

TECHNICAL NOTE**CRIMINALISTICS**

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Discrimination of Transparent Polyethylene Films Based on Identification of Inorganic Antiblocking Agents

ABSTRACT: Several nondestructive and semidestructive analyses were used to discriminate colorless transparent polyethylene bags. Transparent plastic bags made from low-density and linear low-density polyethylene usually contain antiblocking agents to prevent sticking of the film, which makes it difficult to open the mouths of plastic bags. Inorganic antiblocking agents are uniformly dispersed in polyethylene films, so they are easily observed using optical microscopy. The particle size distributions of the antiblocking agents were compared by statistical tests. Particle composition was examined by elemental analysis using energy-dispersive X-ray spectrometry with a scanning electron microscope and by molecular vibration analysis using a sensitive microscopic Raman spectrometer. The compositions could be determined nondestructively on the basis of the results. These data reinforce the morphological discrimination. Morphological discrimination of the dispersed antiblocking agent powders, statistical comparison of particle size distributions, and compositional analysis of the antiblocking agents strengthen the ability to discriminate polyethylene films.

KEYWORDS: forensic science, plastic bag, polyethylene, optical microscope, Welch's *t*-test, SEM-EDX, microscopic Raman spectrometry

Plastic bags made of polyethylene film are common packing materials; they are generally used to package food and medicine. They are also used to contain evidential materials such as illegal medicine or arms. Discrimination among various types of plastic bags containing crime evidence and unused plastic bags from the home of a suspect is often requested.

Comparisons of morphology, color, major components, and trace constituents are often necessary to discriminate forensic materials (1). Whereas colored films can be distinguished by their color, transparent films require other methods of discrimination. For instance, plastic bags are quantitatively differentiated by infrared spectroscopy, thickness measurements, and differential scanning calorimetry; wide-angle X-ray diffraction is also used to trace the source of illegal drugs in and around Europe (2,3). Both nondestructive and semidestructive methods are necessary for analyzing criminal evidence. Antiblocking agent is added to keep the films from sticking to each other and to make it easy to open the mouths of plastic bags. Various inorganic oxides such as silica, aluminosilicate, talc, and zeolite are used. Many polyethylene resins used for plastic bags contain these agents, but they are sometimes added in the blow-molding stage. The identification of antiblocking agents can be one of the most important procedures in differentiating plastic bags.

Vibrational spectroscopy methods such as infrared absorption and Raman scattering are useful for classifying various types of polymer samples. However, because particles of the antiblocking

agents are scattered and buried in the films, it is difficult to apply infrared spectrometry with attachments such as attenuated total reflectance and microscopic Fourier transform infrared spectroscopy instruments (4). On the other hand, microscopic Raman (micro-Raman) spectroscopy might be applicable to the analysis of antiblocking agents in transparent and thin films because of its small focusing area. This method uses a strong scattering intensity that can be controlled by changing the laser intensity of a localized light source in a small target on film samples (5). Antiblocking agents are well known to be dispersed in plastic bags; however, they have never been subjected to spectroscopic and compositional analysis using nondestructive microanalysis.

In this study, we combined several observational and analytical methods to examine many polyethylene resins used for plastic bags in which antiblocking agents are dispersed to improve the forensic discrimination process. First, we conducted morphological analysis using optical microscopy (OM) observations. Then, we used Welch's *t*-test (6) to analyze the dispersion conditions and particle size distributions of antiblocking agents and differentiate the resins. The main components and trace constituent were compared using energy-dispersive X-ray spectrometry with a scanning electron microscope (SEM-EDX). Microscopic Raman spectroscopy was used to analyze the molecular structure of the antiblocking agents and films.

Materials and Methods

Samples

Polyethylene films have been classified into three types: low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE). These types can

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TABLE 1—Components of antiblocking agents and vibrational mode assignments in Raman spectra.

