

TECHNICAL NOTE

Takashi Hashimoto,¹ M.Sc.; David G. Howitt,² Ph.D.; Donald P. Land,³ Ph.D.;
Frederic A. Tulleners,⁴ M.A.; Faye A. Springer,⁵ B.S.; and Shunlin Wang,⁶ Ph.D.

Morphological and Spectroscopic Measurements of Plastic Bags for the Purpose of Discrimination

ABSTRACT: The discrimination of noncolored transparent polyethylene bags was studied by several nondestructive and semidestructive analytical methods. X-ray diffraction, infrared spectroscopy, and optical microscopy (differential interference contrast microscopy and phase contrast microscopy) were applied to polyethylene films. X-ray diffraction was used to distinguish variations in the crystalline phase, infrared spectroscopy was used to distinguish variations in the molecular components, and optical microscopy was used to distinguish the different surface morphologies. The results show that X-ray diffraction classifies the crystalline phase of the film depending on whether it is made from low-density polyethylene, linear low-density polyethylene, or high-density polyethylene; that infrared spectroscopy is useful to distinguish the molecular components and it is the most discriminating technique; and that optical microscopy discriminate films easily by their morphological differences.

KEYWORDS: forensic science, plastic bag, polyethylene (LDPE, LLDPE, HDPE), X-ray diffraction, infrared spectroscopy (FT-IR, ATR), morphology, phase contrast microscope, DIC microscope and discrimination

Plastic bags are often a component of evidence that may be recovered from crime scenes. Therefore, there may be a need to distinguish them when one wishes to distinguish plastic bags from different criminal events. In this study, we chose the colorless, transparent plastic bags that are commonly found at home and are often used to package drugs. Measuring methods that were either nondestructive or consumed only a very small portion of the sample were chosen. As the polyethylene used for these bags is typically a partially crystallized polymer (1), we decided to consider not only the standard spectroscopic and optical methods but also X-ray diffraction.

Polyethylene can be classified into one of three types: low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE). The polyethylene available in Japan includes domestic as well as imported products, particularly from China, South Korea, and Southeast Asia. As we wanted to correlate the results to particular processing methods, we limited our study to Japanese manufacturers from whom we could obtain information on both the grade and quality.

In answer to our request, the five principal domestic manufacturers offered us the polyethylene films manufactured by the inflation method using their own production pellets whose properties are described (Table 1).

¹Forensic Science Laboratory of Hyogo Prefecture Police HQ, 5-4-1 Shimoyamate-dori Kobe, Hyogo Pref., Japan.

²Department of Chemical Engineering, University of California – Davis, Davis, CA 95616.

³Department of Chemistry, University of California – Davis, Davis, CA 95616.

⁴Forensic Science Graduate Program, University of California – Davis, Davis, CA 95618.

⁵Sacramento Laboratory of Forensic Services, Sacramento, CA 95820.

⁶Bruker Optics, Inc., Fremont, CA 94538-6520.

Received 10 Oct. 2006; and in revised form 24 Feb. 2007; accepted 1 April 2007; published 21 July 2007.

TABLE 1—Crystallinity of polyethylene is calculated by diffraction strength and thickness.

Sample name	Grade	Thickness (mm)	Maximum peak height around 21°	Degree at maximum value	Factor of crystallinity
F101-1	LDPE	0.039	3097	21.3	79,410
F218-0	LDPE	0.032	2896	21.32	90,500
F412-1	LDPE	0.03	2220	21.26	74,000
FS140	LLDPE	0.034	4709	21.38	138,500
FS370	LLDPE	0.034	6431	21.4	189,147
FR151	LLDPE	0.032	3568	21.32	111,500
F184	HDPE	0.015	14437	21.5	962,467
F1920	LDPE	0.038	3858	21.26	101,526
M2204	LDPE	0.039	3211	21.3	82,333
F019	LDPE	0.023	4072	21.28	177,043
F022	LDPE	0.028	1955	21.34	69,821
F023	LDPE	0.023	1638	21.12	71,217
F222	LDPE	0.024	1713	21.22	71,375
F522	LDPE	0.023	1395	21.24	60,652
R300	LDPE	0.045	3135	21.34	69,667
R500	LDPE	0.026	2411	21.38	92,731
2100J	HDPE	0.033	11070	21.52	335,455
7000F	HDPE	0.024	13675	21.52	569,792
640UF	HDPE	0.032	9251	21.54	289,094
0134M	LLDPE(C4)	0.03	4484	21.38	149,467
0238H	LLDPE(C8)	0.028	4540	21.38	162,143
0358CN	LLDPE(C8)	0.029	5436	21.48	187,448
SP2040	LLDPE(C6)	0.052	5869	21.4	112,865
SP1520	LLDPE(C6)	0.049	6074	21.38	123,959
20200J	LLDPE(C6)	0.032	4318	21.36	134,938
LF440HB	LDPE	0.024	1624	21.36	67,667
UF421	LLDPE(C4)	0.034	2473	21.38	72,735
SF232	LLDPE(C6)	0.031	3507	21.46	113,129
HF313	HDPE	0.024	22191	21.58	924,625
HF334	HDPE	0.033	4403	21.5	133,424
KF270	LLDPE(C6)	0.058	5212	21.38	89,862

