

Effect of the Composition on the Phase Size in Immiscible Blends with the Viscosity Ratio Close to Unity

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ABSTRACT: The influence of the composition and interfacial tension on the phase size in immiscible polymer blends with a viscosity ratio close to unity has been investigated with poly(methyl methacrylate)/poly(ethylene terephthalate) blends and data from various works. For all the blends considered, the dispersed particle diameter (d) is proportional to the interfacial tension of the system. When the dispersed-phase content (ϕ) is below 1%, there is mini-

mal change of d with increasing ϕ . When ϕ is between 1 and 20%, d is proportional to $\phi^{0.4}$. It seems that the processing conditions do not influence the morphology significantly for blend systems with a viscosity ratio close to unity. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1791–1799, 2003

Key words: blends; tension; dispersion; particle size distribution

INTRODUCTION

Polymer blending has received much attention both in theoretical research and for practical applications because it has been proven to be an efficient way of developing new materials with required properties.^{1,2} Most polymer blends that have commercial value are immiscible. The mechanical properties and the end use of immiscible polymer blends are greatly affected by the morphology, which is usually developed during a melt-blending process carried out with a twin-screw extruder or a batch mixer. The most common case of melt blending is one polymer mechanically dispersed inside another. The drop breakup and coalescence are two competitive processes governing morphology development.^{3,4} The size and shape of the dispersed phase, which are determined during drop breakup and coalescence processes, are controlled by material parameters, such as the interfacial tension, viscosity ratio, composition, and processing conditions.^{5–9}

Many researchers have examined the drop breakup process in polymer blends.^{4,5,7,10,11} Taylor's^{12,13} theory on the deformation and disintegration of a Newtonian fluid is usually applied to polymer blends as a fundamental consideration.^{6,14,15} A relationship was proposed by Taylor to predict the maximum drop size that would be stable in a Newtonian material and under simple shear flow. Under given conditions, drop breakup occurs when the shear forces deforming the droplet are higher than the interfacial forces:

$$d_{\text{Taylor}} = \frac{4\sigma_{12}(\eta_r + 1)}{\dot{\gamma}\eta_m \left[\frac{19}{4}\eta_r + 4 \right]} \quad (1)$$

where d_{Taylor} is the dispersed particle diameter according to Taylor, σ_{12} is the interfacial tension, η_r is the viscosity ratio (η_d/η_m), η_d is the viscosity of the dispersed phase, η_m is the viscosity of the matrix, and $\dot{\gamma}$ is the shear rate.

As Taylor's equation did not provide for the coalescence of the dispersed particle and extension flow in mixing, researchers usually treat d_{Taylor} as the lower limit of the dispersed particle size in polymer blends. Wu,⁷ who studied blends of polyamide or poly(ethylene terephthalate) (PET) with ethylene-propylene elastomers, found that the smallest particles were generated when the viscosities of the components were similar. The influence of σ_{12} and η_r on the dispersed particle diameter (d) can be characterized as follows:

$$d_{\text{Wu}} = \frac{4\sigma_{12}\eta_r^{\pm 0.84}}{\eta_m\dot{\gamma}} \quad (2)$$

where d_{Wu} is the dispersed particle diameter according to Wu. The exponent is positive when η_r is greater than 1, but it is negative when η_r is smaller than 1. Serpe et al.¹⁶ showed that eq. (2) is also valid for polyamide/polyethylene systems if the viscosity of the blend is replaced by η_m . It is evident that the particle diameter of the dispersed phase given by eq. (2) differs from that of eq. (1), although they have the same form for the quantities of the shear stress ($\eta_m\dot{\gamma}$) and σ_{12} .

Nevertheless, drop breakup is not affected by the volume fraction of the dispersed phase (ϕ),¹² and co-

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TABLE I
Basic Properties and Sources of the Polymers Used

Polymer	Supplier	M_n	MFR ^a (g/10 min)	Density at 275°C ^b (g/cm ³)	Viscosities at 243 s ⁻¹ and 275°C (Pa s)	η_r at 243 s ⁻¹ and 275°C ($\eta_{\text{PMMA}}/\eta_{\text{PET}}$)	Calculated σ_{12} at 275°C (mN/m) ^c
PET	Toray Industries, Inc.	20,000		1.22	167		
PMMA	Sumitomo Chemical Co.		5	1.06	211	1.2	1.03

M_n = number-average molecular weight.

^a Melt flow index measured at 230°C according to JIS K7210.

^b Estimated with data from refs. 20 and 21.

