

# Morphological Studies of the Modified Materials: Low-Density Polyethylene/Poly(acrylic acid)/Europium(III) and Low-Density Polyethylene/Poly(acrylic acid)/Uranyl Ion

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## SYNOPSIS

The morphology of low-density polyethylene (LDPE) modified by *in situ* sorption and thermal polymerization of acrylic acid (AA) in the matrix was examined. The microstructure of the LDPE/poly(acrylic acid) (PAA) materials after  $\text{Eu}^{3+}$  and  $\text{UO}_2^{2+}$  ion exchange was investigated. The phase behavior of these materials was analyzed using X-ray diffraction, scanning electron microscopy (SEM), and thermal measurements (DSC). The X-ray diffraction studies showed that PAA is located at amorphous region of the matrix. The LDPE/PAA surface, as investigated by SEM, was apparently homogeneous before and after  $\text{Eu}^{3+}$  and  $\text{UO}_2^{2+}$  ion exchange, respectively. Two  $T_g$  values were found for the LDPE/PAA material before and after  $\text{Eu}^{3+}$  ion exchange. Also, three and four  $T_g$  values were found for LDPE/PAA after  $\text{UO}_2^{2+}$  ion exchange depending on the amount of  $\text{UO}_2^{2+}$  in the modified matrix. This indicates microphase domains in the LDPE/PAA-, LDPE/PAA/ $\text{Eu}^{3+}$ -, and LDPE/PAA/ $\text{UO}_2^{2+}$ -modified materials, although a lack of visible phase separation in the micrographs was observed. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Low-density polyethylene (LDPE) can be modified by the sorption and *in situ* thermal polymerization of vinyl monomers in the matrix at 60–90°C.<sup>1</sup> The method produces the materials LDPE/poly(methyl methacrylate), LDPE/poly(4-vinylpyridine), and LDPE/PAA.<sup>2</sup> The latter, which contains carboxylic groups, is of interest for the studies of rare earth complexes, yielding an organic polymer matrix with fluorescent properties.<sup>3</sup> Fluorescent properties have also been used for the investigation of  $\text{Eu}^{3+}$  ion aggregation formation in this specific ion-containing polymer. Another fluorescent ion,  $\text{UO}_2^{2+}$ , was chosen for the investigation of the  $\text{H}^+ \leftrightarrow \text{UO}_2^{2+}$  exchange in the LDPE-modified matrix.<sup>4</sup> As the hydrated ion radius of the  $\text{UO}_2^{2+}$  and its ion charge (+2) are smaller than those of the  $\text{Eu}^{3+}$  ion, it was

possible to explore the inner layers in the modified matrix.<sup>4–7</sup> In fact, the percentage of the  $\text{H}^+ \leftrightarrow \text{UO}_2^{2+}$  ion exchange in the matrix is twofold higher than that observed for  $\text{Eu}^{3+}$ .<sup>3,4</sup> These studies showed evidence that ion exchange occurs mainly at the surface or at neighboring layers of the modified matrix LDPE/PAA.

Following the goal of investigating the microstructure of the LDPE/PAA material, we aimed in this work to study the morphology of LDPE/PAA, LDPE/PAA/ $\text{Eu}^{3+}$ , and LDPE/PAA/ $\text{UO}_2^{2+}$  to find evidence of inhomogeneities in these materials.

## EXPERIMENTAL

Acrylic acid (AA) was supplied by Aldrich Chemical Co. and Cia. Quimica Rhodia Brasileira. It was distilled under vacuum prior to use and stored at 18°C. Hydroquinone monomethyl ether (HMME) was supplied by Cia. Quimica Rhodia Brasileira. It was purified by successive crystallization in acetone.

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**Table I** Characteristics of the Samples

Sample No./ Specification	% PAA in the LDPE Matrix	% Eu <sup>3+</sup> in the LDPE/PAA Matrix	% UO <sub>2</sub> <sup>2+</sup> in the LDPE/PAA Matrix	Film Thickness (μm)	Ion-exchange Heating Temperature (°C)
S <sub>1</sub> /LDPE	—	—	—	230	—
S <sub>2</sub> /LDPE-PAA	0.3	—	—	250	—
S <sub>3</sub> /LDPE-PAA	1.7	—	—	250	—
S <sub>4</sub> /LDPE-PAA	4.0	—	—	250	—
S <sub>5</sub> /LDPE-PAA	25.7	—	—	150	—
S <sub>6</sub> /LDPE-PAA-Eu <sup>3+</sup>	3.1	14	—	250	60
S <sub>7</sub> /LDPE-PAA-Eu <sup>3+</sup>	4.1	29	—	200	60
S <sub>8</sub> /LDPE-PAA-Eu <sup>3+</sup>	4.5	42	—	200	80
S <sub>9</sub> /LDPE-PAA-UO <sub>2</sub> <sup>2+</sup>	1.1	—	17.8	90	35
S <sub>10</sub> /LDPE-PAA-UO <sub>2</sub> <sup>2+</sup>	1.6	—	41.7	200	35
S <sub>11</sub> /LDPE-PAA-UO <sub>2</sub> <sup>2+</sup>	1.6	—	73.2	250	35

