

The Use of RuO₄ in Studies of Polymer Blends by Scanning Electron Microscopy

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Synopsis

Flat samples of blends of PP and SEBS were contrasted with ruthenium tetroxide and studied in a scanning electron microscope provided with a detector for back-scattered electrons. The images showed the SEBS phase as bright areas with dark dots and the PP phase as dark. The dots in the bright SEBS areas corresponded to the unstained EB-domains of the triblock SEBS polymer. The technique used provided BSE images of high resolution. This is a consequence of the intrinsic electrical conductivity conferred to the sample surface by the ruthenium species deposited there during staining. Treatment with ruthenium tetroxide vapor conferred electrical conductivity to the stained areas, which explains the high resolution obtained with the present technique.

INTRODUCTION

Electron microscopy is an important tool in the study of polymer blend morphology. Although transmission electron microscopy (TEM) provides high resolution, sample preparation requires great skill and is time consuming. In most cases, a selective staining agent must be used. Bromine and osmium tetroxide are common staining agents for polymers containing double bonds. The recent introduction of ruthenium tetroxide as a staining agent has widened the applicability of TEM and made it useful in the studies of many blends of saturated polymers. This is due to the fact that ruthenium tetroxide reacts not only with carbon-carbon double bonds, but also with alcohol, amine, phenyl, and ether groups.¹

Scanning electron microscopy (SEM) is a more simple technique. Using the normal secondary electron detector, SEM provides an insight to the topographical morphology. Thus, this method is useful for blends which can be etched selectively, i.e., blends from which one of the polymers can be removed by a solvent or reagent without disturbing the structure of the remaining insoluble polymer(s).

Using SEM with a backscattered electron detector (BSE), provides an image representing a map of the atomic number contrast in the sample surface.² The signal from the BSE detector also contains a contribution from the sample topography. This can be completely depressed by using flat samples. The use of SEM with a BSE detector for polymer morphology studies has previously been demonstrated using both osmium tetroxide³ and bromine⁴ as the staining agents. The contrast in this case is due to incorporation of heavy atoms in one of the blend phases.

The present work demonstrates that ruthenium tetroxide staining allows the use of a BSE detector in morphology studies of unsaturated polymer blends. It also demonstrates that ruthenium tetroxide confers conductivity to the stained phase. Thus, if a continuous phase is stained, the need for a special conductive layer is eliminated, improving resolution.

EXPERIMENTAL

Electron Microscopy

This study used a Jeol 100U transmission electron microscope and an ISI 100A scanning electron microscope provided with a normal secondary electron detector and an ISI Robinson BSE detector.

Polymers

The polymers used were SBS, SEBS, and blends of SEBS with polypropylene (PP). The SBS was Kraton 1101 from Shell, a triblock thermoplastic elastomer having polystyrene endblocks and a central block of polybutadiene. The SEBS was Kraton G 4609 from Shell, a triblock thermoplastic elastomer prepared by complete hydrogenation of the corresponding SBS polymer. Schematic structures of SBS and SEBS are shown in Figure 1. The PP was PY 6100 from Shell having a melt index of 5.5.

Blends of SEBS or SBS and PP were prepared by first adding a nonaromatic processing oil (Witco Sonneborn Plastic Oil 260) to SEBS or SBS in the weight proportions 90 parts of oil to 100 parts of the thermoplastic elastomer, and then mixing the oil-treated thermoplastic elastomer with PP in a counterrotating, double screw laboratory extruder. In the SBS/PP blend, a filler was incorporated. The filler consisted of fibers of calcium sulfate.

Preparation of RuO₄ (1)

Ruthenium tetroxide is hazardous and should be kept in closed vessels or vented hoods. RuO₄ is unstable and was prepared shortly before use. The RuO₄

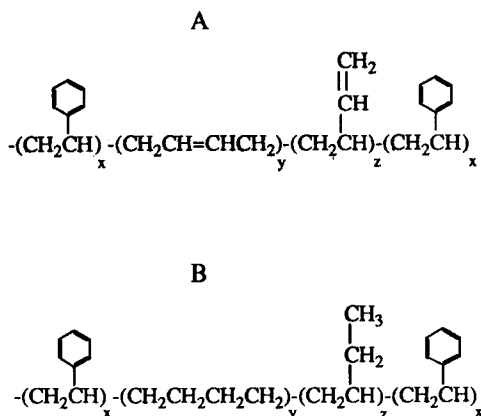
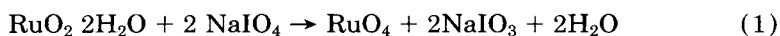


