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On-line morphology measurement during the extrusion of polymer blends

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A light microscope was coupled to the flat sheet die of a laboratory extruder allowing on-line morphology measurements during the extrusion of polymer blends. Polystyrene (PS)/polymethylmethacrylate (PMMA) blends were studied in the concentration range of 5–20 wt% PMMA. Image analysis of the on-line photographs allows a fast and reliable determination of the particle size distribution devoid of systematic errors that are immanent in the evaluation by transmission electron microscopy (TEM). At higher concentrations the particle dimensions are underestimated by TEM even though the dimensions are corrected for the finite thickness of the ultrathin microtome sections. © 1998 Elsevier Science Ltd. All rights reserved.

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Introduction

Polymer blends offer a favourable route to new materials since the relative simplicity of mixing of existing polymers is an attractive alternative to the complex synthesis of new materials. Blending has an economical advantage for improving mechanical properties like impact strength. Most of the common polymers are incompatible and result in multiphase systems when processed by mixing. The morphology is determined by many variables as the material and process parameters[1]. In the case of two components the minor phase is usually dispersed as spherical inclusions of different size in the major phase. The properties, like the rheological behaviour of multiphase polymer systems, are intimately related to their morphology[2,3]. Commonly, the morphology of extruded blends is measured by transmission electron microscopy (TEM) after cooling the extruded specimens. For this purpose microtome ultrathin cuts are prepared and applied on to copper grids. Generally staining is necessary to obtain a contrast. After all of these procedures, images can be taken and quantitatively analysed by use of an image processing system. We want to show that direct on-line measurements can be realized by combining the die of an extruder with a microscope. It is the aim of this paper to introduce a system that combines the advantages of easy handling and fast analysis.

Experiment

Materials. The molecular weights, the polydispersity index and the viscosity of the commercial polymers PS (BASF) and PMMA (Röhm) prepared by anionic polymerization are given in *Table 1*. Three blends with increasing weight fraction of PMMA (5, 10 and 20 wt%) were studied.

Extrusion. The well pulverized homopolymers were mechanically mixed in a cylinder mixer for 30 min and 5 g of the mixture were given into a hopper of a Randcastle Microtruder RCP MT 0250 with four temperature zones between 200 and 220°C at the die. The specially constructed flat sheet die has an optical window (two plates of Spektrosil B, MGT). The variable diameter of the die was 0.2 mm in the experiments. The rotation speed of the extruder screw of 5 rpm (rotations per minutes) remained constant during the extrusion.

Microscope. The light source (Highlight 3001, Olympus) passed the window of the die perpendicular to the extrusion direction, the microscope being positioned on the opposite side. The long working distance objective (Olympus) allowed a required distance of about 5 mm between the heated die and the objective. The coupling of the microscope with a CCD camera (CF 8/1 DXC, Kappa) and a computer allows fast (20 ms) digital images (software DX control, Kappa) to be taken during the experiment. The analogue signal can be controlled qualitatively by a video monitor, and the extrusion process can be recorded on a video tape. Available software offers the possibility of calibrating the dimensions of the digital images with microscope tools (objective micrometer with 10 μm distance, Möller GmbH) allowing quantitative evaluation of the images.

Transmission electron microscopy. After extrusion the samples were cooled to room temperature. Ultrathin cuts were obtained by a Leica Ultracut-E microtome with a diamond knife and applied on to copper grids. The thickness of the sections were about 60 nm as estimated from interference colours. TEM elastic bright field images were taken on a Zeiss CEM 902, operated at 80 kV with monoenergetic electrons (ESI mode). The morphology of the blends were analysed using the SIS image processing system (Soft Imaging System GmbH).

