Morphology development during reactive and non-reactive blending of an ethylene–propylene rubber with two thermoplastic matrices

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The development of morphology from pellet-sized particles to submicrometre droplets during the polymer-blending process is investigated for two pairs of polymer blends. The systems are blends of a rubbery phase in a glassy matrix, namely amorphous nylon/ethylene–propylene rubber and polystyrene/ethylene–propylene rubber blends. In each case the investigation is pursued for a non-reactive blend and a similar reactive blend where the phases may chemically react at the interface during the blending process. The dispersed phase particle size distribution is determined as a function of mixing time for these systems. The behaviour of the blends with matrices of nylon and polystyrene is qualitatively similar. The major reduction in the dispersed phase size is found to occur at short mixing times, in conjunction with the softening process. For example, in the case of a reactive nylon/ethylene–propylene rubber blend, the volume average particle diameter of the dispersed phase is reduced from ~4 mm (pellet size) to ~1 μm within the first 90 s of mixing. At intermediate mixing times, the morphology consists of a large number of small dispersed phase particles (which are about the same size as the particles observed in the final blend) along with a small number of very large particles which constitute most of the volume occupied by the rubber phase. The effect of subsequent mixing is primarily to reduce the size of the largest particles in the size distribution. The interfacial chemical reaction between the phases reduces the dispersed phase size and narrows the size distribution.

(Keywords: polymer blend; morphology development; phase size distribution)

INTRODUCTION

Morphology development is the evolution of the blend morphology from pellet-sized or powder-sized particles to the submicrometre droplets which exist in the final blend. It is widely known that the final morphology of the blend has a controlling influence on the properties of the blend. However, previous studies of how morphology evolves are quite limited. There are many important questions concerning this process which have yet to be addressed. The nature of any intermediate morphologies is unknown. There has been much speculation about the primary mechanisms of particle size reduction but these have not been thoroughly investigated. The effect of interfacial reaction on morphology development is also not known.

Figure 1 presents a simple schematic of a typical polymer-blending operation. Pellets or powders of the two major components, A and B, are dry blended, for example in a tumbling drum. This mixture is then fed to an intensive mixer. In an industrial process the mixer may be a single-screw extruder, twin-screw extruder or batch intensive mixer. In the mixer, the materials are softened or melted and mixed to form the polymer blend. In extruders the feed section of the barrel is commonly kept relatively cool. After feeding, the solid mixture is quickly conveyed down the barrel to the heated sections where melting or softening occurs. Further mixing in the fluid state leads to the final morphology of the blend. There have been many studies which have reported on the influence of processing conditions on the resultant morphology of a blend[1–13].

Unfortunately, very little work has been reported on how the morphology develops as a function of time during polymer blending. Schreiber and Olguin[5] investigated blends of polypropylene with dispersed phases of polystyrene, ethylene–propylene rubber and bromobutyl rubber. Only small differences in the morphology were observed between blends sampled at 10 and 20 min of mixing. Karger-Kocsis *et al.*[6] studied blends of several rubbers dispersed in polypropylene. They reported no significant changes in morphology from 5 to 40 min of mixing. Plochocki *et al.*[14] investigated the blending of polystyrene with linear low density polyethylene in a variety of industrial mixers. They tentatively proposed that the initial dispersion mechanism may be abrasion

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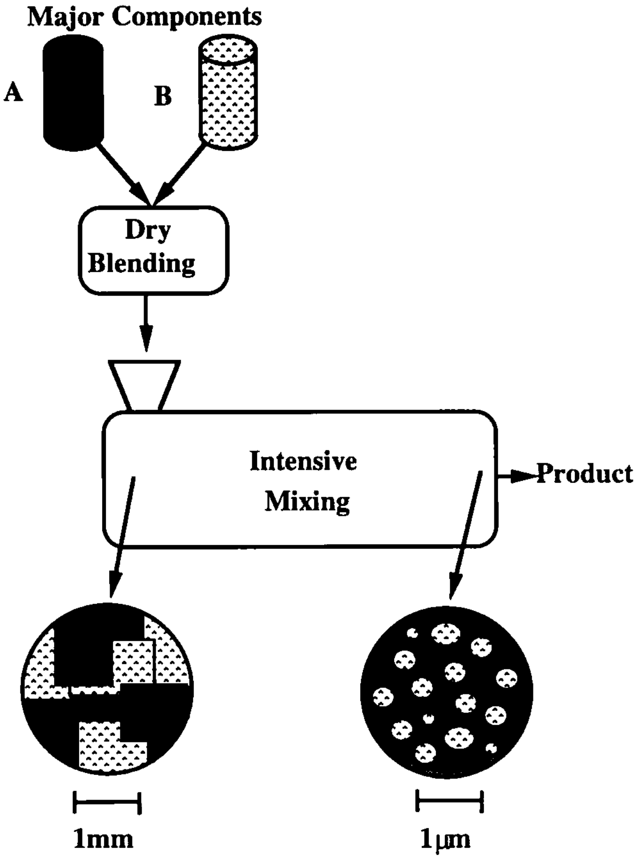

Figure 1 Schematic of the polymer-blending process

of solid or only partially softened pellets against the walls of the processing equipment.

Favis[15] investigated the effect of mixing time on the morphology of blends of polypropylene and polycarbonate. The blends were prepared in a batch mixer with roller blades. The morphology was sampled from 2 to 20 min of mixing and there was very little reduction in size of the dispersed phase over the time period investigated. This was found to be true over a range of mixing torque ratios (approximately equal to viscosity ratios) from 2 to 13. The authors concluded that the most significant changes in morphology occurred during the first 2 min of mixing when melting and softening of the materials were also occurring.

Scott[16] and Scott and Macosko[17] reported the results of model experiments which investigated the initial stages of mixing at very short times. The primary mode of morphology development at short mixing times appeared to be a shearing of the phases into ribbon or sheet structures followed by a shear and interfacial tension driven breakup of these sheets or ribbons. This work considered only a glassy dispersed phase in a glassy matrix. The model experiments were conducted with a nylon dispersed phase which had a T_g higher than that of the matrices which were used. Most of the reduction in the dispersed phase size was demonstrated to occur in the very early stages of mixing. This work has been extended by Sundararaj *et al.*[18].

Shih *et al.*[19] investigated the rheological characteristics of several polymer blends during the compounding process. They identified four characteristic regimes of rheological behaviour. They also observed a phase inversion mechanism when the minor component melted or softened at a lower temperature than the major component.

Lindt and Ghosh[20] investigated the reduction of phase size during blending in a single-screw extruder. They observed the melting of solid polymer particles to form thin lamellar structures similar to those previously reported by Scott[16] and Scott and Macosko[17]. They also developed a model for the conversion of pellets into such striations during melting in the single-screw extruder.

The primary focus of this work is to investigate the mechanism of morphology development during polymer blending of a rubber with a glassy matrix. Knowledge of this mechanism may be used to design intensive mixers with better dispersive mixing capabilities. This information is also important in systems such as reactive blends where the kinetics of creation of interfacial area are critical to the blending process. In addition, such information may be used to design various aspects of the mixing process such as the form and order of addition of components in systems where adequate dispersion is difficult to achieve. Previous work in the area indicates that most of the particle size reduction occurs in conjunction with the melting or softening process. Since the materials used in this study are amorphous, the relevant transition is the softening of the material as the temperature rises above the glass transition temperature. In order to investigate this, samples must be obtained at very short mixing times. Simultaneous measurement of the mixing torque in a batch mixer provides an indication of how far softening or melting has progressed. An additional goal of this work is to compare the development of morphology in non-reactive and reactive polymer blends.

EXPERIMENTAL

Materials

The functionalized nylon (PA) was Zytel 330, kindly provided by DuPont. This material is reported to be functionalized with amine groups on the chain-ends. It is a partially aromatic amorphous nylon. The functionalized polystyrene (PS–Ox) was RPS XUS40056.01, kindly provided by the Dow Chemical Company. This material is reported to be functionalized with 1.0% oxazoline. It is reported to have a molecular weight of 200 000 and a melt index of 7.0. The non-functional polystyrene (PS) was Dow Styron 666D. This is reported to have a melt index of 7.5.

