Particle dimensions in polystyrene/polyethylene blends as a function of their melt viscosity and of the concentration of added graft copolymer

D. Heikens and W. Barentsen*
Eindhoven University of Technology, Eindhoven, The Netherlands
(Received 16 June 1976; revised 27 July 1976)

Apparent particle dimensions in blends of low density polyethylene (PE) and polystyrene (PS) made by mixing in the molten state have been measured and have been shown to depend on the viscosity of the mixed system. At a certain shearing rate small particles of the dispersed polymer are obtained if the polymer in excess has a high viscosity. At a higher concentration however this effect is counteracted completely if the dispersed phase has a low viscosity and thus lowers the overall viscosity. Coalescence is affected in the same way and the size of the particles increases greatly with increasing concentrations. If a highly viscous polymer is dispersed in a low viscosity polymer matrix relatively large particle sizes will be found at the preset shearing rate mentioned above. With increasing concentration of the highly viscous dispersed phase the particle size decreases due to the increasing viscosity. This effect is counteracted by coalescence leading to a relatively slow increase of particle size with concentration. Addition of surfactants such as graft copolymers based on PS and PE leads to smaller particle sizes as expected.

INTRODUCTION

From thermodynamic and diffusion theory point of view molecular dispersion in molten liquid mixtures of polymers can be expected to be the exception rather than the rule.

Upon solidification increasing molecular packing density and crystallization will enhance the tendency for phase separation. Thus most binary blends of thermoplasts are found to be two-phase systems. Often the visible result of this non-molecular mixing is loss of transparancy and gloss of the solid objects obtained. For many purposes this is not a serious drawback as many blends are used because of their mechanical and rheological properties. Non-molecular blends of two polymers combine some of the properties of the pure materials, which cannot be expected to be the case for molecular blends. Thus a blend of poly(vinyl acetate) and polyethylene has a modulus–temperature curve showing contributions from both materials. On the other hand the modulus–temperature curve of the homogeneous ethylene/vinyl acetate random copolymer which can be compared with the hypothetical molecular mixture of the two homopolymers, has its own glass transition region and does not show the contributions of the two homopolymers.

Some mechanical and optical properties of objects made from blends depend on the particle dimensions or in general on the space distribution of both materials in the microphase system. Melt-blended mixtures may show coalescence particularly at greater concentrations of one polymer in another, e.g. at concentrations higher than 15–20%. The objects produced from the melt may show a heterogeneous distribution of particle dimension and of particle shape.

From theory and experiments by Taylor it is known that in mixtures of immiscible liquids, particle dimensions depend on the viscosities of the mixed liquids under mixing conditions and on the interfacial tension. In addition for polymers the condition required to obtain small particle dimensions is supposed to be a high viscosity of the component in excess. Experiments on blends of polyethylene and polystyrene were performed to check this theory for polymeric materials and are described below. It is plausible that conditions to obtain small particles in blending operations will not necessarily produce stable dispersions. Particle dimensions are a function of the magnitude of shearing forces and products made from solid blends, after becoming molten during subsequent processing, may contain particles of dimensions different from those in the original blend.

Experiments are described below which show how particle dimensions can be stabilized by adding compatibilizers. It is moreover found that in the cases studied the presence of a stabilizer also leads to better mechanical properties.

PARTICLE DIMENSIONS IN POLYETHYLENE–POLYSTYRENE BLENDS

All blending techniques have in common the shearing action of polymers in the molten phase (extruders, injection moulding machines, mills). The induced shearing force deforms the dispersed molten polymer into rod-like particles which constrict spontaneously until rupture. A schematic picture of the breaking up of particles under the influence of shear is presented in *Figure 1*. The constrictions are induced by Brownian motion or by local changes in the pattern of the shearing due to changes in the relative positions of the surrounding particles. Size reduction continues till the total force on the particle equals the surface

---

* PC Hooftlaan 28, Hengelo, The Netherlands.

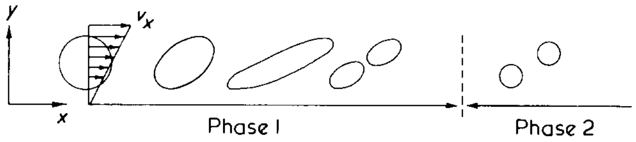

Figure 1 A schematic representation of the disruption of a particle after deformation by shearing forces in a matrix with a shearing rate dv_x/dy. Phase 1, disruption phase; Phase 2, relaxation of the formed particles

tension which is the retracting force in the process.