^c Estimated with data from ref. 19.

alescence is strongly influenced by the blend composition.^{3,4} The size of the dispersed phase increases and the size distribution broadens significantly at higher ϕ values, and this is usually caused by coalescence of the dispersed phase. By considering that the equilibrium particle size is achieved when the rates of breaking down and coalescence are balanced, Tokita obtained an expression for estimating the diameter of the dispersed particles:¹⁷

$$d_{\text{Tokita}} \cong \frac{24P_r\sigma_{12}}{\pi\eta_m\dot{\gamma}} \left(\phi + \frac{4P_r E_{DK}}{\pi\eta_m\dot{\gamma}} \phi^2 \right) \quad (3)$$

where P_r is the probability that a collision will result in coalescence and E_{DK} is the bulk breaking energy. From this equation, one can also conclude that the particle size of the dispersed phase decreases with increasing shear stress and is proportional to σ_{12} . Favis and Willis⁶ found that a master curve was generated by the correlation of the particle diameter to $\phi + \phi^2$, as described by Tokita's theory for eight different blend systems. However, Favis and Willis noticed that the E_{DK} value obtained was unrealistically high and that the influence of power on the breakdown process was also probably overestimated by eq. (3).

The relationship between the composition and diameter of the dispersed particles is one subject of great interest for understanding how the material parameters and processing conditions will influence blend morphology. On the one hand, it is easy to change the dispersed particle size with alterations to the composition for fulfilling some special requirements; on the other hand, no defined relationship between the dispersed-phase size and the composition for immiscible blends has been reported up to now. In this study, we examined the effect of the composition on the dispersed-phase size in a poly(methyl methacrylate) (PMMA)/PET blend system. To simplify the question, we selected a blend system with η_r close to unity for investigation. By combining literature data, we found a simple equation to predict the dispersed-phase diameter with the composition and σ_{12} .

EXPERIMENTAL

Materials and their characterization

For this study, PET and PMMA were used as the matrix and dispersed phase, respectively. They were chosen because of their similar viscosities at the processing shear rate. Some of their basic properties and suppliers are summarized in Table I. The matrix was coded PET, and the dispersed phase was coded PMMA. The blend system is denoted *dispersed phase/matrix* throughout this article.

The rheological analysis was performed with a Capirograph 1B capillary rheometer made by Toyoseike Co. (Aichi, Japan). The capillary diameter was 1 mm, and the length/diameter ratio was 10. The measurement was carried out at a processing temperature of 275°C. The shear viscosity and η_r values of PET and PMMA at 243 s⁻¹ are given in Table I.

σ_{12} between two polymers was not measured directly but calculated with a harmonic mean relationship:¹⁸

$$\sigma_{12} = \gamma_1 + \gamma_2 - 4 \frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - 4 \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad (4)$$

where γ_i is the surface tension of polymer i ($\gamma_i^d + \gamma_i^p$), γ_i^d is the nonpolar fraction of γ_i [$(1 - x^p)\gamma_i$], γ_i^p is the polar fraction of γ_i ($x^p \times \gamma_i$), and x^p is the polarity of polymer i .

Table I gives the calculated σ_{12} values between PET and PMMA at 275°C from eq. (4) and from literature data of the surface tensions and polarities of PET and PMMA.¹⁹ For the conversion of weight fractions into volume fractions, the densities of the two polymers at the processing temperature were calculated by their corresponding coefficients of volume expansion and densities at 25°C,^{20,21} which are also listed in Table I.

Blending

All materials were vacuum-dried for more than 12 h before the blending for the removal of any volatiles. The drying temperature was 150°C for PET and 90°C

for PMMA. The blending of PET with PMMA was carried out with a model MP-2015 twin-screw extruder manufactured by Tsubaco Yokohama Hanbai, Ltd. (Yokohama, Japan). The screw speed was 150 rpm, and the temperature was 275°C. The dry component pellets were fed into the extruder through a feeder blanketed with dry nitrogen for the prevention of moisture absorption. A two-step blending method was taken to ensure good dispersion of the dispersed phase. First, the master blend containing 10% PMMA and 90% PET (by weight) was prepared. Then, blends with the concentrations of the dispersed phase varying from 0.1 to 5% (by weight) were prepared by the mixing of the neat PET and the master blend. The master blend was also repelletized. Two types of blend samples were collected. One was called the TD sample, which was taken from the die immediately after the extrudate came out of the die and was quenched in air. The other was called the P sample, which was collected after it was stretched through a cool-water trough and pelletized. Therefore, the P sample underwent stretching after coming out of the die, whereas the TD sample did not. Moreover, the P sample was cooled faster than the TD sample.

Sample preparation and morphology analysis

The morphology of the blend was observed with scanning electron microscopy (SEM) with an ultrathin microtome section of the extrudate. The section was obtained by either parallel or perpendicular cutting to the extrudate axis. The section thickness was 12 μm . Selective extraction of either the dispersed phase or matrix did not change the morphology, but it made the dispersed-phase domain clearer.^{22,23} Because PMMA can easily be dissolved with many common solvents, we could not find a solvent to selectively dissolve PET and leave PMMA alone. Therefore, after the microtoming, only the dispersed phase was removed from the sample with xylene. Before the SEM examination, all surfaces were coated with platinum/palladium and viewed with a Hitachi S-800 scanning electron microscope.

