separation between highly immiscible components of PBT and PS took place very rapidly. Also, with increasing annealing time the shape for an immiscible polymer blend becomes spherical to

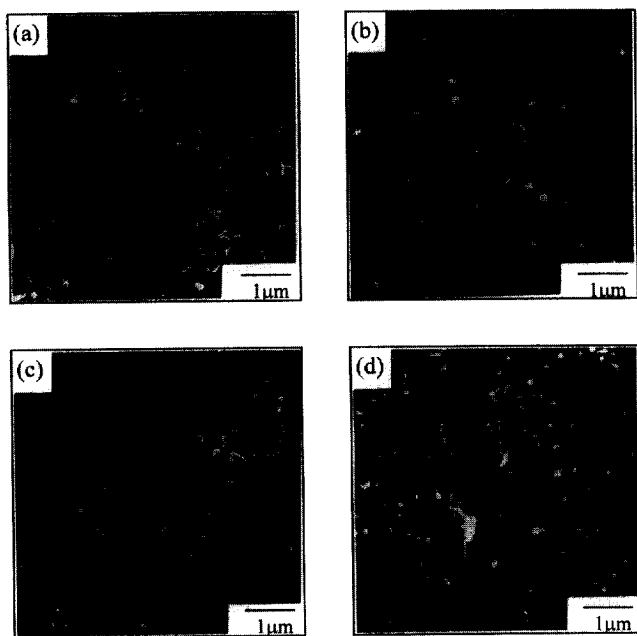


Figure 1 Scanning electron micrographs of fractured surfaces of 75/25 wt/wt PBT/PS blends with various amounts of PS-GMA based on total (PS + PS-GMA) phase: (a) 0, (b) 5, (c) 10, and (d) 20 wt%

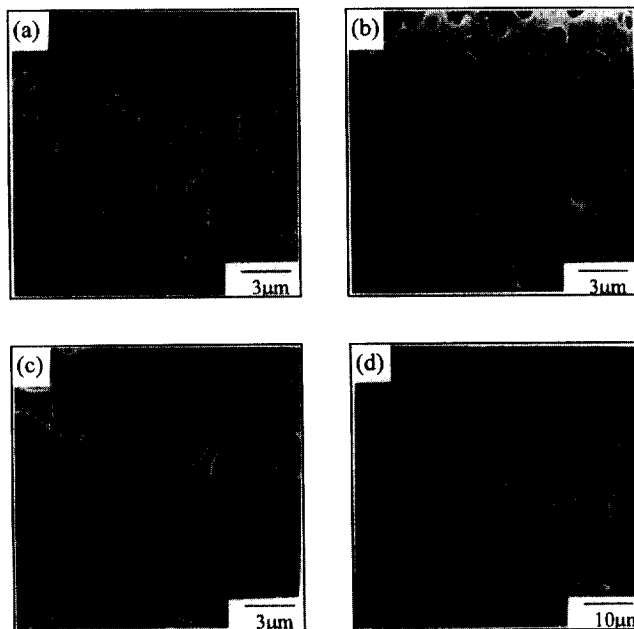
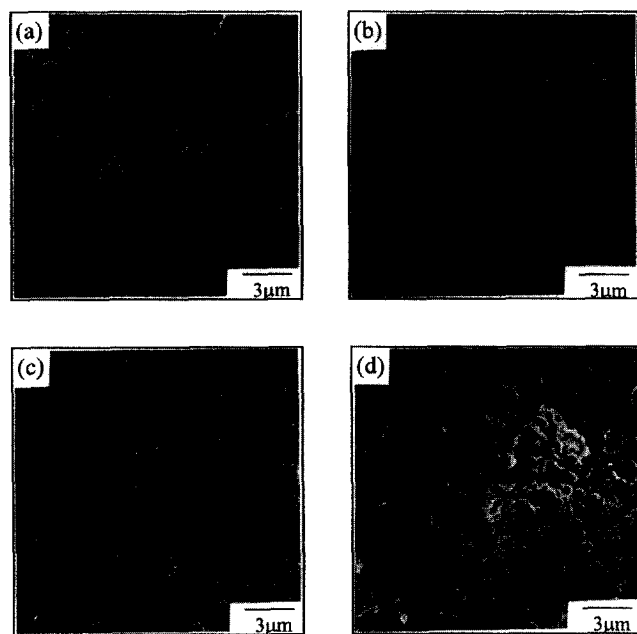


Figure 2 Scanning electron micrographs of 75/25 wt/wt PBT/PS blend without PS-GMA with various annealing times at  $245^\circ\text{C}$ : (a) 30 s, (b) 300 s, (c) 3600 s, and (d) 5400 s

reduce the interfacial energy, and the dispersed domain size keeps increasing. It can be seen in *Figure 1d* and *Figure 3* that, for the blend with 20 wt.% PS-GMA, the dispersed domain size increases from 0.11 to 0.27  $\mu\text{m}$  within 30 s of annealing. The initial growth in the dispersed domain size is because for a very short time phase separation prevailed over the formation of the *in situ* graft copolymer. However, as the annealing time increases further, the dispersed domain size does not change. Moreover, the shape of dispersed domain does not become spherical, i.e. the irregularly shaped dispersed domain remains. This is due to the existence of PBT-*g*-PS formed *in situ* at the interface between PBT and PS phases.