Fig. 1. SBS, styrene-butadiene-styrene block copolymer (A) and SEBS, styrene-ethylene-butylene-styrene block copolymer (B).

solution used for vapor staining was prepared by first dissolving 0.6 g of NaIO₄ in 10 mL of water. The periodate solution was cooled with ice in a vented hood. After adding 0.1 g of RuO₂ · 2H₂O, the beaker was covered. During the reaction period (2–3 h) the solution turned yellow indicating the formation of RuO₄:



This solution was used directly for vapor staining. Except for RuO₄ and the unreacted periodate, the solution contained byproducts from side reactions and from the decomposition of RuO₄. The excess periodate present in the solution increased its stability.

Staining

The solid polymers to be studied by SEM were cooled with liquid nitrogen and cut in a microtome or with a razor blade to obtain samples with flat and smooth surfaces. The samples were mounted on sample holders of aluminium

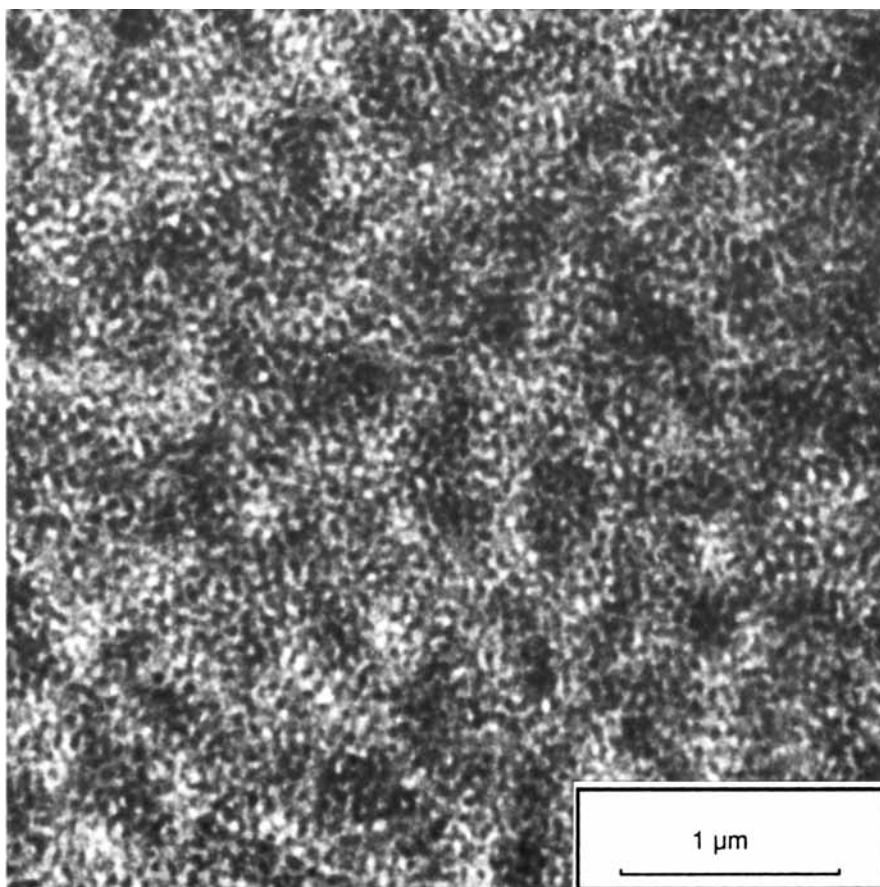


Fig. 2. A TEM image of a RuO₄-stained SEBS film, cast from an SEBS-xylene solution.

