Development of Morphology in Blends of Immiscible Polymers

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Thermoplastic polymer blends often exhibit different microstructures and hence different properties in different directions. This undesirable anisotropy has its origin in the polymer melt-blending process. Model experiments are presented which reveal part of the underlying physics. The experiments show the process of disintegration of an array of parallel, closely spaced molten polymer threads in a matrix of another molten polymer.

From our experiments, it can be seen that the sinusoidal distortions at the surfaces of two adjacent threads develop in modes which are half a wavelength out of phase. The development of these modes is delayed due to the fact that the distortions of the threads have to fit into one another. Once this fit has been reached, the distortions develop just as fast as in the case of a single thread. The length scale of the mutual influence was observed to decrease with a decreasing viscosity level of the matrix polymer. These findings have the important practical implication that in any given blend system that consists of immiscible polymers anisotropy can be avoided by lowering the viscosity level of the matrix polymer.

Polymer blending means combining immiscible materials that have different melting points and different viscosity levels. Granules of the component polymers are brought together and fed as a dry blend to a screw extruder, in which the material is heated, molten, and mixed. As a result, a high-molecular-weight emulsion is formed in which the major phase generally constitutes the matrix or the connected phase. The minor phase is stretched into long threads which will disintegrate into droplets under the influence of the interfacial tension. The final droplet size distribution will be the result of the interplay between breakup and coalescence processes (Rayleigh, 1878; Taylor, 1934; Tomotika, 1935; Grace, 1982; Elmendorp, 1986; Chesters, 1991; Tjahjadi and Ottino, 1991; Janssen, 1993; Sundararaj, 1994).

This is a fairly accurate representation of the process that takes place during melt-blending of systems with dispersed phase fractions as small as 5 to 10 wt. %. In this case, the molten polymer threads can be regarded as isolated liquid cylinders in a sea of surrounding matrix liquid with no other cylinders present. However, in real blends where the dispersed phase fraction is in the range of between 30 to 50 wt. %, the liquid cylinders can no longer be considered to be isolated from one another. In fact, they close together as shown in Figure 1, where some threads are disintegrating while others have coalesced at certain points. Figure 1 was the basis for our studying the simultaneous breakup of several molten polymer threads which are at a close distance to one another, since this was probably the key to the explanation of the anisotropy phenomenon in polymer blends containing large fractions of dispersed phase.

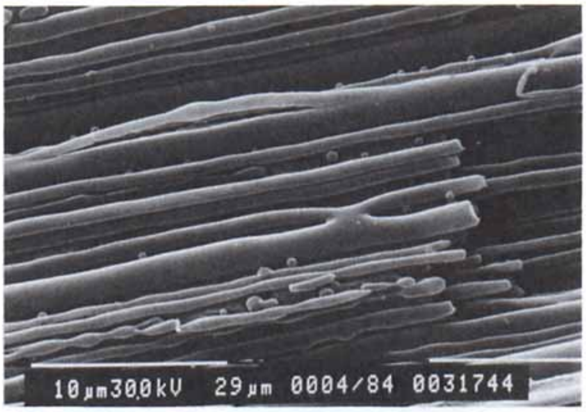

Figure 1. Scanning electron micrograph of the fracture surface, parallel to the direction of extrusion, of the strand of a 45/55 PS/PE blend (Meijer et al., 1990).

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Experimental Studies

As a follow up to earlier work in which the disintegration of one single molten polymer cylinder was studied (Elemans et al., 1990) experiments were performed to study the process of disintegration of an array consisting of several molten nylon 6 threads (BASF Ultramid B3) embedded in a matrix of poly(styrene) (Shell N7000). Threads with a diameter of about 70 micron obtained by melt spinning were carefully wound around an object glass, so that they were close together, parallel, and as evenly spaced as possible. A solution which had

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been prepared by dissolving 8 wt. % poly(styrene) in methyl-ethyl-ketone (MEK) was applied onto the package, and the product was dried under vacuum at ambient temperature for at least one week.

The package was removed from the glass and placed between two poly(styrene) films with a diameter of 10 mm and a thickness of 0.5 mm. The system was enclosed between glass slides and placed under an optical microscope in a Mettler FP52 hot stage, and brought to a temperature of 230°C. At this temperature, the zero shear rate viscosities of the polymers were such that the thread phase was 25 times less viscous than the surrounding matrix phase. During the experiments, the deformation rates associated with the breakup processes were low $(10^{-3}s^{-1})$, so the polymers behaved like Newtonian liquids, and the theoretical background (Tomotika's linear stability analysis of a single Newtonian liquid cylinder in another Newtonian liquid (Tomotika, 1935)) applied.

