# Phase morphology of polymer blends: scanning electron microscope observation by backscattering from a microtomed and stained surface

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A new electron microscopy technique was used to observe two-phase morphology in polymer blends. It consisted of preparing a flat specimen surface by microtoming, staining the unsaturated domains with $OsO_4$, and scanning electron microscope observation of the composition images using backscattered electrons. The new technique was applied to the melt blends of polypropylene (PP)/polybutadiene and PP/ethylene-propylene-diene rubber systems. Compared with conventional scanning electron microscope observation using secondary electron imaging for fractured surfaces, the new technique yielded a much clearer phase contrast.

**(Keywords: scanning electron microscopy; polymer blends; backscattering; staining; polypropylene)**

## INTRODUCTION

Scanning electron microscopy (SEM) is a widely used technique to elucidate the phase morphology of polymer blends. Samples for SEM are easy to prepare and the morphology can be observed under high resolution. Usually, micrographs are obtained by collecting secondary electrons emitted upon bombarding the samples with high energy electrons. This secondary electron image (SEI) gives information about the topography of the sample surface. By SEI-SEM it is often possible to infer the phase morphology of polymer blends.

A common and easy way to prepare samples for SEI-SEM is to fracture the blend above the glass transition temperature ($T_g$) of the low $T_g$ component. When the low $T_g$ component constitutes the dispersed phase, the low $T_g$ particles remain intact in one of the fractured surfaces. Where adhesion failure between the phases occurs, mounds or holes are observed under SEI-SEM[1].

Another procedure is to make a flat surface by fracturing the sample below the $T_g$ of the low $T_g$ component. The fracture usually travels through the low $T_g$ component particles, giving a smooth surface. Then, these particles are removed by selective oxidation or solvent etching, to render the holes which are visualized by SEI-SEM[2].

A very flat surface of a polymer specimen can be prepared by microtome. The microtomed surface provides a more representative view of the two-phase structure under SEI-SEM than the fractured surface[3], when it is followed by some etching of the dispersed phase.

If there are big differences in the atomic numbers of the elements between the two phases, composition images (CI) obtained by collecting backscattered electrons from a flat surface may give a clear phase contrast without etching. It is known that backscattered electrons originate from deeper regions in the sample than secondary electrons, and as a consequence the resolution obtained with them would be slightly lower. The difference in atomic numbers could be enhanced by selective staining of one of the phases using a heavy metal compound. Kishi *et al.*[4] recently employed this technique and observed two-phase morphology in a epoxy/polyimide blend by staining the polished surface with $OsO_4$. However, details of the method were not reported.

In this study, we tried to establish the CI-SEM technique. The results were compared with the above techniques.

## EXPERIMENTAL

### *Materials, blending and pressing*

The polypropylene (PP) used in this study was a commercial polymer (J3HG, $M_w = 350000$, $M_n = 50000$, Mitsui Toatsu Chemical Inc.). The ethylene-propylene-diene (EPDM) rubber was supplied by Japan Synthetic Rubber Co. (JSR EP 21, Mooney viscosity 38, with the diene component being ethylidene norbornene). The polybutadiene (PB) was also a commercial polymer (JSR BR-01, Mooney viscosity 44, *cis* 1-4 content 97%).

The PP and EPDM (70/30 w/w) were melt-mixed at 185°C for 4 min using a Mini Max Molder (model CS-183, Custom Scientific Instruments Inc.). The melt blend was then compression-moulded at 215°C to a 1 mm thick sheet. A 70/30 PP/PB blend was similarly prepared by melt mixing at 200°C for 3 min and then compression moulding at 200°C for 2 min.