We used software (Scion Image Beta 3b acquisition and analysis software) produced by Scion Corp. (Frederick, MA) to perform image analysis on SEM micrographs. Usually, image analysis consists of image processing, measurement, data analysis, and output. Because the primary mode of our image analysis was gray-level thresholding, simple high-contrast images were most appropriate for image analysis. For the SEM micrographs, the contrast between the matrix and the dispersed phase was large enough to be analyzed directly by the software. An HP Scanjet 4S (Houston, TX) with a resolution of 200 pixels per inch was used to digitize the portrait. Digitized images were saved as TIFF files that were imported into the

Scion Image program for further analysis. Thresholding was used to segment an image into objects of interest and background on the basis of the gray level. When thresholding was enabled, objects were displayed in black, and the background was white. Measurements were then carried out on the binary images. About 200–600 particles from at least four different views were measured for 0.5–10% samples. For 0.1% samples, about 50–100 particles from 10 different views were measured.

RESULTS AND DISCUSSION

Morphology of the PMMA/PET blend

For all micrographs of this blend system, the general morphology of the blend is that of discontinuous PMMA spheres or near spheres in a continuous PET matrix with clear borders, regardless of the sectioning direction or sample type. Typical morphologies of the blends after the dispersed phase is removed are shown in Figure 1. With the extraction method described earlier, the PMMA phase on the surface can be removed completely from the blends. This observation confirms that the PMMA/PET blend system is immiscible.

Two types of samples were prepared in this study: TD and P samples. The P sample endured stretching, whereas the TD sample did not, after extrusion. Stell et al.²⁴ proposed an empirical method for the quantitative description of the stretch during the extruding process. They defined the hot stretch ratio (R_{hs}) as follows:

$$R_{hs} = (V_t - V_d) / V_d \quad (5)$$

where V_t is the velocity of take-up (m/min) and V_d is the average polymer velocity in the die, which can be computed by the mass-flow rate of the polymer and the area of the die. R_{hs} for the P sample is about 0.44 for the investigated compositions. The shapes of the dispersed phases in both samples are almost the same (Fig. 1). The extent of deformation can be characterized by the aspect ratio, which is the length (major axis of ellipse) to width (minor axis of ellipse) ratio of the PMMA particles. The aspect ratio is 1–1.5 for both samples at different compositions and from different sectioning directions. This suggests that at small R_{hs} values (e.g., <0.5), the stretch force exerting on the blend extrudate after it comes out of the die is not large enough to cause significant changes in the shape of the dispersed particle. Therefore, the shapes of dispersed-phase particles for both samples can be considered spheres.

For image analysis, the area of each particle was measured, and the particle diameters were determined under the assumption that all the particle im-