Supplier	Sample	Type of PE	Type of Antiblocking Agent (AB) and Analyzed Components	Assignments in Raman Spectra
Sumitomo Chemical	F412-1	LDPE	Silica	Si–O E(t) + E(1) (128 per cm)
	F208-3	LDPE	Silica	A ₁ (205 per cm) A ₁ (463 per cm) (10)
Ube-Maruzen	F019	LDPE	Diatomite	
	F022	LDPE	Diatomite	
	F023	LDPE	Diatomite	
	F222	LDPE	Diatomite	
	F522	LDPE	Diatomite	
Sumitomo Chemical	FR151	LLDPE	Aluminosilicate	Si–O bridging (485 per cm)
	FS153	LLDPE	Aluminosilicate	Al–O (c.700 per cm) (11,12)
	CL1083	LLDPE	Aluminosilicate	
Japan Polyethylene Prime Polymer	UF421	LLDPE	Aluminosilicate (Zeolite)	
	0134M	LLDPE	Aluminosilicate	
	0238M	LLDPE	Aluminosilicate	
Asahi Kasei	F1920	LDPE	Talc	O–H–O (199 per cm) $\nu_5(e)$ SiO ₄ (388 per cm) ν_s Si–O _b –Si (680 per cm) (13,14)
Japan Polyethylene	LF440HB	LDPE	CaSO ₄	ν_2 (SO ₄) (412 per cm, 492 per cm) ν_4 (SO ₄) (605 per cm, 621 per cm) (15)

LDPE; low-density polyethylene; LLDPE, linear low-density polyethylene.

be identified by near-infrared spectroscopy (7). As adhesion of HDPE is rare, most commercial HDPE does not include antiblocking agents. Therefore, we focused mainly on LDPE and LLDPE samples in this study, as illustrated in Table 1. Samples of 15 types of film blow-molded from their own resins were collected from five Japanese suppliers. The suppliers provided information on the antiblocking agents used in the films. Original samples of the antiblocking agents contained in these films were also examined and compared.

Optical Microscope Observation

Because polyethylene films are transparent, antiblocking agents can be observed by OM. The particle size and dispersion of the antiblocking agents were examined by a digital microscope (KEYENCE VHX-1000/1100; Osaka, Japan). All the films were observed at five different places to observe the dispersion condition and obtain reproducibility. The characteristic shapes, morphologies, and diameters of the antiblocking agent particles as observed in OM images were statistically analyzed using the image analysis software Scion Image (Scion Corporation, Frederick, MD). The supplied polyethylene films were *c.* 30 μm thick, and the antiblocking agents were dispersed in every region of the films. The focus point was moved from the lower surface to the upper surface of each film. Several OM images were collected at each location and merged. Consequently, clear images containing all particles in the focusing area could be obtained.

The distributions of the dispersed particles of antiblocking agent obtained from the OM images were statistically analyzed using Welch's *t*-test (6) using macro-calculation in Microsoft Excel 2003 (Microsoft Corp., Redmond, WA). In this calculation, the statistical *t*-values and the associated *p*-values (probabilities) were obtained for the 105 possible combinations of pairs of samples.

Observation and Elemental Analysis Using SEM-EDX

The morphology and components of the antiblocking agents were analyzed by SEM-EDX using a Quanta 200F instrument with an Edax Quanta 400 EDX spectrometer (FEI Company, Hillsboro, OR). The samples were cut into 5-mm squares and mounted on the sample holder using conductive carbon adhesive tape. To avoid

damaging the samples, they were not sputter coated. The acceleration voltage was 15 kV under a low vacuum of 90 Pa to avoid electron charge-up. The magnification during EDX analysis was 800 for most observations.