The ethylene–propylene rubbers were provided by Exxon. The non-functional rubber (EP) was designated as V805 and reported to have an ethylene content of 76%. This was provided in a crumb form. The reactive rubber (EP–MA) was designated as XX1301 and reported to have an ethylene content of 76% and a maleic anhydride content of 0.7 wt% with a molecular weight $M_n = 86\,000$. This was provided in a pellet form.

All materials were dried overnight under vacuum at 80°C before the compounding of blends. For use in some blends the rubbers EP and EP–MA were precompounded in the mixer and recut into cubes as described below. All materials were fed to the mixer in pellet or small cube form.

Table 1 Summary of rubber-toughened blend systems investigated

System	Matrix phase	Dispersed phase (20 wt%)	System type	Mixer wall set temperature (°C)
Nylon/ethylene–propylene rubber	PA	EP	Non-reactive	200
	PA	EP–MA	Reactive	200
Polystyrene/ethylene–propylene rubber	PS	EP–MA	Non-reactive	170
	PS–Ox	EP–MA	Reactive	170

Blending procedure

All of the blends were prepared using a Haake Rheomix 600 batch mixer with a Haake System 90 drive. The mixer set temperature depended on the system being blended, as specified in *Table 1*. Roller blades were employed at 50 rev min^{-1}. At this rotor speed, the maximum drag flow (neglecting pressure flow) shear rate in the mixer was 65 s^{-1}. All of the blends prepared were composed of 20 wt% dispersed rubber phase. Pellets of the components were mixed by hand in a cup before blending in the mixer. The mass of material charged to the mixer was chosen so that a constant volume of 54 cm^3 was achieved for each sample. The densities were estimated using the data given by van Krevelen[21].

At $t=0$, the pellet mixture was fed through a chute into the preheated mixing chamber under a constant force of 5 kg. The stock temperature of the materials and the mixing torque were measured during the blending process. After the specified time of mixing, the roller blades were stopped and the mixing chamber pulled away from the blades, leaving most of the material attached to the blades. The procedure for sampling the material is outlined by Scott[16]. The sample was cut from the large gap region of the roller blades and dropped directly into a bath of liquid nitrogen to freeze the morphology. The time required between stopping the mixer and dropping the sample into the liquid nitrogen bath was 10–15 s. Based on standard heat transfer calculations[22], once the sample is dropped into liquid nitrogen it takes approximately 30 s for the centreline of the sample to be cooled to below 100°C. This should be sufficient to fix the morphology. Mixing times investigated were 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 15.0 min of mixing. Time zero corresponds to the start of feeding of the pellets to the mixer. The time required to feed the entire charge of pellets varied with the system, as specified below.

For the nylon/ethylene–propylene rubber system, the reactive blend was formed by mixing PA with EP–MA, while the non-reactive blend was formed by mixing PA with EP. The fact that the EP material was provided in crumb form and the EP–MA in pellet form was found to make a difference in the rate of feeding to the batch mixer. Therefore, both rubbers were precompounded before use. Both of the rubbers were first softened in the mixer at a wall temperature of 170°C with roller blades at 50 rev min^{-1} for a mixing time of 5 min. The material was then pressed out into plaques of 3.2 mm thickness and cut into small cubes using a machine shop shear. The resulting cubes were fairly monodisperse with sides varying from 3 to 5 mm in length. These fed easily into the mixer in a similar manner to pellets. The time required to feed the entire charge into the mixer averaged 44.5 s and varied from 39 to 51 s.

For the polystyrene/ethylene–propylene rubber system, the reactive blend was formed by mixing PS–Ox and EP–MA, while the non-reactive blend was formed by mixing PS and EP–MA. As used in these experiments, the maleic anhydride functionality of the EP–MA had been partially hydrolysed to the diacid form. The EP–MA pellets were used directly in these experiments. The time required to feed the entire charge into the mixer averaged 35.8 s and varied from 33 to 38 s.

Sample preparation

The quenched blend samples from these rubber-modified thermoplastic systems were prepared for microtoming. Some of the samples retained their shape after being dropped into liquid nitrogen. Other samples spontaneously broke into many small pieces during quenching. For those samples which retained their shape, two sampling planes were investigated from each sample of material. The first sampling plane was parallel to the velocity gradient in the mixer, while the second sampling plane was perpendicular to the velocity gradient. Samples which retained their shape and could be analysed in this way were PA/EP at all mixing times; PA/EP–MA at 1.5, 2.5, 3.0, 4.0, 5.0 and 7.0 min of mixing; PS/EP–MA at 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 min of mixing; and PS–Ox/EP–MA at 5.0 min of mixing. For samples which broke into many small pieces, two perpendicular planes of the material were also investigated, as described above. However, the relationship of these planes to the velocity gradient in the mixer was unknown. Samples which were analysed using this method were PA/EP–MA at 2.0 and 15.0 min of mixing; PS/EP–MA at 7.0 and 15.0 min of mixing; and PS–Ox/EP–MA at 1.5, 2.0, 2.5, 3.0, 4.0, 7.0 and 15.0 min of mixing. After quantifying the morphologies it was determined that there were no qualitative or quantitative differences between the results for the two perpendicular sampling planes. Therefore, the results from the micrographs from all planes of a given sample were lumped together for the analysis.

The samples were cryoultramicrotomed using a Reichert Ultracut E with an FC-4 low temperature attachment at −100°C and a diamond knife to provide flat surfaces for investigation of the morphology. The flat block faces were kept for analysis. The cryoultramicrotomed samples from the nylon/ethylene–propylene rubber systems were exposed to xylene in a Soxhlet apparatus for 6 h to remove the soluble rubber phase. The Soxhlet operated at approximately 138°C. The holes left in the extracted surface represent the former locations of the rubber particles. Micrographs of unextracted surfaces were flat and featureless, demonstrating that the blends were free of air bubbles. The surfaces were coated by evaporation with a 30 nm layer of carbon and then a 10 nm layer

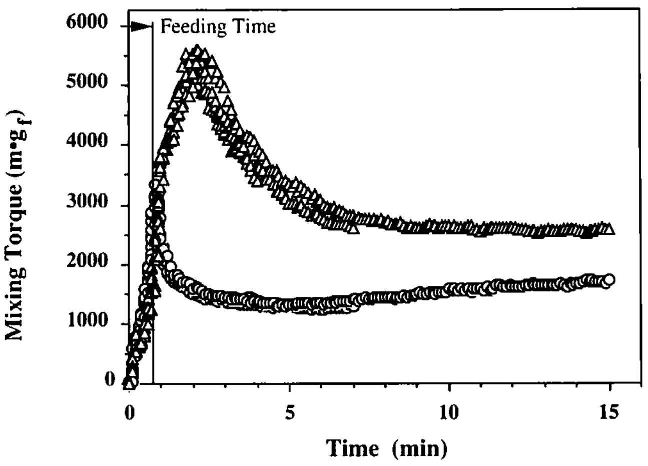

Figure 2 Mixing torque as a function of time for (○) PA/EP and (△) PA/EP–MA. Data from eight runs are overlaid on each curve

of gold. The cryoultramicrotomed samples from the polystyrene/ethylene–propylene rubber systems were exposed to ruthenium tetroxide vapour above a 0.5% aqueous solution (Polysciences Inc.) for 5 min to enhance the phase contrast. The surfaces were then coated by evaporation with a 30 nm layer of carbon. The scanning electron microscopy (SEM) micrographs were obtained with a JEOL 840II HRSEM at 5 kV.

