

Reuse of Plastics Recovered from Solid Wastes. Thermal and Morphological Studies from HDPE / LDPE Blends

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Synopsis

In this work a few observations are made about some microstructural aspects from HDPE and LDPE homopolymers and their blends as virgin materials and also from urban plastic wastes. Micrographs were taken by SEM. Micrographs corresponding to the fracture surface from specimens tested in an impact test clearly show different microstructural features due to polymer which is more than 50%. Parts were injection molded. On the other hand, a discussion is given about crystallization behavior of those materials obtained by DSC. For all blends the same results have been found, i.e., two peaks owing to each of the two polymers which are present in the blends.

INTRODUCTION

Polymer blends exhibit a wide range of morphological states from coarse to fine ones. In addition to the usual possibilities of obtaining separate phases with various size, shape, and geometrical arrangements of inclusions, more complex structures are possible, especially in crystalline polymer blends.

The most interesting aspects of the two-component polyolefin blends concern the influence of composition on the overall morphology, on mechanical behavior, and on quantities such as the melting temperature, the degree of crystallinity, and the crystallization rate from melt of components.¹

Two polymers can be expected to be miscible when a very close match in cohesive energy density or in specific interactions, which produce a favorable enthalpy of mixing, is involved. The ability to cocrystallize can provide an additional driving force for polymer miscibility.

One of the major areas of studies on polymer blends is the dependence of the mechanical properties on composition. This is due to the fact that these complex systems exhibit a behavior that does not simply follow the sum of the properties of the components. In a previous work² Laguna et al, showed the mechanical behavior of LDPE/HDPE blends, pure and from urban plastic wastes film, unmodified and modified with different agents. In the same work a study by optical microscopy of different samples from HDPE, LDPE, and their blends was also carried out.

In an attempt to find out about the waste microstructure, a study was carried out by scanning electron microscopy (SEM) of the fracture surfaces owing to impact tests at -30°C for urban plastic wastes film and HDPE/LDPE blends.²

TABLE I
Physical Properties of Materials Used in the Present Work

Material	Molecular weight		HI	Melt index			ρ (g cm ⁻³)
	\bar{M}_n	\bar{M}_w		P (kg)	T (°C)	(g 10 min ⁻¹)	
LDPE	141.000	19.000	7.5	2.160	190	6.70	0.9160
HDPE	114.700	22.000	5.25	5.000	190	2.33	0.9450
Film plastic wastes	^a	—	—	2.160	190	1.10	0.9407

^a Compared by viscometry with homopolymers.

The existence or not of cocrystallization phenomena for different samples from wastes and LDPE/HDPE blends was also studied by differential scanning calorimetry DSC. Samples were taken from injection-molded parts.

MATERIALS AND EXPERIMENTAL METHODS

The materials studied are described in Table I.

Blends of high and low density polyethylene were prepared on a two roll-mill and fabricated into parts in a single screw injection machine. Specimens from urban plastic wastes film were also molded by this method.

In the roll mill the mixing time was 15 min, and the roll temperature 150–160°C.

Blends prepared were in LDPE/HDPE ratios of 0/100, 14.64/85.36, 50/50, 85.35/14.64, and 100/0, chosen according to a factorial design developed for the study of melt behavior of HDPE/LDPE blends.³

DSC thermograms were used by the authors for determining the weight concentration of each of the crystalline components of PE blends, pure and from urban wastes.⁴ DSC analysis was carried out on a Perkin-Elmer differential scanning calorimeter, DSC-4 Model, at a heating rate of 10°C, under nitrogen atmosphere.

Impact tests were made by a Ceast instrumented apparatus at -30°C. After each test both fragments of the specimen were taken and reserved for their study on fracture surfaces by SEM.

The scanning electron microscope used was an ISI, Model Super Mini SEM. The specimen surfaces' topography was observed by metallization of the samples which were coated with a thin layer of gold of 288 Å. LDPE samples were coated with a thin layer of 432 Å. Observations were made at 25 KV with a work distance equal to 8.

RESULTS AND DISCUSSION

Thermal Studies

Figures 1–6 illustrate the fusion endotherms of the blend from urban plastic wastes and, respectively, for HDPE, HDPE/LDPE ratios 85.36/14.64, 50/50, and 14.64/85.36, and, at last, LDPE. The corresponding values have been put in Table II.

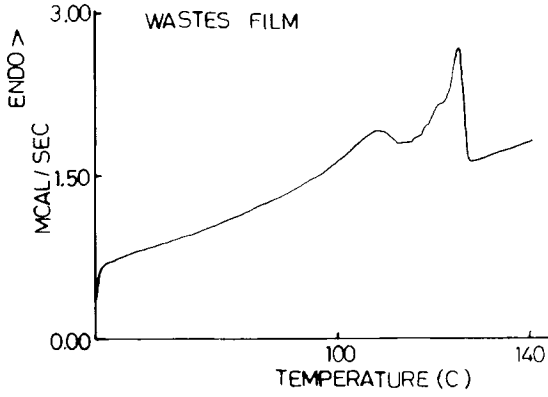


Fig. 1. DSC thermogram from urban plastic wastes film.

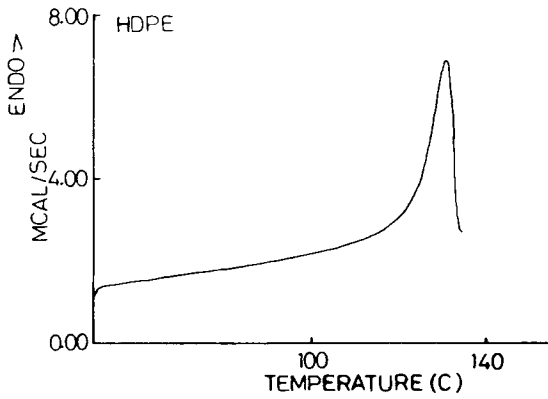


Fig. 2. DSC thermogram from HDPE used at this work.

