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Morphology development during the initial stages of polymer–polymer blending

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The development of morphology from pellet-sized particles to submicrometre droplets during the polymer blending process is investigated for several polymer blends. In order to determine the morphology at short mixing times, a model experiment is developed that allows the matrix to be dissolved away so that the dispersed phase may be observed directly using scanning electron microscopy. The dispersed phase for the model experiments is an amorphous nylon. The matrix phases investigated include polystyrene, an oxazoline functional polystyrene, a styrene–maleic anhydride copolymer, an amorphous polyester and a polycarbonate. These model experiments dramatically reveal the primary modes of particle deformation and the nature of the morphologies at short mixing times.

The major reduction in phase domain size occurs in conjunction with the melting or softening of the components. The initial mechanism of morphology development involves the formation of sheets or ribbons of the dispersed phase. These sheets or ribbons become unstable due to the effects of flow and interfacial tension. Holes develop in the ribbons, which grow in size and concentration until a fragile lace structure is formed. The lace structure breaks into irregularly shaped particles, which are then broken up into nearly spherical particles. This mechanism results in very fast formation of small dispersed-phase particles, which are nearly the same size as those observed at long mixing times. Continued mixing action primarily reduces the size of the largest particles in the size distribution.

(Keywords: blend; morphology development; scanning electron microscopy)

INTRODUCTION

Morphology development is the evolution of the blend morphology from pellet- or powder-sized particles to the submicrometre droplets that exist in the final blend. It is widely known that the final morphology of the blend has a controlling influence on its properties. However, previous studies of how this 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 investigated. The effect of interfacial reaction on morphology development is also not known.

In most blending operations the components are added at room temperature as pellets or powders. They are quickly heated and softened or melted by thermal conduction and viscous heating. The critical temperature near which viscous flow begins is the melting temperature for semicrystalline polymers and the glass transition temperature for amorphous polymers. However, during melting or softening there will be a broad distribution of temperature, stress and strain within the sample. Early in the process some portions of the materials will be exposed to high temperatures and become greatly deformed while other portions will experience little or no deformation at all. This is clearly the case in single-screw extruders due to the formation of the melt pool and solids bed. However, it is also true in twin-screw extruders, batch mixers and other types of mixing equipment. The development of morphology in such equipment is critically dependent on the mechanism of melting or softening.

Knowledge of the mechanisms of morphology development would be useful for the design of processing equipment with improved mixing capabilities. Equipment configurations could be developed to take advantage of the particular mechanisms involved. Advantageous methods could be devised to enable the mixing of materials that are difficult to mix, such as high- and low-viscosity liquids. In addition, the order and form of addition of various formulation components could be adjusted in light of the mechanisms involved. For example, such knowledge could be used to determine whether it is best to add a low-viscosity additive that is solid at room temperature in flake form at the feed hopper or to melt it and pump it into an extruder at a point downstream from the melting zone. It could also be used to determine the optimum point of addition for additives consisting of particles that must be dispersed, such as carbon black or colorants. The understanding of morphology development is important in reactive polymer blend systems where the kinetics of interfacial reaction are critically dependent on the rate of interfacial area generation.

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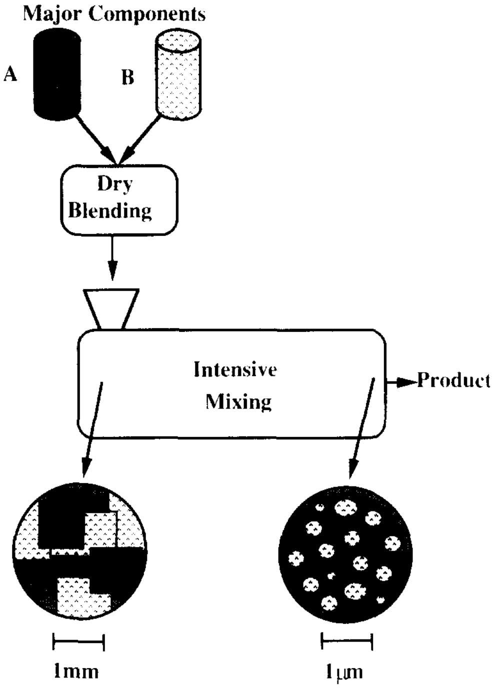

Figure 1 Schematic of the polymer blending process

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 is typically a twin-screw extruder or batch intensive mixer. In the mixer, the materials are softened or melted and mixed to form the polymer blend. There have been many studies that have reported on the influence of processing conditions on the resultant morphology of a blend[1-8].

Unfortunately, very little work has been reported on how the morphology develops during polymer blending. Schreiber and Olguin[9] 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.*[10] studied blends of ethylene–propylene–ethylidenenorbornene, ethylene–propylene–1,4-hexadiene terpolymer and a high-ethylene-content ethylene–propylene block copolymer dispersed in polypropylene. They reported no significant changes in morphology from 5 to 40 min of mixing. Plochocki *et al.*[11] 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 of solid or only partially softened pellets against the walls of the processing equipment.

Favis[12] 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 was also occurring.

Scott[13] reported on morphology development in blends of ethylene–propylene rubber with an amorphous nylon and a polystyrene. The vast majority of the phase size reduction was found to occur during the first 1.5 min of mixing in conjunction with the melting or softening of the polymers. Scott and Macosko[14] reported model experiments on polystyrene/nylon blends, which indicated the formation of sheets or ribbons of the dispersed phase during melting in a batch mixer. This work was extended to a twin-screw extruder by Sundararaj *et al.*[15].

Shih *et al.*[16] investigated the rheological characteristics of several polymer blends during the compounding process. They identified four characteristic regimes of rheological behaviour: elastic solid pellets, deformable solid pellets, transition material and viscoelastic fluid. Morphological changes in these regimes were discussed. In the work of Shih *et al.*, the temperature of the batch mixer was raised slowly from room temperature in order to distinguish these regimes.

Lindt and Ghosh[17] investigated the blending of polystyrene with styrene–butadiene copolymer and with ethylene–vinyl acetate in a single-screw extruder. They observed the formation of fine lamellar structures similar to those observed previously by Scott[13,14], which extended over much of the melting zone and were broken up by capillary forces.

