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Model experiments concerning morphology development during the initial stages of polymer blending

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Summary

In order to investigate the mechanisms of morphology development in polymer-polymer blending, a model experiment is developed which allows the matrix to be dissolved away so that the dispersed phase may be observed directly using scanning electron microscopy (SEM). The dispersed phase for the model experiments is an amorphous nylon. The matrix phase is a polystyrene. These model experiments dramatically reveal the primary modes of particle deformation and the nature of the morphologies at short mixing times. The initial mechanism of morphology development involves the dragging of a large particle of the dispersed phase along a hot surface such as the mixer walls. This dragging action results in the formation of sheets or ribbons of the dispersed phase. These sheets or ribbons become unstable due to the effects of shear and interfacial tension. Holes develop in the ribbons which grow in size and concentration until a fragile lace structure is formed. This lace structure breaks into irregularly shaped particles which are then broken up into nearly spherical particles.

Introduction

Morphology development is the evolution of the blend morphology during intensive mixing from pellet or powder size particles to the submicron 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 this morphology evolves are quite limited.

Schreiber and Olguin(1) 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 minutes of mixing. Karger-Kocsis et al.(2) studied blends of several rubbers dispersed in polypropylene. They reported no significant changes in morphology from 5 to 40 minutes of mixing. Plochocki et al.(3) 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(4) investigated the effect of mixing time on the morphology of blends of polypropylene and polycarbonate. The morphology was sampled from 2 to 20 minutes of mixing and there was very little reduction in size of the dispersed phase over the time period investigated. Thus, several authors have concluded that the most significant changes in morphology occurred during the first few minutes of mixing when melting and softening of the materials was also occurring. 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 primary focus of this work is to investigate the mechanism of morphology development during polymer blending. Previous work in the area indicates that most of the particle size reduction occurs in conjunction with the melting or softening process. Therefore,

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samples must be obtained at very short mixing times. 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 introduced into a relatively cold feeding zone and then quickly conveyed into a hotter zone.

Experimental

The nylon (PA) was Zytel 330, provided by the DuPont Company. This material is a partially aromatic amorphous nylon. The polystyrene (PS) was Dow Styron 666D. This is reported to have a melt index of 7.5. Both materials were provided in pellet form. All materials were dried overnight under vacuum at 80°C before the compounding of blends. Other than this, the materials were used a received.

All of the blends were prepared using a Haake Rheomix 600 batch mixer with a Haake System 90 drive. The set point for the three mixing sections was 200°C. Roller blades were employed at 50 rpm and the torque required for mixing was continuously recorded. At this rotor speed, the maximum drag flow (neglecting pressure flow) shear rate in the mixer was 65 sec^{-1}. All of the blends prepared were composed of 20% wt. dispersed 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. This corresponds to 78% of the mixer capacity. The densities were estimated using the data given by van Krevelen(5). Based on the viscosity data obtained for these materials elsewhere(6) the viscosity ratio, $\eta(PA)/\eta(PS)$, at the processing temperature and 65 sec^{-1} is ≈ 14.

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 of the blades leaving most of the blend 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. Mixing times investigated were 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, and 15.0 minutes of mixing. By definition, a time of zero corresponded to the start of feeding of the pellets to the mixer. The time required to feed the entire charge into the mixer averaged 24.5 seconds and varied from 22 to 26 seconds.

The quenched samples from the model systems were placed into special Soxhlet cups described elsewhere(6). These aluminum cups have a Baxter Scientific Products Grade 362 (qualitative) filter paper "window" which allows methylene chloride to dissolve and remove the polystyrene matrix. For samples which were quenched at short mixing times there was essentially one chunk of material left in the aluminum cup after the Soxhlet procedure. This chunk was simply transferred to an SEM stub for inspection. For samples which were quenched at long mixing times, the contents of the aluminum 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. All 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 5kV.