Maximum peak height divided by thickness is factor of crystallinity.
LDPE, low-density polyethylene; LLDPE, linear low-density polyethylene; HDPE, high-density polyethylene.

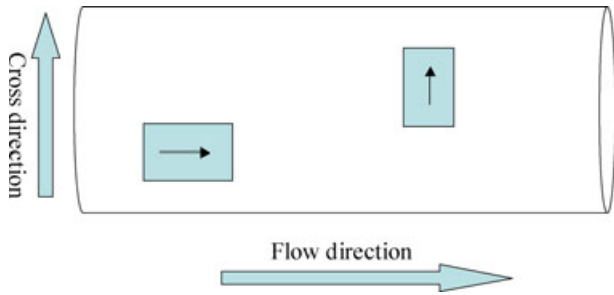


FIG. 1—X-ray diffraction was measured along the flow and cross direction of film sample manufactured by the inflation method.

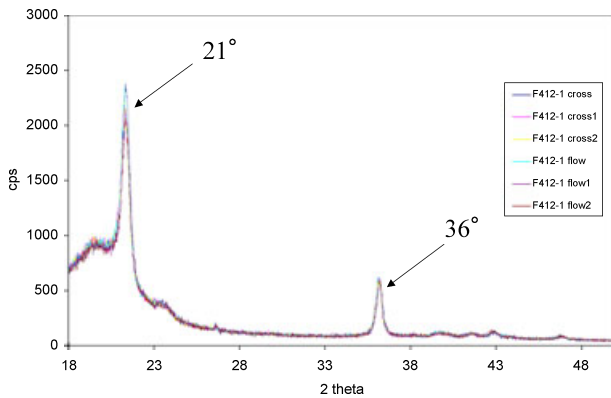


FIG. 2—Comparison of X-ray diffraction to flow and cross direction. Texture of film is not found.

Ultimately 31 samples, including LDPE, LLDPE, and HDPE, were evaluated and compared using the different techniques.

Method

X-ray Diffraction

In fabricating the polyethylene films by the inflation method there is the possibility of texture development, and so diffraction was initially carried out both in the flow and transverse direction.

The measurements were performed using a copper source in an XDS2000 type X-ray diffractometer made by Scintag Inc (Cupertino, CA). The tube voltage was 45 kV and the tube current was 40 mA. The diffraction angle (2θ) was rotated from 4 to 80°. Rectangular sections were cut from the films and mounted on powder diffraction holder.

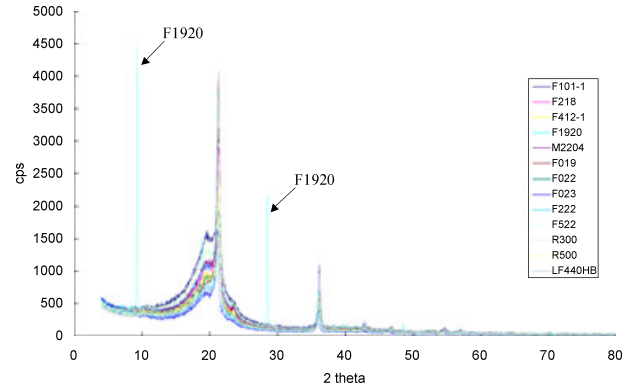


FIG. 4—F1920 is distinguishable to other low-density polyethylene.

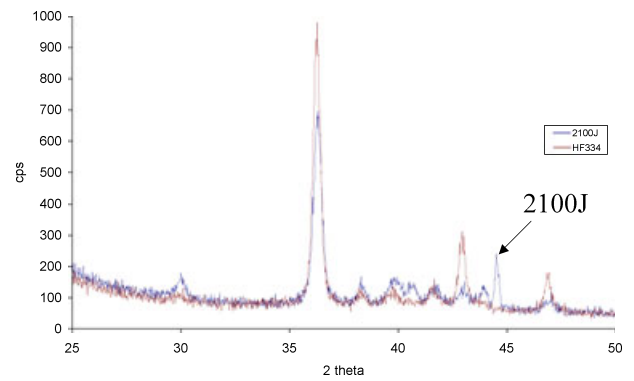


FIG. 5—2100J is distinguishable to other high-density polyethylene.