See Experimental.<sup>3,4</sup>

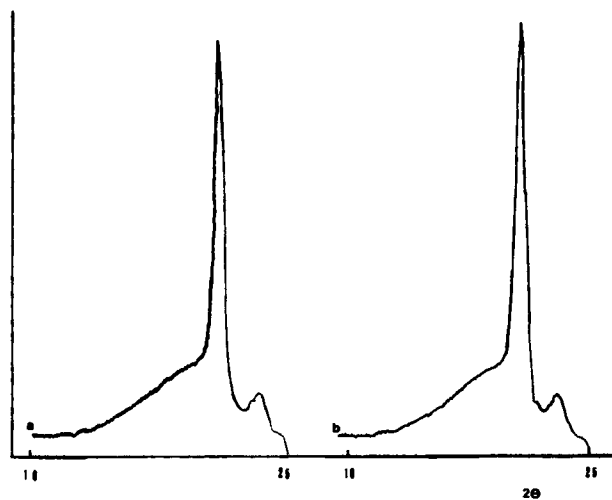
Europium(III) oxide (Eu<sub>2</sub>O<sub>3</sub>), 99.99%, was supplied by Alfa Inorganics Ventron Co. and uranyl chloride (UO<sub>2</sub>Cl<sub>2</sub>) was from BDH Chemical Ltd., Poole, England. They were used without further purification.

Low-density polyethylene sheets (LDPE,  $d = 0.918 \text{ g/cm}^3$ , MI = 1.15 g/min) were supplied by Poliolefinas (São Paulo). The films (3 × 4 cm) were cleaned and characterized by the procedure described previously.<sup>3</sup>

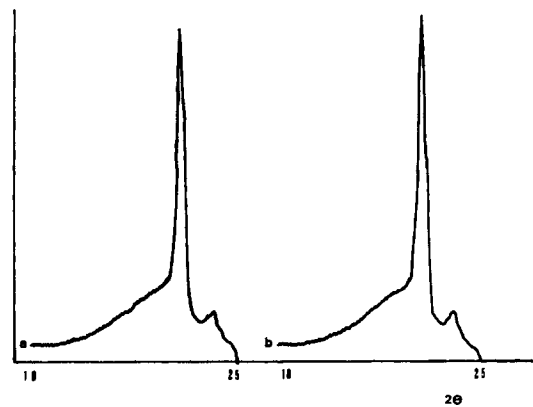
## Methods

### Sorption and Thermal Polymerization of AA in LDPE

The sorption and *in situ* thermal polymerization of AA (80% by unit volume of aqueous solution containing 350 or 500 ppm of HMME) in LDPE films followed the method described in our previous works.<sup>1-3</sup> The mass increase of LDPE films was obtained by gravimetry.<sup>8</sup>



**Figure 1** X-ray diffractograms: (a) LDPE/PAA (S<sub>3</sub>); (b) LDPE/PAA-Eu<sup>3+</sup> (S<sub>6</sub>).



**Figure 2** X-ray diffractograms: (a) LDPE/PAA (S<sub>3</sub>); (b) LDPE/PAA-UO<sub>2</sub><sup>2+</sup> (S<sub>11</sub>).

**Table II Crystallinity Degree of the LDPE-modified Matrix**

Sample (No.)	% PAA in the Matrix	% ion in the LDPE/PAA Matrix	Crystallinity Degree, $X_c$ (%)
LDPE ( $S_1$ )	—	—	51.1
LDPE/PAA ( $S_3$ )	1.7	—	50.8
LDPE/PAA- $\text{Eu}^{3+}$ ( $S_6$ )	3.1	14	50.4
LDPE/PAA- $\text{UO}_2^{2+}$ ( $S_{11}$ )	1.6	73.2	50.7

Film thickness: 250  $\mu\text{m}$ .

### $\text{H}^+ \leftrightarrow \text{Eu}^{3+}$ Ion Exchange in the LDPE/PAA Matrix

A film of LDPE/PAA was carefully folded in several layers and immersed into a quartz cell containing 3.6 mL of a 10 mM  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  aqueous solution. The cell was tightly sealed and heated at specific temperature (60, 70, and 80°C). The fluorescence spectra were taken periodically from the homogenized cell solution at room temperature. The film in the cell was kept out of the optical pathway. The  $\text{Eu}^{3+}$  ions were excited at 394 nm and the fluores-

cence spectra of the solution were obtained in the region of 570–640 nm. The fluorescence intensity of the  $\text{Eu}^{3+}$  ions in the solution showed a linear behavior so that the fluorescence intensity of the peak at 591 nm was used to calculate the percentage of  $\text{H}^+ \leftrightarrow \text{Eu}^{3+}$  exchange. The fluorescence intensity of 10 mM  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  solution was assumed to be 100%. The percent of ions in the solution after each thermal treatment was calculated according Ximenes et al.<sup>3</sup>

The fluorescence spectrum of the dehydrated LDPE/PAA matrix after ion exchange was obtained under the same conditions as those of the solution. The matrix was placed into a sample holder to obtain the maximum fluorescence intensity in the region of 570–670 nm.

### $\text{H}^+ \leftrightarrow \text{UO}_2^{2+}$ Ion Exchange in the LDPE/PAA Matrix

The fluorescence measurements of the  $\text{H}^+ \leftrightarrow \text{UO}_2^{2+}$  ion exchange in the LDPE/PAA matrix followed the procedure described previously.<sup>3</sup> The work

