Confocal laser scanning microscopy: a new method for determination of the morphology of polymer blends

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The use of confocal laser scanning microscopy (CLSM) as a new technique for the determination of the morphology of polymer blends is described. With this technique it is possible to obtain three-dimensional images of the morphology of the blends. An advantage of CLSM, compared to optical and electron microscopy techniques, is that the samples do not have to be prepared. As an example, the morphology of blends consisting of a styrene(ethylene/butylene)styrene (SEBS) block copolymer and a poly(ether ester) as obtained with CLSM is shown to compare well with that obtained by scanning electron microscopy.

(Keywords: confocal laser scanning microscopy; polymer blends; morphology)

Introduction

Blending of two polymers usually results in a heterogeneous mixture, as a result of thermodynamics. Several morphologies can be obtained for the resulting two-phase blend: a dispersed phase/matrix morphology in which the dispersed phase can be spherical, fibrous or lamellar, and a cocontinuous morphology in which both phases are continuous. The type of morphology formed is dependent on the viscosity and elasticity of the blend components at the shear rate and temperature of blending and the interfacial tension between the components. In addition to the processing method and conditions, the morphology is strongly dependent on the volume fractions of the components[1].

Optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are normally used to obtain images of the morphology of polymer blends. Although these are useful methods they possess some drawbacks. The usefulness of optical microscopy is limited by the magnifications that can be obtained. With SEM, and particularly TEM, the preparation of the samples usually causes problems. Moreover, to get good contrast, staining methods have to be applied which could give rise to artefacts. In addition, these methods are destructive methods, i.e. the material has to be broken or cut before the morphology can be examined. Furthermore the electron microscopy methods are time consuming (particularly TEM). Finally, to obtain a three-dimensional picture of the morphology of the blends many different samples are required for these techniques.

A new, non-destructive method for the determination of the morphology of polymer blends is confocal laser scanning microscopy (CLSM)[2]. In confocal microscopy, the object is scanned by the coinciding focal points (confocal) of a point light source and a point detector, both focused on a certain plane in the object. Only light coming from the focal point is detected and, even more important, out-of-focus light is rejected. *Figure 1* shows the principle of the confocal microscope. Because of the strong depth discriminating properties of this technique, images are so-called optical sections, which can be used to study the sample in three dimensions. Because of the inherent high contrast of the images, preparation of the samples is often very simple and takes a very short time. As a result, this method can be used as a very quick and reliable tool for characterization of the morphology of polymer blends. As reported by Thomason and Knoester[3], this method is also applicable for studying the fibre–matrix interfaces in fibre-filled polymers.

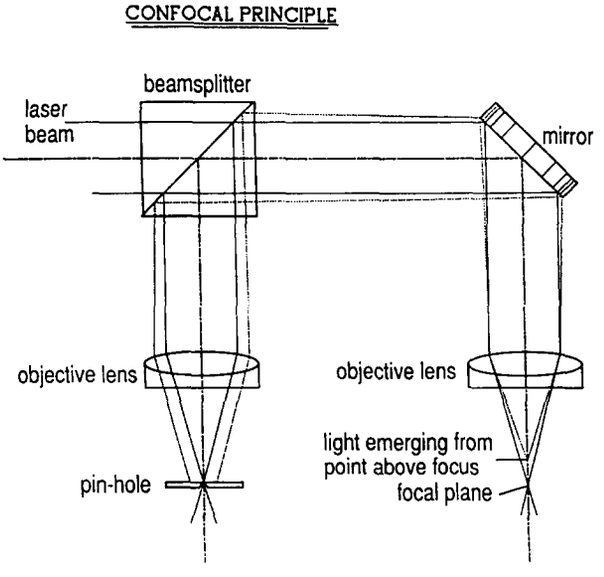

Figure 1 Principle of the confocal reflection microscope with a laser light source (reprinted from reference 2)

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This paper reports the use of CLSM for the determination of the morphology of blends consisting of two thermoplastic elastomers, a styrene(ethylene/butylene)styrene (SEBS) block copolymer and a poly(ether ester). The results obtained with this method are compared with those obtained from SEM micrographs of fracture surfaces of the blends and of the blends from which the SEBS block copolymer is extracted.