The diffraction patterns taken along the direction of flow and the transverse direction were mostly in agreement, and did not show any significant texture (Figs. 1 and 2). Thus, after the first few specimens, the sampling directions of the test pieces for X-ray diffraction were taken at random.

Infrared Spectroscopic Analysis

As the polyethylene films proved to be too thick for transmission analysis and because of the difficulties associated with mounting the films, we resorted to a single bounce attenuated total reflection technique (2). The diamond ATR prism produces a large absorption in the region of interest limiting the available spectral range. However, we had a good success with Zinc selenide at 45° incidence and

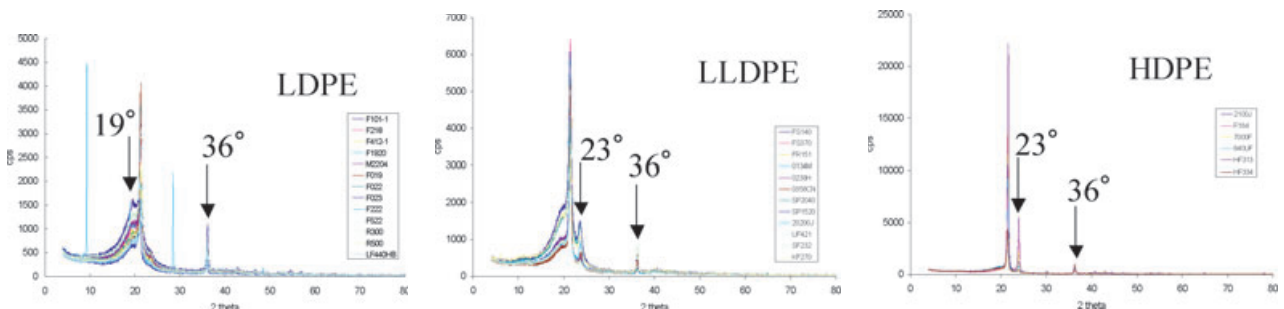


FIG. 3—Comparison of X-ray diffraction patterns according to polyethylene grade, low-density polyethylene, linear low-density polyethylene and high-density polyethylene.

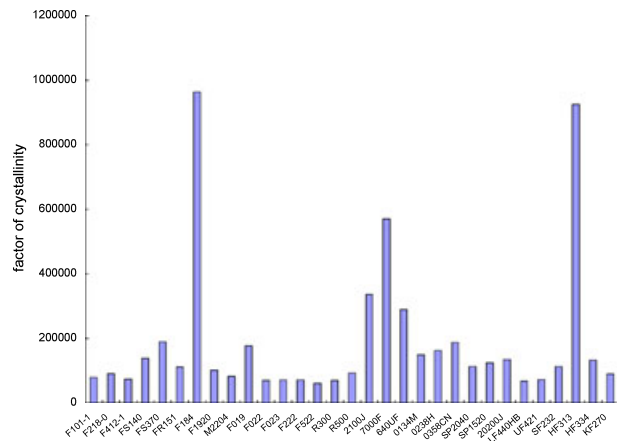


FIG. 6—Crystallinity of all polyethylene film samples.

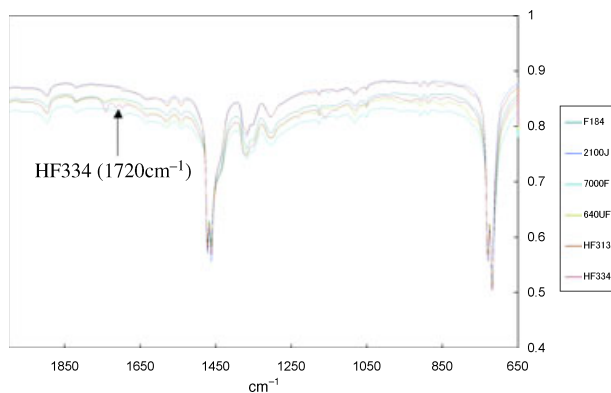


FIG. 9—HF334 is distinguishable from the other high-density polyethylene specimens.

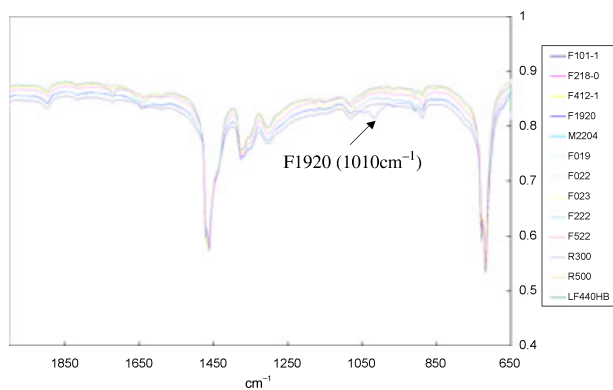


FIG. 7—F1920 is distinguishable from the other low-density polyethylene specimens.