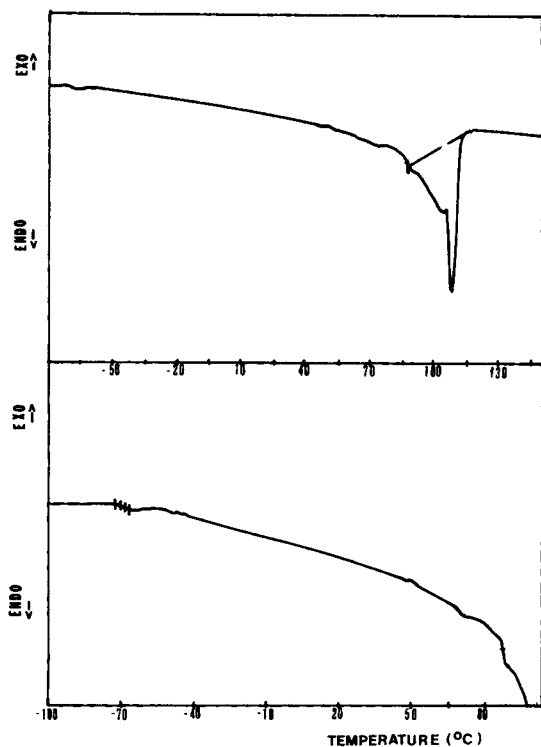


Figure 3 DSC curve: LDPE ( $S_1$ ).

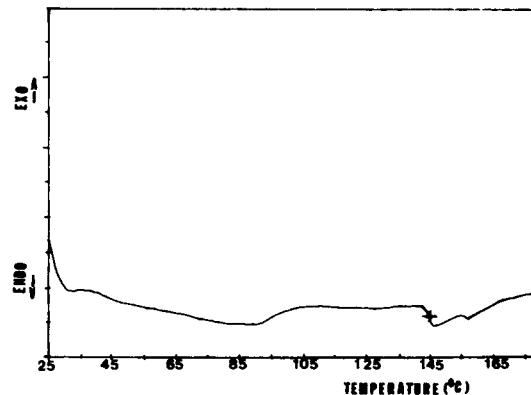


Figure 4 DSC curve: PAA.

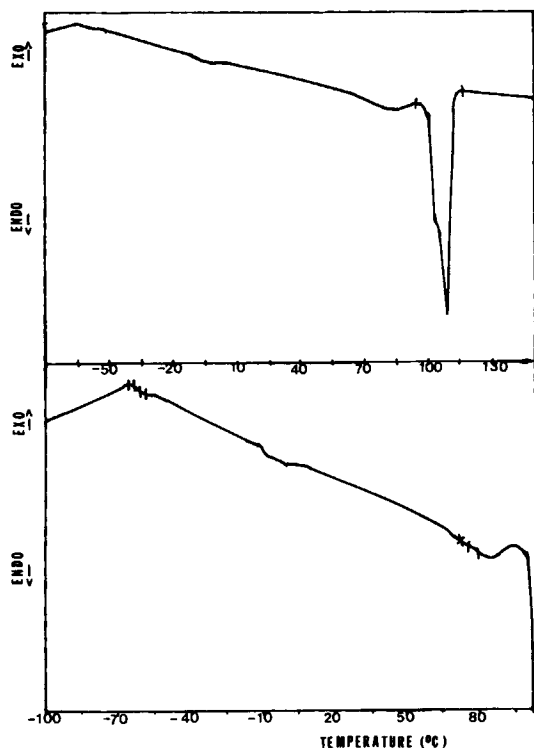


Figure 5 DSC curve: LDPE/PAA ( $S_4$ ).

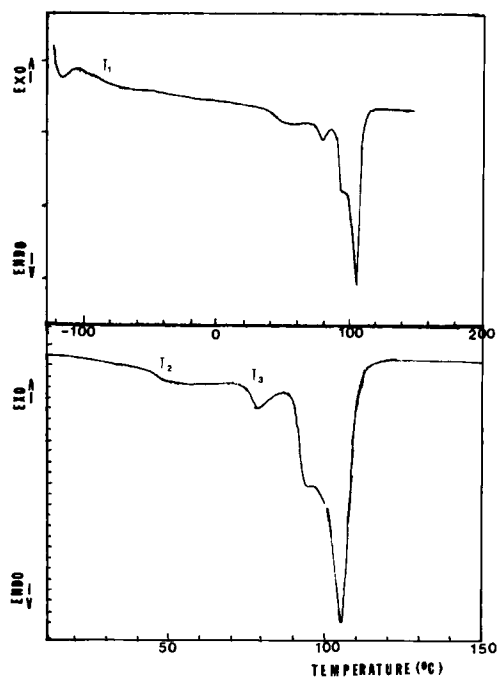


Figure 6 DSC curve: LDPE/PAA- $UO_2^{2+}$  ( $S_{10}$ ).

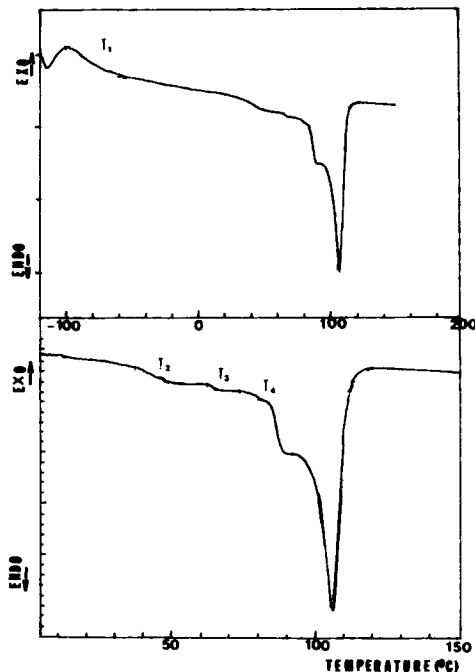


Figure 7 DSC curve: LDPE/PAA- $UO_2^{2+}$  ( $S_{11}$ ).