After these preparatory steps, the disintegration process of a planar array of parallel, closely spaced molten threads could

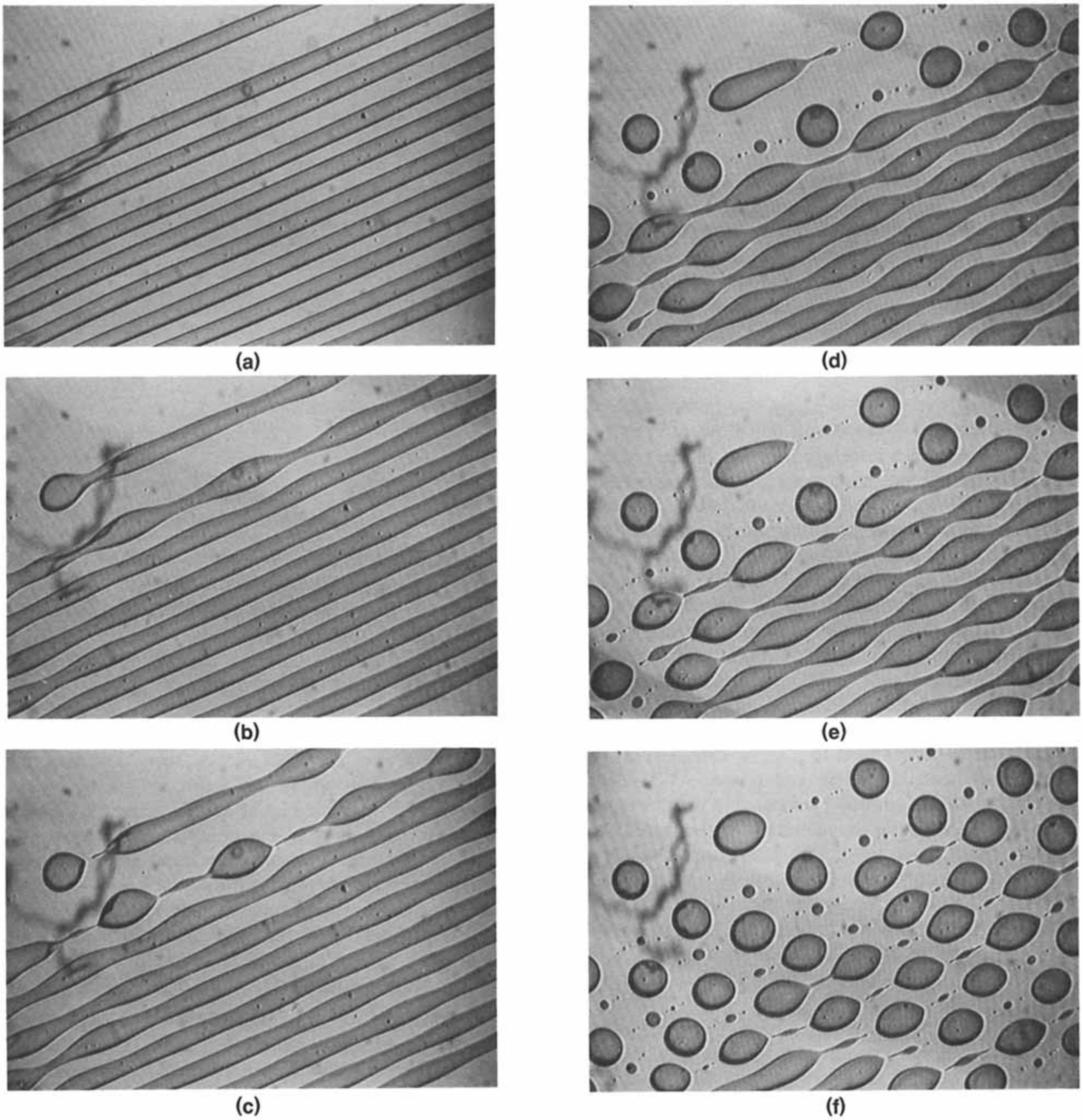

Figure 2. Sinusoidal distortions at the surface of molten nylon-6 threads which are aligned at regular intermediate distances (in one plane) in a poly(styrene) matrix.