These results lead us to consider that the amount of PBT-*g*-PS formed within 30 s is sufficiently large to inhibit the growth of the dispersed domain, and thus stabilize the interface between the irregularly shaped dispersed phase and the matrix. Guegan *et al.*<sup>15</sup> studied the reaction kinetics of epoxy terminated poly(methyl methacrylate) (PMMA-E) and carboxylic acid terminated polystyrene (PS-COOH) at molten states. They also used a random MMA-glycidyl methacrylate copolymer (PMMA-*r*E) instead of PMMA-E to investigate the effect of the copolymer structure on the reaction rate. They found that the reaction rate of PMMA-*r*E and PS-COOH, which is very similar to that of PMMA-E and PS-COOH, is of the order of  $10^{-3} \text{ kgmol}^{-1} \text{ s}^{-1}$ , and this reaction is not diffusion controlled. In order to check whether or not the reaction between PBT and PS-GMA employed in this study is diffusion controlled, we compare the zero viscosities ( $\eta_0$ ) of homopolymers, because the diffusion coefficient can be inversely related to the viscosity. The  $\eta_0$  values at 180°C of PMMA-*r*E with  $M_w$  of 46 000 and PS-COOH with  $M_w$  of 43 000 are calculated to be  $9.4 \times 10^4 \text{ Pa}\cdot\text{s}$  and  $3.6 \times 10^3 \text{ Pa}\cdot\text{s}$ , respectively, obtained from the WLF equation and reference values<sup>37</sup>. The  $\eta_0$  values at 245°C of PBT and PS ( $M_w = 198\,000$ ) employed in this study were  $2 \times 10^3 \text{ Pa}\cdot\text{s}$  and  $9 \times 10^3 \text{ Pa}\cdot\text{s}$ , respectively. These results lead us to consider that the reaction between PBT and PS-GMA is not



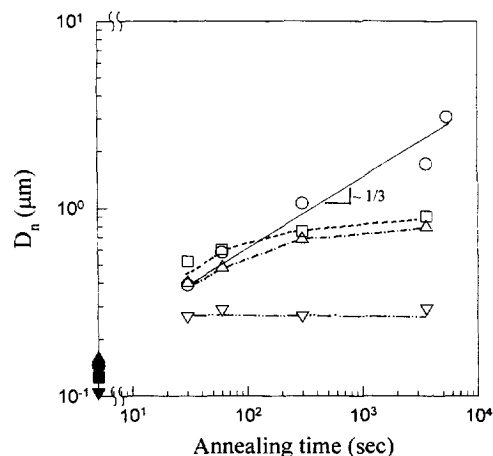
**Figure 3** Scanning electron micrographs of 75/25 wt/wt PBT/PS blend with 20 wt% PS-GMA with annealing times at 245°C: (a) 30 s, (b) 60 s, (c) 300 s, and (d) 3600 s

diffusion controlled. Since the activation energy ( $E_a$ ) was reported to be  $84 \text{ kJ mol}^{-1}$ , the reaction rate at 245°C is about 16 times higher than that at 180°C. Nakayama *et al.*<sup>38</sup> observed that a mixing time of  $\approx 5 \text{ min}$  is sufficient to reach the final particle size for the same blend system at 180°C. When these results are applied to the PBT/PS blend employed in this study, the interface can be stabilized within 20 s at 245°C, and the small domain size can be maintained at longer times. Although the concentration of functional groups is also an important factor affecting the overall reaction rate, and the backbone polymers employed in this study are different from theirs, we can conclude that sufficient PBT-*g*-PS was formed *in situ* within 30 s and covered the interface for the blend with 20 wt.% PS-GMA.

On the basis of results found in *Figures 1–3*, plots of the number average dispersed domain size ( $D_n$ ) versus annealing time for all blend compositions are given in *Figure 4* and the values of the  $D_n$  with standard deviations are listed in *Table 1*. It can be seen in *Figure 4* that  $D_n$  of the blend without PS-GMA increases with annealing time via a coarsening process which results from either a coalescence or an Ostwald ripening (evaporation–condensation) mechanism. Although the two mechanisms are different, the trend of the increase in  $D_n$  with phase separating time is the same, and is given by

$$\bar{r}^3 = \bar{r}_0^3 + Kt \quad (2)$$

where  $r$  and  $r_0$  are the average domain radius at time  $t$  and at initial time, and  $K$  is the coarsening constant. From *Figure 4*, it is noted that for the blend without PS-GMA the growth



**Figure 4**  $D_n$  versus annealing time at 245°C for 75/25 PBT/PS blends with various amounts of PS-GMA: (○) 0, (□) 5, (△) 10, and (▽) 20 wt%. The  $D_n$  values of blends with various amounts of PS-GMA prepared by solution blending followed by precipitation are shown as the filled symbols