David *et al.*[18] used a laboratory tester to study the early stages of mixing of immiscible polymer melts. In these experiments the polymers were fully melted before deformation was initiated. They observed the formation of platelets, which stretched and broke into strings of droplets.

The primary focus of the present work is to investigate the initial mechanism of morphology development during polymer blending. Previous work in the area clearly demonstrates that most of the particle size reduction occurs in conjunction with the melting or softening process. In order to investigate the morphology in this regime, samples must be obtained at very short mixing times. One major challenge for investigations at short mixing times is that it is difficult to observe the complex morphologies that are created. The experimental method used here involves dissolution of the matrix so that the morphology of the dispersed phase may be observed directly. An additional goal of this work is to compare the development of morphology in non-reactive and reactive polymer blends. This paper is an extension of the work done previously by Scott and Macosko[13,14].

EXPERIMENTAL

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

Table 1 Summary of model blend systems investigated. Minor phase is 20 wt% PA

System	Major phase	T_g (major) (°C)	Type	Mixer wall set temperature (°C)
Polystyrene/nylon	PS	99^a	Non-reactive	200
	PS-Ox	107^a	Reactive	200
Styrene–maleic anhydride/nylon	SMA	138^b	Reactive	200
Copolyester/nylon	PETG	81^c	Non-reactive	200
Polycarbonate/nylon	PC	157^a	Non-reactive	230

[a] Dow Chemical product literature, Vicat softening point
[b] Differential scanning calorimetry, 10°C min^{-1}
[c] Eastman Chemical product literature

a melt index of 7.0. The styrene–maleic anhydride copolymer (SMA) was ARCO Chemical's Dylark 290. It has a reported maleic anhydride content of 17 wt%. The amorphous copolyester (glycol-substituted poly(ethylene terephthalate), PETG) was Kodar Copolyester 6763, provided by Eastman Chemical Company. It has a reported glass transition temperature of 81°C and molecular weight $M_n = 26\,000$. The polycarbonate (PC) was Dow Chemical Calibre 300-6. This is a general-purpose polycarbonate with a reported melt index of 6.0 and Vicat softening temperature of 157°C. All materials were dried overnight under vacuum at 80°C before the compounding of blends.

The blends were prepared using a Haake Rheomix 600 batch mixer with a Haake System 90 drive. All materials were fed to the mixer in pellet form. The set temperature depended on the system being blended, as specified in *Table 1*. Roller blades were employed at 50 rpm. At this rotor speed, the maximum drag flow (neglecting pressure flow) shear rate in the mixer was 65 s^{-1}. This was calculated on the basis of the rotor speed and the minimum gap between the rotor tip and the mixing chamber wall. The blends prepared were composed of 20 wt% dispersed phase unless otherwise specified. 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[19].

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 off the blades, leaving most of the material attached to the blades. The sample was cut from the large gap region of the 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 to 15 s. Based on standard heat-transfer calculations[20], 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 1.0, 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 model polystyrene/nylon system, the non-reactive blend was formed by mixing PS with PA and the reactive blend was formed by mixing PS-Ox with PA. The rheologies of the PS and PS-Ox are nearly identical, as demonstrated by Scott[13]. The time required to feed the entire charge into the mixer, averaged over the runs made, was 24.5 s and it varied from 22 to 26 s. The blends with an SMA matrix finished feeding in an average of 37 s; the PETG matrix in 34 s; and the PC matrix in 38 s.

The quenched samples from all of the model systems were placed in the special Soxhlet cups[13]. These are aluminium cups with a piece of filter paper clamped over the top of the cup. The paper allows the solvent and dissolved polymer to pass through, but keeps the insoluble dispersed phase particles in the cup. The paper is reasonably dense but contains holes on the order of 1 μm. Some of the smaller particles in the distribution are expected to be lost through these holes during the extraction procedure. However, many particles smaller than 1 μm are retained by the filter, as demonstrated in several micrographs that follow. The matrix was easily removed in the Soxhlet using methylene chloride for 7 days. For samples that were quenched at short mixing times there was essentially one chunk of material left in the aluminium cup after the Soxhlet procedure. This chunk was simply transferred to an SEM stub for inspection. For samples that were quenched at long mixing times, the contents of the aluminium cup after the Soxhlet procedure was a milky suspension of nylon particles in methylene chloride. A drop of this suspension was placed on an SEM stub and the methylene chloride was allowed to evaporate. These samples were sputter coated with 10 nm of gold using a Denton DV-502 A. The SEM micrographs were obtained with a JEOL 840II HRSEM at 5 kV.

For the model systems with SMA, PETG and PC matrices the sample morphology at 7.0 min of mixing was obtained from fracture surfaces. Small bars (approx. 25 mm by 10 mm by 3 mm) of the sample were prenotched with a razor blade and placed in liquid nitrogen for 10 min. The bars were then fractured by bending. These samples were coated by evaporation with 30 nm of carbon and then 10 nm of gold before observation.

MODEL EXPERIMENTS: DISCUSSION OF THE TECHNIQUE

The morphology of polymer blends is very complex in the initial stages of compounding where an enormous reduction in phase size is taking place. It is difficult to investigate such complex morphologies using standard microscopic techniques, which involve observation of a fracture surface or a microtomed slice of the sample. In order to overcome the difficulties with sample observation, a model experiment was developed that allows dissolution of one polymer phase. Generally it is more practicable to dissolve the matrix phase and leave the dispersed phase. The blend components are selected such that one can be easily dissolved by a solvent that has no effect on the other component. Soxhlet extraction provides for a very gentle treatment of the sample and for that reason it is the technique of choice for removal