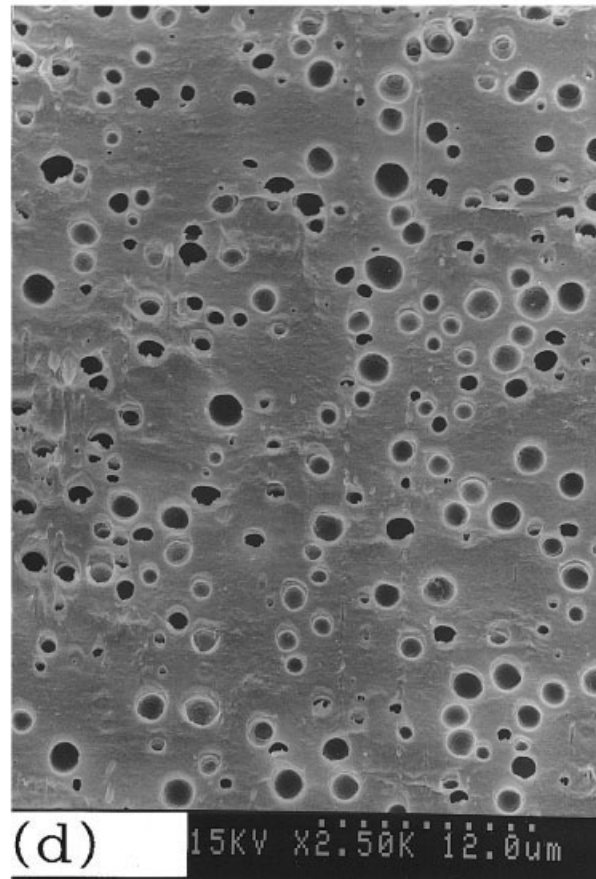
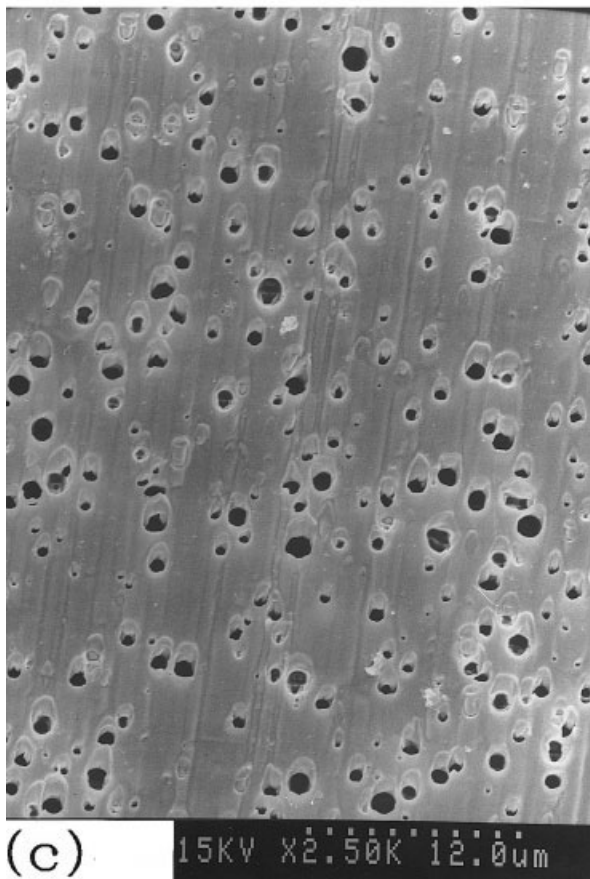
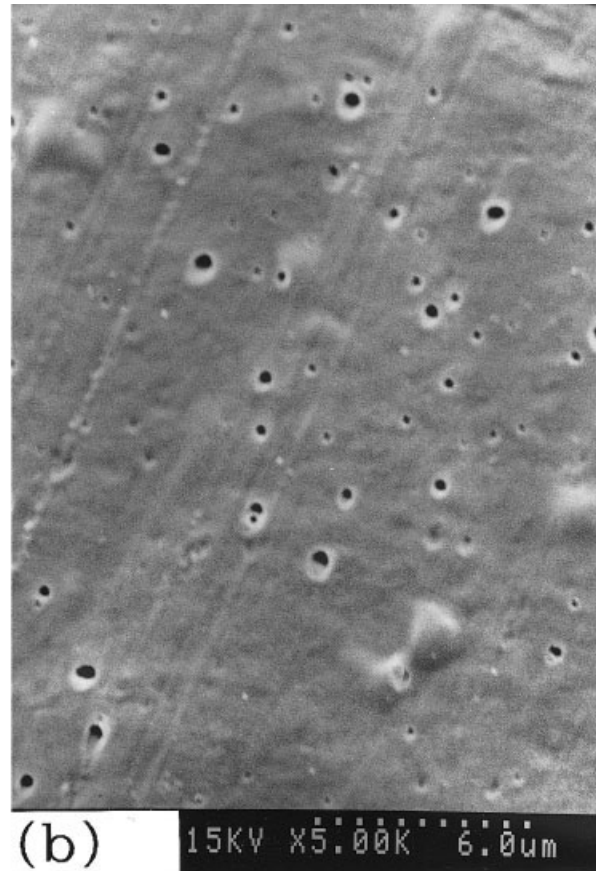
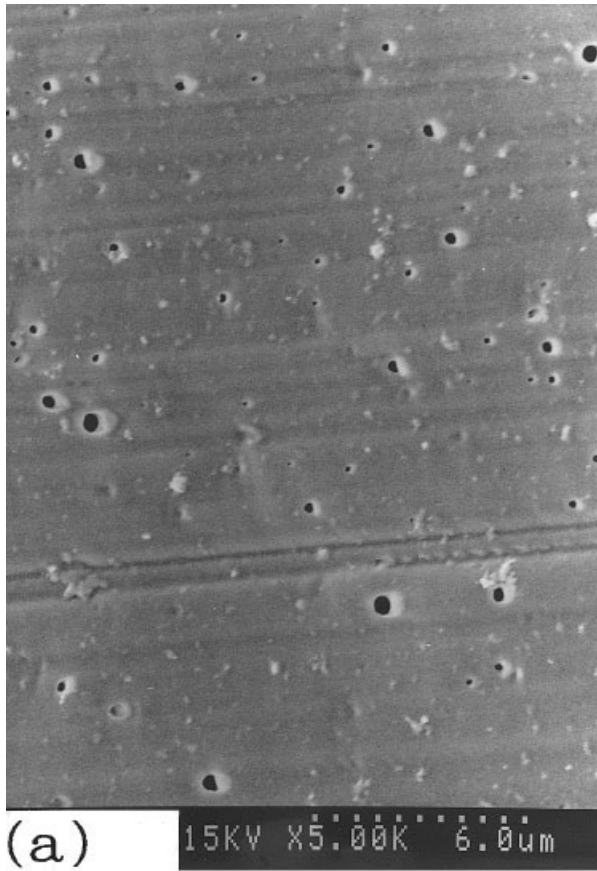


Figure 1 SEM micrographs of the microtome surfaces of PET phases after PMMA extraction in PMMA/PET blends: (a) 1 wt % P sample, (b) 1 wt % TD sample, (c) 10 wt % P sample, and (d) 10 wt % TD sample.