**Table 1** The number average dispersed domain size ( $D_n$ ) with annealing time at 245°C for 75/25 wt/wt PBT/PS blends with various amounts of PS-GMA

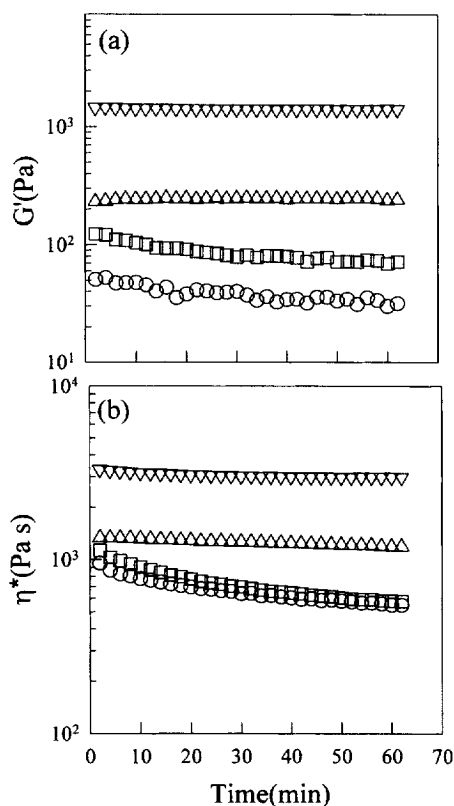
Annealing time (s)	$D_n$ ( $\mu\text{m}$ )			
	PS-GMA0	PS-GMA5	PS-GMA10	PS-GMA20
0	$0.15 \pm 0.08$	$0.13 \pm 0.03$	$0.16 \pm 0.11$	$0.11 \pm 0.07$
30	$0.39 \pm 0.32$	$0.52 \pm 0.24$	$0.40 \pm 0.15$	$0.27 \pm 0.18$
60	$0.58 \pm 0.29$	$0.60 \pm 0.28$	$0.48 \pm 0.15$	$0.29 \pm 0.19$
300	$1.06 \pm 0.49$	$0.75 \pm 0.30$	$0.68 \pm 0.20$	$0.27 \pm 0.19$
3600	$1.71 \pm 1.10$	$0.90 \pm 0.29$	$0.79 \pm 0.22$	$0.29 \pm 0.18$
5400	$3.06 \pm 1.88$	–	–	–

of the dispersed domain is proportional to  $t^{0.34}$ , and so  $D_n$  increases according to a coarsening process. It should be mentioned that  $\bar{r}^3$  was taken as the y-axis in Figure 4, while  $(\bar{r}^3 - \bar{r}_0^3)$  is used in equation (2). However, for the PBT/PS blend without PS-GMA,  $\bar{r}_0^3$  is  $3.8 \times 10^{-4} \mu\text{m}^3$  which is about 4 order of magnitude smaller than  $\bar{r}^3$  ( $=0.63 \mu\text{m}^3$ ) at  $t=1$  h, and thus the exponent (0.34) obtained from the results in Figure 4 remained the same even when  $(\bar{r}^3 - \bar{r}_0^3)$  was used as the y-axis. Although this assumption cannot be suitable for the blends with PS-GMA, these plots are shown in order for comparison with those of the blend without PS-GMA.

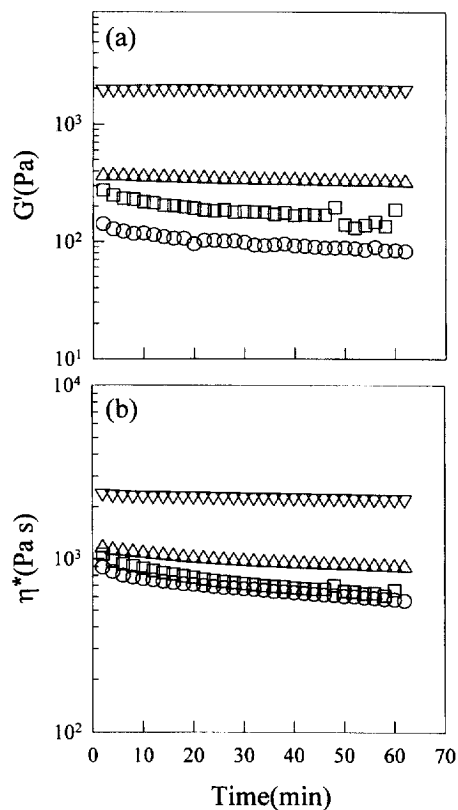
Figure 4 also shows that  $D_n$  of the blends with 5 wt.% and 10 wt.% PS-GMA increases very slowly with time from 30 to 300 s, and then levels off, while that of the blend with 20 wt.% does not change after 30 s. At earlier stages of morphology development (i.e. less than 30 s), a phase separation followed by coarsening and the formation of PBT-g-PS at the interface occur simultaneously. If the amount of PBT-g-PS at the interface were not enough to inhibit the coarsening of the dispersed domain, the domain size would increase steadily until enough of the copolymers had formed by diffusion of PS-GMA in PS phase to the interface. However, as the initial amount of PS-GMA increases, enough of the copolymers are formed at shorter times, and thus the dispersed domain size levels off at shorter times.