Microscopic Raman Spectrometry

Many of the antiblocking agent particles were very small (from a few microns to about 10 μm); however, by OM observation, we were able to obtain characteristic micro-Raman spectra of various antiblocking agents buried in the polyethylene films within a 20-sec exposure time using highly sensitive microscopic Raman equipment. Microscopic Raman spectroscopy was performed using a microscopic laser Raman spectrometer (SENTERRA™; Bruker Optics Inc., Billerica, MA) equipped with a microscope (BX51; Olympus, Tokyo, Japan). Samples were excited by a second-harmonic Nd:YAG laser with a wavelength of 532 nm. Scattered light from the samples was detected by a charge-coupled device with 1024 \times 255 pixels. The laser power and integration time were 20 mW and 2–20 sec, respectively. The laser was focused into an area of *c.* 1 μm \times 1 μm that included a single particle of an antiblocking agent.

Results and Discussion

Optical Microscopy

Digitally merged images of the LLDPE FR151 sample observed by OM are shown in Fig. 1. The internal distribution of antiblocking agents in the transparent plastic film can be observed. The type of antiblocking agent can be determined to some extent by visually observing the shape and size of the particles. The differences between an evidence film and the film to which it is being compared can also be identified. The image was captured in Scion Image, which provided numerical information about the particle sizes.

Figure 2 shows the particle size distributions of two typical films containing aluminosilicate antiblocking agents, FR151 and CL1083. The particle size distributions of these films are obviously different. Such information on the particle size distribution is useful as an approximate discrimination for the first step of the analysis. For all possible combinations (105 pairings) of the 15 different samples,

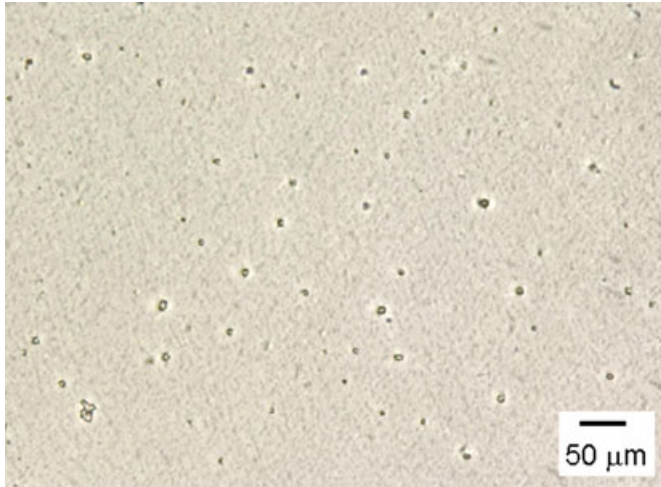


FIG. 1—Digital microscope image of linear low-density polyethylene film FR151 in which the antiblocking agent of aluminosilicate was used.

we used Welch's *t*-test to check for statistically significant differences in the average particle size. The results are shown in Table 2. No significant differences were observed among F019, F022, F023, F222, and F522; among F1920, F019, F022, F023, and F222; and between FS153 and 0238H. However, the other pairs of films could be discriminated because statistically significant differences appeared (*p*-values of <0.05).

Observation and Elemental Analysis of Antiblocking Agents Using SEM-EDX

In the OM observations, a micron-order structure and its size distribution can be discriminated. However, samples of various types have similar size distributions, and sometimes, it is necessary to classify these samples by elemental analysis. As most antiblocking agents consist of light elements, as shown in Table 1, EDX is appropriate for detailed analysis of their components. Figure 3 compares the EDX profiles and size distributions of F208-3, which contains silica, and CL1083, which contains aluminosilicate. Although their size distributions are similar, their differing elemental compositions are evident in their EDX spectra. Moreover, some agents have a peculiar shape owing to the origin of the samples, such as natural diatomite silica mineralized from diatoms, as shown in Fig. 4. Although the compositions of samples of F019, F022, F023, F222, and F522, which contain diatomite silica, are similar to those of films containing silica, such as F412-1 and F208-3, they can be classified by not only compositional analysis but also direct observation under high magnification.