Image analysis

The micrographs were analysed using a semiautomatic method with International Imaging System's 575 software. The method of a guard frame outlined by Russ[23] was used to deal with edge particles. The numbers of particles counted per sample averaged 850 from a total of at least five fields of view for the blends of nylon and ethylene–propylene rubber and 400 from a total of at least three fields of view for the blends of polystyrene and ethylene–propylene rubber. The cross-sectional area of each particle and the total particle area in the region of observation were determined using the computer software. The particle areas were converted to equivalent diameters using

$$d_{\text{equivalent}} = \sqrt{\frac{4}{\pi}(\text{area})} \qquad (1)$$

The diameters reported here are uncorrected equivalent diameters calculated from observations on a two-dimensional surface cut through the blend. However, the diameters observed on a two-dimensional sampling surface are not the actual diameters of the particles. There are several methods presented in the literature for correction of particle size data for three-dimensional effects[23–26]. In order to judge the effect of disregarding the correction on the results of this study, the correction was made on the particle size distribution for the PA/EP–MA blend at 15 min of mixing. The method used here is that of Johnson[27] and Saltykov[24] as described by Underwood[25].

A comparison of the uncorrected and corrected data demonstrated that there is little qualitative difference between the uncorrected and corrected data. In the frequency distribution, the major effect of the correction is to cut off the lower end of the distribution. The uncorrected number average diameter is 0.196 μm compared to the corrected number average diameter of 0.181 μm. This represents an 8% decrease in the number average diameter. There is a small shift of the distribution to lower diameters. The volume average diameter is reduced from 0.333 μm in the uncorrected distribution to 0.304 μm in the corrected distribution. This represents a 9% decrease in the volume average diameter. These comparisons indicate that making the correction would not have a significant effect on the results presented here.

RESULTS AND DISCUSSION

Amorphous nylon/ethylene–propylene rubber blends

The non-reactive blends were formed from PA and EP, while the reactive blends were formed from PA and EP–MA. The chemical reaction between the amine functionality of the PA and the anhydride functionality of the EP–MA has been described in detail elsewhere[16,28–32].

The torque *versus* time and material temperature *versus* time curves for the nylon/ethylene–propylene rubber non-reactive and reactive systems are presented in *Figures 2* and *3*. The curves shown are overlays of traces from the eight runs required to generate the samples. The reproducibility of the torque and temperature is seen to be fairly good.

In the case of the non-reactive PA/EP blend, the torque first rises quickly as the cold material is fed to the mixer. As the material is heated by shear and conduction, it softens and the torque falls. The torque then levels off to a nearly constant value for the remainder of the mixing time. In the case of the reactive PA/EP–MA blend, the torque continues to rise after the feeding is completed because of the chemical reaction. The reaction increases the molecular weight of the polymer and thus raises the required mixing torque. The torque peaks at approximately 2 min of mixing and then falls. This is evidently because of degradation of the higher molecular weight fractions of the interfacial reaction product caused by the intense shearing in the mixer. The torque then levels out to a fairly constant value which is higher than that observed for the non-reactive blend.

The stock temperature in both the non-reactive and reactive blends is initially low as a result of feeding the

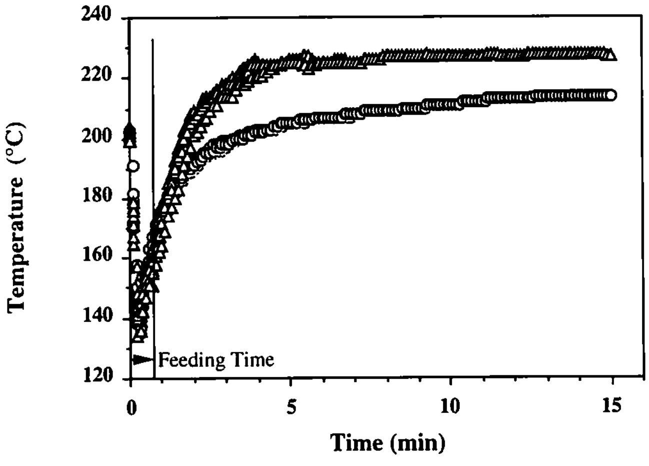

Figure 3 Material temperature as a function of time for (○) PA/EP and (△) PA/EP–MA. Data from eight runs are overlaid on each curve

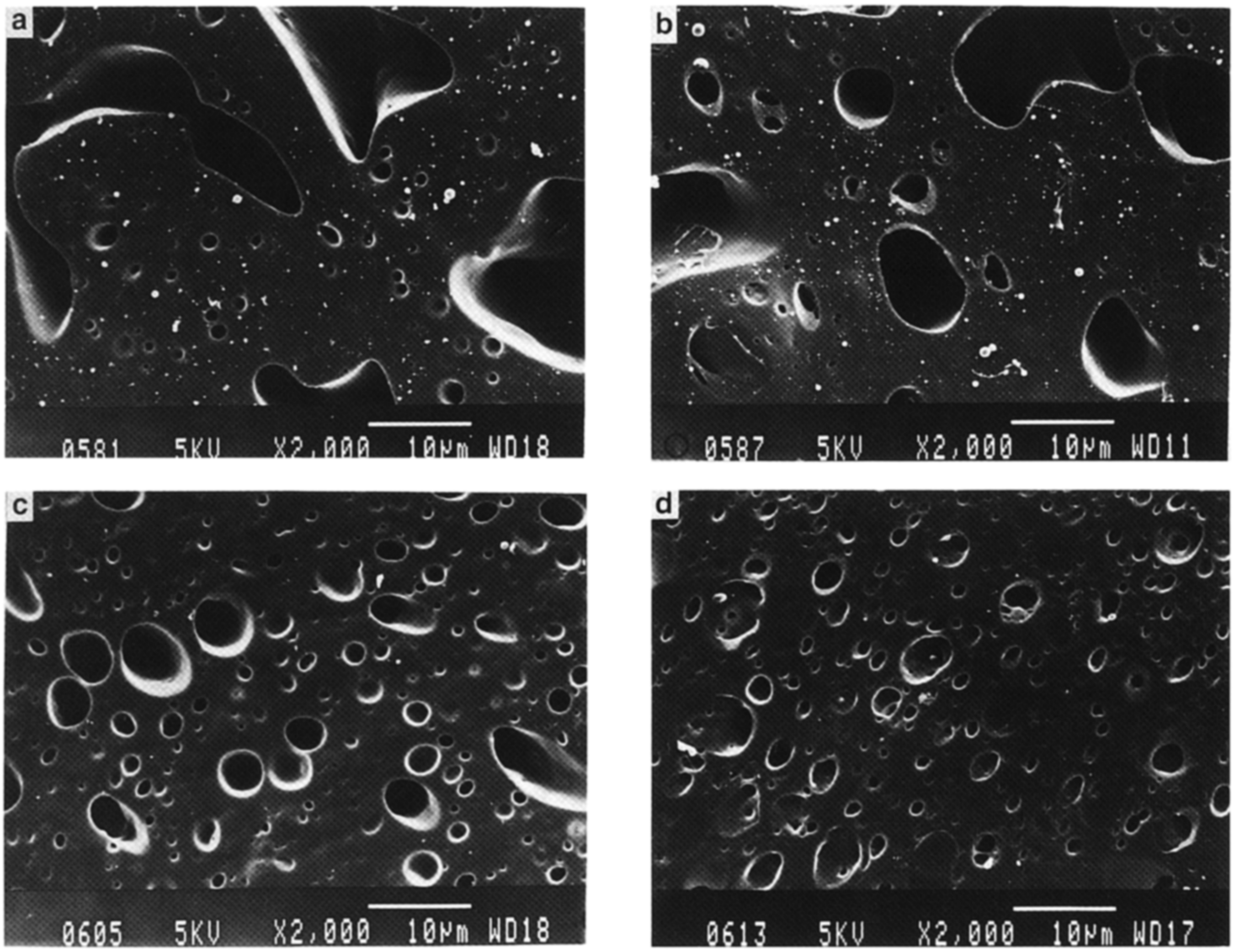

Figure 4 Cryoultramicrotomed surfaces after removal of the soluble rubber phase with xylene from PA/EP after (a) 1.5 min of mixing, (b) 2.5 min of mixing, (c) 5.0 min of mixing and (d) 15.0 min of mixing

material at room temperature. It increases slowly because of the heating action in the mixer. The steady-state temperature of the reactive blend is higher than that of the non-reactive blend because the higher viscosity of the reactive blend results in a greater dissipation of mechanical energy. The temperature of the non-reactive blend levels out to 214°C, while the temperature of the reactive blend levels out to 228°C.