Experimental

The polymers used in this study were Kraton G1657X, supplied by Shell, and Arnitel EM400, provided by Akzo. Kraton G1657X is a thermoplastic elastomer consisting of block segments of styrene (S) units and rubber (ethylene/butylene, EB) units. The ratio of S to EB is 13/87 and the polymer is composed of 70% triblock copolymer S-EB-S and 30% diblock copolymer S-EB. Arnitel EM400 is a semicrystalline poly(ether ester), built up of 40% poly(butylene terephthalate) as the hard, crystalline segments and poly(oxytetramethylene)terephthalate as the soft segments.

Blends were prepared by mixing these polymers on a two-roll mill at a temperature of 200°C and a shear rate of 266 s^{-1}. The compositions of the Kraton/Arnitel blends reported in this paper were 20/80 and 50/50, based on volume fractions. After a blending time of 7 min the blend was scraped off the mill and either (1) quenched in water at room temperature; or (2) pressed into a sheet with a platen press at 200°C. After pressing times of 0.5–1 min the sheet was quenched in water at room temperature.

More information about the preparation of the blends and the rheological, thermal and morphological properties is reported elsewhere[4,5].

Information about the morphology of both types of blends was obtained by selective extraction of the SEBS polymer and from SEM micrographs. Extraction of the SEBS polymer was performed with diethylether at room temperature; the extraction time was 18 days.

A Jeol JSM 35 scanning electron microscope was used to obtain the micrographs. Samples of the fracture surfaces of the blends were prepared, broken in liquid nitrogen. Some samples were prepared of blends from which the SEBS polymer was extracted after cryogenic fracture. The samples were coated with gold in an Edwards Sputtercoater S150B.

A video-rate confocal laser scanning microscope CLSM (prototype of the Odyssey produced by Noran Instruments) was used to determine the morphology of the directly quenched and the pressed blends. Blends were examined in the reflection mode at 488 nm with a 1.25 NA oil immersion objective. The polarization of illumination and detection beams were crossed to prevent strong reflections from interfaces between the two polymer phases reaching the detector. The images were video-recorded, starting from the surface up to a depth of 50 μm. Playing back these tapes gives an excellent view of the morphology of the blends. Image processing of the