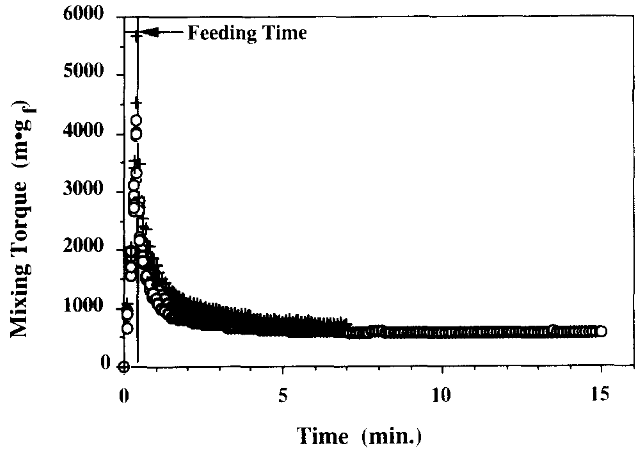

Figure 2 Mixing torque as a function of time for: (○) PS/PA blends (data from seven runs are overlaid); (+) PS-Ox/PA blend (data from two runs are overlaid)

of the matrix phase. By this means, one of the blend components may be removed from the system while the other retains the morphology that it exhibited within the blend. This phase may then be examined directly with scanning electron microscopy. Entire particles of the phase may then be examined, not just a two-dimensional slice or a fracture surface. This allows for observation of complex morphological structures because the large depth of field of SEM enables observation of the whole particle. Tilting or shadowing may be used to obtain the complete dimensions of the particles.

The major disadvantage of this method is that it must be ensured that the dispersed phase retains its shape after dissolution of the matrix. This may be achieved by using a dispersed phase that is glassy at room temperature or a crosslinked dispersed phase. The solvent must be carefully selected to dissolve the matrix completely without swelling or partially dissolving the dispersed phase. Also, there is loss of some spatial information. A long thread of dispersed phase may break up into a series of droplets during blending. The relative positions of the droplets are lost using this procedure.

Model systems with a nylon dispersed phase were chosen for these experiments to minimize the possibility of artifacts due to sample preparation. The PA has a glass transition temperature of 136°C. The matrices used may be dissolved using methylene chloride, which has a boiling point of 40°C. Nylon is very resistant to this solvent. Also, both reactive and non-reactive systems are available. The functionality of the PA will react with the functionalities of both the PS-Ox and the styrene–maleic anhydride copolymer, SMA.

MODEL EXPERIMENTS: RESULTS

A summary of the systems investigated in this study is presented in *Table 1*. The blend systems that were investigated most thoroughly were a PS/PA non-reactive blend and a comparative PS-Ox/PA reactive blend. Scott[13] demonstrates that the PS and PS-Ox are rheologically matched at high shear rates and discusses the interfacial chemistry in the reactive blend. The torque and material temperature–time curves for these experiments are given in *Figures 2* and *3*, respectively. The material temperature of this system levels out to approximately 203°C at 6 min of mixing. The slow approach to the steady-state temperature that is seen in *Figure 3* is typical of all the blends studied here owing to the processing conditions selected. During the early stages of blending, significant temperature gradients are expected within the sample due to heat-transfer limitations. The implications of this are explored further in the 'Discussion' section below. Based on the viscosity data obtained for PA and PS the viscosity ratio, $\eta(\mathrm{PA})/\eta(\mathrm{PS})$, at the steady-state temperature and $65\,\mathrm{s}^{-1}$ is 14. The torque curves for the reactive PS-Ox/PA blend follow fairly closely the curves for the PS/PA non-reactive blends. The only evidence for reaction is a slightly higher torque just after the melting peak. Based on the mixing torques, it appears that the extent of reaction between the two phases has not become significant at 1.0 min of mixing. However, the morphologies of the blends at 7.0 min of mixing clearly indicate an interfacial reaction, as demonstrated below.

The morphologies observed at 1.0 min of mixing in the non-reactive PS/PA blends are presented in *Figure 4*. The micrographs show the nylon phase, which remains after the polystyrene matrix has been removed. Three large chunks of nylon left after dissolution of the matrix from the three pieces of the blend are shown in a low-magnification picture in *Figure 4a*. Each of these chunks was originally a single nylon pellet. The piece in the upper right-hand corner of the picture is a relatively undeformed pellet of nylon. The pieces in the upper left and lower middle of the picture each have a region that is relatively undeformed and another region that has been greatly deformed during the mixing process. *Figure 4b* shows a higher-magnification picture of the piece in the lower middle of *Figure 4a*. In the area of extensive deformation the material has been stretched out into many ribbons or sheets. Closer examination of these ribbons reveals that many of them have holes in them. Higher-magnification pictures of some of these holes are shown in *Figure 4c*. These holes are of the order of 10 μm in diameter. In some areas there are no or only a few holes in the sheet. In other areas the size and concentration of the holes is sufficient to form more of a lace-type structure. *Figure 4c* shows evidence of the fragile lace structure breaking

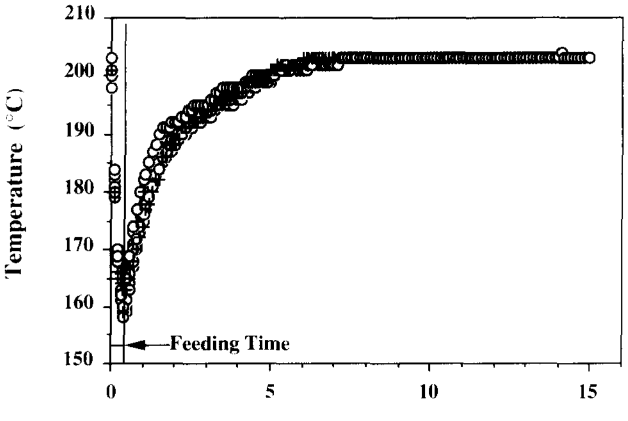

Figure 3 Material temperatures as a function of time for (○) PS/PA blends (data from seven runs are overlaid); (+) PS-Ox/PA blend (data from two runs are overlaid)