Results

A model system with a nylon dispersed phase was chosen for these experiments to minimize the possibility of artifacts due to sample preparation. The PS matrix used may be dissolved using methylene chloride, which has a boiling point of 40°C. Nylon is very resistant to this solvent. The PA has a glass transition temperature of 136°C (the maximum in tan δ as measured by solid state dynamic mechanical spectroscopy in torsion at 1 Hz).

The morphologies observed at 1.0 minute of mixing in the PS/PA blends are presented in Figure 1. Three large chunks of nylon left after dissolution of the matrix from three pieces of the blend are shown in a low magnification picture in Figure 1a. It appears that 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 which is relatively undeformed and another region which has been greatly deformed during the mixing process. Figure 1b shows a higher magnification picture of the piece in the lower middle of Figure 1a. In the area of extensive

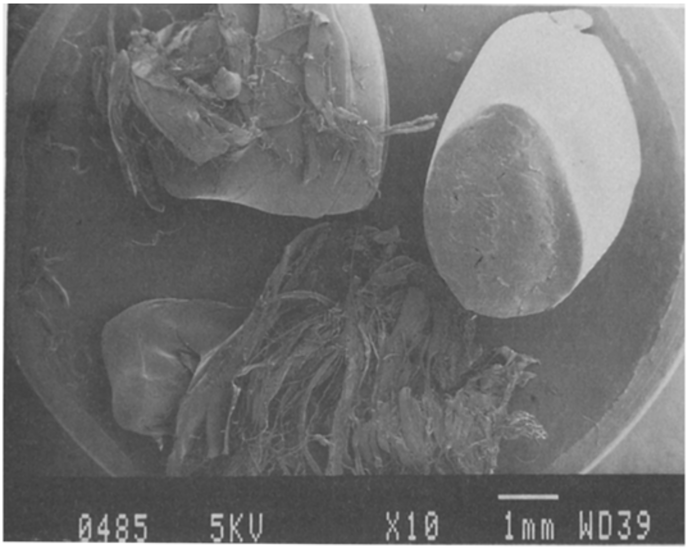

Figure 1a. Low magnification picture of three large pieces of PA after extraction of the PS matix phase. 1.0 minute mixing.

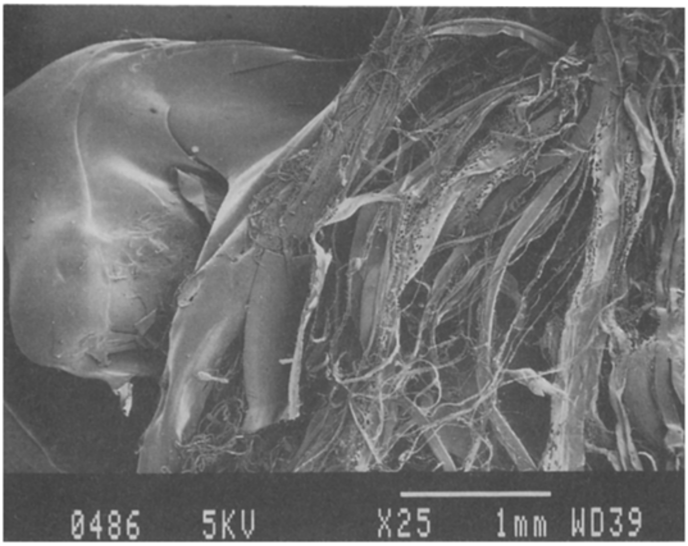

Figure 1b. Closeup of the lower piece in Figure 1a. 1.0 minute mixing.

deformation the material has been stretched out into many ribbons or sheets. Closer examination of these ribbons reveals that many of them have holes which have formed in them. A higher magnification picture of some of these holes is shown in Figure 1c. 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 1c shows evidence of the fragile lace structure breaking up in some regions of the sample. Figure 1d shows a high magnification picture in another 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 μm to 3μm. As shown below in Figure 3, these small spherical particles are the same size as the particles found in the blend at 2.5 to 15.0 minutes of mixing.

