THE EFFECT OF SCALE-UP ON THE PROCESSING BEHAVIOR OF A BLEND EXHIBITING PHASE INVERSION DURING COMPOUNDING

Ram Ratnagiri[1], Chi-Kai Shih[2] and Chris E. Scott[1]
[1]Department of Materials Science and Engineering
Massachusetts Institute of Technology, Cambridge, MA 02139.
[2]Dupont, Central Research and Development
Wilmington, Delaware 19880.

Abstract

Phase inversion during compounding of low-viscosity ratio polystyrene/polyethylene blends was studied in two different batch mixers. Using a constant maximum-shear-rate as the scale-up criterion, longer mixing times were required in the large mixer due to its lower specific area. A new triangular element blade design was used to obtain different batch sizes in the same mixer. On scale-up with these blades, a constant specific area was maintained and equal mixing times to phase inversion were observed.

Introduction

A variety of blends involve the addition of a small amount of a low-viscosity component into a higher viscosity matrix. In the compounding of such blends, it has been observed that the minor component forms the continuous phase at short mixing times. On further compounding the major component pellets soften, deform and coalesce to form the continuous phase. This transformation in morphology as a function of mixing time has been termed phase inversion during compounding. The mixing time required to disperse the minor component was shown to increase with decreasing viscosity ratios and decreasing mixer operating temperatures (1). This work compares the time to achieve this transformation in morphology in two different batch mixers for a polystyrene/polyethylene (major/minor) blend.

For a newly formulated blend, initial compounding is carried out in laboratory scale batch mixers and the process parameters are optimized to achieve the required dispersion of the minor component. Scale-up to larger mixers and extruders is then attempted to bring the blend into production. The scale-up rules specify the rotor speed, temperature, mixing time in the large mixer to achieve the same degree of mixing as with the small mixer. Geometrical similarity is ensured by scaling all the dimensions by the same ratio.

A summary of existing scale-up rules for batch mixers is given in (2). For the mixing of solid additives into rubbers, the most common scale-up rules are based on shear strain or the specific work input (3). Both these criteria do not specify a maximum shear stress to be attained while compounding and could fail to produce the required dispersion of the additive. Zloczower et. al. have proposed a scale-up criterion to achieve the same degree of dispersion of carbon black in rubber, using a theoretical model for the breakup of agglomerates at a certain shear stress (4,5).

At present, there are no scale-up criteria for the compounding of blends with a low-viscosity additive. On scale-up to a large mixer, the area to volume ratio decreases and this reduces the heat transfer by conduction to the batch. The presence of a low-viscosity melt reduces viscous dissipation and heat conduction is expected to play an important role in determining the mixing time to disperse the low-viscosity component.

Experiments

Polystyrene from BASF with a melt viscosity of 716 Pa.s at 180°C and $100s^{-1}$, was chosen as the major component. A series of polyethylenes from Eastman Chemical Company with lower melt viscosities were used as the minor component in the blends. The relevant properties of the blend components are compiled in Table 1. For this system, during compounding at a constant mixer set temperature in a batch mixer, an initial continuous phase of polyethylene was formed. After further mixing the dispersed polystyrene pellets softened, deformed and coalesced to form the continuous phase. This transformation was accompanied by a rise in the torque input to deform the higher viscosity polystyrene.

In a typical compounding run, a mixture of dried pellets of the two components in the correct proportions was hand mixed in a tray. This was then added to the batch mixer preheated to the set temperature. The torque trace and melt temperature were recorded as a function of mixing time. The dimensions of the two batch mixers used here are given in Table 2. Roller blades were used in both the mixers. The large mixer had an available mixing volume of 350 cm^3, while the small mixer had an available volume of 69 cm^3. The batch sizes were chosen so that there was good intermixing between the two halves of the mixing bowl. Batch sizes of 49g in the small mixer and 240g in the large mixer were used. These correspond to a 70% degree of fill based on the total mixer volume available.

Pellets of polystyrene were cylinders of 2.5mm diameter and 3mm height. Polyethylene pellets were spherical with an average diameter of 2.5mm. These dimensions are larger than the minimum gap between the blades and the mixer wall in both the mixers. Initial compounding runs were done in the small mixer at a rotor speed of 50 rpm. To achieve the same maximum shear rate in the large mixer, the drive shaft was run at 42 rpm. The maximum shear rate was calculated assuming pure drag flow at the minimum gap between the blades and the mixer wall.

The melt viscosities of the components were measured using an ARES mechanical spectrometer from Rheometrics, using compression molded disks in a parallel plate fixture. Small strain dynamic shear viscosity was measured and the Cox-Merz rule was used to obtain the viscosity as a function of shear rate. For the PS/PE-D blend the effect of concentration of PE and the mixer set temperature were also studied. In each case, similar compounding runs were performed in both the mixers and the times to phase inversion were compared.