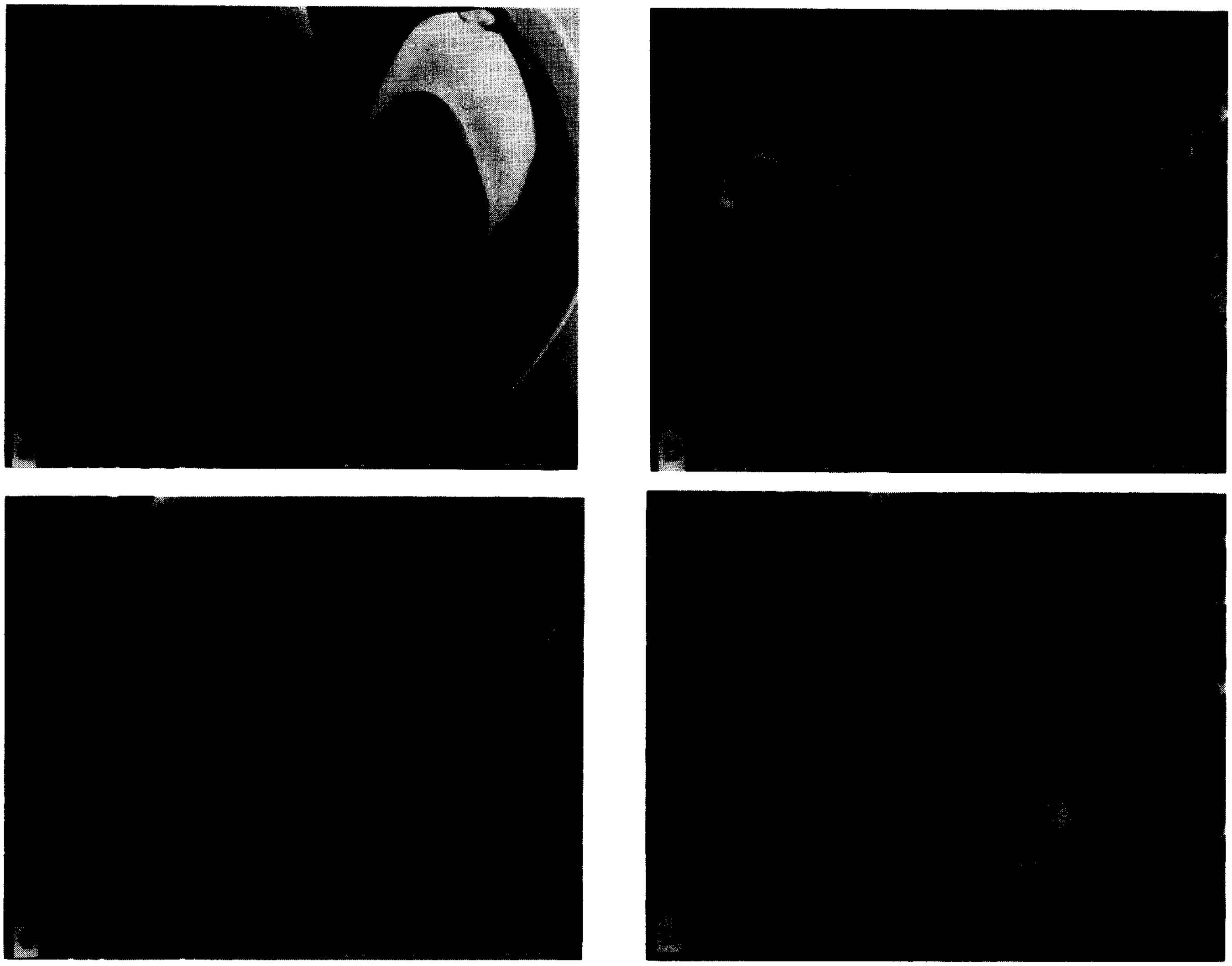

Figure 4 SEM micrographs for PS/PA, 1.0 min mixing. (a) Low-magnification picture of three large pieces of PA dispersed phase after extraction of PS matrix phase. (b) Close-up of one of the pieces from (a). (c) Holes and lace structure observed in ribbons and sheets of the dispersed phase. (d) Broken lace structure and small spherical particles of the dispersed phase

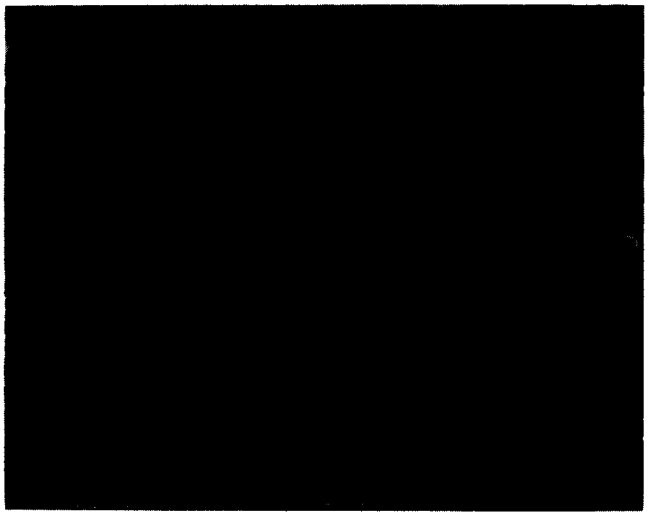

Figure 5 Morphology of dispersed-phase particles from PS/PA blend, 1.5 min mixing

up in some regions of the sample. *Figure 4d* shows high-magnification pictures in a region of this same sample. There are many small irregularly shaped pieces, which appear to have originated from the breaking of the lace structure. There are also many small spherical particles of diameters from 0.5 to 3 μm. As shown below in *Figures 6* to *9*, these small spherical particles are the same size as the particles found in the blend at 2.5 to 15.0 min of mixing. The results given here are for a blend with 20 wt% of PA. Similar results were obtained for a blend with 5 wt% PA in PS.

The morphologies observed at 1.5 min of mixing are presented in *Figure 5*. There are many irregularly shaped particles, which appear to have originated from disintegration of the lace structure shown above. There are also many highly elongated particles as well as many nearly spherical particles. Note that the diameters of the spheres and elongated particles are in the range of 0.5 to 3 μm.

The morphologies observed at 2.5 to 15.0 min of mixing are shown in *Figures 6* to *9*. The particles observed at these mixing times are nearly all spherical. A few drop break-up structures may also be observed. The particle diameters range from 0.5 to 3 μm.

