ELSEVIER

Polymer 40 (1999) 2171–2173

polymer

Polymer Communication

On the use of energy-filtering transmission electron microscopy for analysis of unstained multiphase polymer systems

C.A. Correa*, E. Hage Jr.

Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, Via Washington Luis km 235. CEP 13565-905 São Carlos, SP, Brazil

Received 6 March 1998; accepted 22 May 1998

Abstract

This paper gives further evidence of successful use of energy-filtering transmission elctron microscopy (EFTEM) for studying the polymer morphology of unstained samples. The method presents numerous advantages compared to traditional chemical staining methods using toxically staining agents such as osmium and ruthenium tetraoxide. For this purpose an EFTEM LEO912 equipped with an omega filter was used to produce conventional brightfield unscattered images and inelastic filtered images of high impact polystyrene ultramicrotomed samples. It was shown that morphology details observed in unstained samples are equivalent in quality contrast to those stained with osmium tetraoxide.

Keywords: Multiphase polymers; Transmission electron microscopy; Physical staining

1. Introduction

In principle, image contrast in conventional transmission electron microscopy (TEM) is the result of variations in thickness, objective aperture and local changes in composition among structures present in the sample. The brightfield image is formed by transmitted unscattered and inelastic scattered electrons [1]. Regarding polymer and biological specimens, they are macromolecules commonly constituted of low atomic number elements, thus exhibiting small fluctuations in electron density. Accordingly, the bulk of the polymer and biology morphological studies rely on the use of staining agents to provide differential contrast throughout the sample. In its broader sense, staining involves the incorporation of electron dense atoms into the chemical structure of the sample in order to increase the electron density and thus enhance differential contrast. Staining permits TEM observation of the dispersed phases in multiphase blends. In materials containing unsaturated chemical bonds—such as rubber modified polymers and block copolymers—osmium and ruthenium tetraoxide are the most widely employed stains for this application. In the case of osmium tetraoxide, reaction is by chemical graft and crosslink of double bonds within the rubber phase hardening, and raising its electron density in relation to the unstained matrix [2]. Despite its toxicity and handling difficulties, the osmium tetraoxide staining method, as developed by Kato [3] more than 20 years ago, is currently in use for the characterization of many multiphase polymer systems. Recent developments in TEM technology are opening new possibilities for using physical staining in place of traditional chemical methods. The method has also been used elsewhere for observation of biological samples [4].

In theory, inelastic scattering in TEM is a result of energy-transfer with little change in trajectory (0–1 mrad) of the electrons from the incident beam to the sample. In contrast to the elastic scattering, the inelastic scattering in TEM produces changes in energy of the inelastic electrons which are polyenergetic and therefore can be used for electron spectroscopy in materials microanalysis. Moreover, in conventional TEM the inelastic scattering tends to deteriorate absorption and phase contrast conditions [5].

The LEO912 energy-filtering TEM (EFTEM) consists of a built-in column omega filter of four coupled magnetic sectors. This electron spectrometer bends the electrons successively through 105° and disperses them back into the optic axis of the microscope column forming an energy-loss spectrum. An energy-selecting slit of variable width in the spectrum plane restricts the energy range of electrons that contribute to the image formation. By varying the width and position of the slit, energy-filtered images of

* Corresponding author.

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00423-6

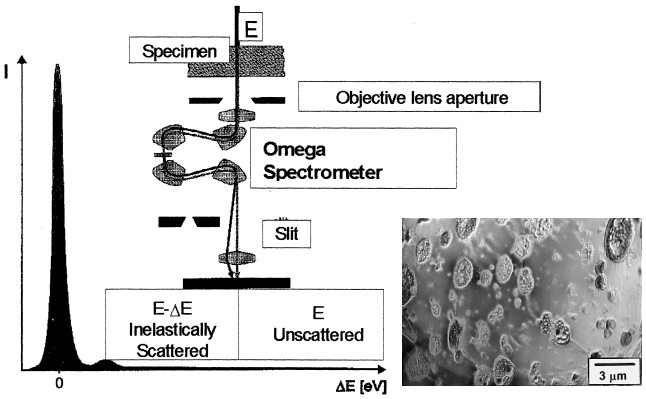

Fig. 1. GBF imaging of HIPS morphology using conventional TEM.