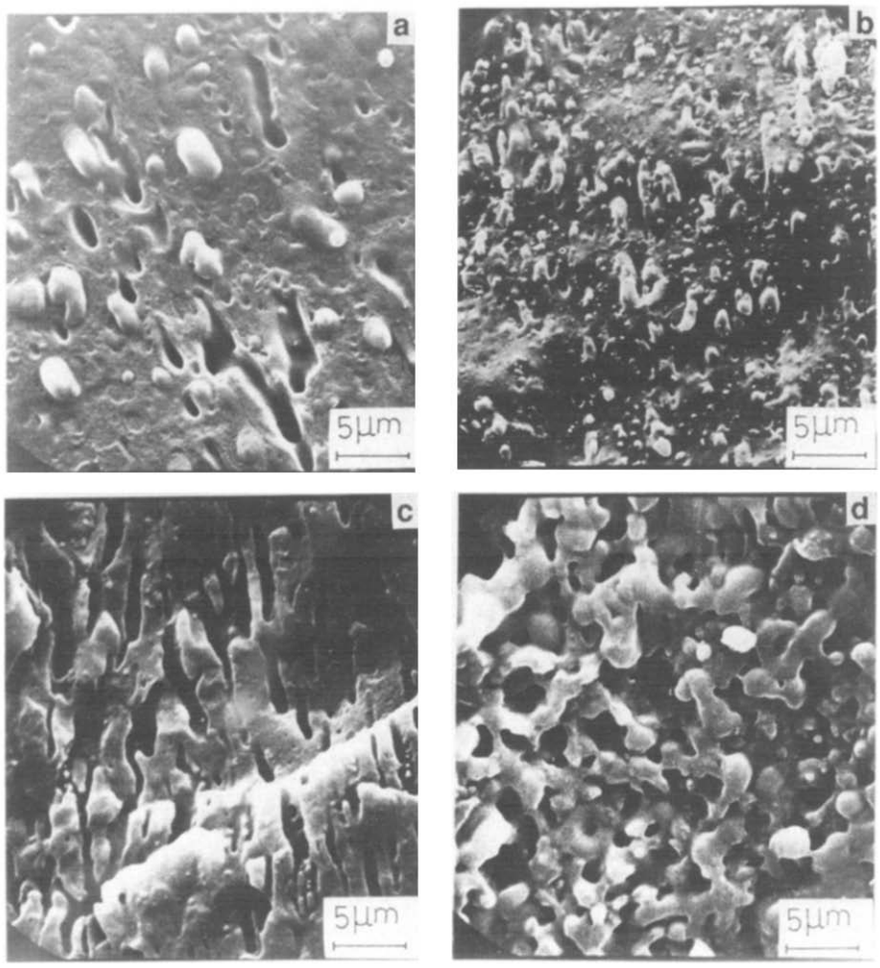

Figure 2 SEM micrographs of the directly quenched SEBS/poly(ether ester) blends with the compositions 20/80 (a, c) and 50/50 (b, d). (a, b) Fracture surfaces; (c, d) fracture surfaces of the extracted blends

video images was performed using the Application Visualization System 3.0 (AVS 3.0) developed by Stardent Computers Inc.

Results

If 90–100% of a polymer can be extracted from a blend it can be concluded that this polymer forms a continuous phase in the blend. When the geometry of the remaining polymer does not change during the extraction, the morphology of the blend must be cocontinuous. *Table 1* reports the percentages of SEBS extracted with diethylether. According to the extraction results, the SEBS polymer forms a continuous phase in the directly quenched blend containing 20 vol% SEBS and in the blends containing 50 vol% SEBS. Because the remaining Arnitel phase is still continuous after the extraction of SEBS, these blends must be cocontinuous. From *Table 1* it can be seen that pressing of the blends changes the continuity of the SEBS polymer in the blend containing 20 vol% Kraton. The geometry of the Arnitel phase does not change during the extraction so this material forms the continuous matrix.

Table 1 Percentage of SEBS extracted from the blends with diethylether

SEBS (vol%)	Directly quenched	Pressed
20	103	67
50	100	107

Figure 2 shows SEM micrographs of the directly quenched SEBS/poly(ether ester) blends with compositions 20/80 and 50/50. *Figures 2a* and *b* show the morphology of the fracture surfaces of the blends; *Figures 2c* and *d* show the morphology of the blends after the extraction of SEBS. It can be concluded that directly after blending on the two-roll mill, the SEBS polymer is already continuous at 20 vol%. As expected, the blend containing 50 vol% Kraton is cocontinuous.

Figure 3 shows SEM micrographs of the pressed blends. Pressing of the blend containing 20 vol% SEBS results in a decrease of the continuity of the SEBS polymer, as confirmed by the extraction result, since only about 70% of the SEBS present is extracted. As expected, a cocontinuous morphology is again found for the blend with the 50/50 composition. In this blend only a limited degree of phase-coarsening occurred during the pressing process.