For our analysis, the SEM-EDX observation was performed under low vacuum conditions at 90 Pa to avoid charge-up of the polymer films without sputter-coating them, so that nondestructive observations can be made. Therefore, SEM-EDX observation of the polyethylene samples is not more significant than OM analysis for forensic purposes when maintaining that the integrity of the original sample is important.

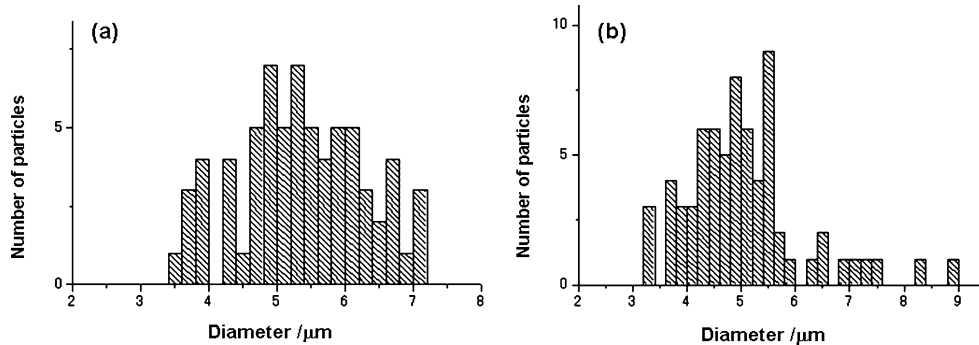


FIG. 2—Particle diameter distributions of antiblocking agent using aluminosilicate in polyethylene films; (a) FR151 and (b) CL1083.

TABLE 2—Values of discrimination by Welch's *t*-test for 15 types of plastic bag using focus-synthesized optical microscopic images.

	F412-1	F208-3	F019	F022	F023	F222	F522	FR151	FS153	CL1083	UF421	0134M	0238H	F1920	LF440HB
F412-1	<i>p</i> -values→0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
F208-3	-9.65	0	0	0	0	0	0	0	0	0	0	0	0	0	0
F019	-22.1	-19.8	0.817	0.970	0.336	0.056	0	0	0	0	0	0	0	0.088	0
F022	-19.3	-17.3	-0.232	0.777	0.532	0.123	0	0	0	0	0	0	0	0.074	0
F023	-26.8	-23.8	0.037	0.283	0.267	0.034	0	0	0	0	0	0	0	0.057	0
F222	-28.0	-25.1	-0.963	-0.626	-1.11	0.256	0	0	0	0	0	0	0	0.002	0
F522	-24.0	-21.7	-1.92	-1.54	-2.13	-1.14	0	0	0	0	0	0	0	0	0
FR151	-48.2	-31.0	11.8	10.5	14.3	15.6	14.1	0	0	0	0	0	0	0	0
FS153	-61.8	-45.0	7.02	6.35	8.40	9.81	9.38	-17.3	0	0	0	0	0.195	0	0.001
CL1083	-41.5	-26.5	12.7	11.2	15.3	16.6	14.9	3.38	19.8	0	0	0	0	0	0
UF421	-72.3	-48.4	8.03	7.20	9.65	11.1	10.4	-16.4	3.53	-19.2	0	0	0.006	0	0
0134M	-66.6	-43.2	9.50	8.47	11.5	12.8	11.8	-10.3	9.23	-13.5	6.78	0	0	0	0
0238H	-80.5	-52.9	7.44	6.70	8.96	10.4	9.81	-19.7	1.30	-22.7	2.85	-10.1	0	0	0
F1920	-31.4	-27.3	1.71	1.79	1.91	3.13	3.94	-15.1	-7.68	-16.4	9.31	-11.6	-8.42	0	0
LF440HB	-43.3	-34.9	5.46	5.04	6.41	7.77	7.80	-15.4	-3.25	-17.3	5.85	-9.67	-4.38	5.16	<i>t</i> -values