The morphologies observed at 1.0 min of mixing in the reactive PS-Ox/PA blend are qualitatively similar to those observed in the PS/PA non-reactive blends. Two pictures from this sample are shown in *Figure 10*. Again, many ribbons or sheets with holes and lace structures

Figure 6 Dispersed-phase particles from PS/PA blend, 2.5 min mixing

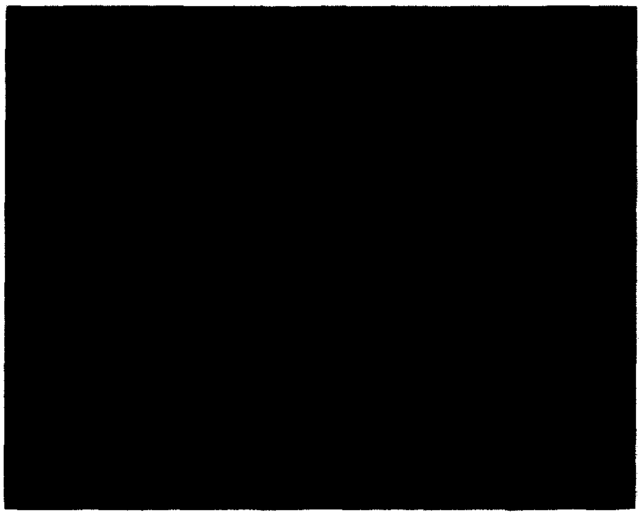

Figure 7 Dispersed-phase particles from PS/PA blend, 3.0 min mixing

are evident. The behaviour is qualitatively the same as that in the PS/PA non-reactive blends. However, at long mixing times, the dispersed phase size in the PS-Ox/PA blends is about 0.1 to 0.3 μm, five to ten times smaller than that in the PS/PA blends, due to the influence of the chemical reaction at the interface.

Similar experiments have been pursued with other matrices in order to determine if these observations hold in other blend systems. The morphologies observed at 1.0 min of mixing with matrices of SMA, PETG and PC were qualitatively similar to those observed with the polystyrene matrices.

The maleic anhydride functionality of the SMA reacts with the amine functionality of the amorphous nylon to form an amide or cyclic imide. This has been demonstrated directly through infra-red studies and indirectly through examination of reactive and non-reactive blend morphologies[13]. *Figure 11a* shows a graphic example of the sheeting structures that were observed in an SMA/PA blend. Strand and spherical structures are also shown in *Figure 11b* from a different portion of the sample at a higher magnification. These two micrographs again illustrate the variety of dispersed-phase shapes and sizes that are present in blends at short mixing times. The diameters of the dispersed nylon phase at 7 min of mixing are in the range of 0.1 to 0.3 μm. This is five to ten times smaller than the size of the dispersed phases observed in the non-reactive PS/PA blends due to the chemical reaction at the interface. However, the morphologies here at short mixing times are qualitatively similar to those observed in other non-reactive blends shown in this section. Evidently, the initial mechanism of morphology development is little influenced by the interfacial reaction.

The PETG/PA blend is not expected to be reactive under the processing conditions used here. There is a potential for the formation of a reactive blend in this case because of the ester–amide interchange reaction between the two polymers. However, this interchange reaction is usually only observed in the presence of a catalyst and at substantially higher temperatures than those used here[21,22]. The PETGA/PA blend exhibited structures including sheets with holes and strands (*Figure 12*). Compared to the other systems investigated here, there appeared to be more strand structures in this particular blend. The fracture surface of a blend at 7.0 min of mixing

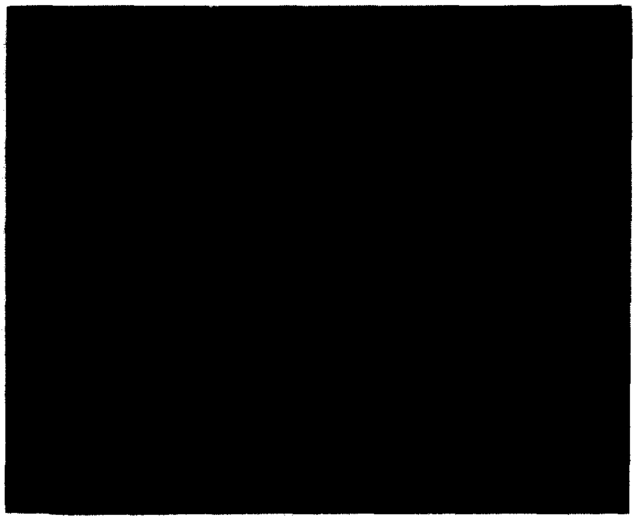

Figure 8 Dispersed-phase particles from PS/PA blend, 7.0 min mixing

Figure 9 Dispersed-phase particles from PS/PA blend, 15.0 min mixing

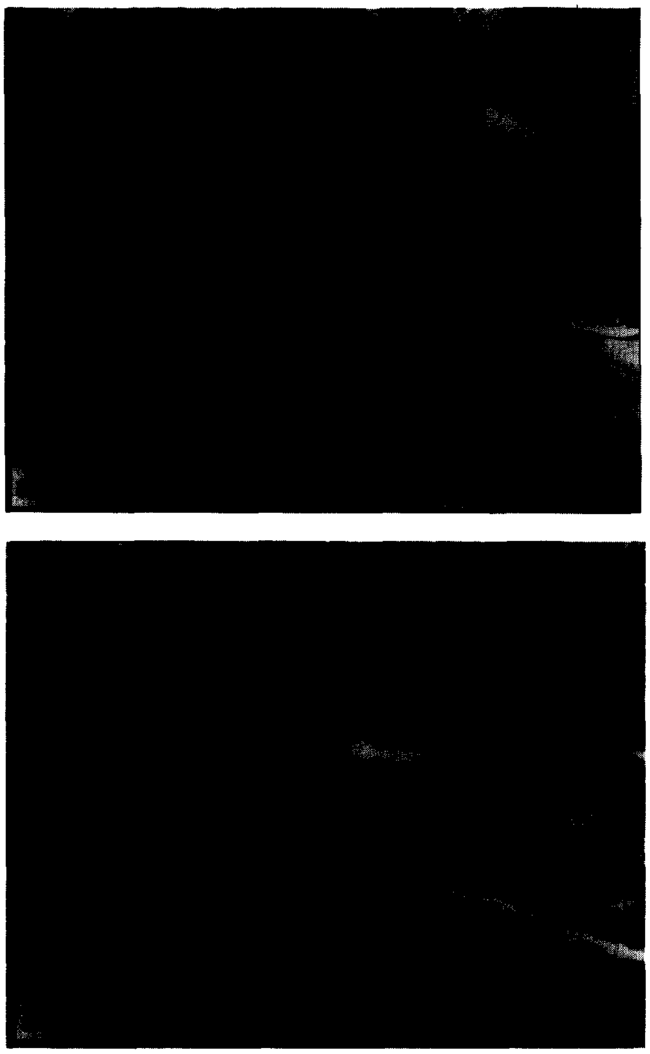

Figure 10 Structure of the PA dispersed phase from a PS-Ox/PA blend, 1.0 min mixing