A novel blade design with triangular elements was used to obtain different batch sizes in the small mixer. A schematic of one such design with six elements on each shaft is shown in Figure 1. By choosing different numbers of elements on each shaft, the available mixer volume could be changed from $8cm^3$ to $64cm^3$. The triangular elements were machined to give the same minimum gap with the mixing bowl as the small roller blades. The batch sizes and geometrical quantities with the triangular blades are summarized in Table 3.

Results

Using the dimensions of the two sets of roller blades and mixing bowls, different geometrical parameters of interest were calculated and these are summarized in Table 2. The minimum gap in the large mixer was 1.5mm compared with 1mm in the small mixer. The mixing blades are not directly heated but they provide additional area for the conduction of heat to or from the batch. For this reason, both the area of the mixing bowl and the area of the blades in contact with the batch were measured. On scale-up to a large mixer the specific area defined as the ratio of area to the volume, decreases. For the two mixers used here, the specific area decreased from $1.2cm^{-1}$ to $0.7cm^{-1}$. On including the area of the blades this value changes from $2.6cm^{-1}$ in the small mixer to $1.6cm^{-1}$ in the large mixer.

The torque traces at constant drive shaft speed for the compounding runs of different PS/PE blends at 180^oC are shown in Figure 2. The torque recorded by the mixer has been normalized by mass of the batch. Each blending run showed a low torque region when polyethylene was continuous and a second torque peak associated with phase inversion to a polystyrene continuous phase. The mixing time at which the second torque peak was observed was labeled “time to phase inversion”. Given the complex nature of morphological transformations accompanying phase inversion, this provides a simple means to identify similar times in the processing history of the blends in the two mixers. As mentioned earlier, it is seen that lowering the viscosity ratio increases the time to phase inversion in both the mixers. For a given blend, longer mixing times are required to achieve phase inversion in the large mixer. For the PS/PE-D blend phase inversion occurred at 14.5min in the large mixer and at 8min in the small mixer.

Five different concentrations of PE-D (0.5, 1, 2, 4, and 7.8wt.%) were compounded with PS and the times to phase inversion were compared in the two mixers. At very low concentrations it is unlikely that PE forms all of the continuous phase. But the torque traces showed a low torque region following the completion of feeding indicating that the presence of a low-viscosity melt has a lubricating effect on the blend. This minimizes the exposure of polystyrene pellets to the high shear regions and delays their deformation and the consequent torque rise, to longer mixing times. In addition, compounding runs at 160, 180 and 200^{o}C were carried out in both the mixers for the PS/PE-D blend. The observed times to phase inversion under different process conditions are compared in Table 4.

The triangular blade design enabled us to study different batch sizes in the same mixer. Three different batch sizes corresponding to 2, 4 and 6 elements on each shaft were studied. The use of identical elements ensured that in addition to geometrical similarity, the specific area (area/volume) remained constant on scale-up. The times to phase inversion and the specific work input until phase inversion for the compounding of PS/PE-D (92.2 / 7.8) blend at 200^{o}C and 50 r.p.m are shown in Figure 3.

Discussion

During mixing in a batch mixer work input through the shafts and heat conduction from the walls of the mixer are the two modes of energy input into the batch. A global energy balance for the batch can be written as (1):

$$\rho C_p \frac{dT}{dt} = \frac{\Gamma \cdot \omega}{V} + h\left(\frac{A}{V}\right)\left(T - T_{wall}\right) \qquad (1)$$

where ρ is the density, V is the volume, C_p is the average specific heat, T is the melt temperature, Γ is the torque, ω is the drive shaft speed and h is an average heat transfer coefficient. The formation of an initial low-viscosity melt of polyethylene reduces viscous heating and heat conduction from the walls is expected to dominate in the low torque regions of Figure 2. The large mixer has a lower specific area and this should delay the heating of the dispersed polystyrene pellets, thus delaying phase inversion. From Table 4, the ratios of time to phase inversion are seen to vary between 1.8 and 2.9. These values are greater than the inverse ratio of specific areas of 1.7.

Specific work input was calculated by integrating the torque trace until the second peak. Compounding in the large mixer required greater specific work input to achieve phase inversion. But the increase was smaller than the increase in the time to phase inversion, and the average rate of work input (last column of Table 4) was lower in the large mixer. This could explain the longer than expected times to phase inversion in the large mixer.