With CLSM it is possible to obtain micrographs of the structure at different levels, starting from the surface to a maximum depth of 50 μm (for the blends described here). As an example, *Figure 4* shows some photographs of the morphology of the directly quenched and the pressed blends at 10 and 20 μm depth. In common with SEM micrographs, these pictures only give some indication of the structure. For instance, from *Figures 4c*,

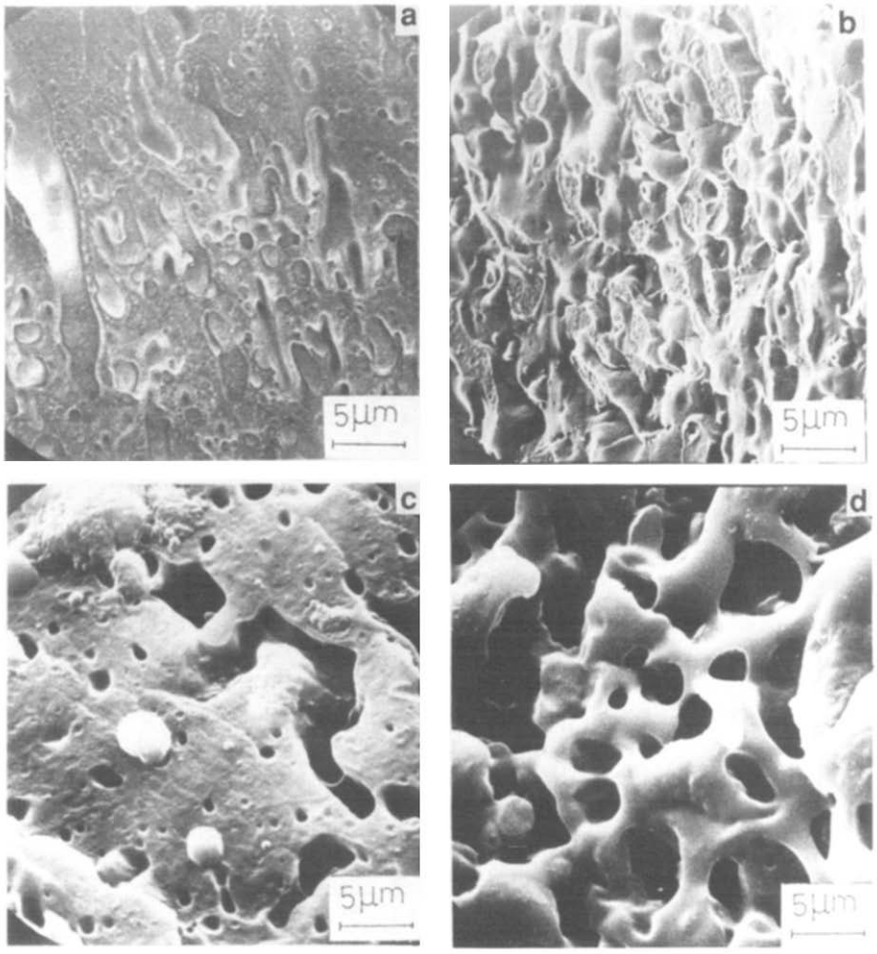

Figure 3 SEM micrographs of the pressed SEBS/poly(ether ester) blends with the compositions 20/80 (a, c) and 50/50 (b, d). (a, b) Fracture surfaces; (c, d) fracture surfaces of the extracted blends