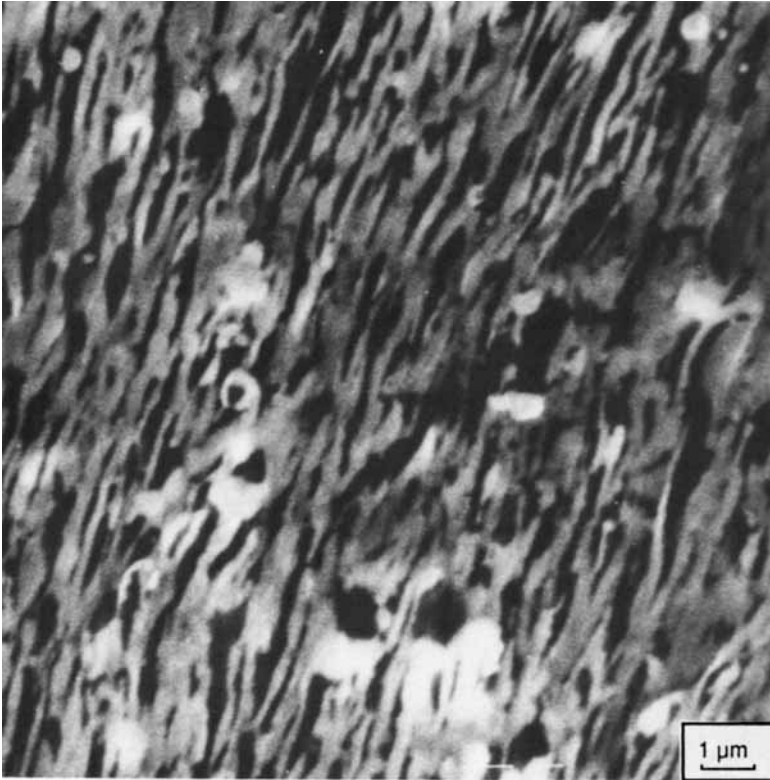


Fig. 3. BSE image of a blend containing (SBS + oil)/PP/filler (50/40/10).

and placed in a staining vessel containing a small beaker. The yellow RuO_4 solution was transferred to the beaker and the staining vessel was covered. The vapor staining time (at room temperature) varied with sample type, but was usually between 3 and 24 h. However, for the thinner TEM samples, the staining times ranged between 15 min and 2 h. Formation of RuO_2 crystals was not observed using this technique.

Selective Etching

The phase structure of the blends was also studied using SEM and the method of selective etching. In this case, blend samples were immersed in xylene (which dissolves the thermoplastic elastomer) for 24 h. The extracted samples were washed with fresh xylene, dried in air, mounted on a sample holder, and covered with Au/Pd by sputtering.

RESULTS AND DISCUSSION

Figure 2 shows a TEM-micrograph from a thin film of pure SEBS, cast from a xylene solution and stained with ruthenium tetroxide. The domain structure can be clearly seen, showing that the ruthenium tetroxide selectively stained the polystyrene domains. The stained polystyrene domains appear dark as they

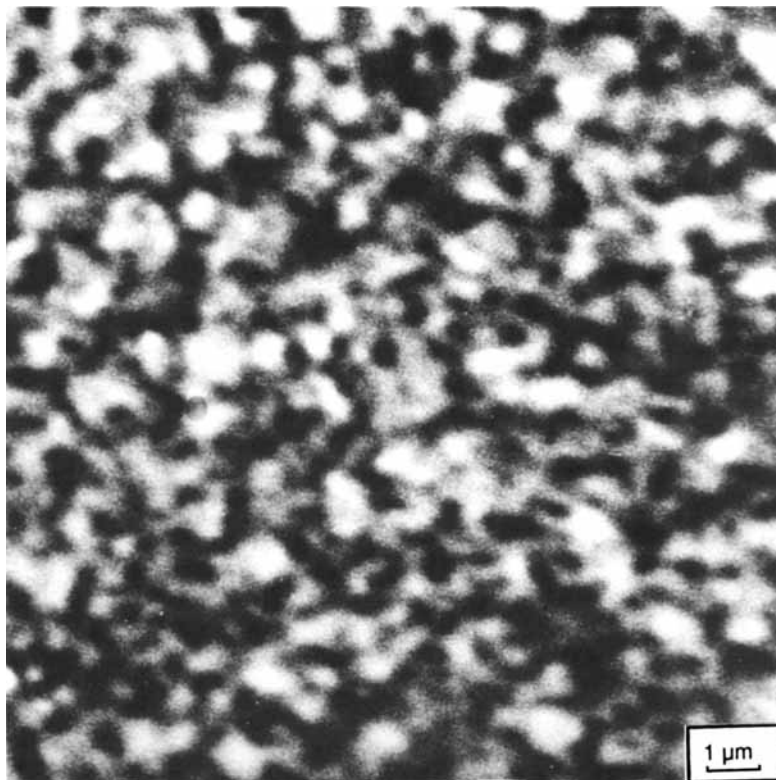


Fig. 4. A BSE image of the atomic number contrast in a (SEBS + oil)/PP blend having the composition, 65/35, using an accelerating voltage of 10 kV.

