Phase morphology of polymer blends: 2. SEM observation by secondary and backscattered electrons from microtomed and stained surface

Graciela Goizueta*, Tsuneo Chiba and Takashi Inoue†
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan
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A recently developed scanning electron microscopy (SEM) technique, which consists of the preparation of a microtomed flat surface, staining with OsO_4 or RuO_4, and compositional contrast observation using backscattered electrons, was applied for high impact polystyrene and propylene–ethylene block copolymer. A clear contrast was obtained for both polymers. By minor revision, i.e. by employing the secondary electron image under a low accelerating voltage, a much better contrast was observed.

(Keywords: scanning electron microscopy; polymer blends; backscattering; staining; polypropylene; copolymers; compositional contrast)

INTRODUCTION

Scanning electron microscopy (SEM) is widely used 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, a topographic contrast is obtained by collecting secondary electrons emitted upon bombarding the fractured or fractured and etched sample with high energy electrons. This information about the topography of the sample surface often allows the phase morphology to be inferred[1–3].

In the previous article[4], we explored a new technique for SEM observation of phase morphology in polymer blends. It consisted of the preparation of a flat specimen surface by microtoming, the staining of unsaturated domains with OsO_4, and the SEM observation of composition image using backscattered electrons. The new technique provided an excellent contrast and a series of reliable results on the two-phase morphology of polypropylene/rubber blends with domain size of a few micrometres.

In the present work, we apply the technique for other blends with finer phase structure and try to improve the technique.

EXPERIMENTAL

Materials, blending and pressing

The polypropylene (PP) used in this study was a commercial polymer (J3HG, Mitsui Toatsu Chemical Inc.) with $M_w = 350\,000$ and $M_n = 50\,000$. Ethylene-propylene-diene rubber (EPDM) was supplied by Japan Synthetic Rubber Co. (JSR EP 21) (Mooney viscosity 38, ethylidene norbornene (ENB)). Polybutadiene (PB) was also a commercial polymer (JSR BR-01) (Mooney viscosity 44, *cis*-1,4 content 97%). PP and EPDM, in a 70/30 wt% ratio, 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 sheet of 1 mm thickness. 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. As will be shown later, the blend specimens prepared at our laboratory have a two-phase structure with domain size of a few micrometres.

Two commercial polymers with finer domains were provided by Idemitsu Petrochemical Co. Ltd: high-impact polystyrene (HIPS); and 'block PP' or high-impact PP, prepared by block copolymerization of propylene with ethylene. HIPS and block PP were compression-moulded at 220°C for 1 and 3 min, respectively.

Surface preparation

A 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 the PP/EPDM blend and −110°C for the PP/PB blend. Then, the microtomed samples were stained with OsO_4 vapour for 14 h at room temperature.

HIPS was stained with OsO_4 vapour for 14 h at room temperature before microtoming. Due to the fixation effect of OsO_4 on the rubber[5], the sample became hard and it was easily microtomed at room temperature.

Block PP was stained with RuO_4 at 50°C for 2 h before microtoming. Since the amorphous regions were hardened by staining[6], it was easily microtomed at room temperature to provide a flat surface.

* On leave from PLAPIQUI, National University of the South, 12 de Octubre 1842, (8000) Bahia Blanca, Argentine
† To whom correspondence should be addressed

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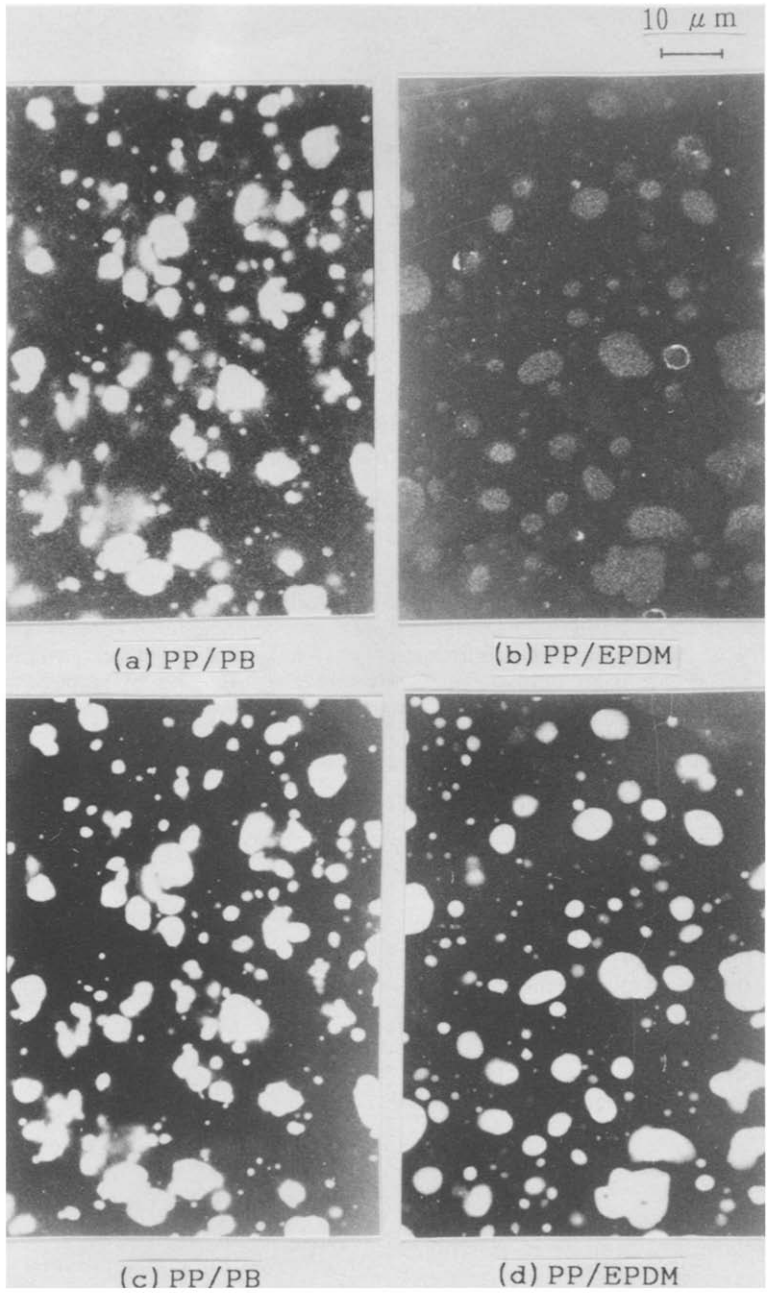