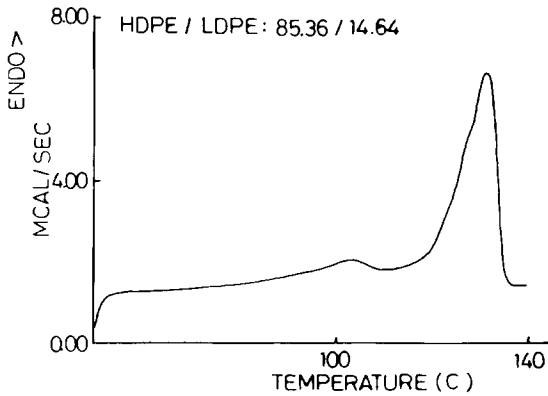


Fig. 3. DSC thermogram from 85.36/14.64 HDPE/LDPE blend.

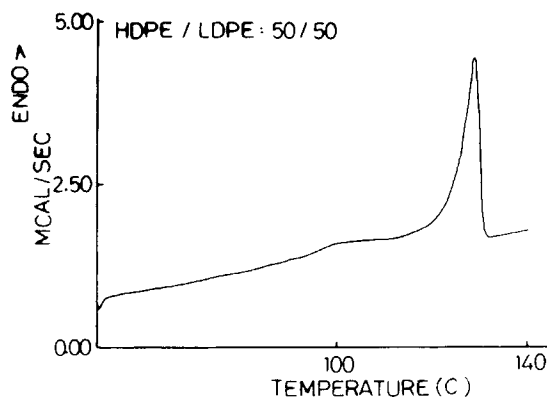


Fig. 4. DSC thermogram from 50/50 HDPE/LDPE blend.

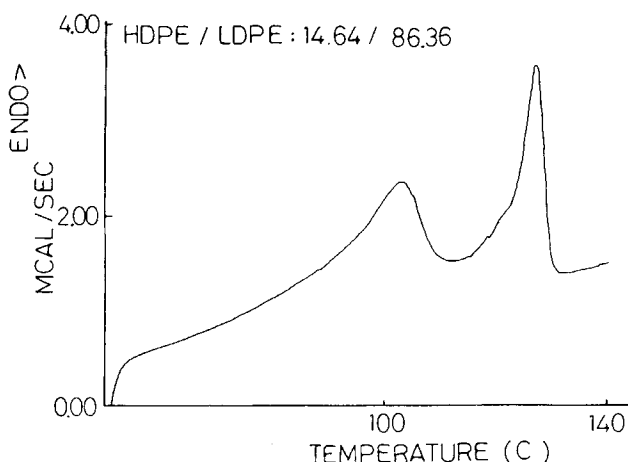


Fig. 5. DSC thermogram from 14.64/86.36 HDPE/LDPE blend.

In both HDPE and LDPE homopolymers, only a single peak appears, whereas the intermediate blends, and those from wastes, show two peaks. Furthermore, endothermic peaks are separated in all cases of more than 10°C.

The peak position of the LDPE appears to remain invariant while the magnitude decreases significantly with decreasing LDPE content. After a slow cooling (1°C/min), this circumstance remains for each sample.

For 50/50 blend (Fig. 4) it is not possible to distinguish the peak corresponding to LDPE but it is possible to determine his existence by peak area method according to Stafford.⁵ The full development was shown in Ref. 4. The existence of two peaks in DSC thermograms has been observed by other authors on studying the crystallization of polyolefin blends⁶ and interpreted as the consequence of a melting endotherm owing to the polymer with the higher crystallization capacity (HDPE at this case), and which is dominant over the LDPE melting endothermic peak.

These melting results are in close agreement with those obtained by Smith and Manley⁷ for mixtures of polyethylenes fractions, Donatelli's results⁸ for LDPE/HDPE and Kyu and Vadhar⁶ for UHMWPE/LDPE blends. Further-

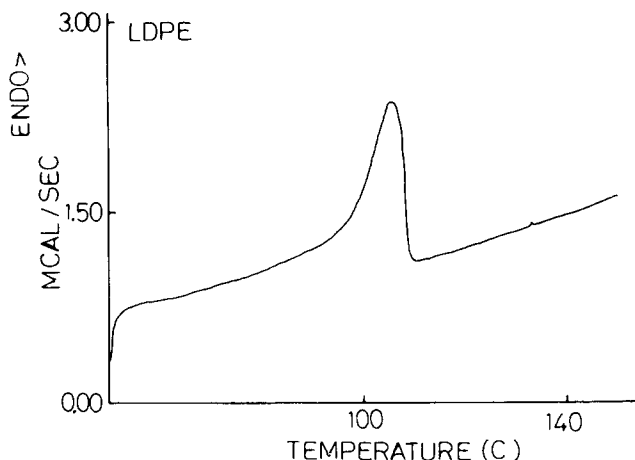


Fig. 6. DSC thermogram from LDPE used in this work.

TABLE II
DSC Data for Pure Polymers and Blends

HDPE/LDPE ratio	T_m ($^{\circ}\text{C}$)		ΔH_m (cal/g)	
	P_1	P_2	P_1	P_2
100.00/00.00	—	131	—	39.86
85.36/14.64	103	131	1.44	23.54
50.00/50.00	—	129	—	19.62
14.64/85.36	103	127	4.70	6.05
00.00/100.00	106	—	16.04	—
20.00 ^a /70.00	106	125	2.78	6.00

^aApproximately corresponding to the average composition from film urban plastic wastes.

more, Kyu and Vadhar found negative deviations from the linearity rule for strength at break and elongation at break for UHMWPE/LDPE blends. The general conclusion may be drawn from those studies that mixtures of linear and linear PE chains have an ability to cocrystallize together, while blends of linear and branched PE tend to form separate crystals.⁶

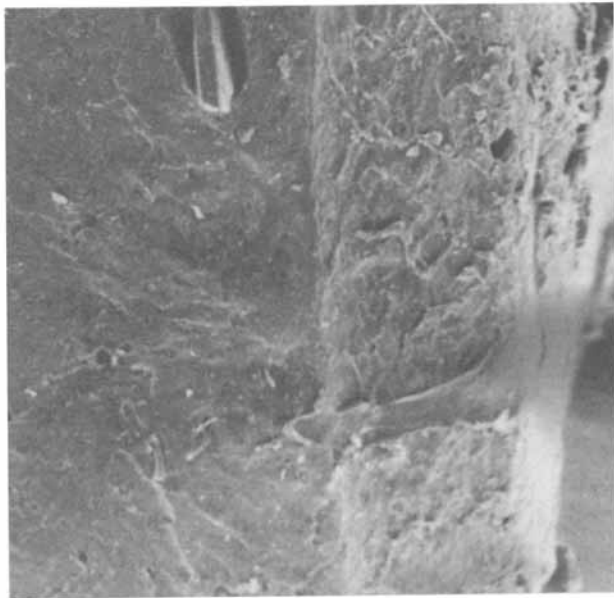
The observations about mechanical behavior of UHMWPE/LDPE blends given in Ref. 6 are in good agreement with results shown by the authors in Ref. 2 which were found for HDPE/LDPE blends.