Taylor has given this process a mathematical treatment[1]. The surrounding material with viscosity η_0 subjected to shearing with a rate dv_x/dy acts on a sphere of radius r and viscosity η_1 with a force:

$$T_\eta = C\frac{dv_x}{dy}\cdot\eta_0 f(\eta_0/\eta_1) \qquad (1)$$

The retracting force resulting from the surface tension can be represented by:

$$T_\gamma = \frac{2\gamma}{r} \qquad (2)$$

If no deformation and rupture occurs then $T_\eta = T_\gamma$ and:

$$r = \frac{C'\gamma}{\eta_0\dfrac{dv_x}{dy}f(\eta_0/\eta_1)} \qquad (3)$$

Experimental evidence on the validity of the relation has been obtained for systems where η_0 and η_1 do not differ very much, the deformation of the sphere is not extremely high and the particle is isolated from other particles[2,3].

The equations explain why smaller particles are formed at higher shearing forces ($\eta_0 dv/dy$) and at lower viscosity of the dispersed polymer (η_1).

Our experiments were carried out with blends of Stamylan 1510 low density polyethylene (ld PE or PE) and general purpose Styron 666, DOW polystyrene (PS). A laboratory blender (Brabender GNF/106/2) at 30 rev/min and 150°C was used. The torque which was recorded is a measure of the overall viscosity. The blends were pressed into plates 3 mm thick.

With the aid of a microtome and a glass knife thin sections were obtained. The section diameters of the particles were estimated from microscopic photomicrographs and were used as a measure for the real particle diameter. The mean diameters and the highest diameters found give an indication about the particle size and the size distribution (*Figure 2*).

At lower concentrations of PE in PS the particle sizes of PE are smaller than the particle sizes of PS at lower concentrations in PE. As in both regions the interfacial surface tension is the same and at this temperature the viscosity of PS is about twice that of PE this result is in general agreement with the formula of Taylor. However at increasing concentrations the sizes of the PE particles are larger than those of PS particles. Increase in size will partly be caused by coalescence at higher concentrations. At the PS matrix side of *Figure 2* however the macroscopic viscosity is decreasing due to the influence of the low viscosity particles of PE. These particles will form semi-continuous microphases at higher concentrations taking up a larger part of the shear strain and diminishing the overall viscosity. Increase in particle dimension from coalescense and from diminishing shearing forces will be the result. At the PE matrix side of *Figure 2* the coalescence will be counteracted by the increase in overall viscosity at higher concentrations of the highly viscous PS particles and only a slight increase in particle diameter will result. The effects described explain the asymmetric diagram of particle dimensions *versus* concentrations if the homopolymers have different viscosity.

STABILIZATION OF POLYMER BLENDS

The results obtained show that a high viscosity of the polymer in excess facilitates the formation of a fine dispersion. If processing conditions are such that during formation of the object the shearing forces are lower than in the blending operation, increase of particle dimensions by coalescence can be expected. Moreover if a difference between the viscosity of the matrix and that of the dispersed phase exists, local differences in overall shearing rate will produce translation of low viscosity material to the regions of higher shearing rate. For example in capillaries low viscosity dispersed phase is transported to the regions near to the wall resulting in inhomogeneous dispersions and an enlargement in average particle dimensions. Thus a high viscosity of the matrix together with a low viscosity of the dispersed phase which is a good condition in the blending operation, may at the same time spoil the blending result during the