The morphologies observed at 1.5 minutes of mixing are presented in Figure 2. There are many irregularly shaped particles which appear to have originated from disintegration of the

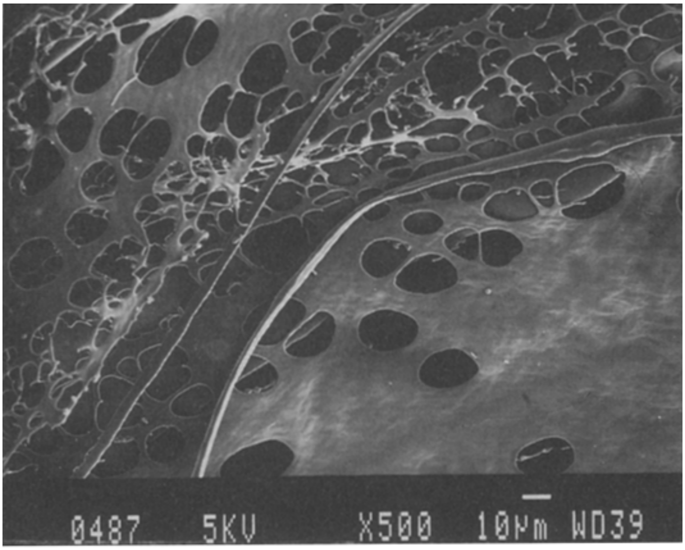

Figure 1c. Holes and lace structure observed in ribbons. 1.0 minute mixing.

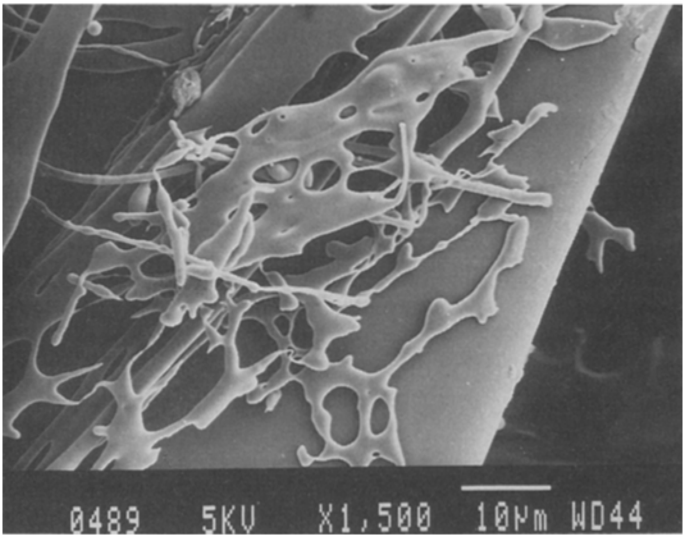

Figure 1d. Broken lace structure and small spherical particles. 1.0 minute mixing.

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 minutes of mixing were very similar. The morphology at t=7 minutes is shown in Figure 3. The pictures look slightly fuzzy because there is a thin layer of polystyrene over the particles. This layer comes from residual dissolved polystyrene left in the methylene chloride suspension. The particles observed at these mixing times are nearly all spherical. A few drop breakup structures may also be observed. The particle diameters range from 0.5 to 3 µm.

The mixing torque and material temperatures as functions of time are presented in Figure 4. The times at which sampling was done are highlighted with arrows. Comparison of the morphology development with the mixing torque and material temperature shown in Figure