It must be noted that crystalline polymer blends consist of both amorphous and crystalline regions in pure components. Therefore, the miscibility studies of crystalline polymer blends are generally very complex and require analysis in both melt and solid states.⁶

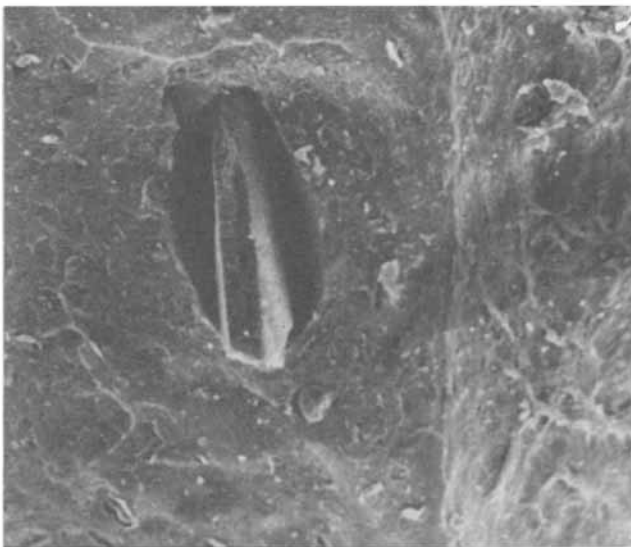
The investigation of melt viscosity has been widely used to study the miscibility of polymer blends, frequently using the additivity scheme for melt viscosity vs. composition. Both positive and/or negative deviations are seen in most blends. Laguna et al.³ showed the results for melt behavior of the HDPE/LDPE blend obtained by using torque-rheometer data. Both positive and negative deviations are found for η_0 vs. % HDPE for this system as was

discussed in Ref. 2 according to the review about this theme given by Utracki.⁹

On the other hand, according to the studies of Paul and Robertson,¹⁰ negative deviations are generally seen in tensile strength and elongation at break vs. composition curves of immiscible HDPE/PP blends. The modulus may vary more or less linearly with the composition regardless of the miscibility between the components. This kind of negative deviation is also observed by the authors in Ref. 2 for the HDPE/LDPE system. Always the validity of the linear additivity rule in the tensile properties vs. composition may be



a



b

Fig. 7. Scanning electron micrographs of fracture surfaces from wastes: (a) $50\times$; (b) $100\times$.

associated with the formation of cocrystals between blend components; on the contrary, the blends of linear and branched polyethylenes tend to form separate crystals.⁶

In the DSC studies shown in Figures 3–5 we observed that in blends of HDPE/LDPE separate crystals are formed and this fact may be attributed to differences in chain linearity since LDPE is of branched type while HDPE is essentially linear. This fact also occurs for urban plastic wastes as it may be seen in Figure 1.

In the cooling runs, two exotherms were evident in all cases; because of this they were not recording. The melting temperature of HDPE component shown in Table II follow a linear variation with composition. The melting

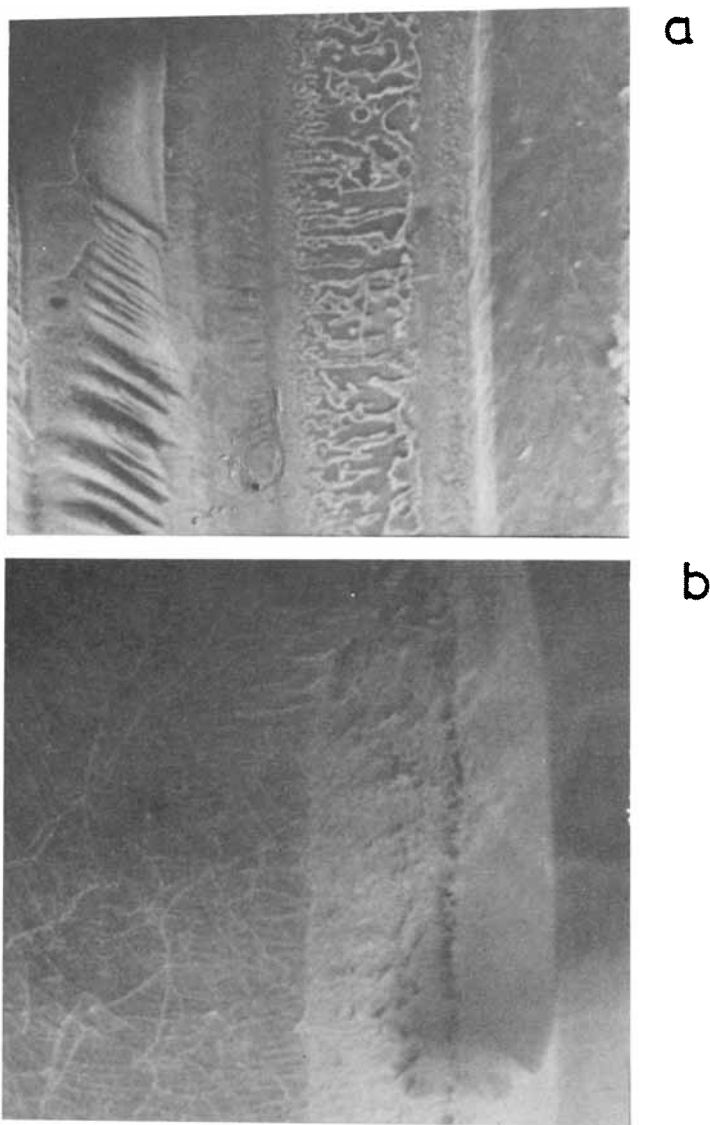


Fig. 8. Scanning electron micrographs of overall fracture surfaces from HDPE (a) and LDPE (b), $30\times$.

temperatures of the HDPE decreases with the addition of LDPE content.⁶ Once more the important conclusion is that separate crystals or separate superstructures are formed between HDPE and LDPE components, as will now be seen by SEM.