shows that the particle diameters are in the range of 0.2 to 1 μm. This is about the same diameter as the strands in *Figure 12b*.

Structures in the PC/PA blend at 1.0 min of mixing are shown in *Figure 13*. The holes in the sheets here appear to be somewhat irregularly shaped. The liquid nitrogen fracture surface of the blend at 7.0 min of mixing shows that the diameters of the dispersed phase vary from 0.2 to 0.7 μm. As shown by *Figure 13*, many nearly spherical particles of this size were observed in the blend at 1.0 min of mixing.

PROPOSED MECHANISM OF INITIAL MORPHOLOGY DEVELOPMENT

The model experiments that have been presented show remarkably similar types of structures at short mixing times. Five different matrices have been investigated. In each case, there is clearly a dramatic reduction in the phase size during the melting or softening phase of compounding. This observation is consistent with findings in several other systems[9–17]. Key aspects of the structure of the dispersed phase are shared by all of the model blend systems that were investigated.

On the basis of the observations presented above, the morphologies that are observed at short mixing times suggest an initial mechanism of morphology development which is summarized in *Figure 14*. This mechanism involves the formation of sheets or ribbons of the dispersed phase in the matrix, which are drawn out of a large mass of the dispersed phase. How the sheet or ribbon is formed is not clear. It could be formed and drawn out in the flow field inside the mixer. Such a structure could also form when a large piece of the dispersed phase is dragged across a hot surface, such as the mixer wall, the mixer blade, or a hotter polymer particle in the mixer. Formation of similar sheets has been observed by Sundararaj[23] in two-component molten systems subject to shear. Owing to the effects of flow and interfacial tension these sheets are unstable and holes begin to form in them. The holes are, of course, filled with the matrix phase, which surrounds the sheet on either side. When the holes in the sheet or ribbon attain a sufficient size and concentration a fragile lace structure is formed, which begins to break apart due to flow and interfacial forces into irregularly shaped pieces. These pieces are of approximately the diameter of the particles that are generated in the blend at long mixing times. These irregular pieces continue to break down until all

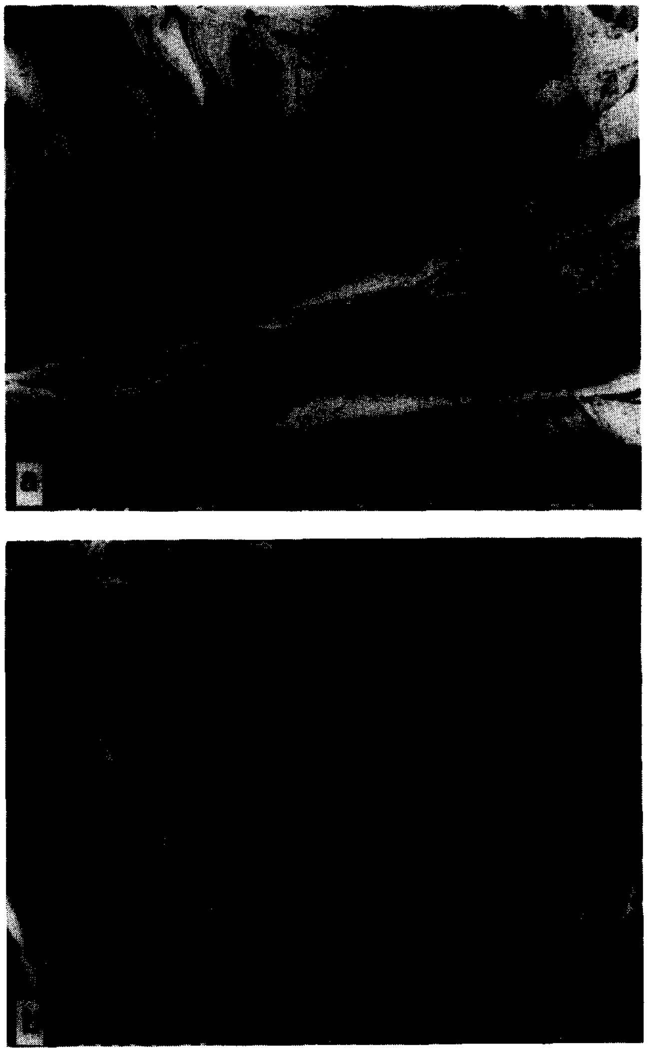

Figure 11 (a) Sheet structures of the PA dispersed phase in a SMA/PA blend, 1.0 min mixing. (b) Strand and ribbon structures of the PA dispersed phase in a SMA/PA blend, 1.0 min mixing