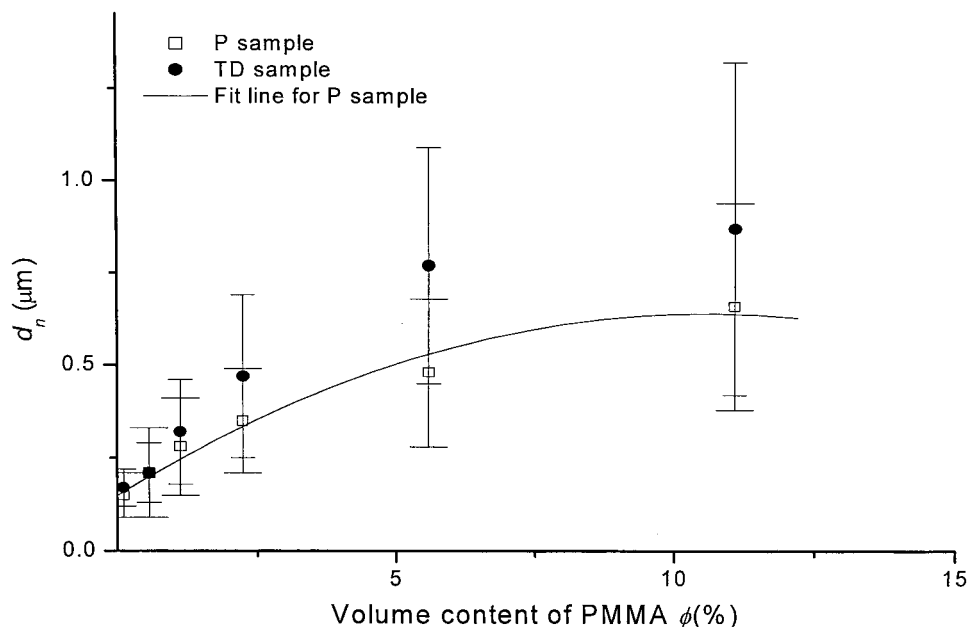


Figure 2 d_n values of the PMMA phase in the PET matrix versus ϕ for P and TD samples. The error bars are standard deviation used for representing the particle size distribution. The real line is the best second polynomial fit for the P sample. The diameters of 0.56 vol % are the same for the two types of samples.

ages were circles. The spherical particles were three-dimensional and could be sectioned at any point. Various solutions to the problem of the determination of the size and size distribution of spherical particles from measurements made on random plane sections have appeared in the literature.²⁵ However, in many cases, the solutions have an unrealistic particle model or a mathematically complex one.²⁶ However, some research work has shown that the corrected values do not differ greatly from the raw data on the average particle size.³ If we consider that the measured particle size may be a compromise between overestimation, as the very small ones may be omitted, and underestimation, because of the section not passing the center of the particles, it is reasonable to some extent for us to directly use the raw data from image analysis in further analysis. Throughout this article, the number-average diameter (d_n) is chosen to represent the dispersed-phase size. Other averages may alternatively be used without the qualitative feature of the analysis being changed.

The relationship between the concentration and size of the dispersed phase is given in Figure 2 for both samples. The standard deviation is shown as error bars for each point in Figure 2 to characterize the broadness of the size distribution. For both samples, with a greater than 1% dispersed phase, the particle size and broadness of the size distribution increase significantly with an increasing content of the dispersed phase, and this can be explained by the fact that pronounced coalescence happens at higher ϕ values. Another interesting point we observed is that the

size and size distribution of the dispersed phase in the TD sample are larger than those in the P sample at high ϕ values. This may be due to the different degrees of coalescence they underwent. According to the sample preparation method described previously, the TD sample has a slow cooling rate and may stay longer in the melt state. Therefore, the dispersed particle in the TD sample may have more time to coalesce. However, at low ϕ values (<1%), P and TD samples have dispersed phases with similar sizes and size distributions (Fig. 1). This suggests that a blend with a very low content of the dispersed phase may have a stable morphology for a longer time period. Because the TD sample has endured some changes after coming out of the die, we use the size and size distribution of the P sample as the dispersed-phase morphology parameters for further analysis.

An estimation of the particle size by Taylor's relationship was performed. As shown in eq. (1), d_{Taylor} was calculated with σ_{12} , η_r , and the shear stress applied to the blend system during extrusion. It is usually thought that γ varies in the range of 100–1000 s^{-1} during extrusion. Because it was difficult to determine the exact γ values for the applied processing conditions, we crudely selected the γ value of 243 s^{-1} for further consideration after considering the screw rate. Under this condition, η_r of the dispersed phase PMMA to the matrix PET is about 1.2. The d_{Taylor} value is 0.02 μm for this PMMA/PET blend, which is far below the measured diameter of 0.15 μm at a very low content of 0.1%. It may be impossible for the coalescence to occur at such a low content. Therefore, the

great difference between the calculated d_{Taylor} value and the measured value may be caused by the viscoelastic properties of the polymer, which are not considered in Taylor's original theory.