On scale-up using the triangular elements, the time to phase inversion was found to vary by less than a minute for the compounding runs shown in Figure 3, with PS/PE-D at 200^{o}C. For this design the specific area remains constant during scale-up. Therefore, this design showed a very strong correlation of the time to phase inversion with the specific area of the mixer. The variation in the specific work input until phase inversion was lowest at the highest concentrations of the PE-D studied here (Figure 3b).

Conclusions

The effect of scale on the time to phase inversion during compounding of a low-viscosity ratio polystyrene/polyethylene blend was studied in two different mixers. Using a constant maximum-strain- rate as the scale-up criterion, longer mixing times were required in the large mixer to achieve a continuous polystyrene phase. The ratio of mixing times was found to be greater than the inverse ratio of specific areas. A new blade design with triangular elements that maintained a constant specific area on scale-up was also used and a constant time to phase inversion on scale-up was observed. Variation in the specific work input until phase inversion was smaller at the largest concentrations of the low-viscosity component studied.

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Table 1: Properties of blend components used in this study

Material	Commercial Designation	Viscosity (180^oC, $100s^{-1}$) Pa-s	Viscosity Ratio (180^oC, $100s^{-1}$)	Transition Temperature (^oC)
PS	BASF 1424	716	-	100 (T_g)
PE-C	Epolene C-13	41	0.05	89 (T_m)
PE-D	Epolene C-10	3.3	0.005	104 (T_m)
PE-E	Epolene C-15	1.9	0.003	101 (T_m)

Table 2: Comparison of the two batch mixers used to study scale-up effects on the processing of polystyrene/polyethylene blends with roller blades

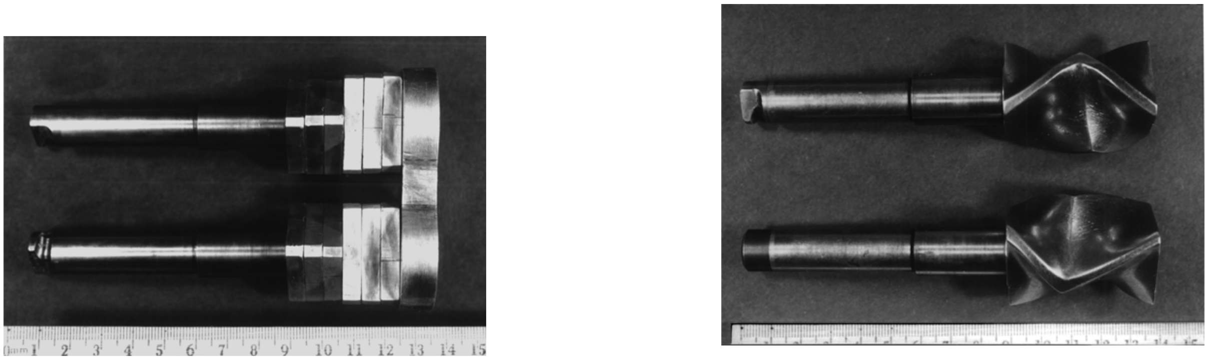
	Small Mixer	Large Mixer	Ratio (Large / Small Mixer)
Mixer Capacity	69 cm^3	350 cm^3	5
Blade Dimensions	3.74 cm dia., 4.67cm long	6.6 cm dia., 8.6cm long	1.76 1.84
Mixing Bowl Dimensions	3.94 cm dia., 4.76 cm long	6.9 cm dia., 8.6 cm long	1.75 1.8
Minimum gap between blades and mixing bowl	1 mm	1.5 mm	1.5
Surface Area of Mixing Bowl	80 cm^2	253 cm^2	3.16
Surface Area of Blades	96 cm^2	317 cm^2	3.3
Specific Area (without blades)	1.2 cm^{-1}	0.7 cm^{-1}	0.6 (= 1/1.7)
Specific Area (including blade area)	2.6 cm^{-1}	1.6 cm^{-1}	0.6 (=1/1.7)

Table 3: Geometrical parameters of the triangular element blades used to achieve different batch sizes in the small mixer

	2 Triangles	4 Triangles	6 Triangles
Batch Size	12 g	23 g	35 g
Mixing Volume	16 cm^3	32 cm^3	48 cm^3
Surface Area of Mixing Bowl	18.5 cm^2	37 cm^2	55.4 cm^2
Surface Area of Blades	21 cm^2	42 cm^2	63 cm^2
Specific Area (including the blades)	2.5 cm^{-1}	2.5 cm^{-1}	2.5 cm^{-1}