temperatures were 35 and 45°C. The area of the fluorescence complex band of the  $UO_2^{2+}$  ion in solution (at the range in between 440 and 660 nm) showed a linear behavior with the ion concentration (excitation at 420 nm). Thus, the relative areas were used to calculate the percent of  $UO_2^{2+}$  ions in the solution, after each thermal treatment, considering the area of the fluorescence complex band of a 10 mM  $UO_2Cl_2$  solution as 100%.<sup>4</sup>

The percent of ions in the LDPE/PAA matrix after  $UO_2^{2+}$  ion exchange was calculated as described for the  $Eu^{3+}$  exchange. The fluorescence spectrum of dehydrated LDPE/PAA matrix after the  $UO_2^{2+}$  ion exchange was obtained under the same conditions as described above for emission at the region 440–660 nm and excitation at 420 nm according to previous work.<sup>4</sup>

### Physical Measurements

X-ray studies were performed using a Rigaku diffractometer system Model Geigerflex D/Max III A with a  $CuK\alpha$  tube operating at 20 mA and 40 kV. Scanning electron microscopy (SEM) was performed using a JEOL JSM-840A operating at 5 kV. The samples were fractured after being frozen in

liquid nitrogen. The specimens were prepared for SEM by mounting then on an aluminum stub using silver paint. The specimens were coated with gold in a sputter coater SCD 050 Balzers.

The DSC thermograms were obtained using a DSC V40B DuPont 2000 calorimeter. The temperature range employed was  $-150$  to  $150^\circ\text{C}$  with a scanning rate of  $10^\circ\text{C}/\text{min}$ . Sample amounts of  $4.5$ – $9.5$  mg were used for the analysis.

## RESULTS

LDPE modified by *in situ* sorption and thermal polymerization of AA, LDPE/PAA after  $\text{Eu}^{3+}$  ion exchange, and LDPE/PAA after  $\text{UO}_2^{2+}$  ion exchange were previously prepared.<sup>3,4</sup> The morphology and microstructure of these materials were investigated. Their characteristics are described in Table I.

### X-Ray Studies

The X-ray diffraction patterns of LDPE/PAA before and after the  $\text{Eu}^{3+}$  ion exchange are shown in Figure 1. There are two main apparent features in these scans: a broad amorphous halo centered at about  $2\theta = 19.1^\circ$  and a sharp diffraction peak at  $2\theta$

$= 20.9^\circ$ . Both are characteristics of an LDPE diffraction pattern.<sup>9</sup> The shape and position of the peaks of the diffractograms observed for LDPE, LDPE/PAA, and LDPE/PAA/ after  $\text{Eu}^{3+}$  ion exchange are identical. No evidence of changes of the crystallinity degree of LDPE was observed in the LDPE/PAA before and after the  $\text{Eu}^{3+}$  ion exchange as calculated according to Aggarwal and Tilley.<sup>9</sup> It was roughly the same as that obtained for the pure matrix (51.1%) (Table II).

The diffraction patterns clearly indicate that PAA is located at the amorphous domains of the LDPE matrix. The evidence also confirmed the  $\text{H}^+ \leftrightarrow \text{Eu}^{3+}$  ion exchange at these domains. The X-ray diffraction patterns of LDPE/PAA before and after the  $\text{UO}_2^{2+}$  ion exchange are shown in Figure 2. The shape and position of the peaks observed for LDPE, LDPE/PAA, and LDPE/PAA after  $\text{UO}_2^{2+}$  ion exchange are identical. Also, the crystallinity degree of LDPE ( $X_c$ ) remained the same after AA sorption and thermal polymerization in the matrix and after  $\text{UO}_2^{2+}$  ion exchange in the LDPE–PAA composite matrix (Table II).

The diffraction patterns indicate that PAA is located at the amorphous domains of the LDPE matrix and, consequently, the  $\text{UO}_2^{2+}$  ions. Possibly, ion clusters might exist in these domains, although preliminary data obtained from simultaneous ion ex-

**Table III Thermal Measurements (DSC) of LDPE-modified Matrix**

Sample (No.)	% PAA in the Matrix	% $\text{Eu}^{3+}$ in the LPDE/PAA Matrix	% $\text{UO}_2^{2+}$ in the LDPE/PAA Matrix	$T_m$ ( $^\circ\text{C}$ )	$T_g$ ( $^\circ\text{C}$ )	$H_f$ ( $\text{Jg}^{-1}$ )
PAA	—	—	—	—	144.4	—
LDPE ( $S_1$ )	—	—	—	108.3	−70.1	64.3
LDPE/PAA ( $S_4$ )	4.0	—	—	109	−61.2 +72.9	75.6
LDPE/PAA– $\text{Eu}^{3+}$ ( $S_8$ )	4.5	42	—	107.4	−69.9 +88.4	67.4
LDPE/PAA– $\text{UO}_2^{2+}$ ( $S_{10}$ )	1.6	—	41.7	105.3	−85.9 47.0 76.5	61.6
LDPE/PAA– $\text{UO}_2^{2+}$ ( $S_{11}$ )	1.6	—	73.2	105.8	−80.1 44.9 64.6 78.8	36.4

change of  $\text{Eu}^{3+}$  and  $\text{UO}_2^{2+}$  did not show evidence of ionomer aggregates in the modified LDPE/PAA matrix.<sup>4</sup> Whatever the ion exchange in the matrix LDPE/PAA ( $\text{Eu}^{3+}$  or  $\text{UO}_2^{2+}$ ), the X-ray patterns are quite similar.