Using eq. (2), we obtained the d_{Wu} value of $0.12 \mu\text{m}$, which is comparable to the experimental lower limit ($0.15 \mu\text{m}$). However, Wu's expression was obtained from a blend system with a 15% concentration of the dispersed phase. For this system, the dispersed particle size of the blend with around 10% PMMA is $0.65 \mu\text{m}$, about 5 times greater than that predicted by Wu's equation. It seems clear to us that although Wu's equation gives a qualitative understanding of the effect of η_r on the particle size of the dispersed phase for the polymer blend system, further development is needed.

We also carried out the nonlinear fitting of the data points with the P sample by correlating them with a second-order polynomial equation (the solid line in Fig. 2). Although the data fit into a second-order polynomial equation, the coefficient to ϕ^2 is negative. The negative coefficient in Tokita's equation is unreasonable.¹⁷ Therefore, Tokita's equation cannot be applied to our measurements.

From this discussion, we have concluded that no appropriate theory can predict these results well. This may be due to the different blend systems used for the study, the difficulty in understanding coalescence, the uncertainty of the effective shear rate in extrusion or mixing, and the complexity of the viscoelasticity of the polymers used. From a practical view on the subject, it is of great interest to be able to predict the dispersed particle size on the basis of the dispersed-phase concentration. To simplify the question, we confine our study to the blend system with η_r close to unity to examine the effect of the composition on d .

Blend system with η_r close to unity

The blend system with η_r close to unity is thought by some researchers to be able to get the finest dispersion.^{7,8,17} To make a comparison with other researchers' results on the same problem, we have collected results of the dispersed-phase diameter versus the concentration of the dispersed phase from the literature on blend systems with η_r about unity. Table II gives source materials and processing temperatures as well as the mixing equipment used for collecting the data. These blend systems were prepared over a large temperature range and with different mixing equipment. Detailed processing results and the predictions of d are listed in Table III. The predicted dispersed-phase diameters obtained from Taylor's relation are always far less than the measured data (Table III). It is also unsatisfactory to use Wu's experimental relationship to estimate the diameter of the dispersed phase if the concentration (15%) originally used by Wu⁷ for

TABLE II
Sources of Materials and Processing Conditions Used by Several Authors for Studying the Blend System with a η_r Close to Unity

Researchers	Blend system	Material	Mixing temperature (°C)	Mixing equipment	Reference
This study	PMMA/PET	PMMA: from Sumitomo Chemical Co. PET: from Toray Industries, Inc.	275	MP-2015 twin-screw extruder manufactured by Tsubaco Yokohama Hanbai, Ltd	3
Sundararaj and Mocosko	PP/PS	PP: PP3050 from Elf Atochem PS: PS6666D from Dow Chemical	200	Haake system 90 torque rheometer with a series 600 batch mixer and roller blades	3
Wu	PS/PP	PS: PS6666D from Dow Chemical PP: PP3050 from Elf Atochem	200	Haake system 90 torque rheometer with a series 600 batch mixer and roller blades	7
Wallheinke	EPR/PET	EPR: not referred PET: not referred	325	Corotating intermeshing twin-screw extruder ZSK28D (Werner and Pfleiderer)	15
Favis and Willis	PE/TPU	PE: Lupolen 4261A from BASF AG TPU: Elastollan C64D from Elastogran GmbH	230	Corotating intermeshing twin-screw extruder ZSK30 (Werner and Pfleiderer)	6
	PA/PP	PA: Zytel 211 from Dupont PP: ProFax 6501 from Himont	250	Brabender mixing chamber	

PP = polypropylene; PS = polystyrene; EPR = ethylene-propylene rubber; PE = polyethylene; TPU = thermoplastic polyurethane; PA = polyamide.

TABLE III
Experiments of Several Authors for Studying the Blend System with a η_r Close to Unity

Blend system	η_m at process condition (Pa s)	η_r at process condition	γ used for calculation (s^{-1})	σ_{12} (mN/m)	d_{Taylor} (μm)	d_{Wu} (μm)	Minimum d_n measured (μm)
PMMA/PET	167	1.2	243	1.03	0.02	0.12	0.15
PP/PS	950	0.9	65	5.0	0.08	0.35	0.35
PS/PP	840	1.1	65	5.0	0.09	0.40	0.39
EPR/PET	~ 150	1.2	100	5.7	0.34	1.8	—
PE/TPU	791	1.6	200	9.4	0.05	0.36	0.77
PA/PP	320	1.0 ^a	100	13.5	0.39	1.7	—

^a Torque ratio.