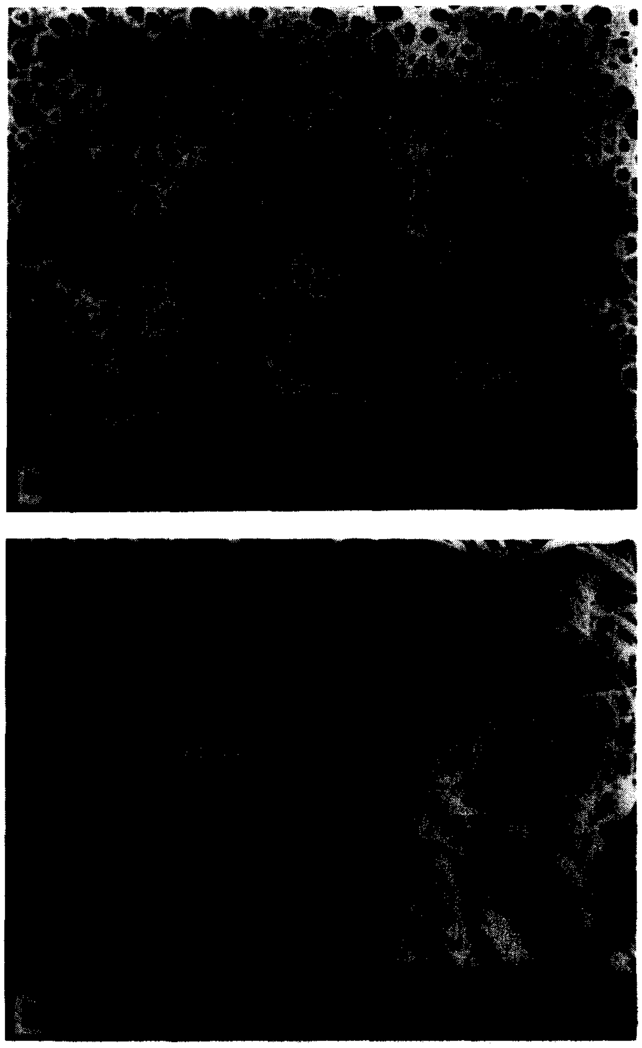

Figure 12 (a) Sheet of PA dispersed phase in PETG/PA blend, 1.0 min mixing. (b) Strands of PA dispersed phase in PETG/PA blend, 1.0 min mixing

of the particles become nearly spherical. *Figures 4* and *12* also indicate that the direct formation of strands or formation of strands from break-up of the sheets during the process may also be important.

This proposed mechanism results in the generation of very small particles at very short timescales. As a piece of dispersed phase undergoes this deformation mechanism, many very small particles may be generated very quickly. As the mixing time proceeds, more and more of the quantity of dispersed phase is cycled through this mechanism.

Of particular interest in this proposed mechanism is the formation of holes in the sheets or ribbons of dispersed phase. It has been speculated here that this has been caused by instabilities due to interfacial tension. However, further investigation is definitely warranted. The time required for quenching the sample may also be critical to formation of holes. Sundararaj[23] identified several systems where sheets were stable under shear but spontaneously developed holes when the shearing was stopped. The rupture of liquid sheets or films has been the focus of many publications[24–30]. Most of these studies have focused on the rupture of sheets or thin films of low-molecular-weight materials that are free-standing (gas on both surfaces), floated on another liquid (gas on one surface, liquid on the other), or on a solid surface (solid on one surface, gas on the other). Application of these results to polymer blends would be tenuous because of the differences in boundary conditions and differences in the relative importance of the material viscosities. Mansour and Chigier[30] investigated the disintegration of liquid sheets issuing from a two-dimensional air-assisted nozzle. They observed the formation of small cell structures, which were bounded by large-diameter ligaments containing thin membranes inside. The appearance of these cells is similar to the holes and lace structure shown in *Figures 4* and *10* except that there is no thin membrane inside of the lace structures observed here. However, the relevance of Mansour and Chigier's work to polymer blends is questionable because their studies were conducted under conditions where air friction and inertial effects were important. Elemans[31] showed the break-up of a small sheet of nylon-6 inside of polypropylene. This sheet broke up by the formation of droplets at the edges rather than by the formation of holes in the middle of the sheet. Qualitatively similar break-up of expanding fluid sheets was observed by Taylor[24].

DISCUSSION

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 solids. As they are heated by conduction and mastication they become deformable solids. The materials are then softened and/or melted to become viscoelastic liquids. The model experiments presented here conclusively demonstrate that the intermediate structures formed during polymer blending may be very complex. The solids conveying and melting processes for the case of a homogeneous material in extruders have been studied extensively[32–34]. However, very little analogous information is available for blend systems.

Owing to the large number of variables involved in these experiments, the time of mixing has been selected in order to analyse and discuss the results. This is somewhat unsatisfactory, since it would be preferable to