Morphological Study

As has been said in the introduction, in a previous work,² Laguna et al. showed morphological features for HDPE/LDPE blends from two homopoly-

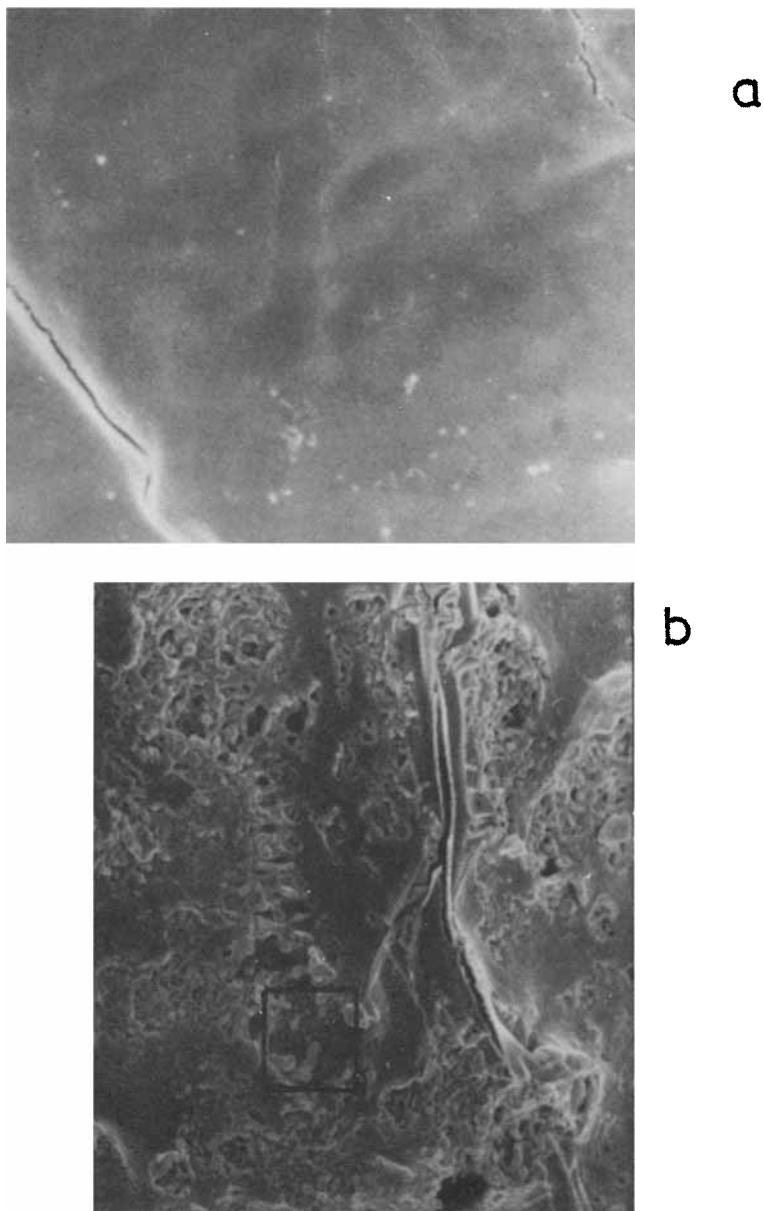


Fig. 9. Scanning electron micrographs of fracture surfaces from LDPE: (a) nonetched sample (1000 \times); (b) xylene-etched sample (1000 \times); (c) xylene-etched sample (7000 \times).

mers by using interferential contrast microscopy based on polarized light. Whereas for samples from plastics wastes it was not possible to carry out the morphological studies by this technique because the optical behavior in transmitted light microscopy of these materials is destroyed by the numerous impurities incorporated in them.

On the other hand, scanning electron microscopy (SEM) is a valuable tool for anyone interested in the surface features of materials and so was considered by the authors in an attempt to find out about the plastic waste microstructure.

A first observation of fracture surfaces obtained from waste samples may be seen in the micrographs of Figure 7, which shows fracture surface from the impact test taken at lower magnifications. Both the micrographs show little solid particles and one bigger insertion inside the polymer blend matrix.

Micrographs of overall fracture surfaces from HDPE and LDPE, respectively, taken at lower magnifications may be seen in Figure 8. These micrographs show differences between the overall fracture surfaces for both HDPE and LDPE homopolymers. This fact is in agreement with the mechanical behavior found by the authors and discussed in Ref. 2. There, a different mechanism of impact toughening for HDPE and LDPE was proposed and Figure 8(a) shows the fracture surface for a brittle material (HDPE) tested to -30°C . At this temperature, LDPE did not break and so Figure 8(b) shows the smooth fracture surface for LDPE taken off a cryofracture (liquid nitrogen).

The observation of fracture surfaces from wastes, HDPE, LDPE, and blends of these latter polymers carried out at higher magnifications showed very little definition and for this reason the fracture surfaces were treated with xylene at 60°C for 1 min in an etching or attack to reveal fine detail in