### Thermal Measurements

DSC thermograms were obtained for pure LDPE, pure PAA, LDPE/PAA, and LDPE/PAA/ $\text{Eu}^{3+}$ . LDPE exhibited a smooth curve with a best-adjusted fit for the  $T_g$  transition at  $-70.1^\circ\text{C}$ , the melting temperature,  $T_m$  at  $108.3^\circ\text{C}$ , and a heat fusion of  $64.3 \text{ J g}^{-1}$  ( $\Delta H_f$ ) (Fig. 3).

Figure 4 shows the DSC curve of PAA with  $T_g$  at  $144.4^\circ\text{C}$ . The DSC curve of the LDPE/PAA-modified matrix showed again a smooth curve with two best-adjusted  $T_g$  values at  $-61.3$  and  $72.9^\circ\text{C}$  (Fig. 5). The LDPE/PAA after the  $\text{Eu}^{2+}$  ion exchange ( $S_g$ ) exhibited a similar DSC curve with two  $T_g$  values at  $-69.9$  and  $88.4^\circ\text{C}$ . For both cases, the transitions are in between the  $T_g$  obtained to the pure linear polymers (LDPE and PAA).

The thermograms of the materials LDPE/PAA containing 41.7 and 73.2% of  $\text{UO}_2^{2+}$  ion exchange in the matrix (samples  $S_{10}$  and  $S_{11}$ ) are shown in Figures 6 and 7. A broadening of the transition region was observed. Three  $T_g$  values were fitted for sample  $S_{10}$  and four  $T_g$  values were adjusted for sample  $S_{11}$ .

These data reflect a microheterogeneity of phase domains of all the systems studied. The constants obtained by the thermal measurements (DSC) for the several materials analyzed are listed in Table III.

### Scanning Electron Microscopy (SEM)

SEM micrographs of the pure matrix LDPE are shown in Figure 8. A smooth and homogeneous surface showing a wavelike morphology is observed for the LDPE matrix [Fig. 8(a)]. However, some small dispersed "lumps" can be noticed [Fig. 8(b) and (c)] which have been explained by the presence of detached LDPE chain segments in the surface of the matrix.

Figure 9 shows the micrographs of LDPE containing 0.3, 4.0, and 25.7% of PAA in the matrix. They showed a similar wavelike surface morphology as compared to that of the LDPE matrix. All display an apparently homogeneous surface. It can be seen that the sorption and *in situ* thermal polymerization