#### Morphological development under an oscillatory shear

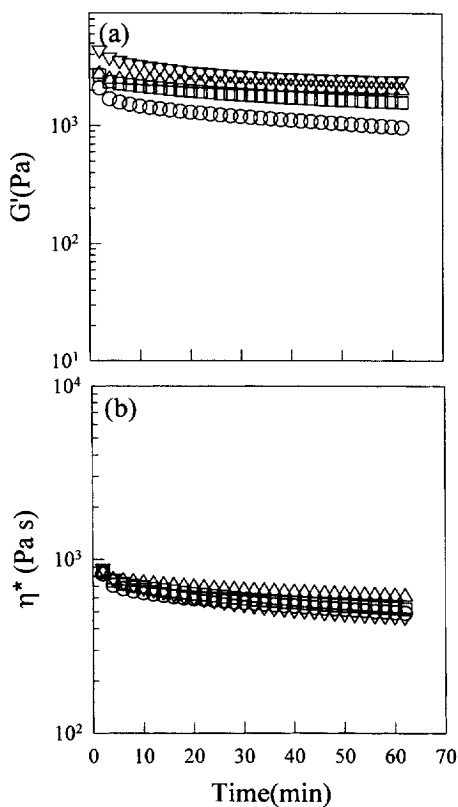
The time evolution of the rheological properties ( $\eta^*$  and  $G'$ ) under an oscillatory shearing for 75/25 wt/wt PBT/PS with various amounts of PS-GMA is given in Figure 5 for



**Figure 5** The time evolution of (a)  $G'$  and (b)  $\eta^*$  at  $\omega = 0.5 \text{ rad s}^{-1}$  and  $245^\circ\text{C}$  for 75/25 PBT/PS blends with various amounts of PS-GMA: (○) 0, (□) 5, (△) 10, and (▽) 20 wt%. First data are shown at 2 min due to sample loading in RDS before the oscillatory shearing measurement



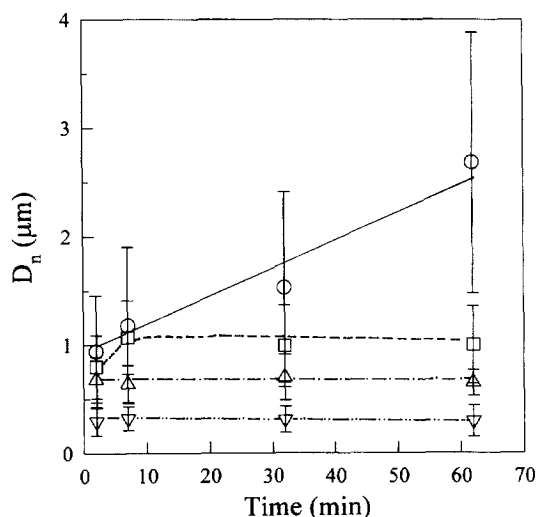
**Figure 6** The time evolution of (a)  $G'$  and (b)  $\eta^*$  at  $\omega = 1.0 \text{ rad s}^{-1}$  and  $245^\circ\text{C}$  for 75/25 PBT/PS blends with various amounts of PS-GMA: (○) 0, (□) 5, (△) 10, and (▽) 20 wt%. First data are shown at 2 min due to sample loading in RDS before the oscillatory shearing measurement



**Figure 7** The time evolution of (a)  $G'$  and (b)  $\eta^*$  at  $\omega = 10 \text{ rad s}^{-1}$  and  $245^\circ\text{C}$  for 75/25 PBT/PS blends with various amounts of PS-GMA: (○) 0, (□) 5, (△) 10, and (▽) 20 wt%. First data are shown at 2 min due to sample loading in RDS before the oscillatory shearing measurement

$\omega = 0.5$ , in Figure 6 for  $\omega = 1.0$ , and in Figure 7 for  $\omega = 10.0 \text{ rad s}^{-1}$ , respectively. One may expect that since the initial morphology appears to be similar,  $\eta^*$  and  $G'$  at the initial state would have the same value regardless of the amounts of PS-GMA. However, since the sample loading time in the RDS-II was at least 2 min, and there was a temperature fluctuation of  $\pm 10^\circ\text{C}$  before steady temperature was reached, sufficient interfacial reactions might occur during that time especially for a blend with a large amount of PS-GMA. Thus, at the beginning of rheological measurement the blend with 20 wt.% of PS-GMA exhibits higher values of  $\eta^*$  and  $G'$  than those for the blend without PS-GMA.