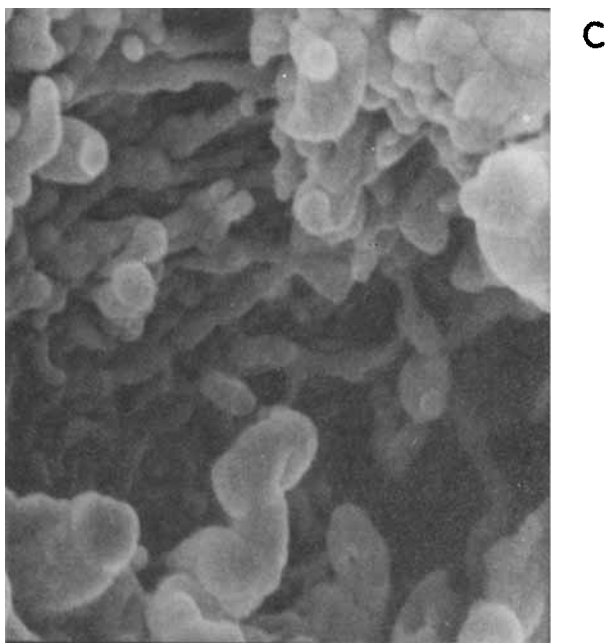
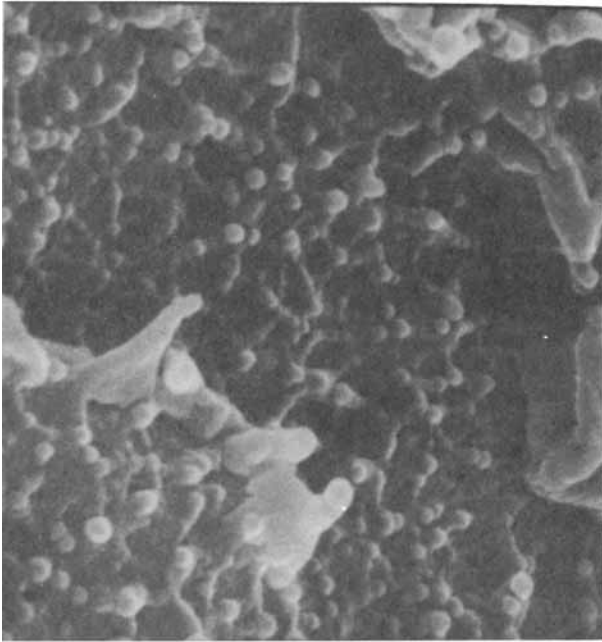
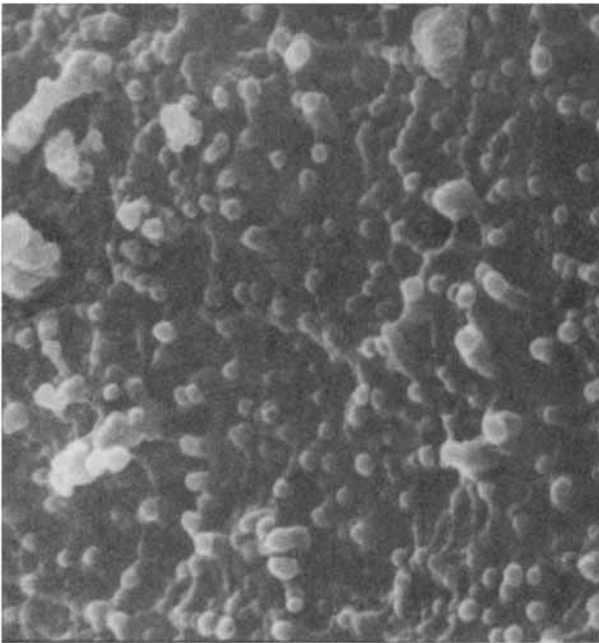


Fig. 9. (Continued from the previous page.)



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Fig. 10. Scanning electron micrographs of fracture surfaces from HDPE: (a) nonetched sample ($7000\times$); (b) xylene-etched sample ($7000\times$).

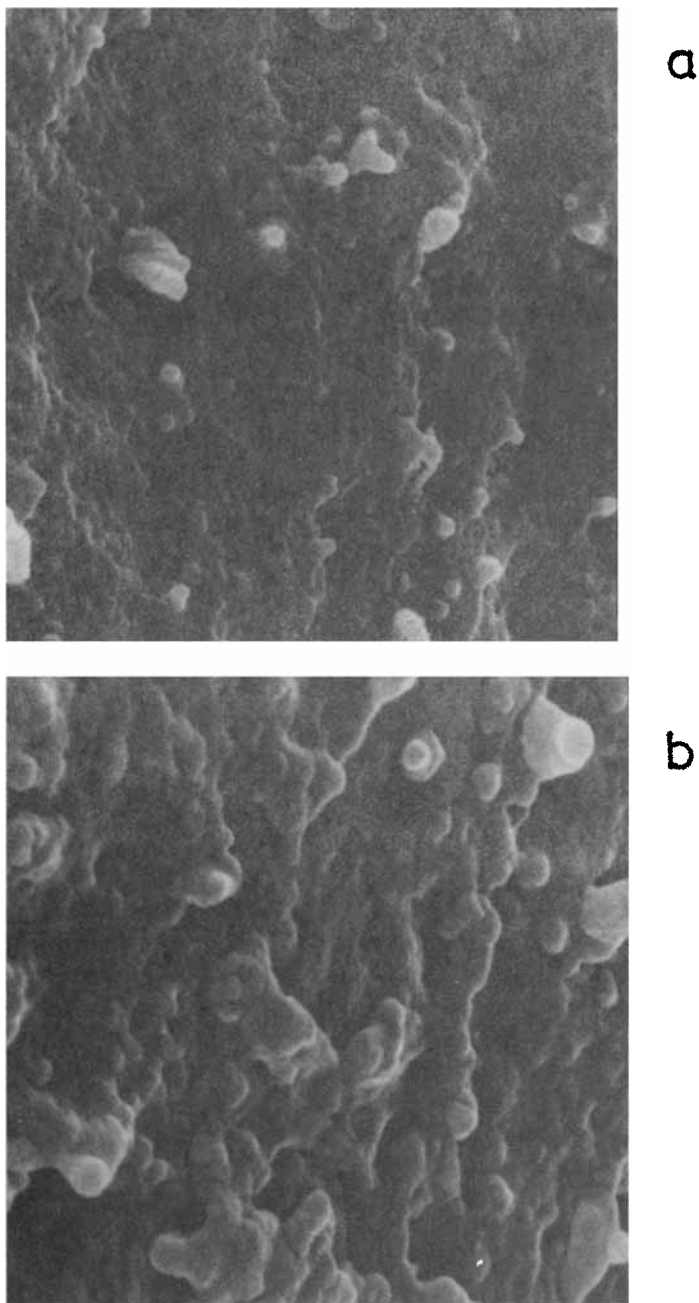
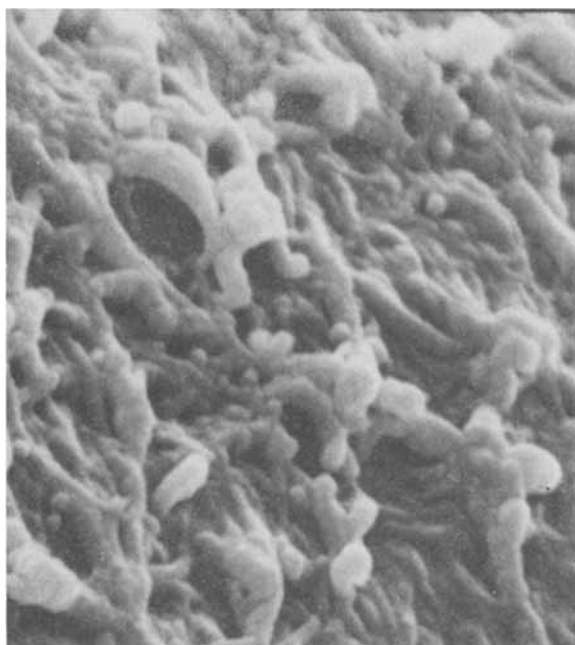