Figure 1 SEM by SEI and CI: (a) SEI of PP/PB blend microtomed at −110°C and stained with OsO_4; (b) SEI of PP/EPDM blend microtomed at −90°C and stained with OsO_4; (c) CI of PP/PB blend, same area as (a); (d) CI of PP/EPDM, same area as (b)

SEM observation

Micrographs were obtained using a scanning electron microscope (Jeol JSM-T220). All the samples were made conductive by deposition of a layer of carbon. Both secondary electron images (SEI) and composition images (CI) using backscattered electrons were obtained.

RESULTS AND DISCUSSION

Figures 1a and *b* show the SEI micrographs of PP/PB and PP/EPDM samples. One can see that the surfaces are flat and show no severe distortion by the microtoming procedure. The flatness of the surface was confirmed by SEI observation of the tilted sample with respect to the incident beam to increase the topographic contrast[7]. It is very important to know the flatness of the surface before obtaining CI. This image is not dependent on the roughness of the surface but on the composition distribution. Hence using CI alone, it is not possible to determine whether or not the cutting action has deformed the rubber particles[4]. *Figures 1c* and *d* show the CI micrographs of the same areas of the samples used to obtain *Figures 1a* and *b*, respectively. The contrast is better than that by SEI. Note that the micrographs in *Figure 1* were observed under a high voltage of 15 kV.

Figures 2a and *b* show SEI and CI micrographs of the same area in the block PP. The acceleration voltage used was 15 kV. *Figures 2c* and *d* show SEI and CI micrographs of the same sample using a voltage of 5 kV. One can see that the contrast observed by SEI under a low voltage (*Figure 2c*) is better than those obtained by SEI under a high voltage (*Figure 2a*) and by CI at both low