When  $\omega$  is  $0.5 \text{ rad s}^{-1}$ ,  $\eta^*$  at  $t = 2 \text{ min}$  of the blend with 5 wt.% PS-GMA is slightly higher than that of the blend without PS-GMA, but after 10 min there is no difference in  $\eta^*$  between the two blends. However,  $G'$  of the former blend is greater than that of the latter blend at longer times. With increasing oscillatory shearing time, values of  $G'$  of the blends without and with 5 wt.% PS-GMA decrease and then level off, but those of the blends with 10 wt.% and more PS-GMA do not decrease. It is well known that the smaller the dispersed domain size, the larger is  $G'$  for an incompatible or phase-separated polymer blend at the same dispersed volume fraction<sup>39</sup>. This suggests that the dispersed domain size of the blend without PS-GMA will be the largest among all blends investigated in this study, and this will increase with an oscillatory shearing time. These will be corroborated later by comparing the dispersed domain size measured by SEM. The fact that  $G'$  of the blend with 5 wt.% PS-GMA is higher than that for the blend without PS-GMA is explained by the *in situ* formation of PBT-*g*-PS at the interface. However, for the blend with 5 wt.% PS-GMA  $\eta^*$  decreases with oscillatory shearing time, indicating that the dispersed domain size grows slowly with oscillatory shearing time. This is attributed to the fact that, even if some PBT-*g*-PS copolymers were formed at the interface, these are not sufficient to suppress completely the coalescence between dispersed domains. For the blends with 10 and 20 wt.% PS-GMA, sufficient amounts of PBT-*g*-PS copolymers are formed before the rheological properties



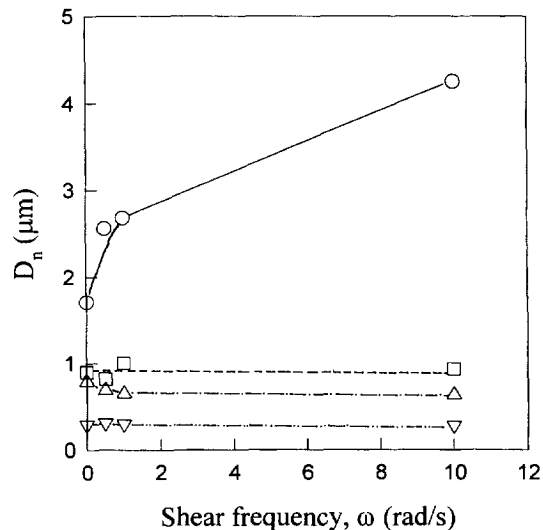
**Figure 8**  $D_n$  versus oscillatory shearing time at  $\omega = 1.0 \text{ rad s}^{-1}$  and  $245^\circ\text{C}$  for 75/25 wt/wt PBT/PS blends with various amounts of PS-GMA: (○) 0, (□) 5, (△) 10, and (▽) 20 wt%.  $D_n$  at 2 min was obtained after sample loading in the rheometer and just before the oscillatory shearing measurement

are first measured (i.e. during the sample loading in RDS), and thus  $G'$  does not change any further with time.

It can also be seen in Figures 5–7 that for a fixed amount of PS-GMA  $\eta^*$  decreases (namely shear thinning behaviour) as  $\omega$  increases from  $0.5 \text{ rad s}^{-1}$  to  $10 \text{ rad s}^{-1}$ . Of course, it is noted that at a fixed  $\omega$ ,  $G'$  increases with increasing amount of PS-GMA since larger amounts of *in situ* graft copolymers are formed near the interface. This shear thinning behaviour appears to be more evident for the blends with larger amounts of PS-GMA. This indicates that the dispersed domains in blends containing the higher amount of PBT-*g*-PS are more easily deformed by a shearing flow.

Figure 8 gives the change in  $D_n$  with oscillatory shearing time at  $\omega = 1 \text{ rad s}^{-1}$  for blends with various amounts of PS-GMA. The value of  $D_n$  for each blend at  $t = 2 \text{ min}$  was measured when the sample was loaded completely in the RDS-II, thus just before starting the oscillatory shearing measurement. This domain size change of each blend with oscillatory shearing time is in agreement with the change of rheological properties given in Figures 5–7.

The effect of shear frequency on  $D_n$  for blends with various amounts of PS-GMA is shown in Figure 9 and the values of  $D_n$  with standard deviations are listed in Table 2. All values of  $D_n$  were obtained after the oscillatory shearing for 1 h. For the blend without PS-GMA,  $D_n$  and its standard deviation become larger as  $\omega$  increases. By varying the viscosity ratio ( $\eta_r$ ) of the dispersed phase to the matrix phase, Ghodgaonikar and Sundararaj<sup>32</sup> reported that  $D_n$  decreases with shear rate for the blends with  $\eta_r \geq 1.0$ . Their results are at variance with the results in Figure 9. This difference can be explained by (i) different flow field and