Based on the temperature *versus* time curves the calculated viscosity ratios between the two phases during the later stages of mixing are[16]

$$\frac{\eta^*(\text{EP; }214^\circ\text{C})}{\eta^*(\text{PA; }214^\circ\text{C})} = 0.36 \quad \text{at } 65\,\text{s}^{-1}$$

$$\frac{\eta^*(\text{EP-MA; }228^\circ\text{C})}{\eta^*(\text{PA; }228^\circ\text{C})} = 0.69 \quad \text{at } 65\,\text{s}^{-1}$$

The viscosities of the rubbers are matched at the high shear rates experienced during blending. However, as discussed above, the temperature is higher in the reactive blends. This accounts for the difference in the viscosity ratio between the reactive and non-reactive blend systems. The applied shear stress during blending is also greater in the reactive blends, as evidenced by the higher mixing torque.

The morphologies of the blends at several times of mixing are presented in *Figure 4* for PA/EP and *Figure 5* for PA/EP-MA. Scale bars are given at the bottom of each micrograph. Some general trends shared by the non-reactive and reactive blends are evident. At short mixing times the morphology is characterized by a few very large particles along with a large number of small particles which are nearly the same size as the particles observed at long mixing times. The major influence of additional mixing time is the reduction in size of the largest particles in the distribution. The dispersed phase particles in the reactive blends are smaller than in the non-reactive blends. Also, the distribution of particle sizes is narrower.

Figure 6 compares the particle size distributions of the non-reactive PA/EP blend and reactive PA/EP-MA blend at 15.0 min of mixing. Note that the diameter scale is logarithmic. The major effects of the chemical reaction at the interface are a reduction in the average size of the dispersed phase particles and a narrowing of the size distribution. The smaller dispersed phase size in the reactive blends compared to the non-reactive blends probably arises through several different effects: (1) reduction of the effective interfacial tension between the phases; (2) inhibition of particle coalescence by the

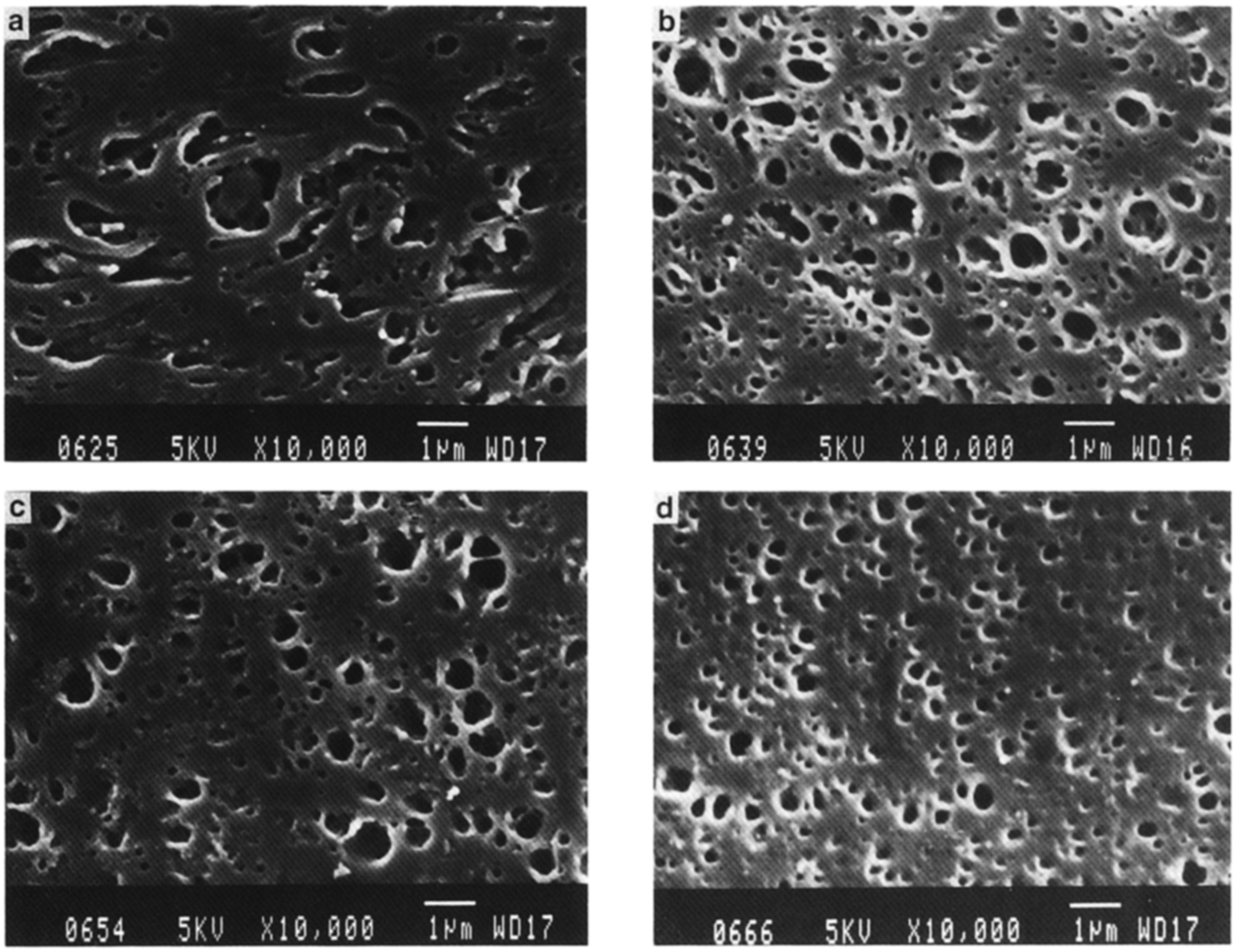

Figure 5 Cryoultramicrotomed surfaces after removal of the soluble rubber phase with xylene from PA/EP–MA after (a) 1.5 min of mixing, (b) 2.5 min of mixing, (c) 5.0 min of mixing and (d) 15.0 min of mixing

presence of the copolymer at the interface; (3) differences in the effective shear stress applied to the blends during mixing; and (4) differences in the viscosity ratio between the two phases caused by temperature[16].

Representative data for the morphology development for the PA/EP non-reactive blends are given in *Figure 7*. The frequency distributions of the samples obtained at 1.5 and 15.0 min of mixing are presented. In addition to this, *Figure 7* also presents the volume of the rubber phase occupied by particles of a given diameter. This more accurately portrays the importance of the small number of very large rubber particles clearly visible in *Figure 4*. The major effect of increased time of mixing over the time period shown here is a reduction of the small number of very large particles in the distribution.