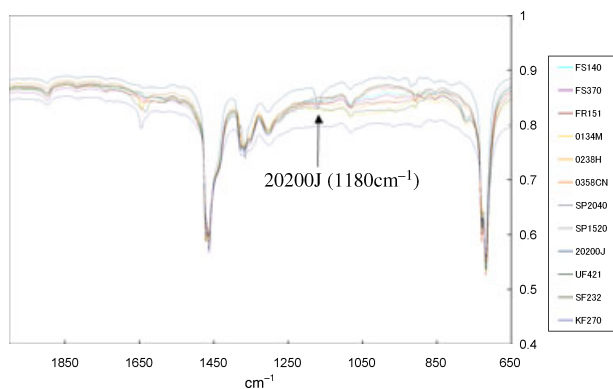


FIG. 8—20200J is distinguishable from the other linear low-density polyethylene specimens.

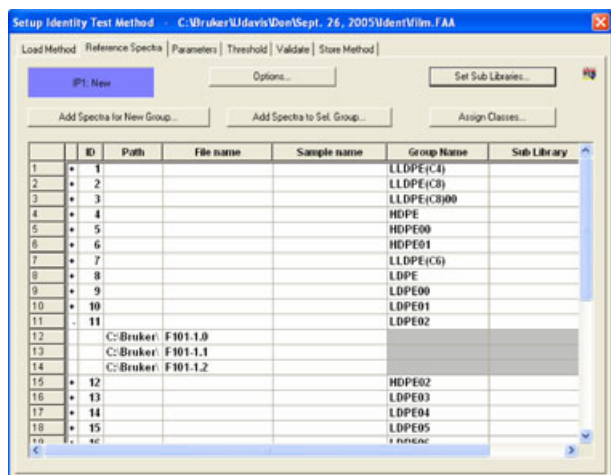


FIG. 10—Library—LDPE02 corresponds to real sample F101-1.

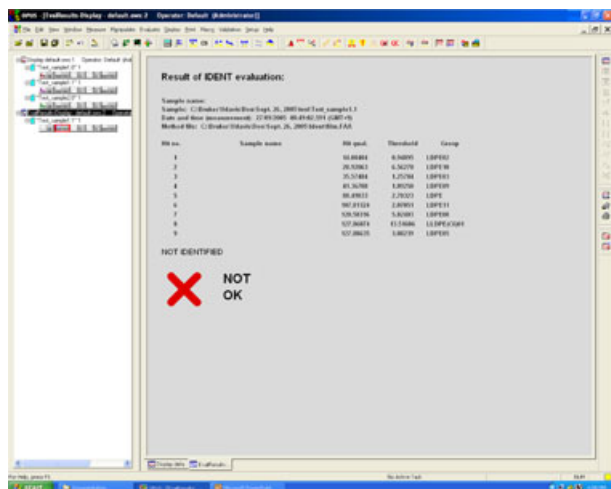


FIG. 11—Test sample no.1, which hits LDPE02 in the Library as the best hit. The test sample is F101-1. This illustrates that the hit is correct.

measurements were taken utilizing a Pike Technologies constant-pressure gauge (Pike Technologies, Madison, WI) in conjunction with the Bruker Tensor 37 FT-IR (Bruker Optics Inc., Fremont, CA).

For each sample, 64 scans were co-added to enhance the signal-to-noise ratio for the smaller absorption features as the major spectral features showed little variation.

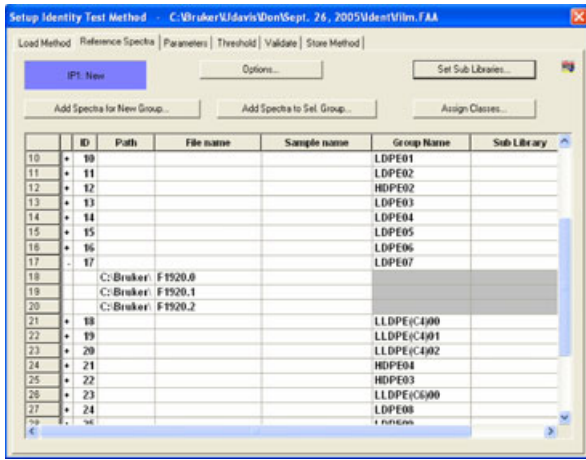


FIG. 12—Library—LDPE07 corresponds to real sample F1920.