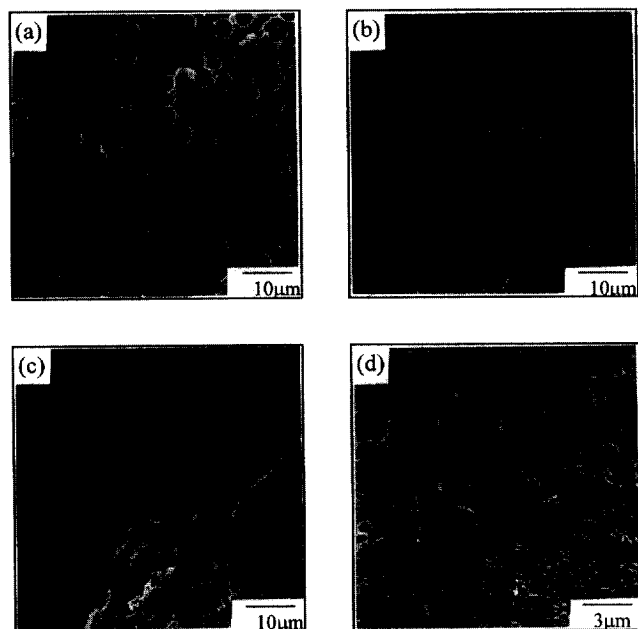


**Figure 9**  $D_n$  versus  $\omega$  for 75-25 wt/wt PBT/PS blends with various amounts of PS-GMA after 1 h of oscillatory shearing at  $245^\circ\text{C}$ : (○) 0, (□) 5, (△) 10, and (▽) 20 wt% of PS-GMA

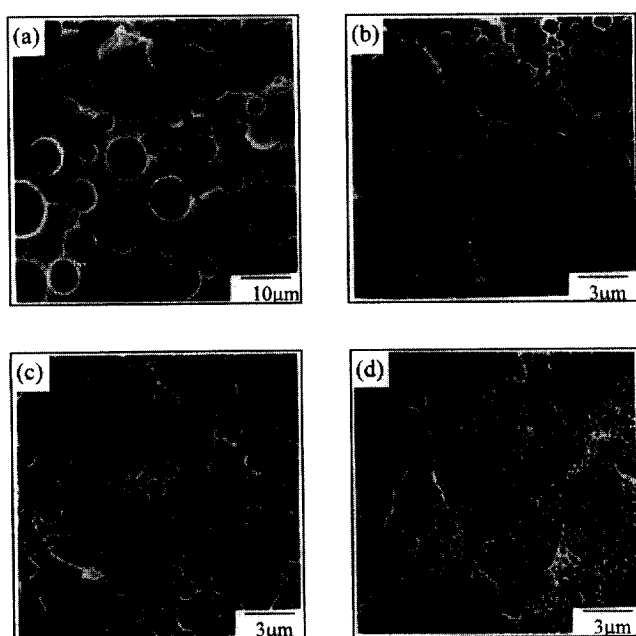
**Table 2** The number average dispersed domain size ( $D_n$ ) with oscillatory shear frequency ( $\omega$ ) at  $245^\circ\text{C}$  for 1 h for 75/25 PBT/PS blends with various amounts of PS-GMA

$\omega$ ( $\text{rad s}^{-1}$ )	$D_n$ ( $\mu\text{m}$ )			
	PS-GMA0	PS-GMA5	PS-GMA10	PS-GMA20
0	$1.71 \pm 1.10$	$0.90 \pm 0.29$	$0.79 \pm 0.22$	$0.29 \pm 0.18$
0.5	$2.56 \pm 1.04$	$0.82 \pm 0.35$	$0.69 \pm 0.23$	$0.31 \pm 0.11$
1.0	$2.68 \pm 1.20$	$1.00 \pm 0.36$	$0.65 \pm 0.12$	$0.30 \pm 0.15$
10.0	$4.25 \pm 2.72$	$0.93 \pm 0.17$	$0.63 \pm 0.17$	$0.28 \pm 0.18$

shear rates, and (ii) different dispersed phase volumes between theirs and our experiment. The blends studied in Ref. 32 were prepared by an internal mixer, in which the flow type and the magnitude of shear rate are not well defined. Although they considered the flow as an shear with shear rate greater than  $40 \text{ s}^{-1}$  the elongational flow effect should also be considered. Also, the weight percent of the dispersed phase for their blend is below 5%, and thus the coalescence effect is not observed even at higher shear rates. We speculate that, if the weight fraction of the dispersed phase for the blend employed in this study were decreased to 5%, we might not observe a shear-induced coalescence. It is



**Figure 10** Scanning electron micrographs for 75/25 wt/wt PBT/PS blends with various amounts of PS-GMA after 1 h of oscillatory shearing at  $\omega = 0.5 \text{ rad s}^{-1}$  and  $245^\circ\text{C}$ : (a) 0, (b) 5, (c) 10, and (d) 20 wt% of PS-GMA



**Figure 11** Scanning electron micrographs for 75/25 wt/wt PBT/PS blends with various amounts of PS-GMA after 1 h of oscillatory shearing at  $\omega = 10 \text{ rad s}^{-1}$  and  $245^\circ\text{C}$ : (a) 0, (b) 5, (c) 10, and (d) 20 wt% of PS-GMA