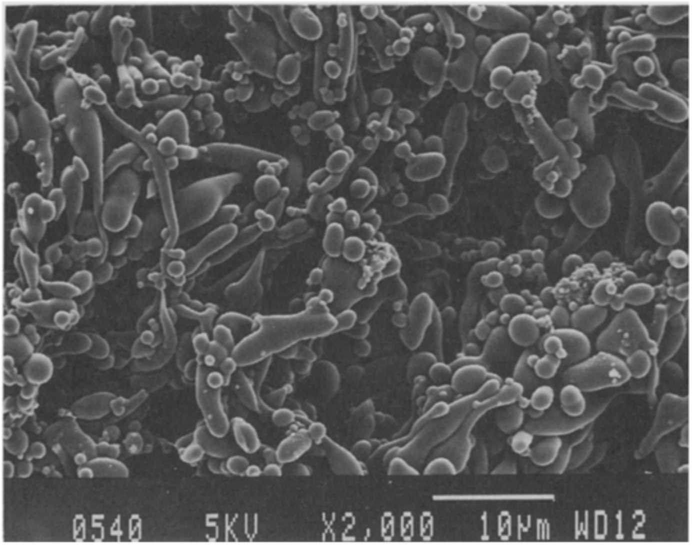

Figure 2. Morphology of the dispersed phase particles at 1.5 minutes mixing.

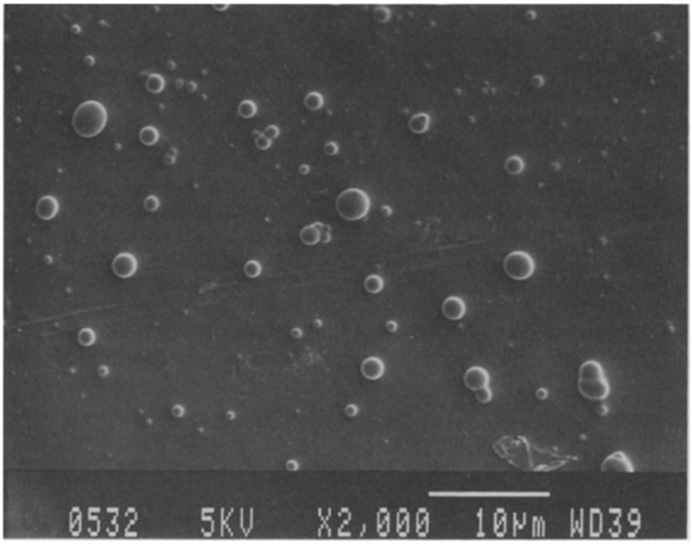

Figure 3. Morphology of the dispersed phase particles at 7.0 minutes mixing.

4 shows that the majority of reduction in the phase size occurs at very short mixing times in conjunction with the softening or melting of the materials.

Discussion

The morphologies which are observed at short mixing times suggest a mechanism of initial morphology development which is summarized in Figure 5. A large piece of the dispersed phase is dragged across a hot surface, such as the mixer wall. This dragging action causes the formation of a large number of sheets or ribbons of the dispersed phase in the matrix. Due to the effects of interfacial tension these sheets are unstable and holes begin to form in them. 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 shearing and interfacial forces into irregularly shaped pieces. These pieces are of approximately the diameter of the particles which are generated in the blend at long mixing times. These irregular pieces continue

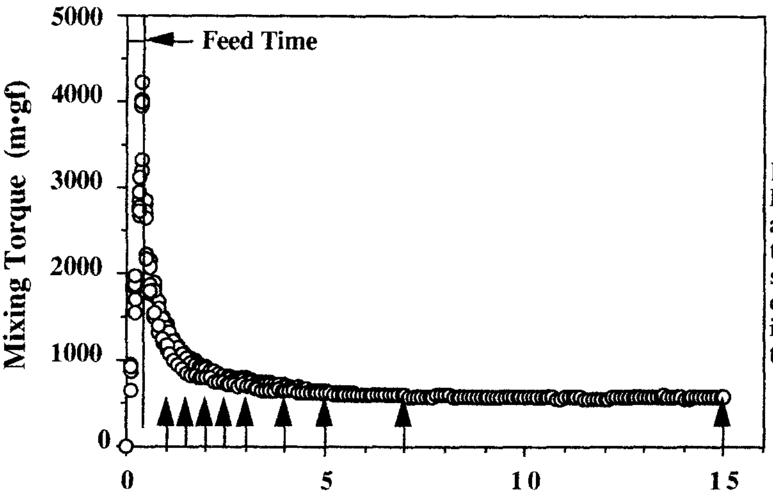

Figure 4a. Mixing torque as a function of time. Data from seven runs are overlaid. Arrows indicate sampling times.