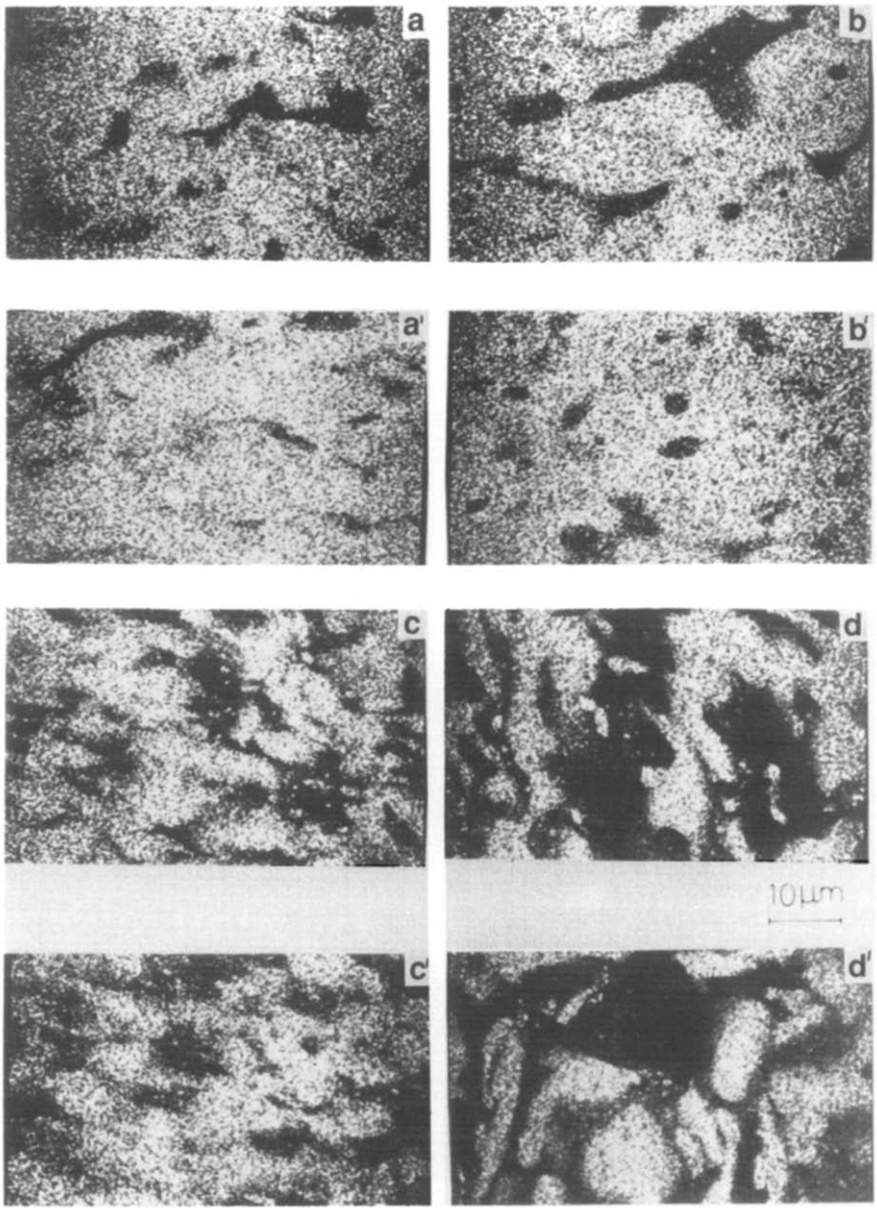

Figure 4 Micrographs obtained with CLSM of the SEBS/poly(ether ester) blends: (a, a') 20/80 composition, directly quenched; (b, b') 20/80 composition, pressed; (c, c') 50/50 composition, directly quenched; (d, d') 50/50 composition, pressed. (a–d) Morphology at a depth of 10 μm; (a'–d') morphology at a depth of 20 μm

c', *d* and *d'* it can be concluded that it is likely that both types of blend containing 50 vol% SEBS possess dual-phase continuity.

By recording the images of the morphology with a video recorder while moving from the surface to a depth of 50 μm, an impression of the three-dimensional structure of the blends is obtained. From the recordings it becomes clear that the directly quenched blend with 20 vol% SEBS possesses dual-phase continuity while the pressed blend containing 20 vol% SEBS consists of a dispersed SEBS phase in a poly(ether ester) matrix. The video recordings also confirm that both types of 50/50 blend possess dual-phase continuity. These results agree with those obtained from extraction experiments and SEM.