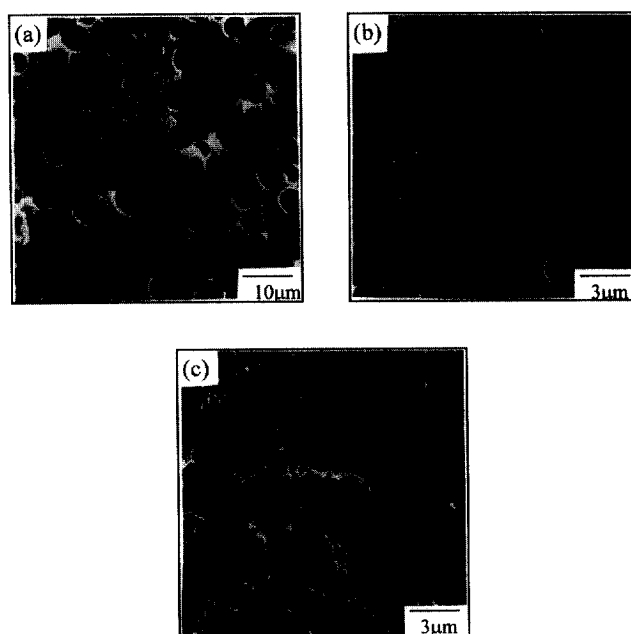
interesting to verify whether or not an oscillatory shearing frequency in the range of  $\omega$  greater than  $10 \text{ rad s}^{-1}$  can decrease the dispersed domain size for a blend with the weight fraction of the dispersed phase smaller than 5%. However, for the blends with PS-GMA, no shear-induced coalescence was observed. Therefore, the PBT-g-PS copolymers located at the interface play a role effectively as a barrier against the shear-induced coalescence of dispersed domains.

Figures 10 and 11 give SEM images of blends with various amounts of PS-GMA after oscillatory shearing at  $\omega$  of 0.5 and  $10 \text{ rad s}^{-1}$  for 1 h, respectively. When  $\omega$  is  $1 \text{ rad s}^{-1}$ , SEM images of blends are very similar to those at  $\omega$  of  $0.5 \text{ rad s}^{-1}$ . At each  $\omega$ ,  $D_n$  decreases with increasing amount of PS-GMA. For the blend with 20 wt% PS-GMA the dispersed domain with irregular shapes persists since more of the PBT-g-PS copolymers is formed at the interface at very short times.

Figure 12 shows SEM images of the blends with 0, 5 and 20 wt% PS-GMA after a steady shear rate ( $\dot{\gamma}$ ) of  $0.5 \text{ s}^{-1}$  was applied for 1290, 1157, and 116 s, respectively. The shearing time is different for each blend since each shearing was stopped before the edge failure occurred. It is very interesting to note from Figures 10, and 12 that, for the blend without PS-GMA after the steady shearing of  $\dot{\gamma} = 0.5 \text{ s}^{-1}$  for 1290 s, the dispersed domain size ( $D_n = 4.05 \pm 1.17 \mu\text{m}$ ) is larger than that ( $D_n = 2.56 \pm 1.04 \mu\text{m}$ ) after the oscillatory shearing at  $0.5 \text{ rad s}^{-1}$  for 1 h. Although this implies that for the blend without PS-GMA a steady shearing induces the coalescence of dispersed domains more strongly than an oscillatory shearing, more investigations both experimental and theoretical sides are needed. However, the blend with PS-GMA does not show the growth of the dispersed domain during the steady shearing time.

## CONCLUSIONS

A controlled initial morphology with finer dispersed domains was prepared by the solution blending method



**Figure 12** Scanning electron micrographs of 75/25 wt/wt PBT/PS blends with various amounts of PS-GMA after the steady shearing at  $\dot{\gamma} = 0.5 \text{ s}^{-1}$  and  $245^\circ\text{C}$ . The amount of PS-GMA in the blend is: (a) 0, (b) 5, and (c) 20 wt%. The shearing times for blends with 0, 5, and 20 wt% of PS-GMA are 1290, 1157, and 116 s, respectively

for 75/25 wt/wt PBT/PS blends regardless of the amount of PS-GMA used as an *in situ* compatibilizer.

For the blend without PS-GMA,  $D_n$  increases with annealing time, and the irregular shape of the dispersed domains becomes spherical within 30 s in order to reduce the interfacial tension.  $D_n$  of the blend without PS-GMA increases with annealing time via a coarsening process, i.e.  $D_n$  is proportional to  $t^{1/3}$ . However, for the blend with PS-GMA,  $D_n$  increases slowly until sufficient amounts of PBT-g-PS copolymers to inhibit effectively the coarsening are formed at the interface, and then  $D_n$  levels off. As the initial amount of PS-GMA in the blend increases, enough of the copolymers for the dispersed domain size in the blend to level off are formed at shorter times.

When an oscillatory shearing is applied to blends with PS-GMA, the time evolution of rheological properties ( $\eta^*$  and  $G'$ ) is affected by blend morphology and the amount of PS-GMA, namely the extent of the reaction between carboxylic acid in PBT and epoxy group in PS-GMA. An increase in the frequency of oscillatory shearing from 0.5 to 10 rad s<sup>-1</sup> can induce the coalescence of dispersed domains of the blend without PS-GMA. However, for the blend with PS-GMA the shear-induced coalescence of the dispersed domain is successfully suppressed by the *in situ* graft copolymers formed at the interface.