Similar plots are presented for the PA/EP–MA morphology development in *Figure 8*. Qualitatively, the results are similar to those of the non-reactive blend. However, the interfacial chemical reaction tends to reduce the number of very large particles at the high end of the distributions. This is illustrated more clearly in the log–normal plots shown in *Figure 9*. Especially at long mixing times, the rubber phase size distributions form nearly straight lines, indicating that the particles form a log–normal distribution similar to that observed by other workers[10,15,33]. Inspection of the high end of the distribution shows clearly that one effect of the chemical reaction at intermediate mixing times is to reduce the number of very large particles in the distribution relative

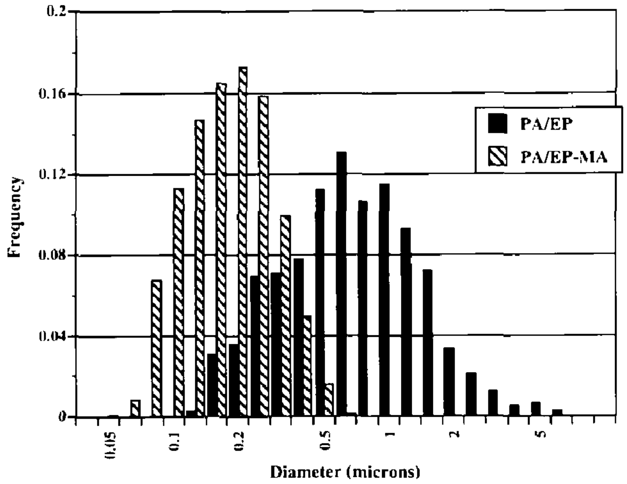

Figure 6 Comparison of dispersed phase diameter distributions for PA/EP and PA/EP–MA blends at 15.0 min of mixing

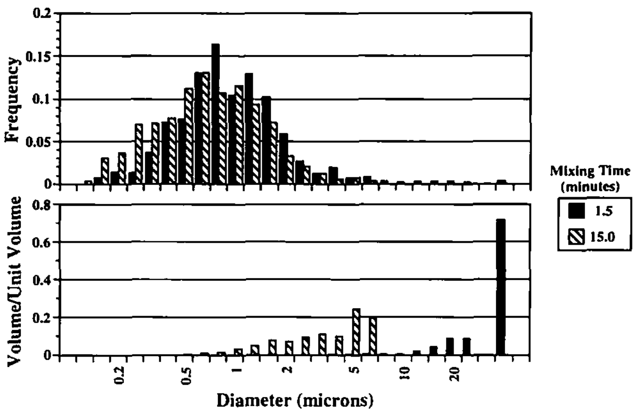

Figure 7 Particle diameter distributions for the PA/EP blend at 1.5 and 15.0 min of mixing

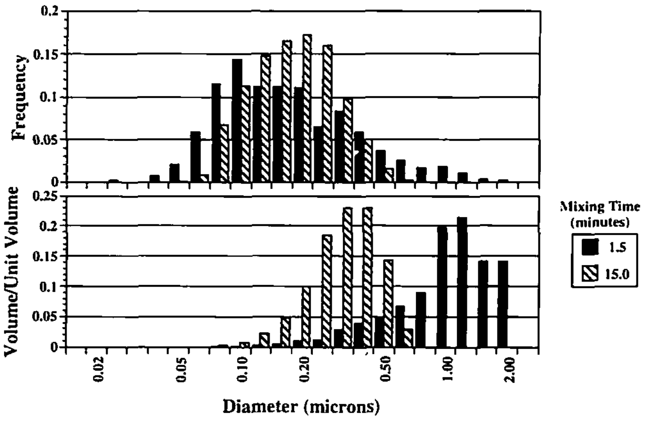

Figure 8 Particle diameter distributions for the PA/EP–MA blend at 1.5 and 15.0 min of mixing

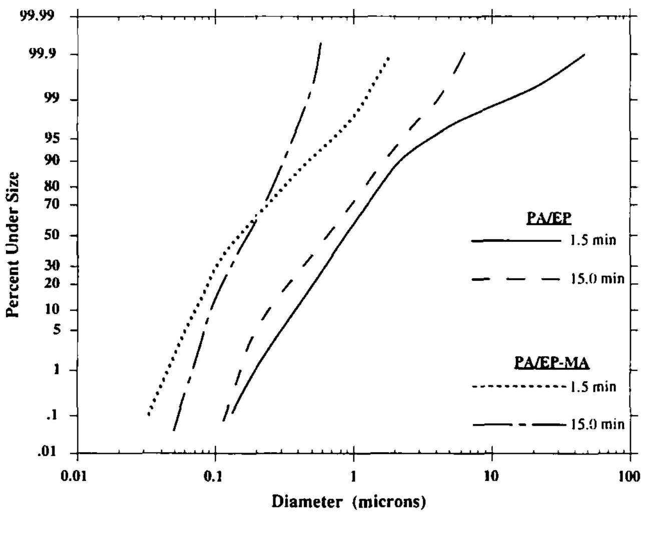

Figure 9 Comparison of rubber phase diameter distributions for PA/EP and PA/EP–MA blends

to the non-reactive case. Thus, the interfacial chemical reaction significantly aids the mixing process.

For the case of the reactive PA/EP–MA blends the distribution curves on the log–normal plot cross each other. This means that there are more very small particles in the distribution at 1.5 min of mixing than in the blends at 15.0 min of mixing. The reason for this is not obvious. It is unlikely that they have coalesced to form larger particles. Coalescence is known to be retarded by the presence of stabilizing interfacial agents such as the product of the interfacial reaction here[16,34,35]. It is possible that in the course of blending these small particles have reacted to such an extent that they are no longer detectable by the phase contrast technique used here. Specifically, the copolymer of nylon and ethylene–propylene rubber may not be soluble in xylene. This possibility may be tested by measurement of the total area fraction of dispersed phase detected on the micrograph sampling surface. This area fraction is equal to the volume fraction of the dispersed phase in the blend[23,25].

The measured area fractions of dispersed phase as a function of mixing time are given in *Figures 10* and *11*. The dashed lines through the experimental data are least-squares fits. The solid lines indicate the theoretical values as determined from the density data presented by van Krevelen[21]. The measured area fraction of EP in the non-reactive PA/EP blends is nearly constant at 0.224

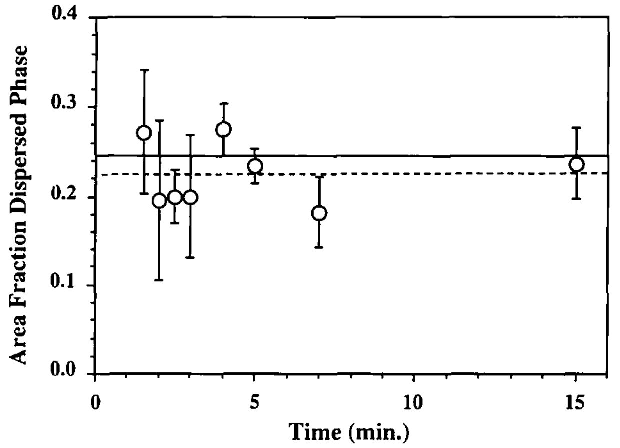

Figure 10 Measured area fraction of dispersed phase in PA/EP non-reactive blends as a function of time (○): (– – –) least-squares fit through data; (——) theoretical value based on composition

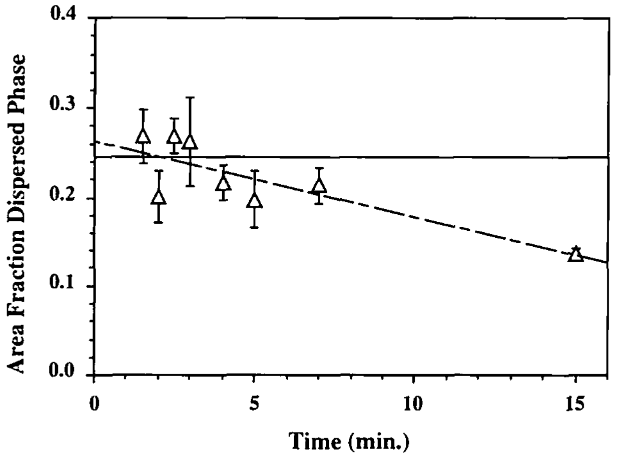

Figure 11 Measured area fraction of dispersed phase in PA/EP–MA reactive blends as a function of time (△): (— — —) least-squares fit through data; (——) theoretical value based on composition