^b The abbreviations for polymers are the same as in Table II.

investigating is considered (d_{Wu} in column 7 of Table III and d_n at 15% in Fig. 3). Furthermore, we found that the minimum particle diameter increases with an increase in σ_{12} . The minimum particle diameters listed in Table III are obtained at a concentration of about 0.1%, at which point it is assumed that no coalescence occurs. Because every system has almost the same value of η_r , it seems that the minimum particle diameter is influenced by σ_{12} to a large degree.

The data from the literature and this study are plotted in Figure 3. It should be noted that the concentration of the dispersed phase used in some research is not the volume ratio. However, the differences in the densities of the different polymers are not large, and directly treating the weight fraction as the volume concentration may not cause great error. Therefore, we take the weight fraction as the volume concentration directly if no volume concentration is available in the literature. All the blend systems show almost the same behavior in Figure 3. At a lower concentration of the

dispersed phase, there is a minimum change in the particle diameter with an increasing concentration of the dispersed phase. When the concentration of the dispersed phase is greater than 1%, the particle diameter increases quickly with the concentration of the dispersed phase. Another point is that the particle diameter of the dispersed phase at a high concentration of the dispersed phase also shows a positive dependence on σ_{12} . This reminds us that there may be a clearer relationship between the diameter and the composition if we filter the interfacial tension effect.

By plotting d/σ_{12} versus ϕ , we obtained Figure 4. Unexpectedly, all the collected data points from the literature almost fall on one curve. The new generated curve for the collected data shows a two-stage behavior. At a concentration of the dispersed phase below 1%, the connecting line of the data is almost parallel to the abscissa. This suggests that the diameter of the dispersed phase at a very low concentration, which is usually taken as the lower limit size of the dispersed

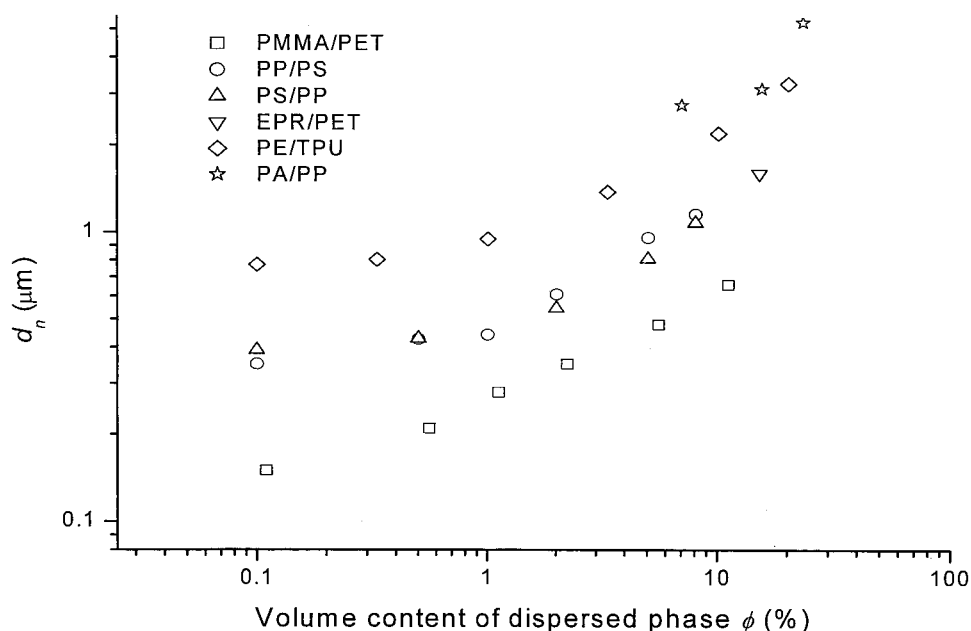


Figure 3 d_n values of the dispersed particles versus ϕ for several blend systems with η_r values close to unity. These were obtained from different authors' works, including this study. Numbers in parentheses indicate σ_{12} (mN/m).