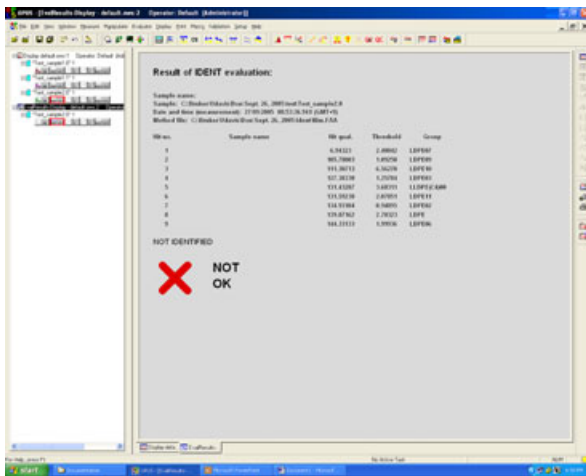


FIG. 13—Test sample no.2, which hits LDPE07 in the Library as the best hit. The test sample is F1920. This illustrates that the hit is correct.

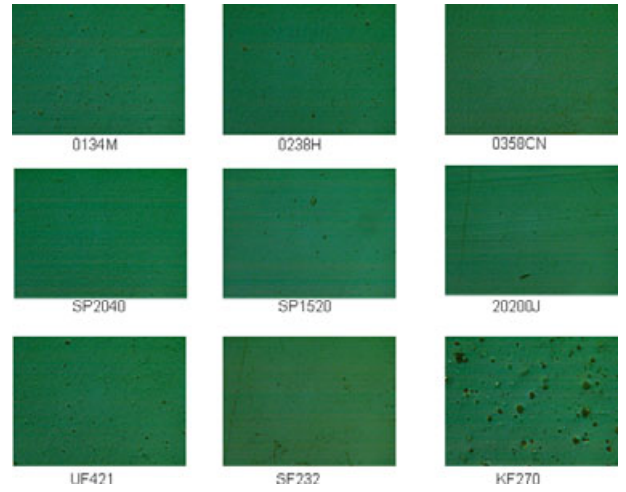


FIG. 15—DIC images of all linear low-density polyethylene. Three combinations (FS140-0358CN, FR151-UF421, UF421-0238H) are indistinguishable in all of the possible 66 paired polyethylene samples.

Optical Microscopy

Samples were observed using differential interference contrast (DIC) microscopy and phase contrast microscopy to highlight differences in the microstructure, refractive index, and surface morphology, the most useful magnification range being around 200 times.

The DIC observation that can visualize surface concavity and convexity was performed using a Nikon LaBOPHOT-2 microscope (Nikon, Melville, NY) and the pictures were taken by PAXCAMERA (MIS Inc., Villa Park, IL).

Phase contrast observations that can visualize the difference in density (3) were performed using an OLYMPUS BX51 microscope (Olympus America Inc., Center Valley, PA) with a UPlanApo20x/0.70Ph2 objective lens (Olympus) and was conducted in the Sacramento County Laboratory of Forensic Services.