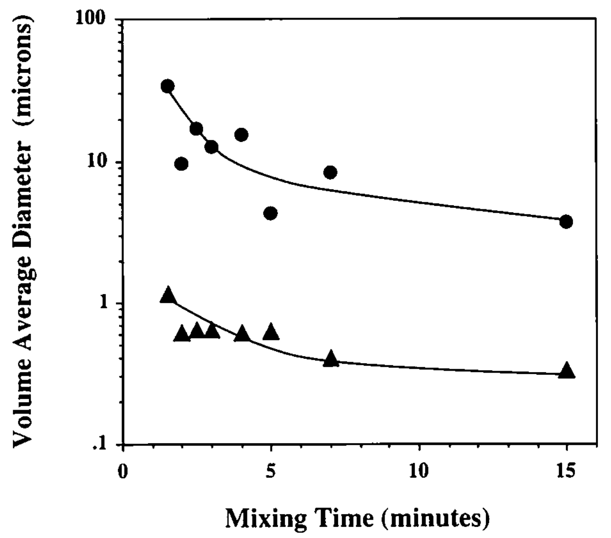

Figure 12 Volume average diameter of rubber particles as a function of mixing time for (●) PA/EP and (▲) PA/EP-MA

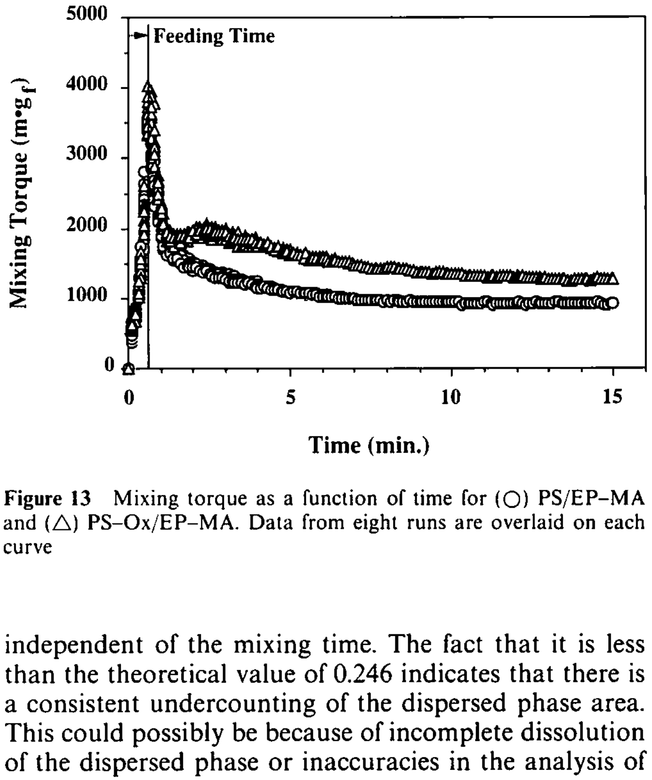

Figure 13 Mixing torque as a function of time for (○) PS/EP-MA and (△) PS-Ox/EP-MA. Data from eight runs are overlaid on each curve

independent of the mixing time. The fact that it is less than the theoretical value of 0.246 indicates that there is a consistent undercounting of the dispersed phase area. This could possibly be because of incomplete dissolution of the dispersed phase or inaccuracies in the analysis of the particles. It could also be because of small particles or sections through particles which are not resolved in the photographs.

The least-squares fit to the data from the reactive PA/EP-MA blends in *Figure 11* shows that the measured area fraction decreases as a function of time. At short mixing times, it is nearly equal to the theoretical value. However, at long mixing times the observed area fraction of the dispersed phase decreases significantly. It is unlikely that the observed reduction in the area fraction of dispersed phase is simply because of limited resolution in the micrographs or image analysis method. The observed reduction in area fraction must arise from some other effect, such as the technique used to achieve phase contrast. Evidently, a significant portion of the copolymer of nylon and ethylene-propylene rubber which is produced by the chemical reaction at the phase interface is not soluble under the extraction conditions used here. This would explain the loss of small particles in the measured particle size distribution and the reduction in the measured area fraction of the dispersed phase with mixing time. If this is indeed true, then *Figure 11* shows that a significant amount of the dispersed phase, nearly half, has been incorporated into copolymer which is insoluble in xylene at 15.0 min of mixing.

Summaries of the changes in volume average diameter as a function of mixing time are presented in *Figure 12*. (The number average diameters change little over the mixing times investigated here.) The interfacial reaction has a dramatic influence on the dispersed phase size, even at very short mixing times. However, the shapes of the curves in both the reactive and non-reactive cases are similar. The breadth of the particle size distribution may be roughly gauged by d_v/d_n, the ratio of volume average to number average diameters. In the non-reactive blend, d_v/d_n falls from 22.7 at $t=1.5$ min to 4.3 at $t=15.0$ min. In the reactive blend, d_v/d_n falls from 4.9 at $t=1.5$ min to 1.7 at $t=15.0$ min. Thus, the particle size distribution narrows at longer mixing times. Also, the interfacial chemical reaction narrows the size distribution of the reactive blend compared to the non-reactive blend.

Polystyrene/ethylene-propylene rubber blends

The torque *versus* time and material temperature *versus* time curves for the polystyrene/ethylene-propylene rubber non-reactive and reactive systems are presented in *Figures 13* and *14*, respectively. The chemical reaction between the oxazoline functionality of the PS-Ox and the functionality of the EP-MA has been described elsewhere[16,36,37]. The curves shown are overlays of traces from the eight runs required to generate the samples. The reproducibility of the torque and temperature is quite good. The temperatures of the two systems are very close under the processing conditions used here. Again, the torque for the reactive blend is higher because of the chemical reaction, which increases the viscosity of the blend. Note that this effect is not nearly as large as observed in the nylon/rubber blends (*Figure 2*). Also, there is a longer delay in time before the difference in torque between the two systems becomes apparent. This

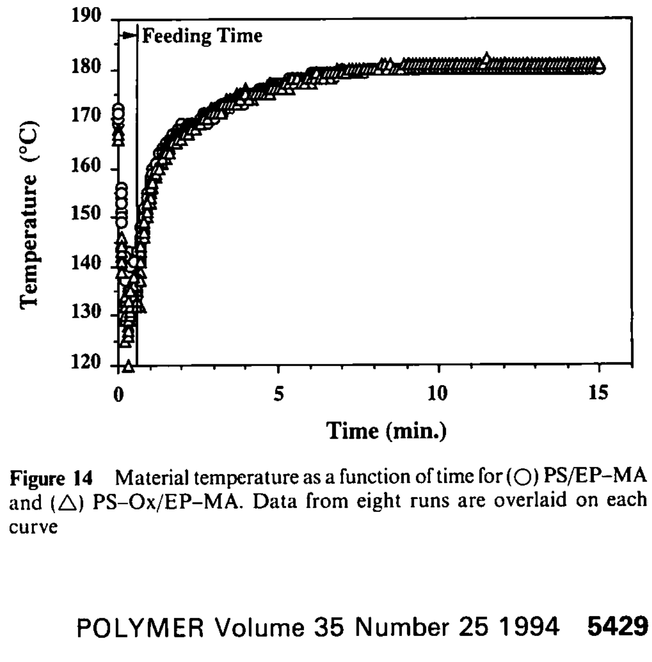

Figure 14 Material temperature as a function of time for (○) PS/EP-MA and (△) PS-Ox/EP-MA. Data from eight runs are overlaid on each curve