Results and discussion

Since the viscosity ratio of the homopolymers, as calculated by zero shear viscosity (*Table 1*), is large ($\eta_{0,PMMA}/\eta_{0,PS} = 200$) a morphology of hard PMMA spheres in a soft PS matrix[4] is expected. A photograph of a blend containing 10% PMMA is shown in *Figure 1*. The image is an example of a series of images taken in intervals of 0.5 s

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Table 1 Molar masses M_w, M_n, polydispersity index *PD* and zero shear rate viscosity η_0, $T_{ref} = 180°C$ of the blend components

Polymer	M_w	M_n	$PD = M_w/M_n$	η_0/Pas
PS (BASF)	54 000	51 000	1.05	7.5×10^2
PMMA (Röhm)	53 800	43 200	1.25	1.5×10^5

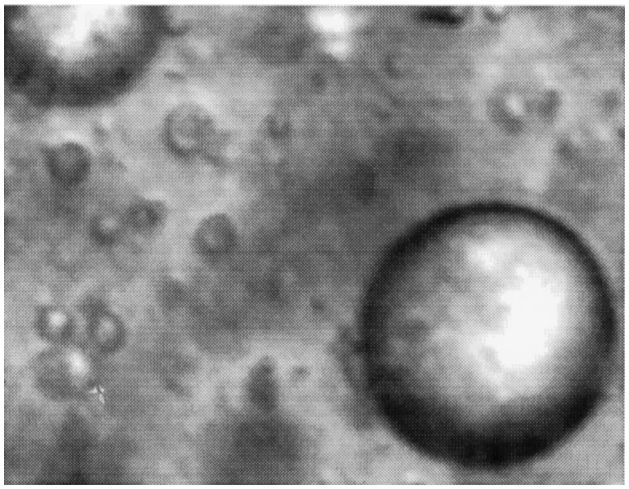

Figure 1 Example of an on-line image of a blend containing 10% PMMA. The dimension of the image is $65.6 \times 50.9\ \mu m^2$

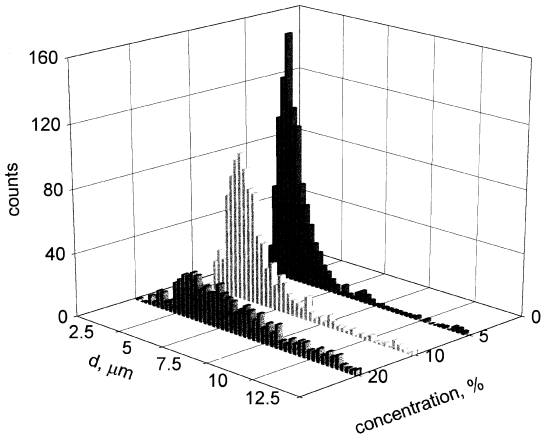

Figure 2 Histograms of the particle size distribution for blends with 5, 10 and 20% PMMA

Table 2 Volume-averaged particle diameters *d* from on-line optical measurements in comparison with diameters obtained by direct evaluation of TEM micrographs and cut-corrected TEM values[5]

Blend	d(on-line)/μm	d(TEM)/μm	$d(TEM_{corr})/\mu m$
5% PMMA	3.27	2.91	3.30
10% PMMA	4.67	3.25	3.97
20% PMMA	7.87	5.62	6.36

during the extrusion. In all cases ideal undeformed PMMA spheres were found. The poor sharpness of the images is caused by the motion of particles getting out of focus or by the turbidity of the blends due to the strong refractive index difference of the polymers. The quantitative analysis of the sphere dimensions is not affected, because unsharp particles were not considered. From each blend up to 150 representative images were taken and about 1000 sharp