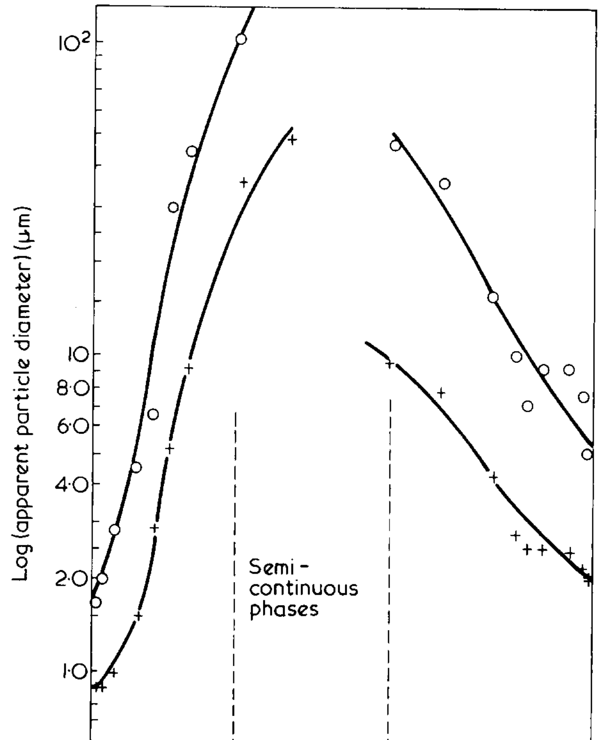

Figure 2 Apparent particle dimensions in PS/ld PE blends made in a Brabender blender at 30 rev/min and 150°C. +, Mean; ○, maximum apparent particle dimensions on a logarithmic scale

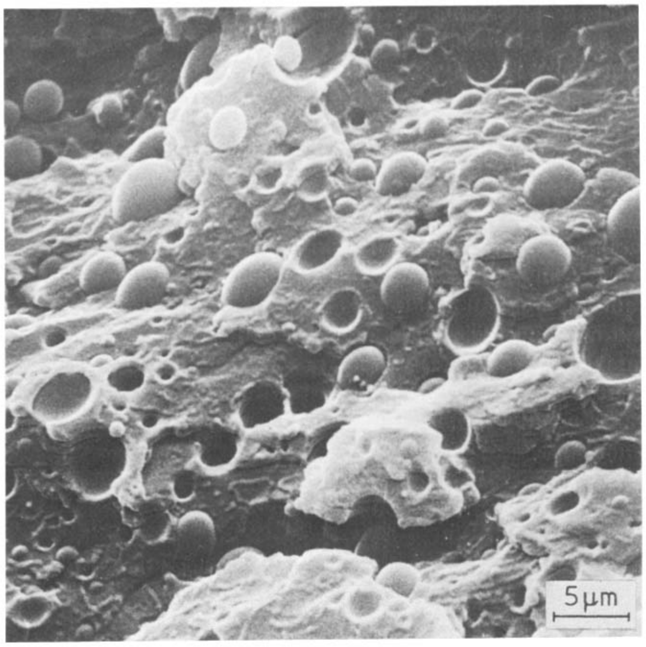

Figure 3 Scanning electron micrograph of a fracture surface of a blend of PS/ld PE90/10 by wt

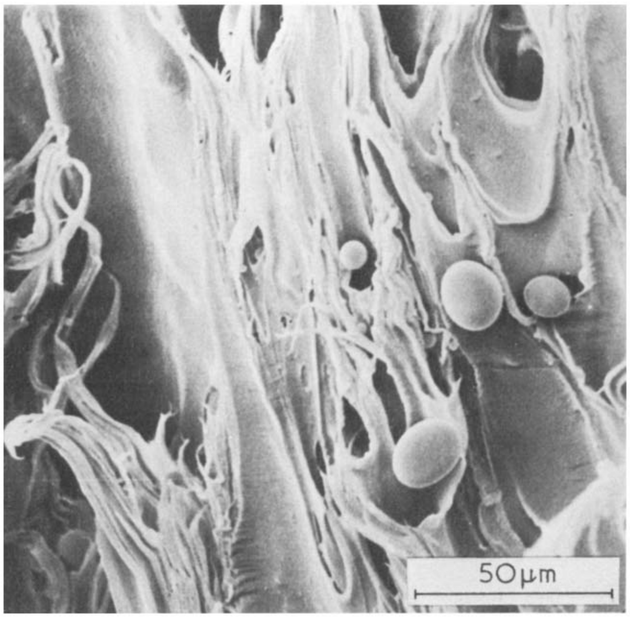

Figure 4 Scanning electron micrograph of a fracture surface of a blend of PS/ld PE 30/70 by wt. Most PS particles are flung away during breaking

processing that may follow. In order to stabilize the blends produced, surface active compounds can be added in the blending operation. In general these compounds diminish surface tension and in accordance with Taylors formula, the minimum particle size. Furthermore if a real interlayer of a certain thickness around the dispersed particles is formed the process of coalescence due to local differences in shearing rate, may be hampered. These two effects thus stabilize preformed dispersions to be processed in a second operation. In our case graft copolymers based on low density polyethylene and polystyrene were chosen as surface active compounds. These materials were prepared by reacting the ld PE with the PS in a cyclohexane solution under the influence of $AlCl_3$ as catalyst. The copolymer was isolated and contained practically equal weight fractions of ethylene and styrene monomeric units. In previous publications it was shown that the copolymer blended with PS and ld PE on a mill was situated at the interfaces of the particles[4,5].