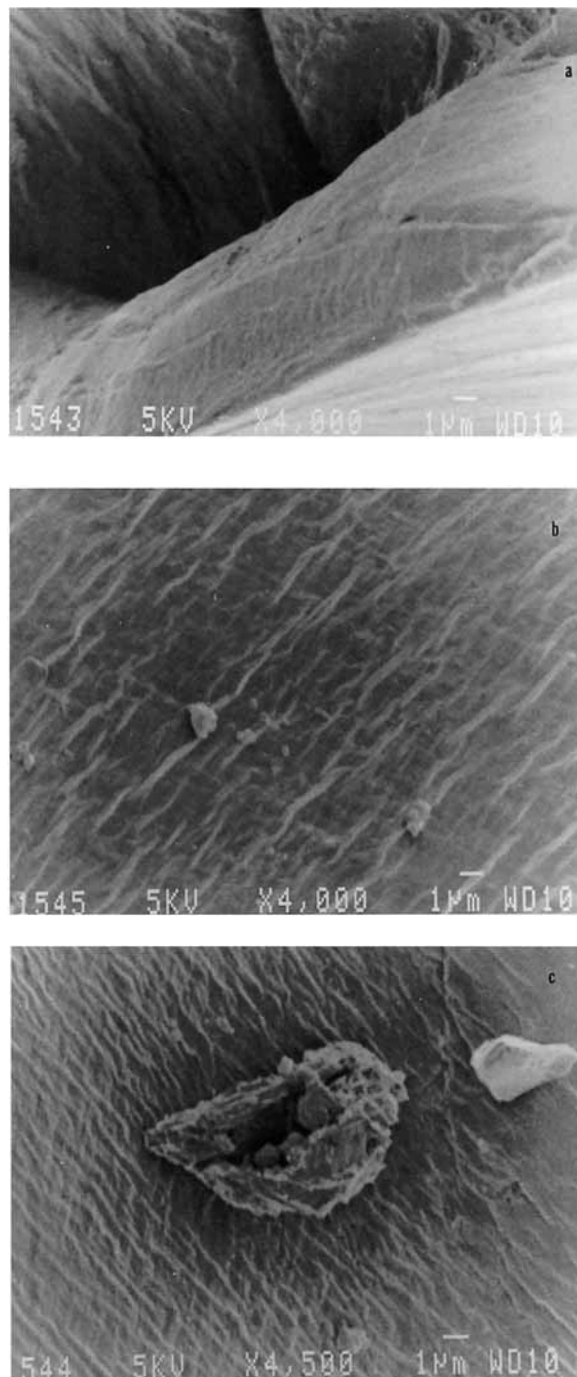
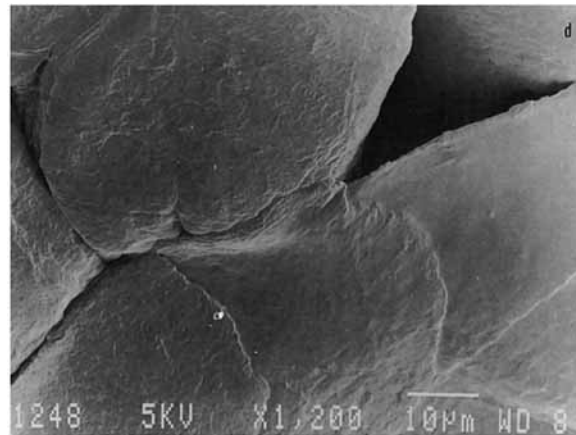
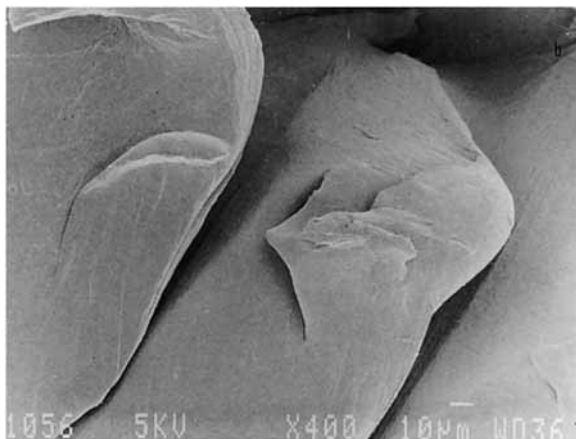
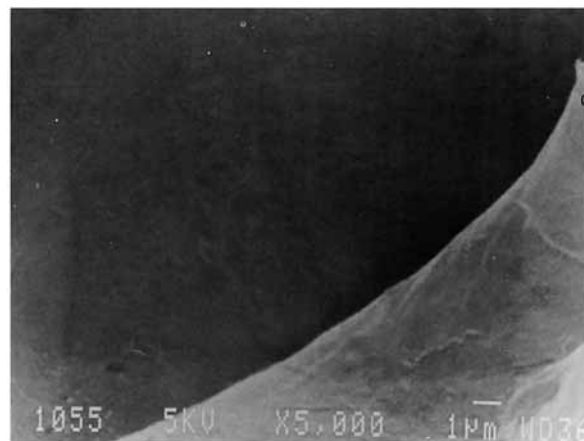
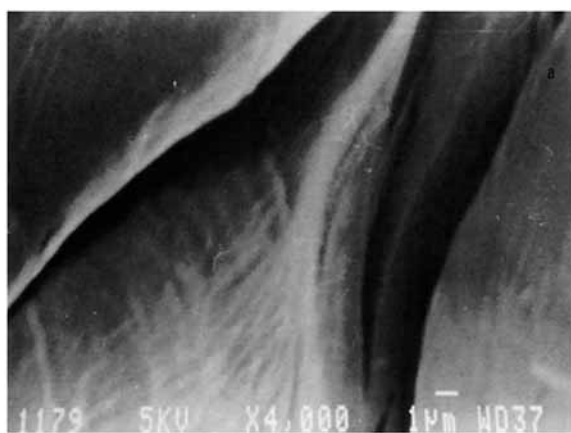
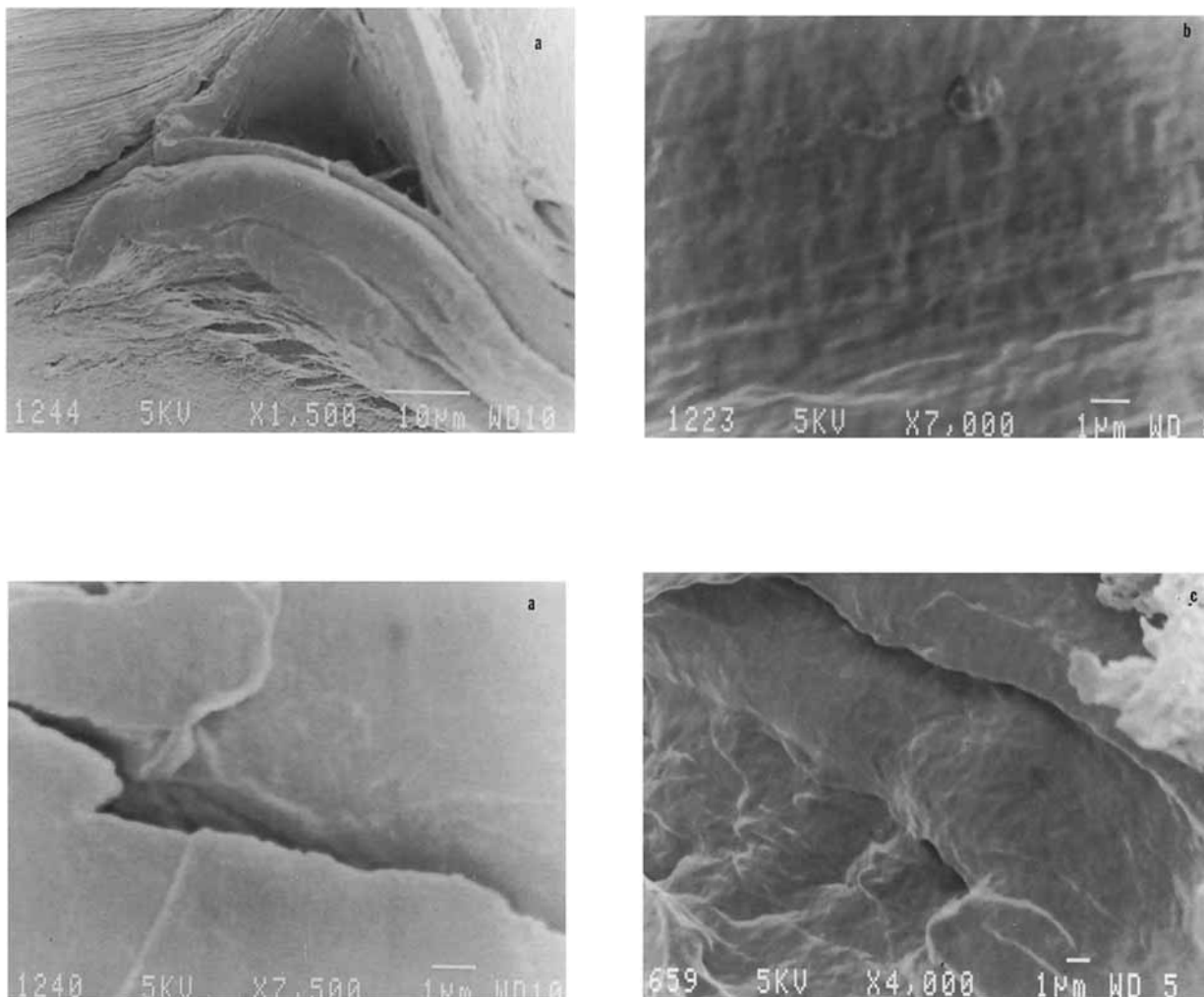