contain strongly absorbing ruthenium atoms, whereas the unstained EB-domains are white.

Figure 3 shows a SEM image of a flat sample of a filled SBS-PP blend, obtained with the use of a BSE detector. In this case, stained areas (staining time 18 h) appear bright instead of dark as in the previous TEM case. The unstained PP is dark, the stained SBS phase is grey, and the white spots originates from the filler particles. The absence of structure in the SBS phase is due to the fact that both the polystyrene and polybutadiene domains of the SBS phase were stained. Due to their composition and density the filler particles (calcium sulfate fibers) are effective electron scatterers. Figure 3 indicates that both polymer phases in the blend are continuous. This means that the SBS-PP blend had the structure of a physically crosslinked interpenetrating network (IPN).

Complete hydrogenation of a SBS polymer gives the corresponding SEBS polymer. With this polymer, ruthenium tetroxide can only react with the phenyl groups present in the polystyrene domains. Figure 4 shows a BSE image of a stained (staining time 24 h) blend of SEBS and PP. The white areas with dark spots represent the SEBS phase and the dark areas PP phase. The dark spots in the SEBS phase correspond to the unstained EB domains. These are surrounded by stained and, hence, white polystyrene domains. Obviously, in this

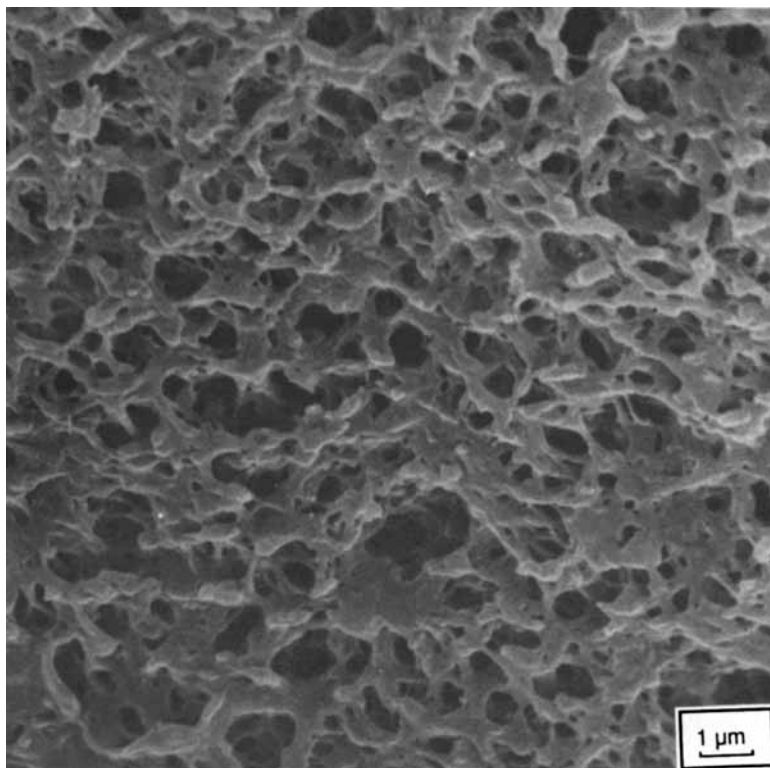


Fig. 5. A secondary electron image of a xylene extracted (SEBS + oil)/PP blend (65/35). The PP network is shown.

case, the BSE image revealed the domain structure of the rubber phase. The reason for this is that with ruthenium tetroxide, in contrast to the more well known osmium tetroxide, the stained layer is extremely thin. In fact it is comparable in size to the size of polystyrene domains. This has been confirmed by TEM studies on thin sections, cut at right angle to the stained surface of samples of the same kind as that used in preparing Figure 4. Such measurements indicated that the penetration depth of ruthenium tetroxide was about 80 nm.⁶ The intense back scattered electron signal, which makes the polystyrene domains in Figure 4 to appear as bright, thus should originate almost entirely from stained polystyrene domains present in the surface layer of the sample.