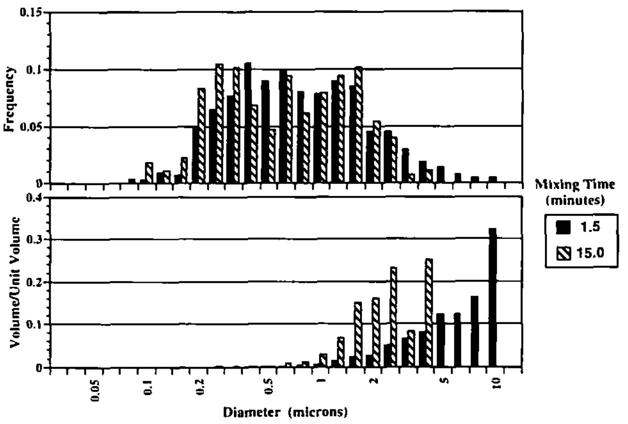

Figure 15 Particle diameter distributions for PS/EP-MA blends at 1.5 and 15.0 min of mixing

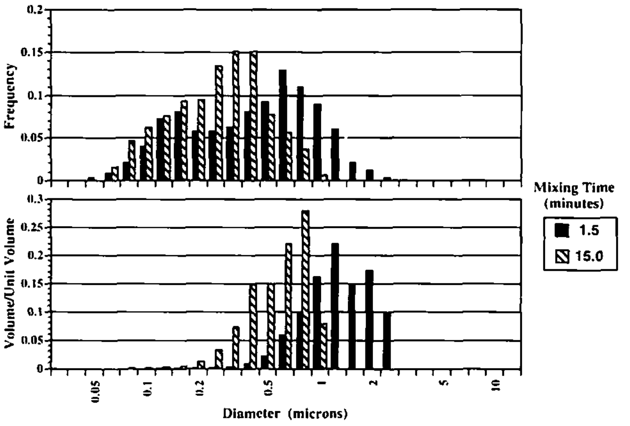

Figure 16 Particle diameter distributions for PS-Ox/EP-MA blends at 1.5 and 15.0 min of mixing

is because the PS-Ox/EP-MA reaction takes place more slowly than the PA/EP-MA reaction under the conditions of temperature and mixing which are used here. Since the viscosities of the polystyrenes are matched at the high shear rates experienced during blending, the viscosity ratios of the two blend systems are also matched[16]. The viscosity ratio $\eta^*(\text{rubber})/\eta^*(\text{polystyrene})$ is approximately 1.9 at around 180°C, the temperature reached by both systems near 5.0 min of mixing.

The comparisons between particle size distributions at 1.5 and 15.0 min of mixing are given in *Figures 15* and *16*. The behaviour is qualitatively similar to that observed in the nylon/ethylene–propylene rubber blends. However, the difference between the reactive and non-reactive blends in terms of particle size is not nearly as large as in the case of the nylon/ethylene–propylene rubber blends. The comparison between the reactive and non-reactive systems is similar to that observed in the nylon/ethylene–propylene rubber blends.

The measured area fraction of the dispersed phase is plotted as a function of time in *Figures 17* and *18*. For the non-reactive system the measured area fraction again agrees well with the theoretical volume fraction. In the case of the reactive system the measured area fraction decreases slightly as a function of time. As in the nylon/ethylene–propylene rubber system, this may be caused by loss of contrast of the copolymer. Summaries of the changes in volume average diameter are given in *Figure 19*. In this figure, a linear diameter scale has been used. Qualitatively, changes in the diameter as a function of time are similar to those observed in the nylon/ethylene–propylene rubber blends. However, the difference in particle size between the reactive and non-reactive blends is not as great in these polystyrene/ethylene–propylene rubber blends as in the nylon/ethylene–propylene rubber blends. The interfacial chemical reaction is not as potent in this case as it is in the nylon/rubber system.

Mechanism of morphology development

The experiments described here have successfully determined the evolution of the blend morphology from approximately 1.5 to 15.0 min of mixing in the batch mixer. However, most of the reduction in size of the rubber phase had already occurred before the first data point was taken. *Figure 20* puts this in perspective with the data collected for the PA/EP-MA blend system. The rubber cubes fed to the mixer averaged 4 mm. The volume average diameter is reduced by nearly four orders of magnitude within the first 2 min of mixing. Subsequent mixing is important because it reduces the size of the largest particles in the size distribution and this could be

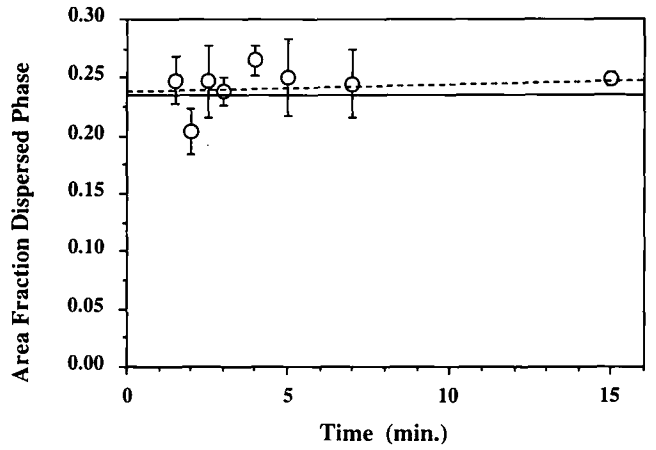

Figure 17 Measured area fraction of dispersed phase in PS/EP-MA non-reactive blends as a function of time (○): (– – –) least-squares fit through data; (——) theoretical value based on composition

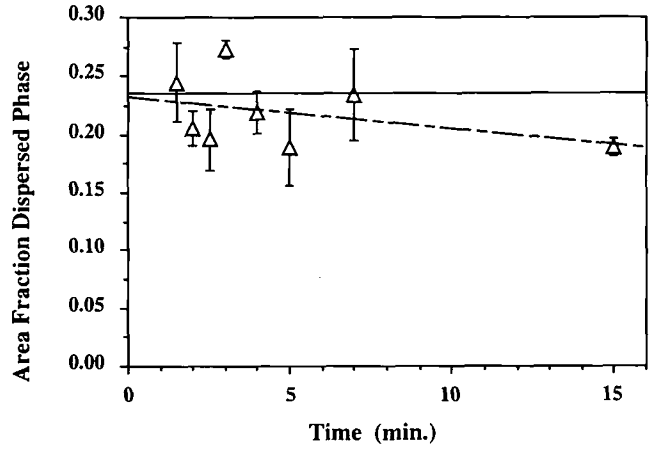

Figure 18 Measured area fraction of dispersed phase in PS-Ox/EP-MA reactive blends as a function of time (△): (— — — -) least-squares fit through data; (——) theoretical value based on composition

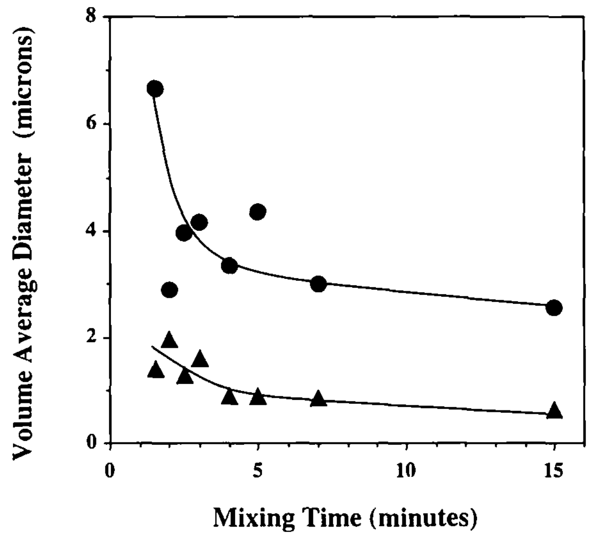

Figure 19 Volume average diameter of rubber particles as a function of mixing time for (●) PS/EP-MA and (▲) PS-Ox/EP-MA

critical for mechanical properties. However, it is clear that most of the morphology development occurs even before the first data points which were presented above. Comparison of the phase size curve with the torque curve in *Figure 20* clearly shows that this process must take place in conjunction with the softening process. A similar conclusion may be drawn with the other three blends investigated in this work. This conclusion is consistent with the observations of previous workers who investigated morphology changes at relatively long times and concluded that the morphology changed little at long mixing times[5,6,15].