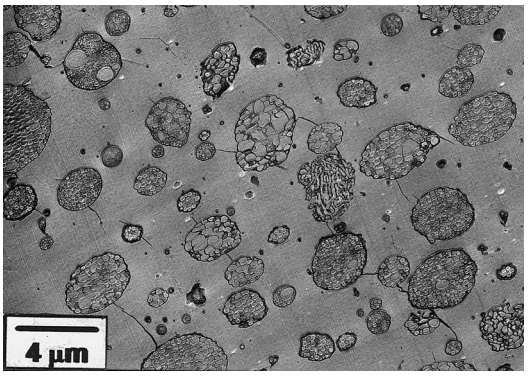

Fig. 3. HIPS samples stained in osmium tetraoxide for 72 h and ultramicrotomed at room temperature. EBF images of 100 nm slices.

different energy-loss or selective contrast can be obtained. For best results in terms of contrast and resolution, specimen thickness should be minimized and a slit aperture within 15–25 eV is recommended [1,4,5]. Despite the fact that the imaging process in EFTEM is a result of very basic physical principles, there are not yet found in the literature references of its application as a physical stain for polymer samples.

In this work the prospective use of EFTEM for observation of the morphology of stained and unstained multiphase polymers is presented. A LEO912 EFTEM equipped with omega filter and a LaB_6 electron source was used to produce energy-filtered images of high impact polystyrene (HIPS) samples ultramicrotomed cryogenically and at room temperature. The lower work function of the LaB_6 source compared to the traditional tungsten filament provided a more intense and homogeneous illumination of the whole sample surface. The HIPS unstained samples were ultramicrotomed cryogenically, while a second set of samples was stained in osmium tetraoxide for over 72 h and ultramicrotomed at room temperature. The rubber crosslinking by osmium staining allowed ultramicrotomy at room temperature without major damage to the samples. Specimen blocks were ultramicrotomed to 100 nm thick slices. Global brightfield imaging (GBF mode) of unstained HIPS morphology is presented in Fig. 1 as acquired using the omega filter. Electron scattering intensity is also shown in the same scheme highlighting the zero-loss peak from unscattered electrons. Contrast tuning using a small objective (30 m) aperture and energy-loss slit (15–25 eV) in the omega filter was employed to filter inelastic scattering and generate elastic brightfield images (EBF mode) as shown in Figs 2 and 3.

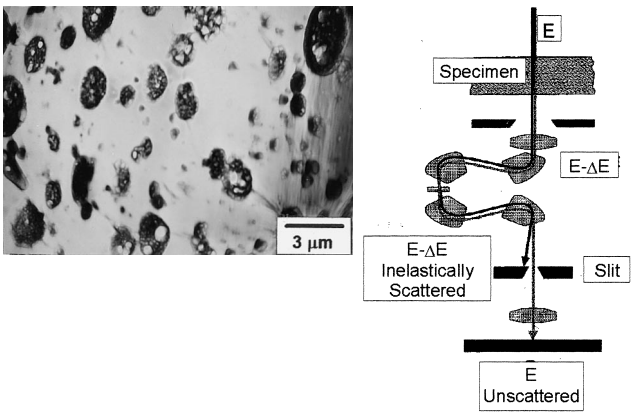

Fig. 2. EBF mode of HIPS morphology—this image is formed by unscattered electrons only.

2. Results

In the GBF mode (Fig. 1) all electrons which pass the specimen and the objective aperture contribute to the final image. The result is poor contrast and bad resolution. In the EBF mode (Fig. 2) all energy-loss electrons are blocked away by the slit aperture of the omega filter, significantly improving the contrast in the final image. Basically, phase contrast is enhanced by elimination of chromatic aberrations produced by inelastic scattering. The EBF mode also compensates for sections presenting variations in thickness, as the ratio of inelastically scattered electrons (plasmon peak) to the unscattered electrons in the spectrum is a function of the specimen thickness. For ultramicrotomed samples this can be very useful, as compression forces during slicing may induce changes in thickness. In multiphase polymers systems inelastic filtering seems to play a very important role as small changes in electron densities tend to give poor contrast in GBF mode. In the HIPS case mass–thickness is the only source of contrast in the specimen. To illustrate Kato's technique, EBF images of HIPS stained with osmium tetraoxide are shown in Fig. 3. As extensively reviewed in the literature, in these images rubber domains are stained black by increased electron scattering from osmium atoms grafted to the polybutadiene double bonds [6,7].

By comparing the images shown in Figs 2 and 3 it is possible to observe that the contrast obtained in EFTEM unstained samples is equivalent to that obtained in those that are chemically stained. Further applications of the physical staining method are under investigation for more complex

multiphase polymer systems, particularly those containing phases with strong scattering elements in their chemical structures. The results of the EFTEM analysis of rubber toughened polypropylene and polycarbonate/ styrene–acrylonitrile blends will be the subject of a forthcoming paper.

Acknowledgements

The authors gratefully acknowledge the fellowship and financial support given by FAPESP (Brazil) and the Centro de Caracterização e Desenvolvimento de Materiais (CCDM/ UFSCar) for the use of the LEO912 EFTEM.

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