The photos represent images on a video monitor screen which were photographed at the following times: $t = 0$, 210, 270, 360, 390 and 510 s. The initial thread diameter was about 70 micron. The measurement was performed at 230°C.

be visualized, as shown in Figure 2. The array essentially consisted of nine parallel threads spaced at the same small distance and one thread which was situated on the outside at twice this distance from the next one. Due to the interfacial tension, this latter thread started to exhibit periodical distortions, followed by the threads on the outside of the equidistant array (Figures 2a to 2c). Satellite and subsatellite droplets were formed at regular positions along a sinusoidally curved line, indicating material displacement in the matrix phase (Figure 2d). Although the viscosity ratio is 0.04 in this case, the number of satellites and subsatellites compares well with results from experiments using a system with viscosity ratio 0.067 (Tjahjadi et al., 1992).

After some delay, the threads within the array started to disintegrate in a symmetrical fashion (Figures 2d to 2e), and the positions of the satellite droplets were located along a straight line (figure 2f). Moreover, the distortions of two adjacent threads developed in modes which were half a wavelength out of phase. A maximum diameter at some point along one thread opposed a minimum diameter along neighboring threads. The wavelength of the distortions at the surfaces of the central threads was smaller than that of the outer threads. This can be understood by considering the system of matrix plus threads as an emulsion whose concentration is proportional to the distance between the threads. The greater the distance between the threads, the more dilute the system is, and the closer its effective viscosity approaches the viscosity of the matrix polymer. It then follows from Tomotika's theory (Tomotika, 1935) that the wavelength of the threads within the array is smaller than that of those outside it.

Note that the satellite droplets formed as a result of the disintegration of the upper thread are on a straight line, indicating that the disintegration process of this thread was not influenced by the other ones.

In another set of experiments in which we employed a much less viscous poly(styrene) as matrix material, the distortions grew faster, as expected (Janssen, 1993) and a mutual influence was observed only when the threads were at very close intermediate distances, which can be understood from the fact that the stress distribution around each thread is transmitted into the matrix over a length scale which depends on the level of viscosity of the matrix polymer.

Conclusions

These somewhat preliminary experiments show that the simultaneous breakup processes of liquid cylinders which are surrounded by others are slightly different from the breakup process of a single liquid cylinder of a comparable diameter. The start of the large-amplitude distortions is delayed for a certain period of time due to the presence of neighboring threads. For the threads to exhibit sinusoidal distortions, the surrounding liquid has to be deformed, but periodic distortions along neighboring threads have to be initiated as well. However, once this accommodation stage has been completed, the growth rate of the distortions is the same for all threads, regardless of their position inside or outside the array, as can be calculated from the photographs.

The process of accommodation can take much time and could be the basis for an explanation for the occurrence of the anisotropy phenomenon in blends of immiscible polymers. At low dispersed-phase fractions, the extended domains are relatively far apart, and their simultaneous disintegration processes are not significantly delayed by each other. At higher dispersed-phase fractions, the interparticle distance between the cylinders gets smaller and smaller until some critical distance is reached (depending on the viscosity of the matrix polymer) where the accommodation process inevitably has to take place, leading to the out-of-phase disintegration.

In the blend system used in the model experiment, the intermediate distance between the cylinders was about 80% of the cylinder diameter, corresponding more or less to a blend system containing a dispersed-phase fraction of about 30%, as calculated from a hexagonal packing of equally sized cylinders.

Therefore, if we made a series of blends consisting of the highly viscous poly(styrene) and nylon-6 as the dispersed phase, we would expect anisotropy at nylon-6 fractions around 30%. This is, of course, an estimate: the domains in such a blend are not hexagonally packed, they are not equally sized, and the viscosities at the temperatures and shear rates in the mixer do not completely correspond to the ones in the model experiment.

The anisotropy could be avoided by switching to a similar blend system which contains a less viscous continuous phase. In that case, the intermediate distance between adjacent molten polymer cylinders is too large for the accommodation process to contribute significantly to the total disintegration time, and the growth rate of the distortions is increased, as can easily be derived from Tomotika's theory (Tomotika, 1935; Janssen, 1993).

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