During this work, samples were taken at mixing times of less than 1.5 min. However, these could not be cryoultramicrotomed because the samples tended to fray or fall apart during cutting. In order to obtain information at these short mixing times, model experiments such as those described by Scott and Macosko[17] must be used. Despite the fact that measurements could not be made at the very short mixing times, some important conclusions may be made.

The morphology development of polymer blends is certainly expected to be a complex process. The pellets are fed into a batch mixer or an extruder as elastic solids. As they are heated by conduction and shear working they become deformable solids. The materials are then softened and/or melted to become viscoelastic liquids. Recent work indicates that under some circumstances a phase inversion may occur during the melting or softening process[19]. The solids-conveying and solids-melting processes for the case of a homogeneous material in extruders have been studied extensively[38-41]. However, very little analogous information is available for blend systems.

At short mixing times, there is a broad distribution of temperature, stress and strain throughout the volume of the sample. Some portions of the sample will be melted or softened and sheared to a great extent while other portions will not. The flows in the mixer used here are sufficiently complex that the distributions of these parameters are unknown. The mechanism of morphology development at short mixing times must be concerned with the mixing action on soft, deformable solids. It is obvious that much work remains to be done in order to understand the process fully. However, the results presented in this work demonstrate that intensive mixers such as extruders should be designed to generate dispersion in the solids-melting zone as well as in the melt phase. Dispersion does not occur only after both phases have been fully melted or softened. Instead, it starts along with the melting process. Thus, it is important to design compounding equipment to mix polymers effectively during the melting or softening process, not just after melting has occurred.

The micrographs and particle size distributions which reveal the nature of the development of morphology clearly show that during the softening process dispersion is not a gradual reduction in particle size from large to medium to small. Instead, very small particles are generated quickly in the mixing process and coexist with very large particles. As mixing proceeds, these very large particles are transformed into smaller ones. A similar transformation has been observed by David *et al.*[42] in a model mixing experiment where the components were completely melted before mixing was initiated.

Based on model experiments, Scott[16] and Scott and Macosko[17] have recently proposed a mechanism of morphology development for the initial stages of polymer blending. These experiments suggested a mechanism where a particle is dragged against a hot surface. This hot surface could be the mixer wall, the mixing blade or another hotter mass of polymer. This causes the formation of a sheet or ribbon of the phase. Owing to interfacial and shearing forces, holes form in the ribbon and grow until a lace structure is formed. This lace is then broken down into irregularly shaped particles and finally nearly spherical particles.

This proposed mechanism is consistent with the morphologies observed in the nylon/ethylene-propylene

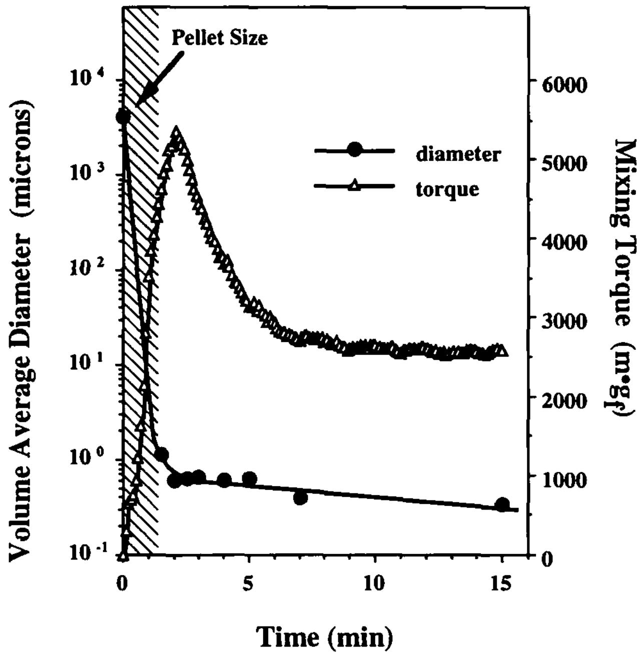

Figure 20 Overview of morphology development results for the PA/EP-MA blend system with 20 wt% EP-MA. In the hatched region the samples could not be analysed using the cryoultramicrotome technique

rubber and polystyrene/ethylene–propylene rubber blends which have been studied here. It explains the existence of very small particles of dispersed phase at very short mixing times. The large particles observed in the nylon/ethylene–propylene rubber and polystyrene/ethylene–propylene rubber blends at intermediate mixing times are those which have not undergone this mechanism of deformation. Another potential mechanism for initial morphology development is the abrasion of solid or partially softened pellets against the mixer wall, as suggested by Plochocki *et al.*[14].

The work reported here has only dealt with one type of dispersed phase polymer. The type of deformation which occurs early in the softening or melting process may be dependent on the polymer molecular weight and level of crystallinity, among other things. The experiments described in this paper have dealt only with a dispersed phase with a significantly lower T_g than that of the matrix. The relative values of the glass transition temperatures of the two polymers are critical because they determine which phase softens first. In this work, the dispersed phase is well above its glass transition temperature throughout the experiment. However, the matrix phase softens during the compounding process as its temperature rises above its glass transition temperature. The morphological transitions which may occur under such circumstances have been explored in detail by Shih *et al.*[19]. However, the rate of heating was very different in the experiments conducted by Shih *et al.* They used a very slow rate of heating during the blending experiments. In the experiments reported here, the cold pellets have been quickly force-fed into a hot mixer. This is intended to model the extrusion process where the pellet mixture is typically fed into a relatively cold feeding zone and then quickly conveyed into a hot barrel zone. Of course, after both phases have softened or melted, it is actually the melt rheology of each phase rather than the relative values of the glass transition temperatures which is critical to determining the morphology.

The mechanism of morphology development may also depend on the type of mixer which is used. However, similar results have been obtained recently on a twin-screw extruder by Sundararaj *et al.*[18] and on a single-screw extruder by Lindt and Ghosh[20].

The discussion in this paper has focused on short and intermediate mixing times. However, later on in the mixing process the mechanism of breakup of a fluid drop in a fluid matrix is certainly important in morphology development. It would be expected to grow in importance at intermediate and long mixing times. Consideration of the problem of the breakup of a drop or filament of one fluid inside another has been the topic for a large number of investigations. Excellent reviews of the literature are given by Rallison[43,44] and Bentley and Leal[45]. There is also a general consensus in the literature that coalescence of droplets during blending may be important. Unfortunately, there are relatively few published investigations of this phenomenon[46–48].

CONCLUSIONS

The dispersed phase morphology as a function of mixing time was investigated for two rubber-modified thermoplastics, namely nylon/ethylene–propylene rubber blends and polystyrene/ethylene–propylene rubber blends. The behaviour of these two systems was qualitatively similar. Most of the reduction in the dispersed phase size was found to occur at short mixing times, in conjunction with the melting or softening process. At intermediate mixing times, the morphology consisted of a large number of small dispersed phase particles (which were about the same size as the particles observed in the final blend) along with a small number of very large particles which constituted most of the volume occupied by the rubber phase. The effect of subsequent mixing was primarily to reduce the size of the largest particles in the size distribution.

The initial mechanism of morphology development was intimately connected with the melting or softening process. The mechanism must be concerned with the mixing action on soft, deformable solids. In addition, the state of temperature, stress and strain varied widely throughout the sample at short mixing times. Further investigation of these aspects of the mixing process is necessary in order to understand them more thoroughly.

The effects of the chemical reaction at the interface on the morphology development of reactive blends were three-fold. Firstly, it reduced the average size of the dispersed phase. Secondly, it tended to accelerate the breakup of the largest particles in the size distribution. Thirdly, it narrowed the size distribution of the dispersed phase. It was possible in some cases to quantify the extent of reaction between the two phases of a reactive blend by following the reduction in apparent area fraction of the dispersed phase. The effect of the chemical reaction was much greater in the PA/EP–MA system than in the PS–Ox/EP–MA system.

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