Figure 8 SEM micrographs: LDPE.

of PAA in the LDPE does not change the surface morphology as compared to the LDPE matrix itself (Fig. 8). No lumps appeared for the three different percentages of PAA in the matrix.



**Figure 9** SEM micrographs: LDPE/PAA: (a) 0.3% PAA; (b) 4.0% PAA; (c) 4.0% PAA; (d) 25.7% PAA.



**Figure 10** SEM micrographs: LDPE/PAA-Eu<sup>3+</sup>: (a) 3.1% PAA, 14% Eu<sup>3+</sup> (S<sub>6</sub>); (b) 4.2% PAA, 29% Eu<sup>3+</sup> (S<sub>7</sub>); (c) 4.5% PAA, 42% Eu<sup>3+</sup> (S<sub>8</sub>).

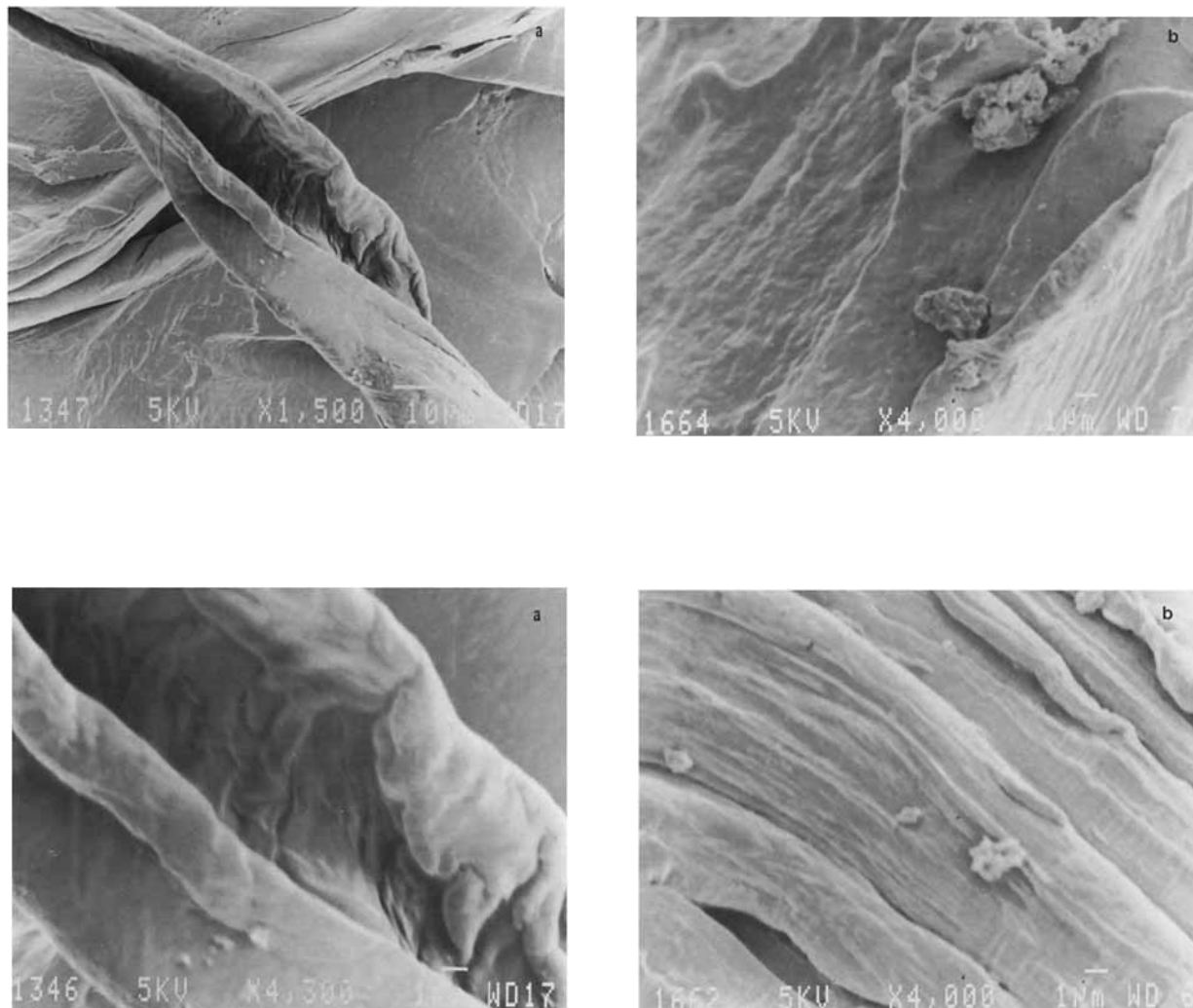
The scanning electron micrographs of LDPE containing 3.1, 4.2, and 4.5% of PAA and 14, 29, and 42% of Eu<sup>3+</sup> after ion exchange are shown in Figure 10. The phase morphologies of these materials, whatever the amounts of Eu<sup>3+</sup> in the matrix, appeared very similar. Also, in some micrographs, the presence of a small globule dispersed in the surface of the modified matrix was noticed [Fig. 10(b)]. Despite this lump, the material seemed to have no hint of phase separation.