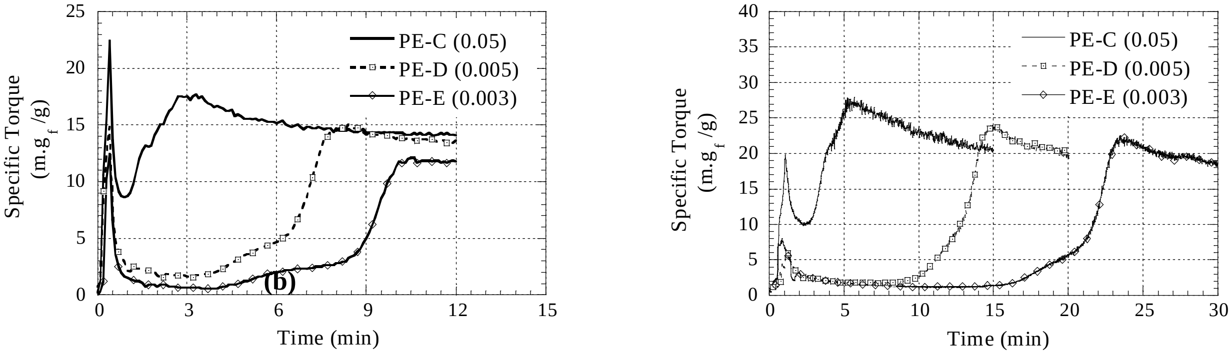
Table 4: Variation in the "time to phase inversion" $t_{P.I.}$, and the specific work input until phase inversion on scale-up to a large mixer using roller blades.

Parameter	Value	$t_{P.I.}$ Small Mixer (min)	$t_{P.I.}$ Large Mixer (min)	Ratio of Times to Phase Inversion (Large/Small Mixer) (a)	Ratio of Specific Work Input until Phase Inversion (Large/Small Mixer) (b)	(b) / (a)
Viscosity Ratio (η_{PE} / η_{PS})	0.05	3.0	5.5	1.8	1.8	1
	0.005	8.0	14.5	1.8	1.49	0.83
	0.003	10.5	24.0	2.3	2.6	0.83
Volume Fraction of PE-D (wt. %)	0.5	2.0	5.0	2.5	2.53	1
	1.0	3.0	8.0	2.7	2.14	0.8
	2.0	3.5	10.0	2.9	2.80	0.97
	4.0	5.0	14.5	2.9	2.47	0.85
	7.8	8.0	14.5	1.8	1.49	0.83
Mixer Temperature (^{o}C)	160	15.0	37.0	2.5	2.1	0.84
	180	8.0	14.5	1.8	1.49	0.83
	200	4.0	9.0	2.2	2.2	1



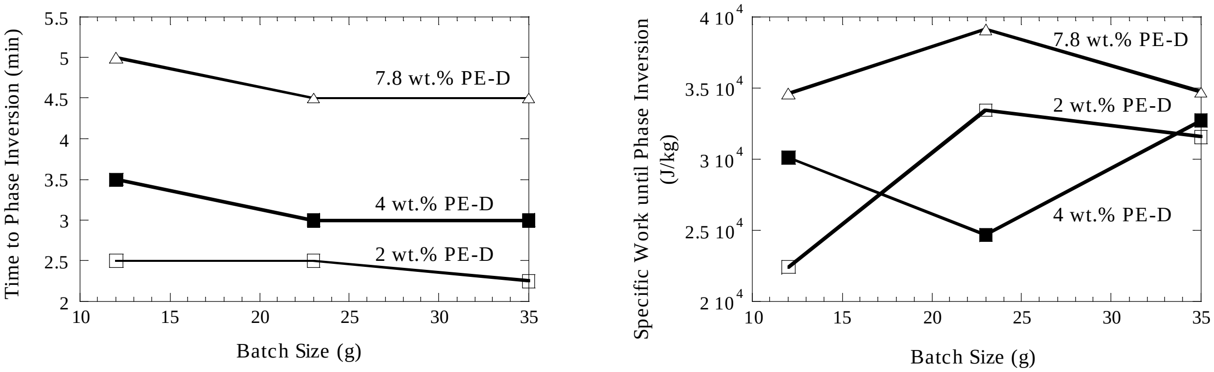
(a)

Figure 1: A comparison of (a) the triangular blade design with six elements on each shaft and (b) the roller blades, used in different compounding runs in the small mixer. The small ruler marks correspond to 1mm.



(a) **(b)**

Figure 2: Comparison of the effect of viscosity ratio on the torque traces for compounding PS/PE (92.2/7.8) blends at 180°C in the (a) small and (b) large mixers. The melt viscosity ratio (η_{PE} / η_{PS}) at 180°C and 100s^{-1} is indicated in parenthesis.



(a) **(b)**

Figure 3: Summary of compounding runs with triangular element blades at 200°C and 50 rpm for three different batch sizes in the small mixer. Variation of the time to phase inversion (a) and the specific work input until phase inversion (b).