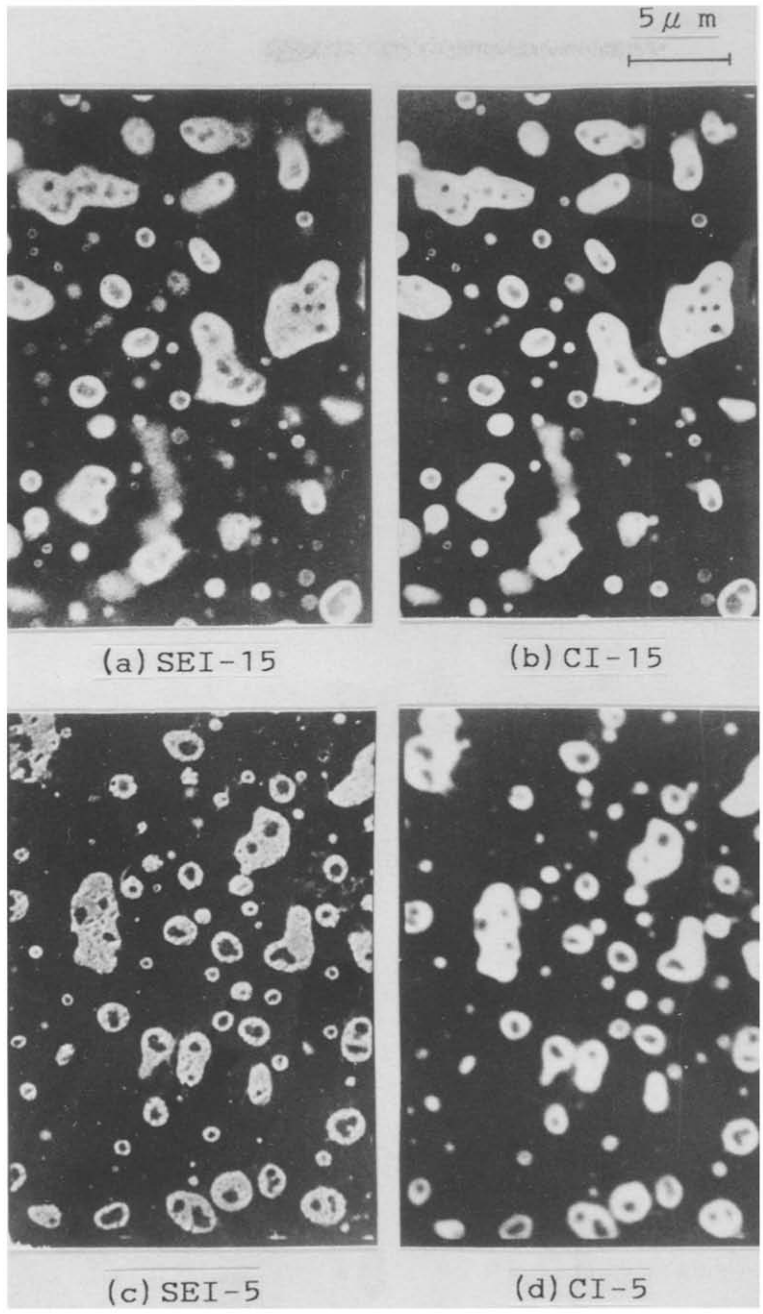

Figure 2 SEM of block PP, stained with RuO_4 and microtomed at room temperature, by SEI and CI: (a) SEI using 15 kV; (b) CI using 15 kV, same area as (a); (c) SEI using 5 kV; (d) CI using 5 kV, same area as (c)

and high voltages (*Figures 2b* and *d*), and the fine morphology inside the dispersed particles is more obvious.

Figures 3a and *b* show SEI and CI micrographs of the same area in HIPS. The voltage used was 15 kV. *Figure 3c* shows the SEI micrographs of the same sample using a voltage of 5 kV. The CI micrograph obtained at this low voltage was completely undefined (it is not shown here). That is, a tendency similar to block PP is seen for HIPS; the secondary electrons become more dependent on the atomic number at a low voltage than the backscattered electrons and provide a clearer compositional contrast. The results may seem unexpected, because generally the resolution diminishes when the voltage used decreases. The strong dependence of the secondary electrons on the atomic number at low voltages and the higher resolution in the images obtained using the secondary electrons than using the backscattered electrons may cause this better observed contrast.

CONCLUSION

The CI of the flat microtomed and stained sample are very clear. For samples with finer domains, SEI under low voltages provides a better contrast than CI.

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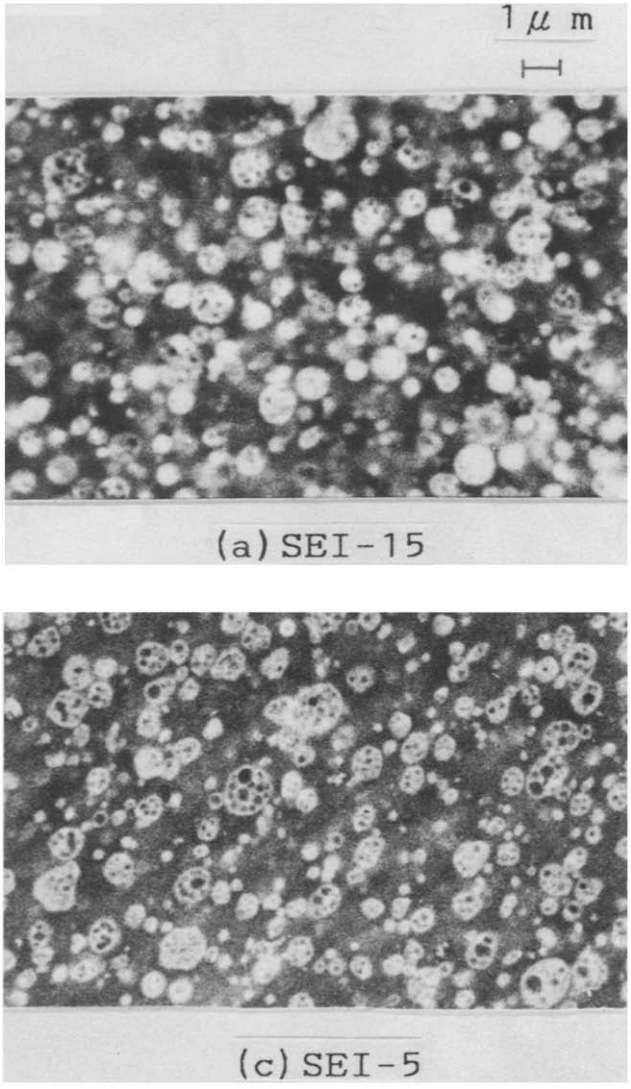

Figure 3 SEM of HIPS, stained with OsO_4 and microtomed at room temperature, by SEI and CI: (a) SEI using 15 kV; (b) CI using 15 kV, same area as (a); (c) SEI using 5 kV

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