A true three-dimensional picture of the morphology of the blends was obtained by computer-aided image-processing of the CLSM recordings as a function of the depth in the sample. With the aid of the Application Visualization System 3.0 (AVS 3.0) it was possible to process the video images into a form suitable for reproduction. Examples of the result of this processing are given in *Figures 5* and *6*. *Figure 5* shows the interface between the Arnitel and the Kraton polymer in a 50/50 pressed blend. It can be clearly seen that this blend indeed has a cocontinuous morphology. From *Figure 6* the geometry of the SEBS in the 20/80 blend can clearly be inferred from the interface between the two components: SEBS forms loose, continuous parts that are oriented into the direction of deformation. This blend does not show three-dimensional dual-phase continuity.

Figures 5 and *6* clearly demonstrate the unique advantages of CLSM over other imaging techniques such as SEM and TEM:

1. processed CLSM images give a direct, fully three-dimensional picture of the blend morphologies;

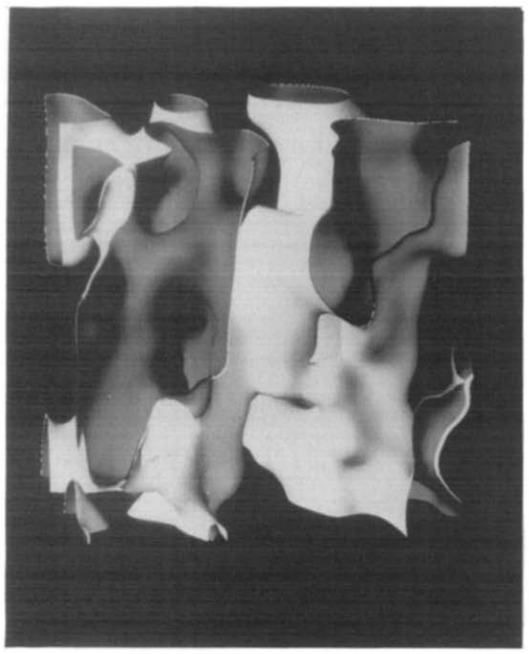

Figure 5 Three-dimensional reconstruction of the interface between the Arnitel polymer and the SEBS polymer in the 50/50 pressed blend

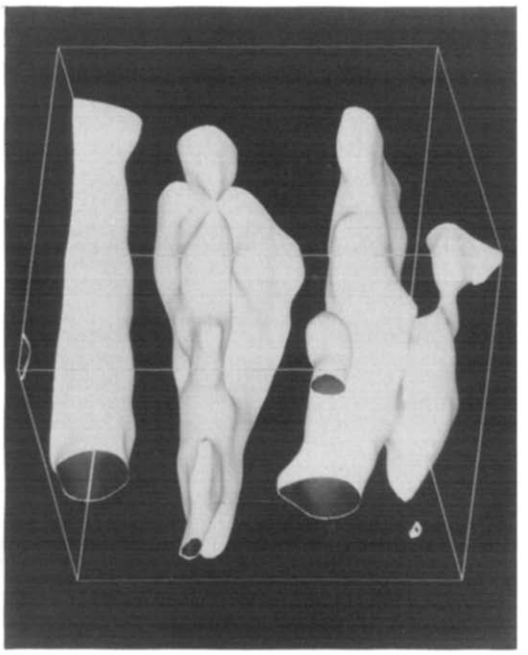

Figure 6 Three-dimensional reconstruction of the interface between the Arnitel polymer and the SEBS polymer in the 20/80 pressed blend

2. uncertainties and ambiguities due to effects of sample preparation and due to the limited number of cross-sections inherent to SEM and TEM, are avoided;
3. no additional information, for example from extraction experiments, is necessary for interpretation of the images in terms of three-dimensional structures.

Conclusions

1. Pictures of the internal structure of bulk samples of polymer blends can be obtained by confocal laser scanning microscopy (CLSM).
2. The pictures are in agreement with results obtained by scanning electron microscopy combined with extraction experiments.
3. The CLSM technique has distinct advantages: it is non-destructive; it requires no sample preparation; it gives images of the real internal structure; and image processing produces fully three-dimensional pictures.

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