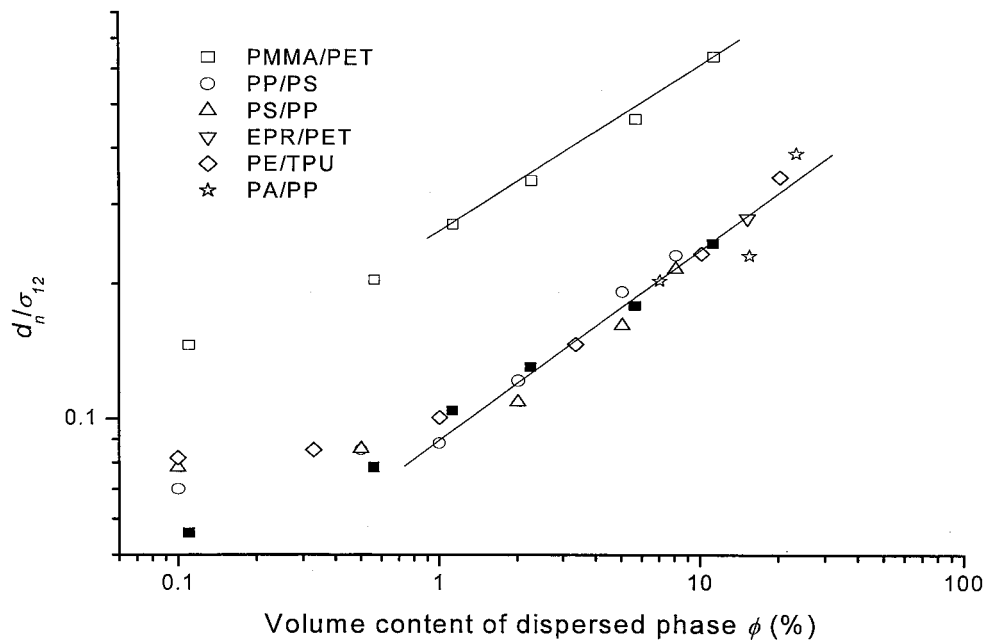


Figure 4 Plots of d_n/σ_{12} versus ϕ for the data sets given in Figure 3.

phase, is proportional to σ_{12} and does not change significantly with an increasing concentration of the dispersed phase. This may be due to the fact that there is no coalescence and that the main process is the dispersed drop breakup, which is a balance of the interfacial force and the shear force applied to the blend system and is not affected by the composition. When the concentration of the dispersed phase goes above 1%, all the collected data fall into a straight line. With the least-square method, the best fit line is found with a slope of 0.4, and this means that the diameter of the dispersed phase is proportional to $\phi^{0.4}$ for η_r around unity. The data set of this study does not fall into the collected data set curve. However, the data obtained from the PMMA/PET blend are parallel to the collected data. With the same fitting method used for collecting the data, the slope for the system with concentrations above 1% of the PMMA/PET blend is also about 0.4, the same as that for the data from the literature. Therefore, we suppose that σ_{12} between PMMA and PET used in this study may not be estimated correctly. Two factors may account for the deviation of estimating σ_{12} : the commercial PET and PMMA used in this study might have contained processing agents, and there was a molecular weight difference between the literature data used for calculation and the materials investigated.

From Table III, we know that γ varies over a large range for the collected data and the PMMA/PET blend system. It seems that there is no significant effect of the shear force on the final d value for the system with η_r around unity. Favis⁵ reported that making the mixing shear rate up to four times larger

and increasing the mixing time had no significant effect on the particle size of the dispersed phase. According to the previous work, we can at least confirm that for the blend system with η_r around unity, it is easy for the dispersed phase to disperse inside the matrix. This means that the energy required to reach the dispersion equilibrium is relatively small. Further study is needed on the viscoelasticity of the components in the blend to explain the fact that the size of the dispersed phase at an equilibrium dispersion depends on the composition and σ_{12} at the power of 0.4.

In conclusion, we have the following experimental expression for the blend system with η_r close to unity:

$$d|_{\eta_r=1} = \begin{cases} K_1\sigma_{12}\phi^{0.4} (1\% < \phi < 20\%) \\ K_2\sigma_{12} (0 < \phi < 1\%) \end{cases} \quad (6)$$

where K_1 and K_2 are constants independent of σ_{12} and the composition. Using eq. (6), one can determine the dispersed particle size over a wide composition range (0–20%) if σ_{12} is known. In this study, the dispersed-phase diameter proportional to σ_{12} is proven by the experimental data for the blend system with η_r close to unity. However, the theoretical explanation for this numerical analysis should be explored further. It seems that K_1 and K_2 may be independent of processing conditions over a wide range of γ values (Table II). This means that the dispersed particle size and nearest neighbor distance may be independent of the processing conditions for systems investigated in this study. This may be due to the ease of dispersion for the system with η_r close to unity. However, a further examination should be carried out because there may

exist lower and upper limits of shear stress between which eq. (6) is tenable.

CONCLUSIONS

For a PMMA/PET blend system with η_r close to unity, the effect of the composition on the dispersed particle size has been investigated. The results from different series of blend samples show the cooling rate effect on the composition–size relationship. Coalescence does not occur at very low concentrations of the dispersed phase PMMA at slow cooling rates, but it does happen at higher concentrations of PMMA. Small R_{hs} values do not cause significant changes in the dispersed particle size.

Looking at the literature data on blend systems with η_r close to unity, we found that the dispersed-phase size has no obvious change with increasing composition when the concentration of the dispersed phase is below 1%. When the composition of the dispersed phase is larger than 1% and up to about 20%, the dispersed particle size is proportional to $\phi^{0.4}$ and σ_{12} of the system. Although further experiments and theoretical studies are needed, these results can be used as a rough approach to predict the dispersed particle size in a blend system with η_r close to unity.

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