The micrographs, at the fractured surfaces, of the LDPE/PAA/UO<sub>2</sub><sup>2+</sup> complex showed a similar wavelike surface morphology as described previously. Figure 11 shows the morphology of the mod-

ified matrix LDPE/PAA containing 1.1 and 1.6% of PAA and after 17.8, 41.7, and 73.2% of UO<sub>2</sub><sup>2+</sup> ion exchange. It can be seen that the percentage of the UO<sub>2</sub><sup>2+</sup> ion exchange did not change the morphologies of the samples. No distinguishable phase separation or inhomogeneities is observed, although some small dispersed lumps can be noticed.

Within the limits of the magnitude used, these lumps, observed occasionally in the modified matrix, seem to be morphologically identical to those found on the pure matrix. They were attributed to chain segments of the pure matrix itself which could be eventually detached from it during the preparation procedure of the modified material.





**Figure 11** SEM micrographs: LDPE/PAA- $\text{UO}_2^{2+}$ : (a) 1.1% PAA, 17.8%  $\text{UO}_2^{2+}$  ( $S_9$ ); (b) 1.6% PAA, 41.7%  $\text{UO}_2^{2+}$  ( $S_{10}$ ); (c) 1.6% PAA, 73.2%  $\text{UO}_2^{2+}$  ( $S_{11}$ ).

## DISCUSSION

The investigation of the morphology of the modified LDPE by *in situ* sorption and thermal polymerization of acrylic acid in the matrix showed no evidence of phase separation in the modified matrix even after the  $\text{Eu}^{3+}$  or  $\text{UO}_2^{2+}$  ion exchange. This fact together with the data that PAA is located at the surface or at neighboring layers<sup>8</sup> suggest that the modified region displays an apparently homogeneous surface.

However, the two  $T_g$  values obtained by the thermal measurements (DSC) for the LDPE/PAA are indicative of phase domains on this material, corresponding probably to the inner layers of LDPE

and to the surface or neighboring layers of the modified material LDPE/PAA. The same behavior was observed on the LDPE/PAA- $\text{Eu}^{3+}$ .

The material LDPE/PAA after 41.7 and 73.2% of  $\text{UO}_2^{2+}$  ion exchange presented three and four  $T_g$  values, respectively. In all materials, the lowest  $T_g$  value is located at the boundaries of the  $T_g$  found for LDPE and the two and three remaining transitions at intermediate values found for LDPE and PAA. The presence of phase microheterogeneity at the surface or at neighboring layers region of these materials was evident.

The lack of phase separation in the micrographs cannot necessarily be conclusive and is indicative of

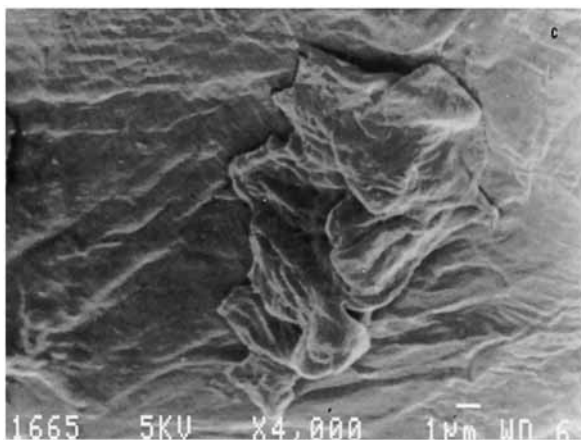
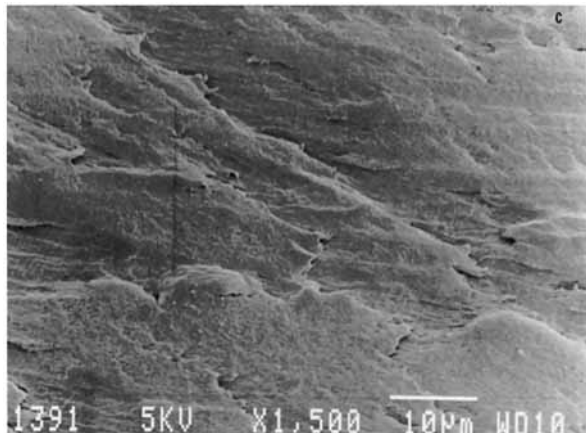


Figure 11 (Continued from the previous page)

the absence of inhomogeneities in these materials. In fact, multiphase behavior where the glass transition is broadened is commonly observed for blends exhibiting partial miscibility.<sup>10,11</sup>

Further morphological studies on LDPE/PAA before and after  $\text{Eu}^{3+}$  and  $\text{UO}_2^{2+}$  ion exchange by TEM is underway. Also, the morphological studies of the simultaneous  $\text{Eu}^{3+}$  and  $\text{UO}_2^{2+}$  ion exchange are under investigation.

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