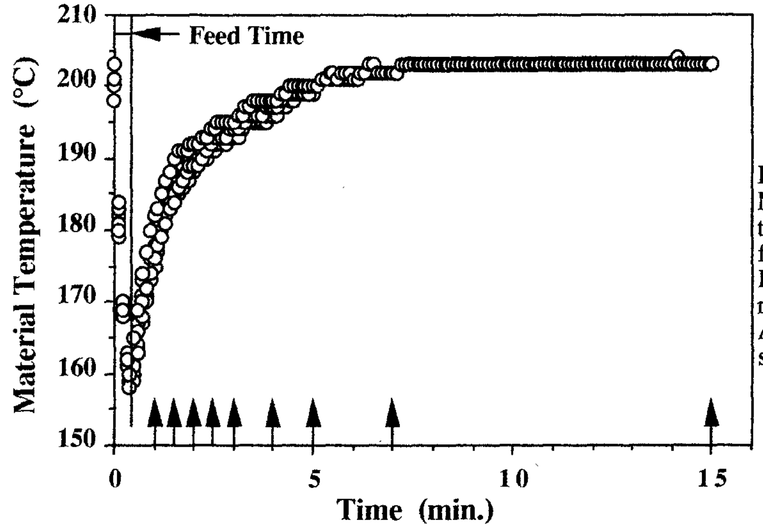

Figure 4b. Material temperature as a function of time. Data from seven runs are overlaid. Arrows indicate sampling times.

to break down under the action of shear and interfacial forces until all of the particles become nearly spherical. The direct formation of strands during the dragging process may also be important.

The proposition of the dragging of material along a hot mixer wall is certainly plausible considering the size of the pellets and the gap between the roller blades and the mixer wall. The minimum gap between the roller blades and the chamber wall is 1.42 mm. The shape of the nylon pellets is nearly cylindrical. The size scale of the pellet dimensions is about 2.6 mm. Therefore, the pellet could be dragged by the rotating blade across the chamber wall, as illustrated in Figure 6. A similar dragging mechanism has been speculated upon previously with respect to blending in an extruder(3).

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. The model experiment presented here conclusively demonstrates that the intermediate structures formed during polymer blending may be very complex. Also, through comparison of the changes in dispersed phase size with the mixing torque and material temperature, it is clear that the mechanism of morphology development must be concerned with the mixing action on soft deformable solids.