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*Surface preparation*

The following four methods were used:

1. The film specimen was fractured after placing in a bath of ethanol–carbon dioxide ( $\sim -65°C$ ) for 30 min.
2. The film specimen was fractured after placing in liquid nitrogen for 30 min. Surfaces of fractured specimens were etched by dipping in cyclohexane for 20 h at room temperature. They were then rinsed with fresh cyclohexane to remove the dissolved polymer.
3. The sheet specimen was mounted on an ultramicrotome (Ultracut E, Reichert-Jung) equipped with a cryostat (FC4E, Reichert-Jung) and microtomed to provide a new surface. The sample temperature was set at $-90°C$ for PP/EPDM and $-110°C$ for PP/PB, respectively*. The microtomed samples were then (i) etched with cyclohexane as described in reference 2 or (ii) stained with $OsO_4$ vapour for 14 h at room temperature.

*SEM observation*

Micrographs were obtained using a scanning electron microscope (Jeol JSM-T220).

Samples obtained by methods 1, 2 and 3i were made conductive by the deposition of a layer of gold, then SEIs were produced. With the samples prepared by method 3ii, both SEIs and CI using backscattered electrons were obtained after coating with a carbon layer ( $\sim 10$ nm thick).

The incident beam was perpendicular to the surface and the voltage used was 15 kV.

* The surfaces were always distorted when higher temperatures (including room temperature) were used. Note that the $T_g$s of PP, EPDM and PB by d.s.c. were $-10$, $-60$ and $-100°C$, respectively

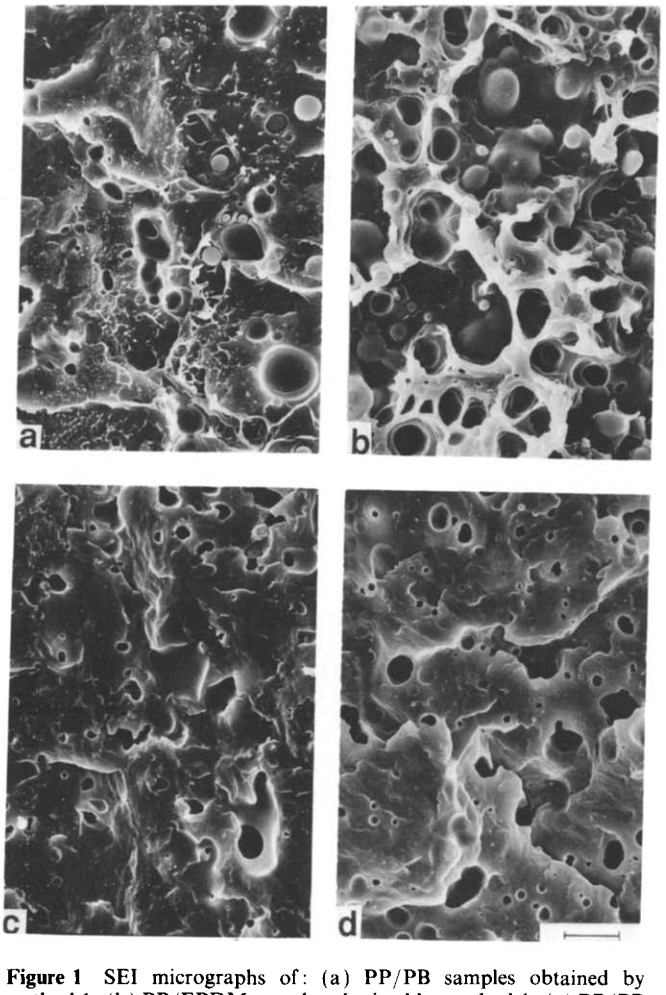


**Figure 1** SEI micrographs of: (a) PP/PB samples obtained by method 1; (b) PP/EPDM samples obtained by method 1; (c) PP/PB samples obtained by method 2; (d) PP/EPDM samples obtained by method 2. Scale bar = 10 $\mu$m