Measurements of these very small particle sizes obtained was not possible under the optical microscope. The sizes were measured therefore with a scanning electron microscope on surfaces of broken strips of blends. The application of this method is restricted to blends with dispersed polyethylene. Surfaces of broken blends with dispersed styrene in excess of PE are distorted. Most PS spheres are flung away during the breaking process, as can be seen by comparing *Figures 3* and *4*.

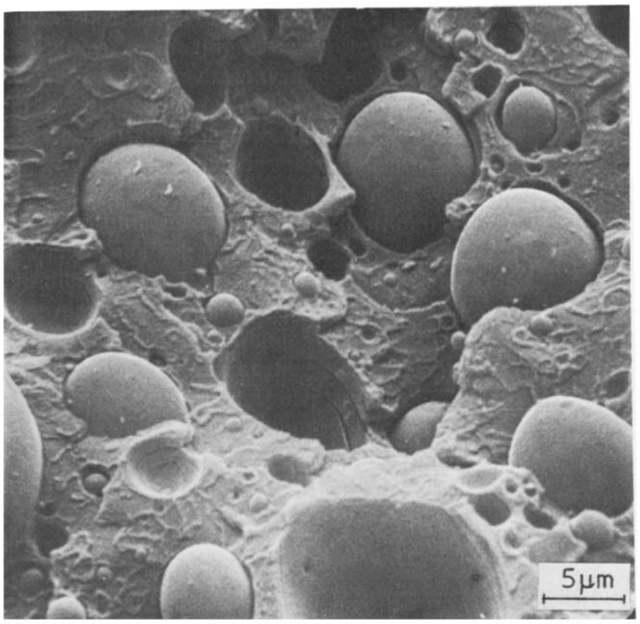

Figure 5 Scanning electron micrograph of a fracture surface of a blend of PS/ld PE 75/25 by wt

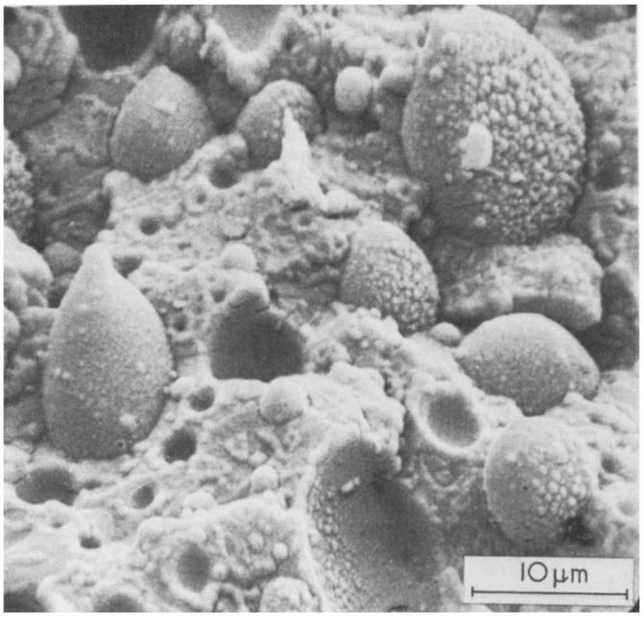

Figure 6 Scanning electron micrograph of a fracture surface of a blend of PS/ld PE/graft copolymer 75/23.75/1.25 by wt. The graft copolymer of PS/ld PE can be seen to be present on the particles of PE and in the half spherical holes from which the particles are pulled out

Table 1 Particle sizes and mechanical properties of ld PE/PS blends with and without added copolymer

Blend	$\bar{d}$ (μm)	Yield stress (kg/cm^2)	Elongation at yield (%)
75% PS +	2.03	163.1	2.2
25% 1d PE	2.06	170.0	2.3
	2.09	164.1	2.2
75% PS +	1.45	200.0	2.6
25% (95% ld PE +	1.48	204.0	3.2
5% copolymer)			
75% PS +	0.78	257.0	2.9
25% (70% ld PE +	0.83	262.0	2.8
30% copolymer)			