Fig. 11. Scanning electron micrographs of fracture surfaces from 85.36/14.64 HDPE/LDPE blend: (a) nonetched sample (5000 \times); (b) xylene-etched sample (5000 \times); (c) xylene-etched sample (10,000 \times).



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Fig. 11. (Continued from the previous page.)

surface characteristics. The attack is derived from the etchant removing disordered or "defective" material which would be disturbing the resolution of the images. The development of a relief showing the morphology is sometimes possible by selective etching (by ions, or by gas discharge, or chemically) of a smooth or brittle fracture surface.¹¹

Figure 9 shows the micrographs by SEM for cryofracture from LDPE. Figure 9(a) shows the surface before the treatment and Figure 9(b) the surface after the treatment. This seems to be very effective for this material and lets us see an internal microstructure damaged as a consequence of the attack, whereas samples from HDPE (Fig. 10) do not seem to be affected by the same treatment, and before and after for the latter, they look the same. At this magnification rather rounded features as well as numerous small cavities may be seen. These rounded features are very different from those found for LDPE after the treatment at the same magnifications [Fig. 9(c)] and are absent without the treatment. LDPE exhibits as fibrilar elements which show evidence of considerable localized plastic deformation before the instantaneous cryofracture.

For HDPE/LDPE blends we found that the cavities are considerably more visible at still higher magnifications. So, in Figure 11(a), corresponding to the HDPE/LDPE blend with a ratio 85.36/14.64, one may see the poor resolution owing to the presence of smooth component, i.e., LDPE, and the holes left between a network or entanglement structure with the above-mentioned rounded features forming as the knots of this network. These observations about the fracture nature are in accord with mechanical behavior from impact test previously discussed in Ref. 2. In fact, for HDPE/LDPE blend with a 14.64/85.36 ratio (Fig. 12) the microstructure is not similar to the above

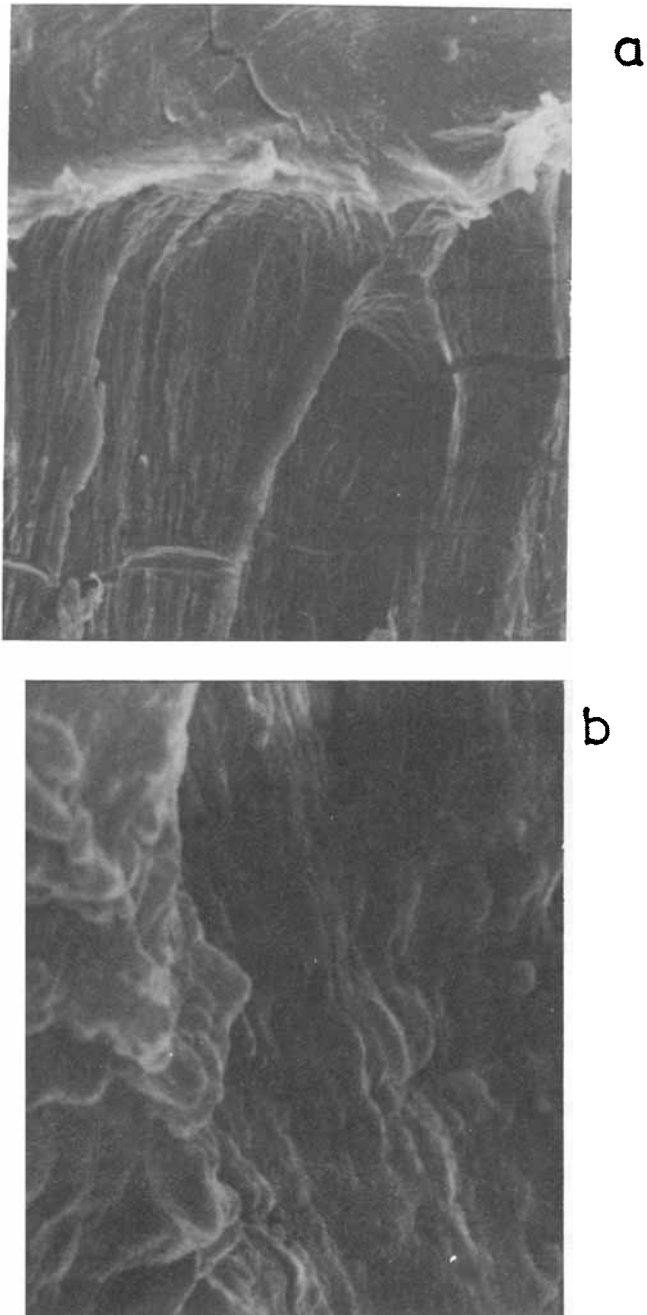
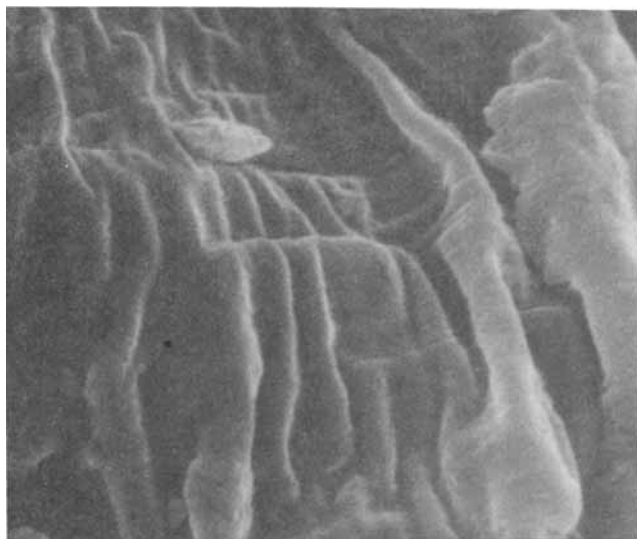


Fig. 12. Scanning electron micrographs of fracture surfaces from 14.64/85.36 HDPE/LDPE blends: (a) nonetched sample (400 \times); (b) xylene-etched sample (5000 \times); (c) xylene-etched sample sample (5000 \times).