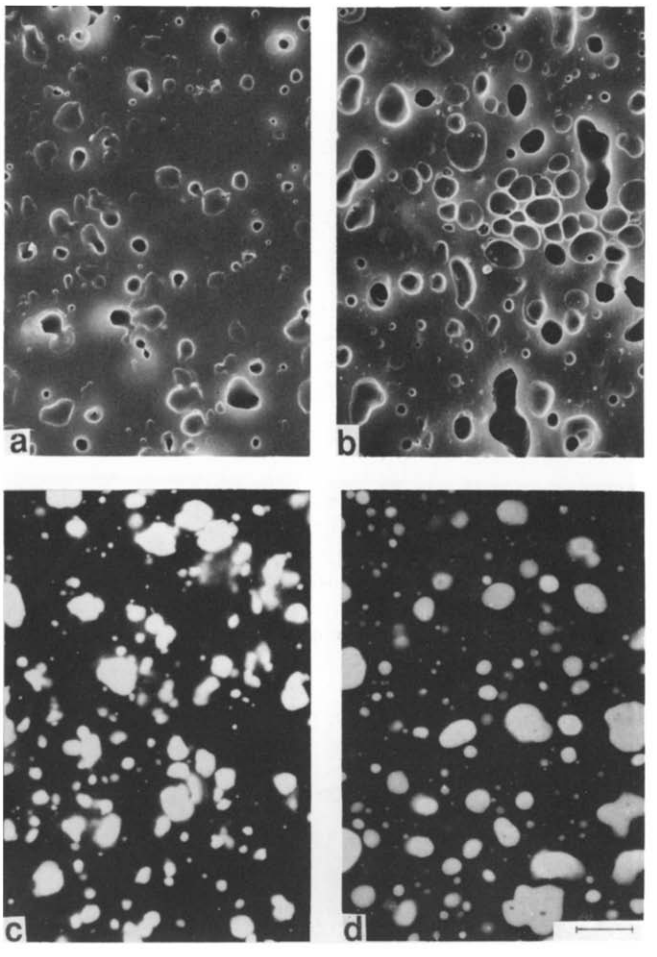


**Figure 2** SEI micrographs of: (a) PP/PB samples obtained by method 3i; (b) PP/EPDM samples obtained by method 3i. CI micrographs of: (c) PP/PB samples obtained by method 3ii; (d) PP/EPDM samples obtained by method 3ii. Scale bar = 10 $\mu$m

## RESULTS AND DISCUSSION

*Figures 1a* and *b* show the SEI micrographs of PP/PB and PP/EPDM samples obtained by method 1. Holes and mounds are observed where the interphase failure has occurred between the PP matrix and the rubbery domains.

*Figures 1c* and *d* correspond to SEI micrographs obtained with surfaces prepared by method 2. Surfaces are flatter than observed in *Figures 1a* and *b* indicating that a more representative view of the two-phase structure is obtained.

*Figures 2a* and *b* show the SEI micrographs of the microtomed and etched surfaces, i.e. from using method 3i. The phase morphology is clearer than with the fractured surfaces in *Figure 1*.

The CI micrographs of the microtomed and stained samples using method 3ii are shown in *Figures 2c* and *d*. This method gives the best phase contrast.

It is very important to know how flat the surface is before obtaining CI. These images are not dependent on