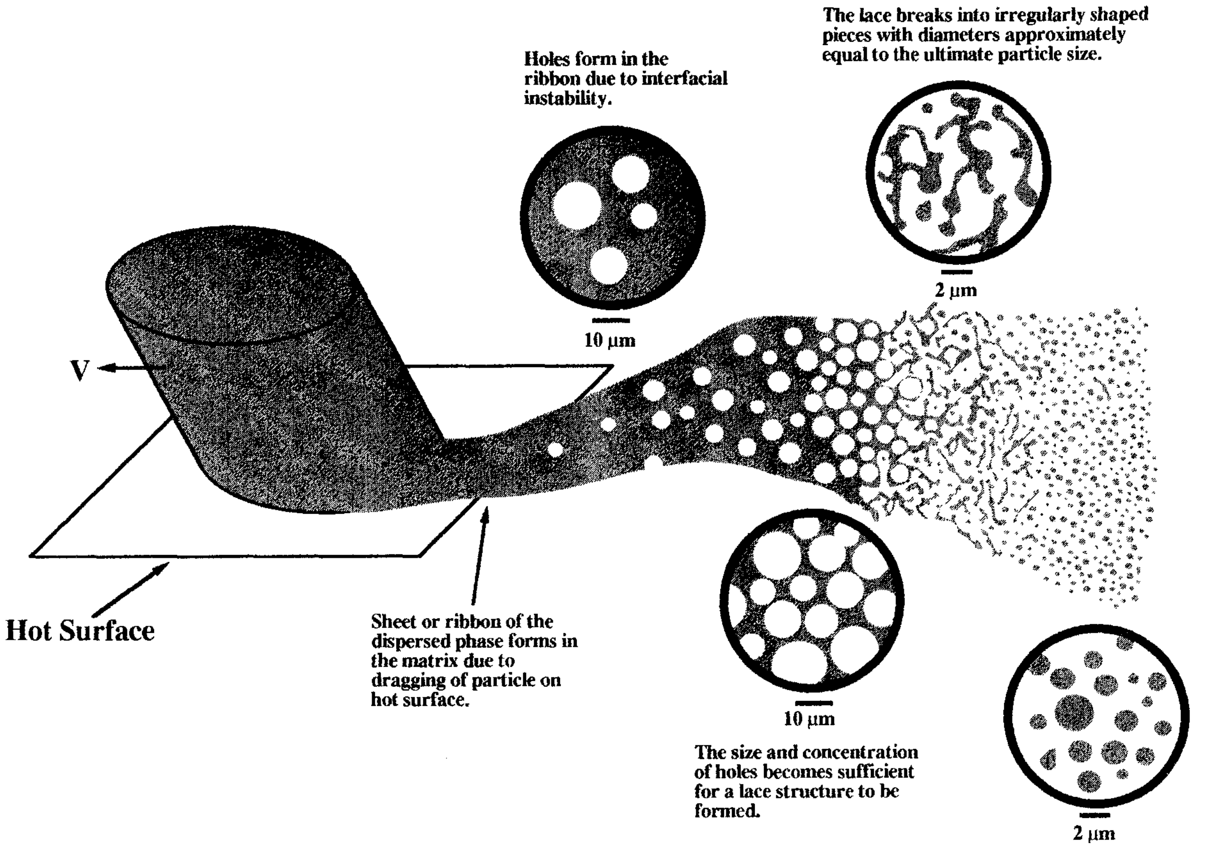

Figure 5. Proposed mechanism for initial morphology development in polymer blends.

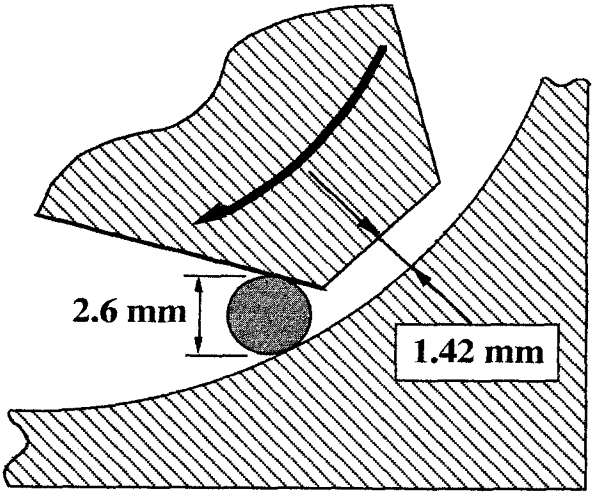

Figure 6. Possible mechanism of dragging a pellet against the chamber wall. (Drawing to scale).

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. The type of deformation which occurs early in the melting process may also be dependent on the polymer molecular weight and level of crystallinity, among other things. However, qualitatively similar results have been obtained on several model systems(6). The mechanism may also depend on the type of mixer which is used.

Conclusions

In order to investigate the mechanisms of morphology development in polymer-polymer blends, a model experiment is developed which allows the matrix to be dissolved away so that the dispersed phase may be observed directly using scanning electron microscopy. The initial mechanism of morphology development is found to be intimately connected with the melting or softening process. The intermediate morphologies have been demonstrated to be quite complex. These model experiments dramatically reveal the primary modes of particle deformation and the nature of the morphologies at short mixing times. The electron micrographs suggest a mechanism for morphology development at short mixing times which is summarized in Figure 5. The dragging of a dispersed phase particle against a hot surface such as the mixer wall causes the formation of a sheet or ribbon of the dispersed phase. Due 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.

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