Figure 13 Structure of PA dispersed phase in PC/PA blend, 1.0 min mixing

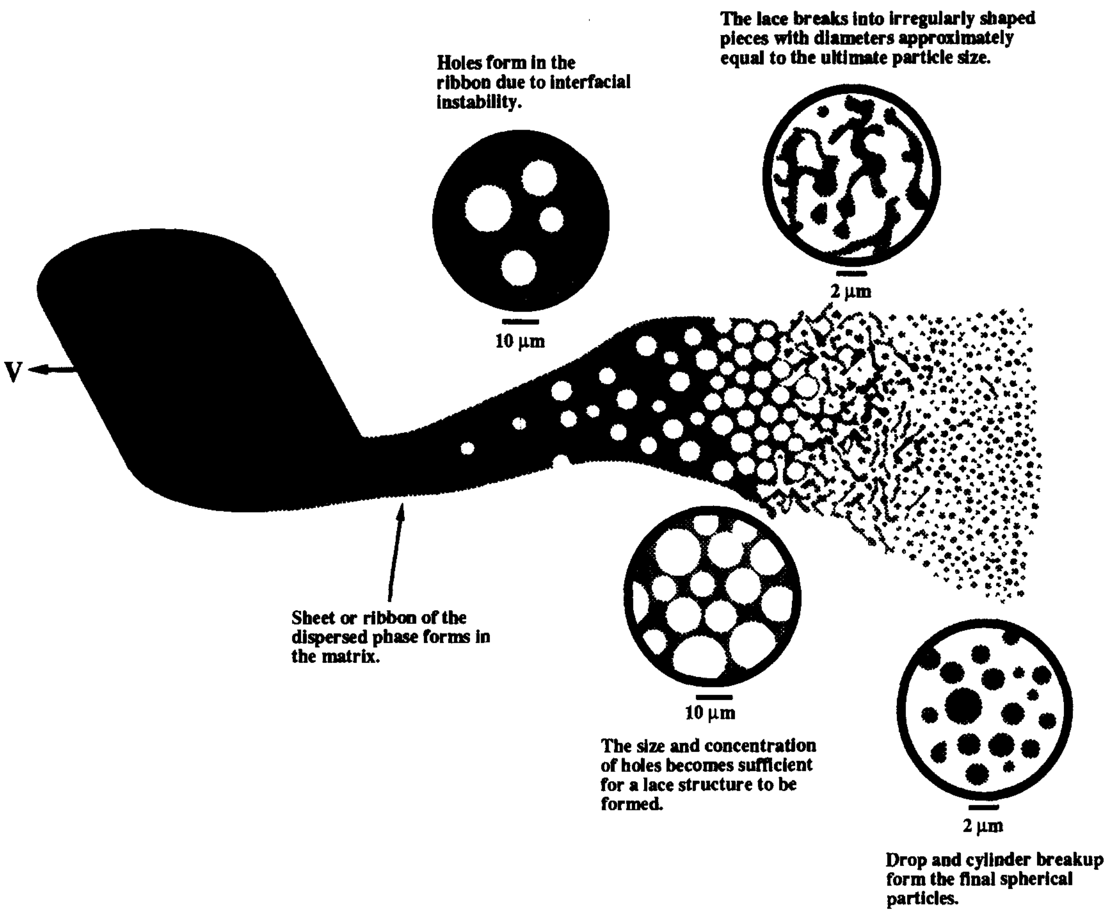

Figure 14 Proposed mechanism for initial morphology development in polymer blends

use parameters such as stress, deformation rate, or total strain, which are more closely related to material deformation processes. However, owing to the complex nature of the flow field in this mixer and the coupling with heat-transfer considerations, the distribution of such parameters throughout the sample is unknown. The time of mixing is the only parameter that is accurately known for every portion of the sample. Experiments utilizing more simple flow fields will be required in order to investigate the effects of the more fundamental parameters.

Heat-transfer considerations are critical in determining the morphology development at short mixing times. There is substantial variation in temperature, stress and strain from one location in the sample to another. Extensive deformation and domain size reduction occur in the regions that have been heated above their softening or melting points and have been exposed to high stresses. Interfacial tension effects become more important as the phase sizes are reduced. In addition, the effects of compatibilizing interfacial reactions will not become significant until large amounts of interfacial area have been created. The SMA/PA system reported in the present work is a fast reacting system. However, it exhibited the same mechanism of morphology development at short times as that observed in similar non-reactive systems.

In the experiments reported here, the solid mixture of pellets was quickly heated in the mixer. The cold pellets have been force fed into a hot mixer. This is intended to model the extrusion process where the pellet mixture is typically fed into a relatively cool feeding zone and then quickly conveyed into a hot barrel zone. As discussed above, localized heating of the sample is a critical component of the mechanism observed here. Thus, different results may be obtained in isothermal studies or with different modes of sample heating. For example, Shih *et al.*[16] have used a much slower heating rate on blends that included a rubbery minor phase. They identified several morphological transformations that occurred under those conditions. Such transformations would be obscured in experiments similar to the present study where heating rates are very fast and localized heating is important.

It is not clear how general the morphologies observed here or the mechanism proposed here may be. The relative softening or melting rates of the blend components could be important. For the materials investigated here, the relative softening rates are probably well described by the glass transition temperatures. As shown in *Table 1*, in the model systems presented here the glass transition temperature of the matrix was varied over a substantial range. Qualitatively, the mechanism of deformation appears to be the same for these blends in which the glass transition temperature of the dispersed phase is higher than or near that of the continuous phase. However, for systems such as dispersion of rubbers in thermoplastic matrices where the glass transition temperature of the minor phase (rubber) is significantly lower than that of the major phase, a phase inversion such as that described by Shih *et al.*[16] is expected to be part of the mechanism. In this case, the minor phase softens first and initially becomes the continuous phase. After melting or softening of the major phase, phase inversion occurs so that the major phase becomes the continuous phase.

The work reported here has only dealt with one dispersed-phase polymer. The type of deformation that occurs early in the melting process may be dependent on the polymer molecular weight and level of crystallinity, among other things. The drawing behaviour of the polymer is a critical element in the proposed mechanism. The rheology of the polymer as a function of temperature and shear may be critical. Unfortunately, the selection of model systems for these particular experiments is constrained by several practical considerations.

The mechanism may also depend on the type of mixer that is used. However, Sundararaj *et al.*[15] have observed the same mechanism of morphology development with a twin-screw extruder. Lindt and Ghosh[17] have also observed sheet formation during blending in a single-screw extruder.

The classic mechanism of drop break-up is certainly important in morphology development. Extensive literature exists concerning this mechanism and excellent reviews are given by Rallison[35,36] and Bentley and Leal[37]. This would occur as an integral part of the mechanism that has been proposed above. It would be expected to grow in importance at intermediate and long mixing times. Consideration of the problem of the break-up of a drop or filament of one fluid inside another has been the topic for a large number of investigations. 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[38–40].

CONCLUSIONS

In order to determine the morphology at short mixing times, model blend systems are investigated, which allow the matrix to be dissolved away so that the dispersed phase may be observed directly using scanning electron microscopy. The dispersed phase for the model experiments is an amorphous nylon. The matrices include polystyrene, an oxazoline functional polystyrene, a styrene–maleic anhydride copolymer, an amorphous copolyester and a polycarbonate. These experiments dramatically reveal the primary modes of particle deformation and the nature of the morphologies at short mixing times. The intermediate morphologies have been demonstrated to be quite complex. The electron micrographs suggest a mechanism for morphology development at short mixing times that is summarized in *Figure 14*. Reduction of phase domain size begins primarily from the formation of a sheet or ribbon of the dispersed phase. Owing to interfacial and flow 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 into nearly spherical particles.

The initial mechanism of morphology development is certainly intimately connected with the melting or softening process. Significant differences in temperature, stress and strain lead to large differences in phase size morphology from location to location within a sample.

These results suggest that compounding equipment and operations may be designed to promote particle size reduction in the melting stage in order to take advantage of the mechamisms outlined here. Understanding the mechanism of morphology development may also have important implications for optimizing the form and order of addition of various components during blending operations.

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