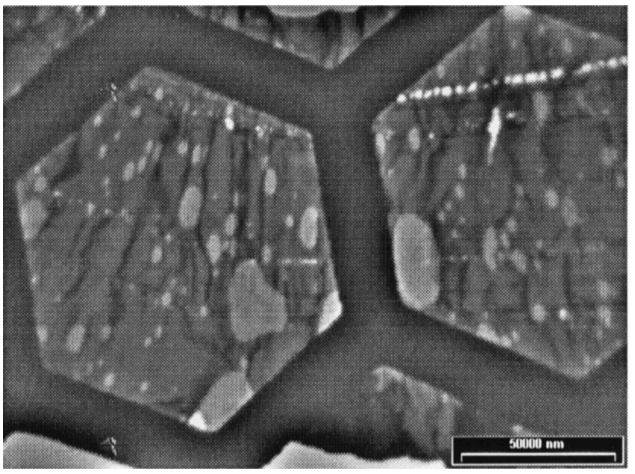

Figure 3 TEM image showing a blend morphology (20% PMMA) and the copper grid

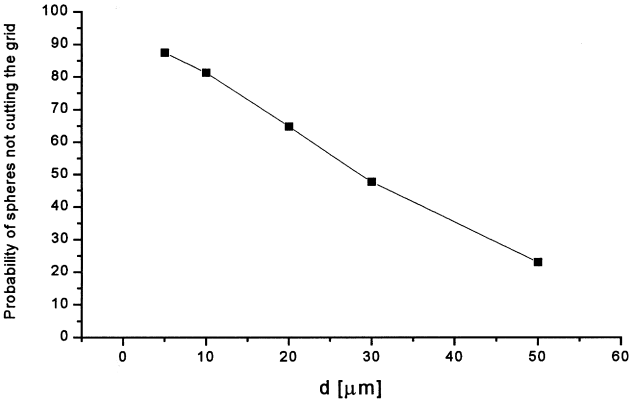

Figure 4 Probability *p* of spheres not cutting the grid independent of the particle diameter

particles were analysed to get good statistics of the particle diameter without further data treatment. The sphere size distribution of the different blends are shown in *Figure 2*, and the volume-averaged diameters are given in *Table 2* in comparison to the diameters obtained from TEM measurements. The diameters from TEM are cut-corrected values which were obtained from the apparent observed diameters by a regularization method[5]. Because of the cutting process the spheres are deformed to ellipsoids. The problem is solved by the software, which calculates the equivalent circle diameter.

An additional difficulty in the TEM analysis arises because of the large polydispersity of the particle dimensions which excludes an easy and fast image analysis. For this reason only 250 particles of each blend could be counted. The results given in *Table 2* show an excellent agreement for the 5% PMMA blend. At higher concentrations the average diameters determined by TEM are smaller than the diameters evaluated from the optical on-line measurements. The effect could be caused by the light microscope, where particles with diameters smaller than 800 nm are not visible. However, since only a few particles of this size were found by TEM, the deviation between both methods must have another reason. In order to explain the problems of the TEM analysis a TEM image at small magnification is shown in *Figure 3*.

Obviously the large particles are strongly deformed, and with increasing area of the particles the probability

increases that they cut the copper grid that occupies 33.6% of the total area. Deformed particles that are only partly visible cannot be counted. *Figure 4* shows the result of a simple statistical calculation. With increasing size of the spheres the probability that particles are not hidden by the grid or are overlapping decreases strongly. Apparently the number of larger particles is underestimated by TEM. For this reason on-line measurements with light microscopy give more reliable results than TEM in the range of particle sizes that are accessible by the optical microscope.

The morphology of the blends can also be measured by light microscopy in an off-line experiment after cooling the blend to room temperature. The advantage is that the static sample can be observed in different depths. The sharpness of the images is improved because the particles are not moving and can be focused more precisely. In comparison with the on-line experiment no changes in the dimensions of the PMMA particles were observed. Therefore, the off-line experiment demonstrates that deformation of the particles observed by TEM is caused by the microtome cutting. This has to be taken into account when blends with a lower viscosity ratio are analysed where the particles may be deformed[6]. In an a posteriori TEM analysis the effect of the secondary deformation by the microtome cutting cannot be distinguished from the deformation in the shear flow of the die. Only on-line measurements afford information about shear-induced deformations.

Conclusion

We have shown that the combination of an extruder with a microscope can be a powerful alternative to the common use of TEM to characterize the morphology of polymer blends resulting from the extrusion process. The resolution of the light microscope, the turbidity of the samples, and the accessible flow velocities will limit the application of the method. We are presently testing these limits by varying the processing parameters and by extending the concentration range of the blends.

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References

1. MacDonald, W. A., *TRIP*, 1995, **3**, 212.
2. Utracki, L. A., *J. Rheol.*, 1991, **8**, 35.
3. Utracki, L. A., *Polym. Networks Blends*, 1991, **1**, 69.
4. Wu, S., *Polym. Eng. Sci.*, 1987, **27**, 335.
5. Friedrich, Chr., Gleinser, W., Korat, E., Maier, D. and Weese, J., *J. Appl. Polym. Sci.*, 1994, **53**, 39.
6. Sundararaj, U., Makosco, C. W., Nakayama, A. and Inoue, T., *Polym. Eng. Sci.*, 1995, **35**, 100.