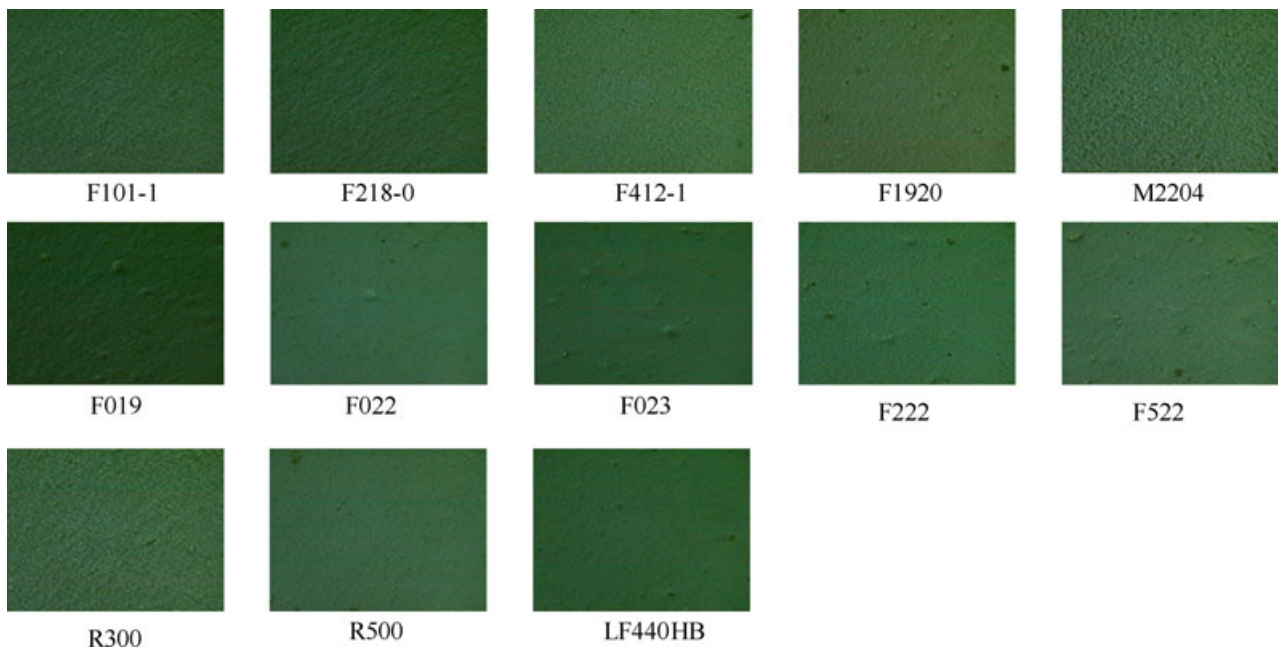


FIG. 14—DIC images of all low-density polyethylene. Five combinations (F101-1-R300, F1920-F522, F022-F023, F023-F522, F522-LF440HB) are indistinguishable in all of the possible 78 paired polyethylene samples.

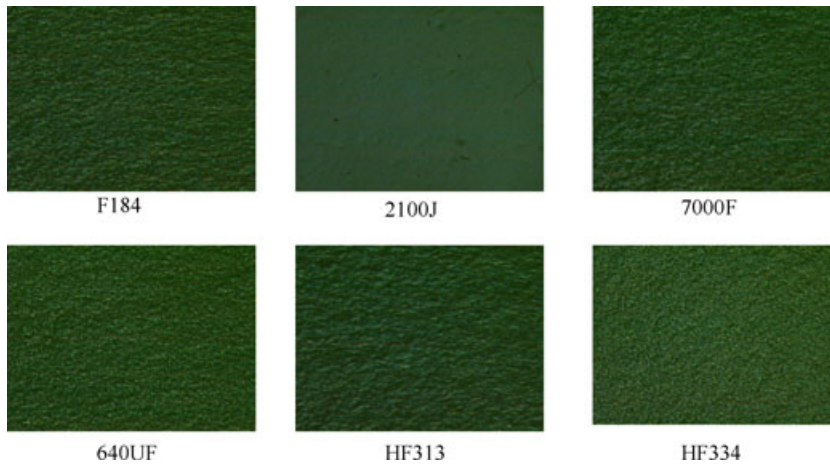


FIG. 16—DIC images of all high-density polyethylene. Four combinations (F184-22100J, 184-7000F, F184-HF313, HF313-7000F) are indistinguishable in all of the possible 15 paired polyethylene samples.