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Fig. 12. (Continued from the previous page.)

shown. When LDPE is more than 50%, even after the attack, it is not likely that a microstructure cannot be identified. This microstructure is from blends whose HDPE component is in the majority.

The polycrystalline polymeric solid shows a distinct lamellar morphology of crystalline lamellae intercalated by so-called "amorphous," less ordered regions.^{12,13} The flat shape of lamellae favors parallel packing into crystal stacks usually producing a local ordering and orientation. The lamellae themselves have a mosaic block superstructure.^{14,15} Nevertheless, the connection of crystalline lamellae through a network of tie molecules and entanglements significantly contributes to the mechanical strength of the polymeric solid.¹⁶

In 50/50 blend, whose micrographs are shown in Figure 13, it is necessary to employ the highest magnifications to appreciate the network or entanglement microstructure and, as was observed in Ref. 2 for the optical behavior of this blend, the holes have the same dimensions of distances between the network knots.

Micrographs in Figure 14 show the fracture surfaces for specimens from wastes. Micrographs 14(a) 14(b) are very similar to those obtained in blends where LDPE is more than 50%, and, furthermore, the presence of smaller impurities may be clearly seen.

At higher magnifications it is possible to distinguish a globular structure in accord with that found in the HDPE/LDPE system. An exhaustive discussion over this morphology is given in Ref. 17.

CONCLUSIONS

—The present work lets us conclude that there are the similar microstructures between HDPE/LDPE blends and a fraction of urban solid wastes which constitutes plastic waste film. This observation is in good agreement

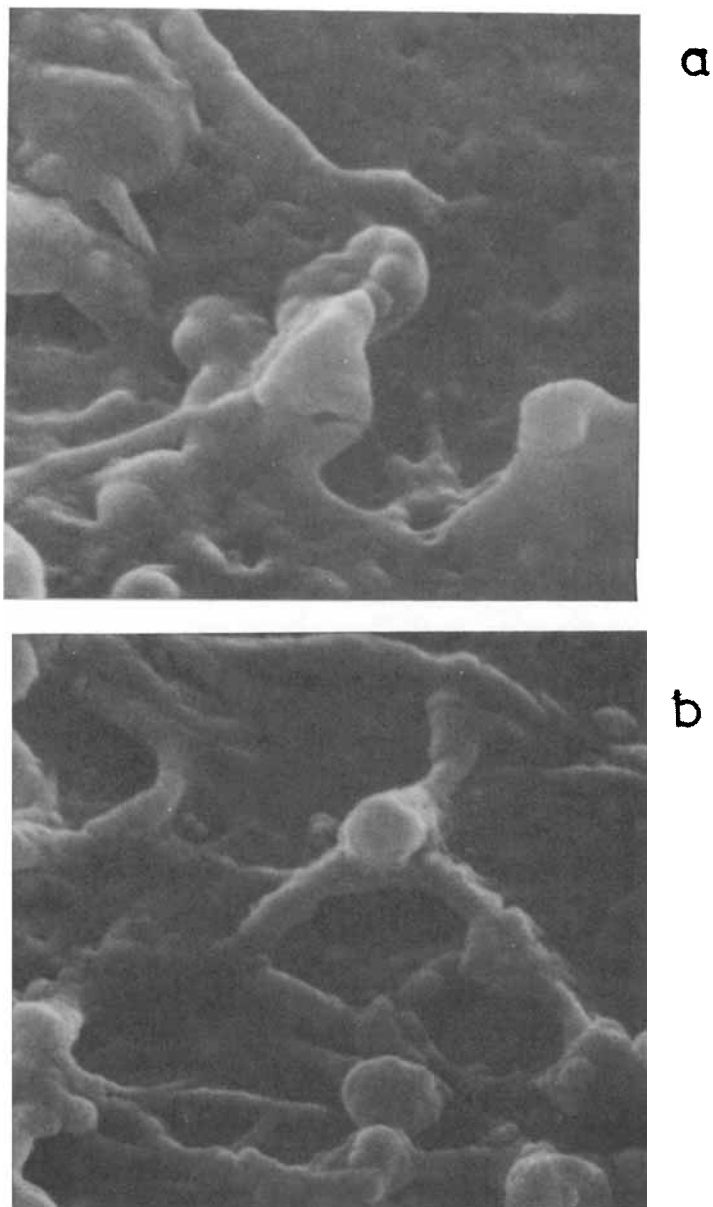


Fig. 13. Scanning electron micrographs of fracture surfaces from 50/50 HDPE/LDPE blend: (a) nonetched sample (10,000 \times); (b) xylene-etched sample (10,000 \times); (c) xylene-etched sample (1000 \times).