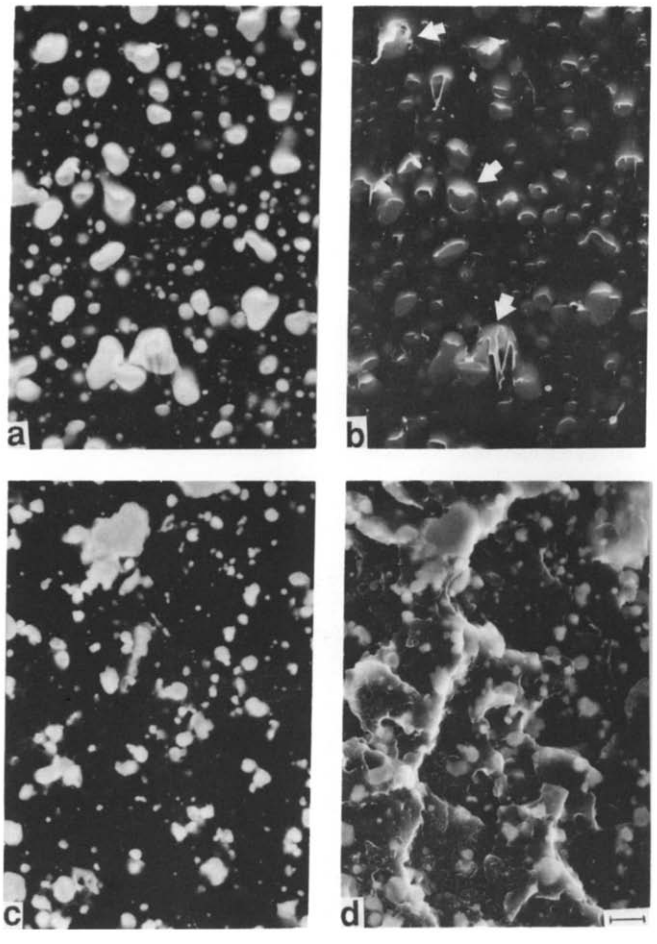


**Figure 3** (a) CI and (b) SEI micrographs of a PP/EPDM blend. (c) CI and (d) SEI micrographs of a PP/PB blend. Scale bar = 10 $\mu$m

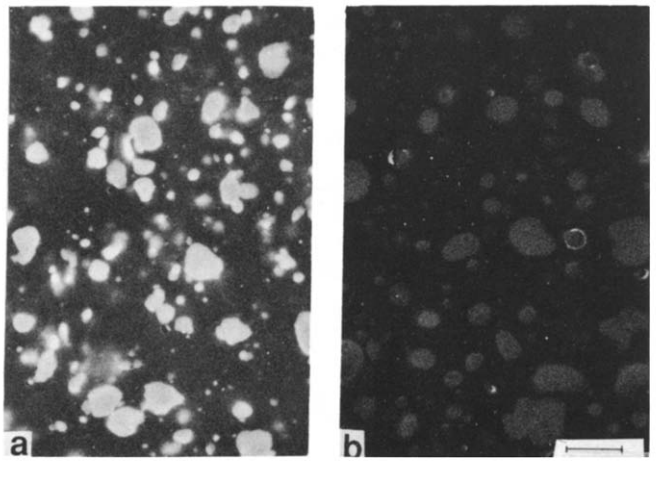


**Figure 4** SEI micrographs of the same areas of the samples used to obtain (a) *Figure 2c* and (b) *Figure 2d*. Scale bar = 10 $\mu$m

the roughness of the surface but on the composition distribution. Hence it is not possible to know whether the cutting action has deformed (or removed) the rubber particles or not. The situation is demonstrated in *Figure 3*. *Figure 3a* shows a CI micrograph of a PP/EPDM blend. The rubber domains were hardened by staining with $OsO_4$ vapour for 14 h after the blend was microtomed at room temperature. *Figure 3b* is the SEI micrograph of the same area as in *Figure 3a*. It is possible to observe the completely deformed EPDM domains which are debonded from the PP matrix (indicated by arrows). This distortion is probably due to insufficient hardening of EPDM domains to be cut at room temperature. The distortion and debonding are not so clear using CI.

Another example is shown in *Figures 3c* and *d* for the PP/PB blend. The PP/PB film was fractured in liquid nitrogen and stained with $OsO_4$ vapour for 24 h. The CI micrograph (*Figure 3c*) shows very clear phase contrast. The SEI micrograph of the same area (*Figure 3d*) shows that the surface is not smooth and the distortion may create an artifact for the CI.

*Figures 4a* and *b* show the SEI micrographs of the same areas of the samples used to obtain *Figures 2c* and *d*. One can see that the surfaces are flat and without severe distortion by the microtoming procedure. The flatness of the surface was confirmed by SEI observation of the tilted samples with respect to the incident beam to increase the phase contrast[5]. Note that the phase contrast by SEI is weaker than by CI. The reason why the EPDM phase is bright using SEI is not obvious at present. This will be discussed in a forthcoming paper.

## CONCLUSIONS

Method 3ii, i.e. CI observation of the flatly microtomed and stained sample, provides the best phase contrast and the most reliable results on the two-phase morphology of PP/rubber blends.

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