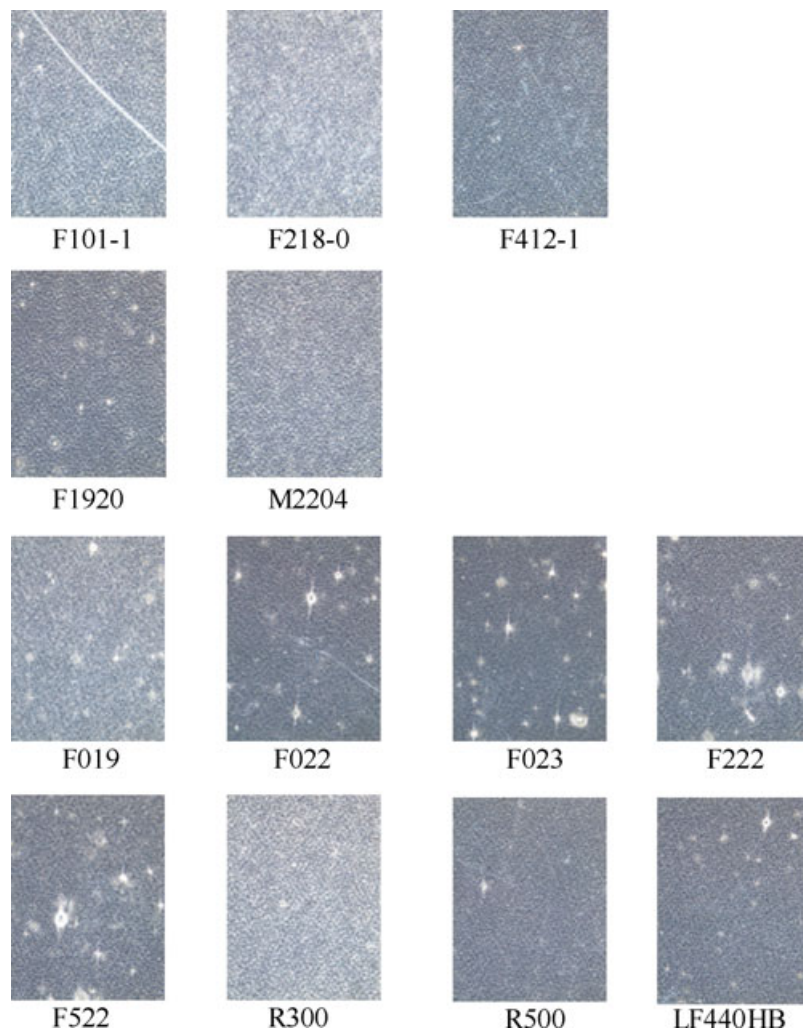


FIG. 17—Phase contrast images of all low-density polyethylene. One pair (F022-F023) is indistinguishable in all of the possible 78 paired polyethylene samples.

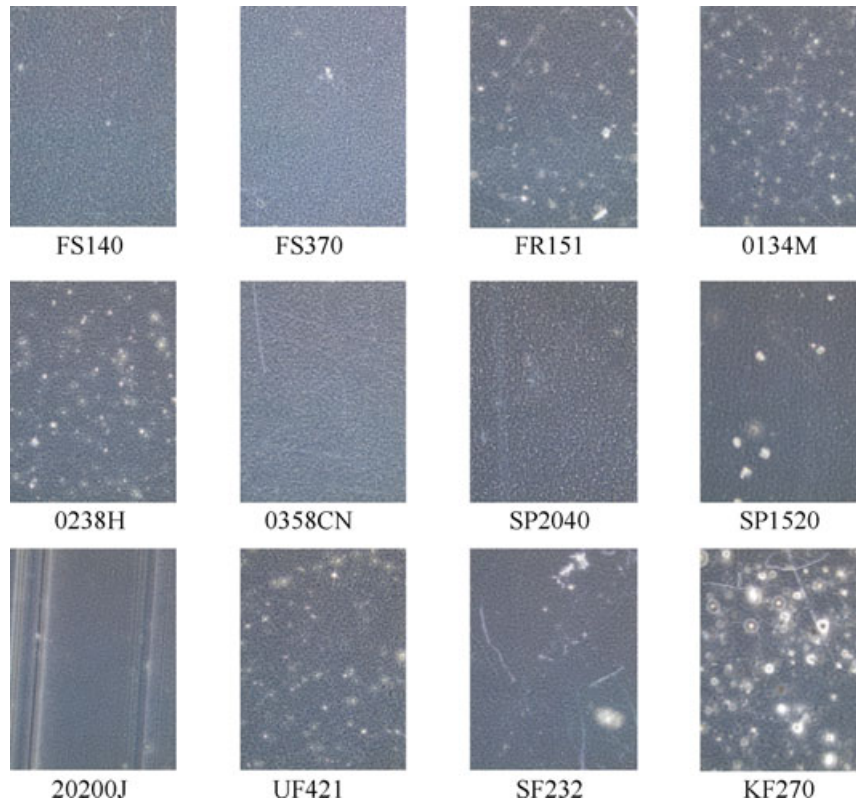


FIG. 18—Phase contrast images of all linear low-density polyethylene. One pair (0134M-0238H) is indistinguishable in all the possible 66 paired polyethylene samples.

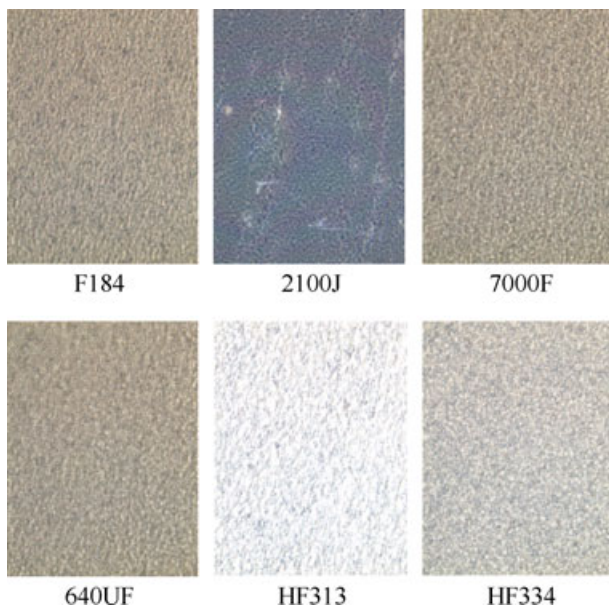


FIG. 19—Phase contrast images of all high-density polyethylene. One pair (F184-7000F) is indistinguishable in all possible 15 pairs.