#### ACKNOWLEDGEMENTS

This work was supported by the Advanced Material Program (1996) of the Ministry of Education.

#### REFERENCES

- Paul, D. R. and Newman, S., *Polymer Blends*. Vol. 1. Academic Press. New York, 1978.
- Utracki, L. A., *Polymer Alloys and Blends*. Hanser. New York, 1989.
- Ouhadi, T., Fayt, R., Jerome, R. and Teyssie, Ph., *J. Polym. Sci. Polym. Phys. Ed.*, 1986, **24**, 973.
- Plochocki, A. P., Dagli, S. S. and Andrews, R. D., *Polym. Eng. Sci.*, 1990, **30**, 741.
- Brahimi, B., Ait-Kadi, A., Ajjji, A. and Fayt, R., *J. Polym. Sci. Polym. Phys. Ed.*, 1991, **29**, 945.
- Montaudo, G., Duglisi, C., Samperi, F. and Lamentia, F. P., *J. Polym. Sci. Polym. Chem. Ed.*, 1996, **34**, 1283.
- Cigana, P., Favis, B. D. and Jerome, R., *J. Polym. Sci. Polym. Phys. Ed.*, 1996, **34**, 1691.
- Macosko, C. W., Guegan, P., Khandpur, A. K., Nakayama, A., Marechal, P. and Inoue, T., *Macromolecules*, 1996, **29**, 5590.
- Xanthos, M., *Polym. Eng. Sci.*, 1988, **28**, 1329.
- Xanthos, M. and Dagli, S. S., *Polym. Eng. Sci.*, 1991, **31**, 929.
- Liu, N. C. and Baker, W. E., *Adv. Polym. Tech.*, 1992, **11**, 249.
- Ide, F. and Hasegawa, A., *J. Appl. Polym. Sci.*, 1974, **18**, 963.
- Willis, J. M. and Favis, B. D., *Polym. Eng. Sci.*, 1990, **30**, 1073.
- Takeda, Y. and Paul, D. R., *J. Polym. Sci. Polym. Phys. Ed.*, 1992, **30**, 1273.
- Guegan, P., Macosko, C. W., Ishizone, T., Hirao, A. and Nakahama, S., *Macromolecules*, 1994, **27**, 4993.
- Sundararaj, U. and Macosko, C. W., *Macromolecules*, 1995, **28**, 2647.
- Beck Tan, N. C., Tai, S.-K. and Briber, R. M., *Polymer*, 1996, **37**, 3509.
- Shull, K. R. and Kramer, E. J., *Macromolecules*, 1990, **23**, 4769.
- Shull, K. R., Kramer, E. J., Hadziioannou, G. and Tang, W., *Macromolecules*, 1990, **23**, 4780.
- Noolandi, J. and Hong, K. M., *Macromolecules*, 1982, **15**, 482.
- Noolandi, J., *Polym. Eng. Sci.*, 1984, **24**, 70.
- Leibler, L., Orland, H. and Wheeler, J. C., *J. Chem. Phys.*, 1983, **79**, 3550.
- Campbell, J. R., Hobbs, S. Y., Shea, T. J. and Watkins, V. H., *Polym. Eng. Sci.*, 1990, **30**, 1056.
- Jeon, H. K. and Kim, J. K., submitted to *Macromolecules*.
- Taylor, G. I., *Trans. R. Soc. London. Ser. A*, 1932, **138**, 41.
- Taylor, G. I., *Trans. R. Soc. London. Ser. A*, 1934, **146**, 501.
- Scott, C. E. and Macosko, C. W., *Polym. Bull.*, 1991, **26**, 341.
- Sundararaj, U., Macosko, C. W., Rolando, R. J. and Chan, H. T., *Polym. Eng. Sci.*, 1992, **32**, 1814.
- Scott, C. E. and Macosko, C. W., *Polymer*, 1994, **35**, 5422.
- Scott, C. E. and Macosko, C. W., *Polymer*, 1995, **36**, 461.
- Sundararaj, U., Dori, Y. and Macosko, C. W., *Polymer*, 1995, **36**, 1957.
- Ghodgaonkar, P. G. and Sundararaj, U., *Polym. Eng. Sci.*, 1996, **36**, 1656.
- Kim, J. K. and Lee, H., *Polymer*, 1996, **37**, 305.
- Kim, J. K., Kim, S. and Park, C. E., *Polymer*, 1997, **38**, 2155.
- Kim, S., Kim, J. K. and Park, C. E., *Polymer*, 1997, **38**, 1809.
- Kim, S., Kim, J. K. and Park, C. E., *Polymer*, 1997, **38**, 2113.
- Onogi, S., Masuda, T., Toda, N. and Koga, K., *Polym. J.*, 1970, **1**, 542.
- Nakayama, A., Inoue, T., Guegan, P. and Macosko, C. W., *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1993, **34**(2), 840.
- Han, C. D., *Multiphase Flow in Polymer Processing*. Academic Press. New York, 1981.