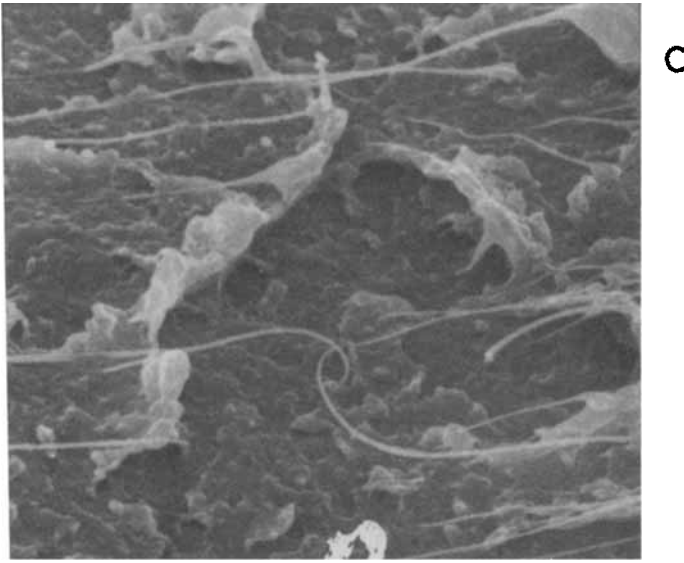
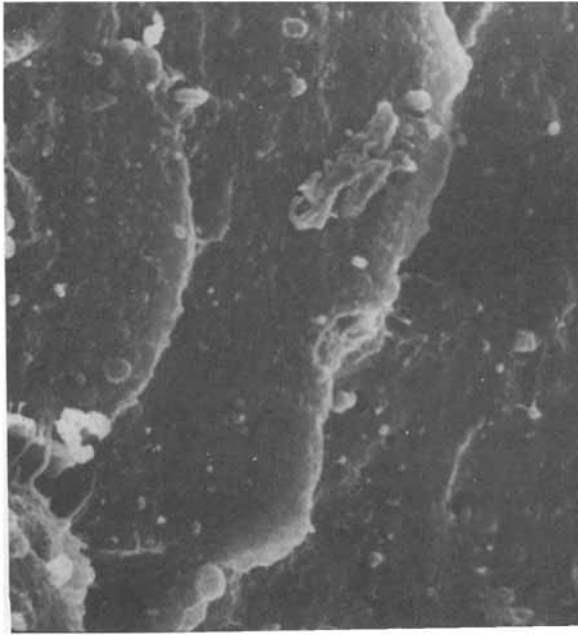


Fig. 13. (Continued from the previous page.)

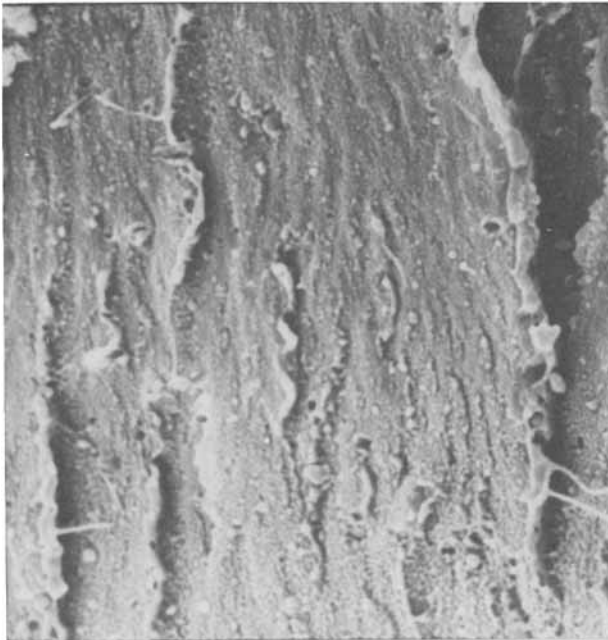
with the analysis of composition from these wastes and with their mechanical behavior previously studied.

- The results from DSC analysis are consistent with the studies from several authors, who found that separate crystals are formed in polyolefin blends in which one of the two components was LDPE, i.e., a branched-type polyolefin. This may be attributed to differences in chain linearity.
- The micrographs from the HDPE/LDPE system, obtained by SEM, show a network or entanglement microstructure which breaks in a brittle way. The rather rounder features forming the knots are smaller when the LDPE content is lower. These knots are not distinguished when LDPE content reaches 85% or more.
- The cryofracture of LDPE does not show globular structure. It shows, in treated samples, damages forming cavities in the microstructure, but not rounder features as seen in HDPE and HPDE/LDPE blends. This may be due the smooth fractures for LPDE in front of a brittle fracture when HPDE is present.
- SEM has demonstrated the presence in wastes of smaller solid particles, different from the polymers, that may be considered as impurities owing to inorganic fillers, pigments, etc.
- SEM micrographs from HPDE/LDPE system are in good agreement with observations previously determined for these blends made about micrographs obtained from optical microscopy of the samples.

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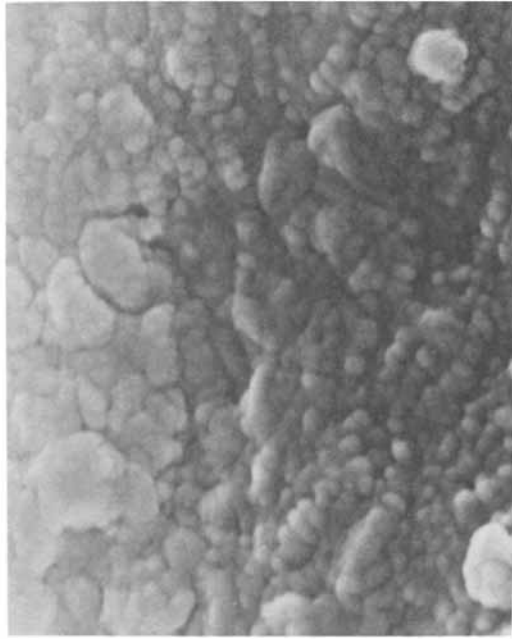


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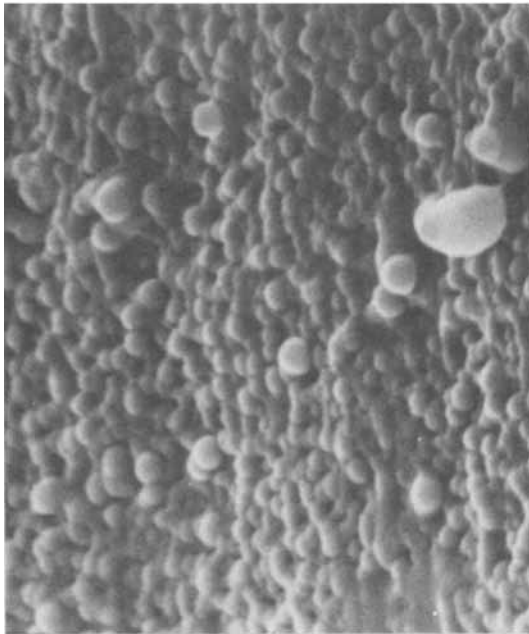


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Fig. 14. Scanning electron micrographs of fracture surfaces from wastes: (a) nonetched sample (1000 \times); (b) xylene-etched sample (1000 \times); (c) nonetched sample (10,000 \times); (d) xylene-etched sample (10,000 \times).



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Fig. 14. (Continued from the previous page.)

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