Results and Discussion

X-ray Diffraction

X-ray diffraction is an excellent method for distinguishing the different types of polyethylene (Fig. 3). In the LLDPE and HDPE, there are recognizable, peaks around 23° and 36°, the former being

more pronounced in the high-density form, with the linear low-density having an additional shoulder peak at 19°.

The peak at 19° appears alone in the general LDPE, and as a general rule one can fairly easily recognize the different types.

In LLDPE, a peak appears near 23° and the peak near 36° decreases.

In HDPE, the peak near 23° becomes larger, and the peak near 36° decreases further.

In terms of distinguishing the products from the different manufacturers in LDPE and HDPE, there was one sample in each batch that could be clearly distinguished, but the rest were similar. These were samples F1920 among the 13 samples of LDPE (Fig. 4) and sample 2100J from the six samples of HDPE (Fig. 5). In LLDPE, none of the 12 samples showed any individuality that could be recognized.

All of the samples also displayed a peak at about 21°, and the degree of crystallinity in the samples may well be a method by which one could distinguish them if the data is normalized to the specimen thickness (Table 1, Fig. 6). Nevertheless, such distinctions would certainly not be obvious.

Infrared Spectroscopic Analysis

The infrared spectra from the samples produced similar results in that in LDPE, one of the 13 samples was clearly distinguishable (Fig. 7) as was one of the 12 samples of LLDPE (Fig. 8), and one of the six samples of HDPE (Fig. 9).

Using the Bruker classification software (Bruker Optics Inc.), all the 31 samples were recognized individually. The difference in the spectra was subtle and, for the most part, not recognizable by the naked eye.

When arbitrary searches were executed on spectra taken from samples, correct polyethylene samples were identified (Figs. 10–13).

Optical Microscopy

Using DIC images and phase contrast images, each image was compared with the others in the same type of polyethylene: LDPE, LLDPE, and HDPE.

There are 78 combinations in LDPE, 66 combinations in LLDPE, and 15 combinations in HDPE.

Optical microscopy (DIC and phase contrast microscopy) was the most powerful of the discriminatory tools.

From DIC observation, 72 of the 78 combinations in the LDPE group (Fig. 14), 62 of the 66 combinations in the LLDPE group (Fig. 15), and 11 out of the 15 combinations in the HDPE group were distinguishable (Fig. 16).

Using phase contrast observations, in each of the groups LDPE (Fig. 17), LLDPE (Fig. 18), and HDPE (Fig. 19), all but one of the combinations were distinguishable.

Conclusions

In conclusion, X-ray diffraction would seem to be effective in classifying the type and category to which the polyethylene belongs, that is, low-density, linear low-density, or high-density.

In terms of individualizing these films, there is reasonable discrimination using ZnSe ATR infrared spectroscopy. Using classification software, one can easily classify samples individually.

If standards are available, optical microscopy would seem to be by far the best method for discrimination. Clearly the structural and chemical differences between the films are somewhat marginal, but the different manufacturing processes clearly produce distinctly different morpho-

logies and textures in the films that can be readily identified using optical microscopy. Phase contrast microscopy may be a little better than DIC microscopy

Acknowledgments

The authors appreciate polyethylene manufacturers in Japan, Sumitomo, Ube-maruzen, Prime polymer, Asahikasei and Nippon polyethylene for supplying test samples (polyethylene films).

Most of this study was conducted at the University of California – Davis through an International Training and Research Award in Forensic Science awarded to T. Hashimoto, conferred by the Japan National Police Agency (The Training Center of Forensic Science) to visit the U.S. during the summer of 2005.

References

1. Furuheim KM, Axelson DE, Antonsen HW, Helle T. Phase structural analyses of polyethylene extrusion coatings on high density papers: I. Monoclinic crystallinity. *J Appl Polymer Sci* 2004;91:218–25.
2. Hartshorne AW, Laing DK. The identification of polyolefin fibres by infrared spectroscopy and melting point determination. *Forensic Sci Int* 1984;26:45–52.
3. Abramowitz M. Phase contrast microscopy. *Contrast methods in microscopy-Transmitted light-Vol 2: Phase contrast*. Center Valley, PA: Olympus America Inc, 1987;19–23.

Additional information and reprint requests:

Takashi Hashimoto, M.Sc.
Forensic Science Laboratory
Hyogo Prefecture Police HQ
5-4-1 Shimoyamate-dori
Chuo-ku Kobe 650-8510
Japan
E-mail: takashihashimoto@hkg.odn.ne.jp