By selective etching, using xylene as a selective solvent, it was shown that the SEBS and the processing oil could be quantitatively removed from the blend of Figure 4, leaving a residue of the same size and shape as those of the original sample. This proves that the blend had a bicontinuous structure, i.e., that both the PP and the SEBS phases were continuous. The structure of the remaining PP phase is shown by the topographic image in Figure 5.

The fact that the internal structure of the SEBS phase could be seen in Figure 4 indicates that a very good resolution was obtained. The images in this figure were obtained with samples that were not covered with a conducting layer. Despite this, no charging problems were observed using an accelerating voltage of 10 kV. This indicates that staining with ruthenium tetroxide confers

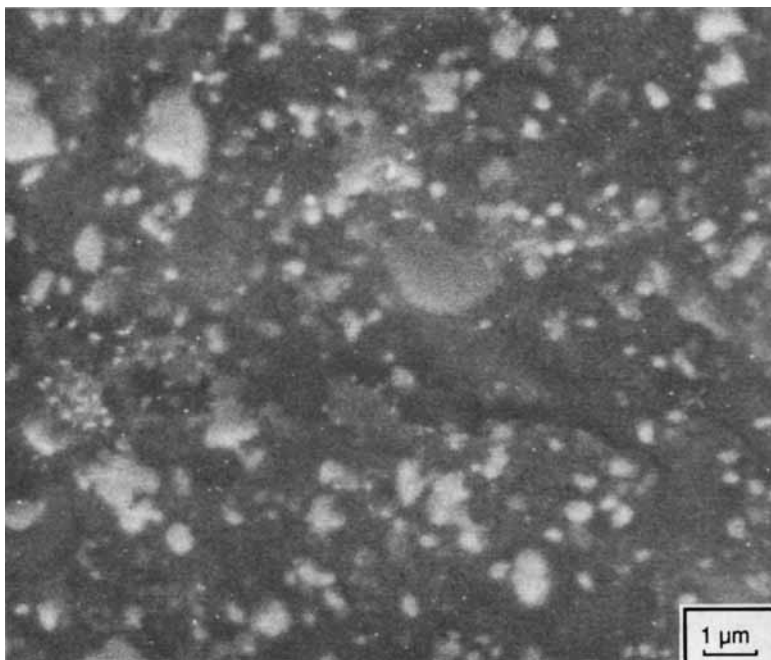


Fig. 6. BSE image of an (SEBS + oil)/PP, 25/75 blend recorded using a very low (5 kV) accelerating voltage to minimize the effect of sample charging.

sufficient electric conductivity to the surface layer to counteract charging of the sample. However, charging problems did occur with samples of blends of compositions, in which the SEBS phase was discontinuous. Even with such samples, BSE studies could be made on uncovered samples by lowering the acceleration voltage. An example of a BSE image demonstrating this is shown in Figure 6.

The fact that ruthenium tetroxide staining gives a thin surface layer with intrinsic electric conductivity is a considerable advantage. With nonconductive samples, the surface must be covered with a thin layer of carbon, or the experiment must be performed using an environmental cell^{2,5} in which the surface charge is dissipated by ionized gas molecules. Both of these methods give reduced contrast and resolution. Moreover, carbon covering is experimentally difficult, since the layer thickness and carbon particle size cannot be easily controlled.

CONCLUSIONS

Polymer blend morphology can be studied by SEM using a BSE detector and ruthenium tetroxide staining. The samples should be flat in order to reduce the topographic contribution to the BSE signal.

Ruthenium tetroxide has a very low penetration depth in polymers, allowing selective staining of the surface layer.

Ruthenium tetroxide staining confers electrical conductivity to the stained phase. If the latter is continuous, a separate conductive layer need not be used. This improves resolution and contrast.

The SEM-BSE method is simple and fast. The resolution is poorer than with TEM, but generally quite sufficient for polymer blend studies.

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