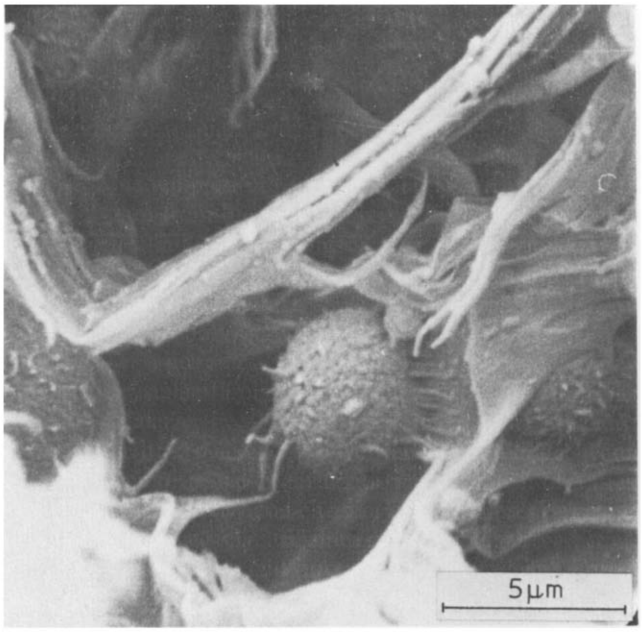

Figure 7 Scanning electron micrograph of a fracture surface of a blend of PS/graft copolymer/ld/graft copolymer PE 17.5/7.5/75 by wt. The particle of PS clearly adheres to the PE matrix. This picture may be compared with *Figure 4* where no copolymer is present

Photographs of several areas of the surface at various magnifications were used to calculate the mean particle diameter *d* and size distribution. This was carried out for blends of 75% PS and 25% 1d PE and for blends of 25% 1d PE in which 5 and 30% of the dispersed 1d PE was replaced by the graft copolymer. From *Table 1* it can be seen that even at low concentrations of graft copolymer the particle size diminishes.

If it is assumed that the graft copolymer is present at the interfaces between the dispersed particles and the matrix, causing a lowering of the surface tension this result is in formal accord with the equation of Taylor (equation 3). On scanning electron micrographs of fracture surfaces the graft copolymer is shown to be present on the dispersed particles and on the surface of the holes from which the particles were pulled during the fracture process. *(Figures 5–7.)*

The addition of copolymer also results in an improved yield stress which may be due to improved adhesion between both pure polymers or the formation of a transition layer or to both effects. Macroscopic peeling off experiments, reveals that the copolymer acts as an adhesive for 1d PE/PS layers[6].

Paul and coworkers also investigated the influence of graft copolymers of PS and PE (prepared by the action of Co^{60} radiation on PE swollen in styrene monomer) on the mechanical properties of PS/PE blends. They found greater elongation and strength values, which were assumed to be a result of better adhesion between the mutually imcompatible polymers PS and PE[7,8].

Generalizing it may be inferred that a high viscosity matrix and a low surface tension will lead to small particle sizes. In our case surface energy was diminished by using a suitable graft copolymer as an emulsifier and still smaller particles resulted. However in the case of a reasonable compatibility as is known for some homopolymer combinations not leading to molecular mixing, or in general, at low concentrations of one of the polymers in the blend the addition of additives may be unnecessary. At higher concentrations addition of a third compound to hamper coalescence will often be necessary. A research program on the influence of copolymer structure on dispersion and on mechanical properties of homopolymer blends is in progress.

REFERENCES

1 Taylor, G. J. *Proc. Roy. Soc. (A)* 1932, **138**, 41

2 Taylor, G. J. *ibid.* 1934, **146**, 501

3 Rumscheidt, F. D. and Mason, S. G. *J. Colloid Sci.* 1961, **16**, 238

4 Barentsen, W. M. and Heikens, D. *Polymer* 1973, **14**, 579

5 Barentsen, W. M., Heikens, D. and Piet, P. *ibid.* 1974, **15**, 119

6 Barentsen, W. M. *Thesis* Eindhoven University of Technology (1972)

7 Locke, C. E. and Paul, D. R. *J. Appl. Polym. Sci.* 1973, **17**, 2597

8 Locke, C. E. and Paul, D. R. *ibid.* 1973, **17**, 2791