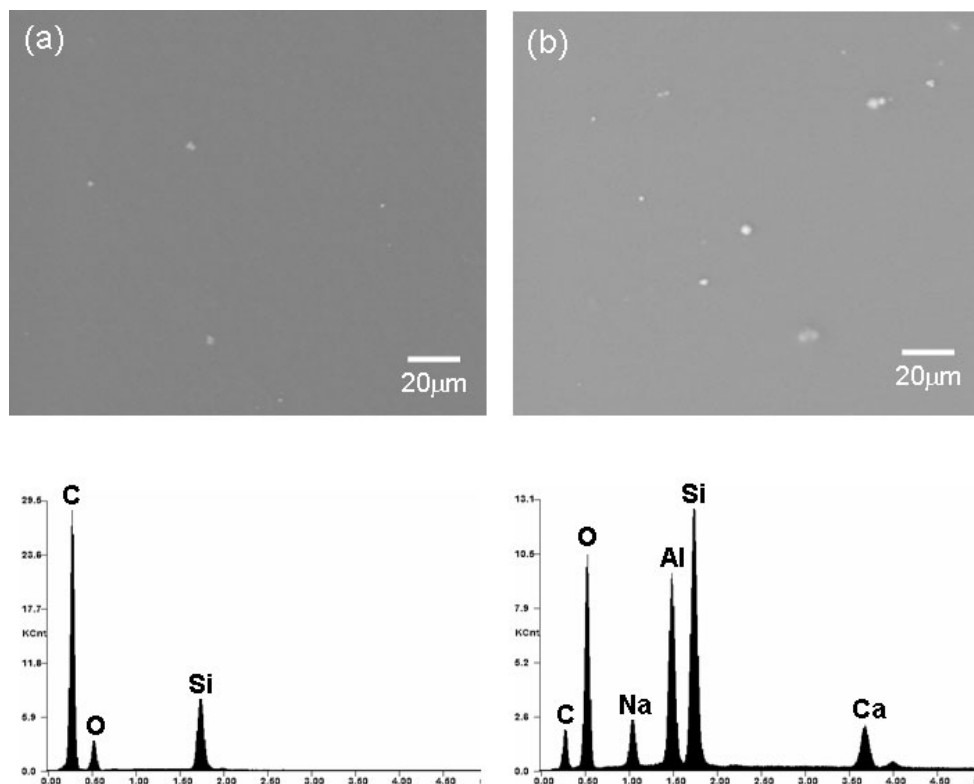


FIG. 3—SEM images and energy-dispersive X-ray spectrometry spectra of antiblocking agent in polyethylene films; (a) F208-3 and (b) CL1083.

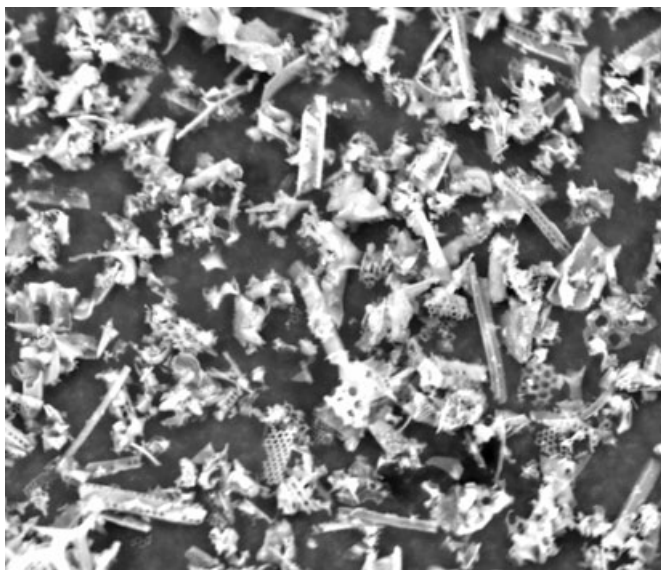


FIG. 4—Characteristic morphological discrimination of natural diatomite silica mineralized from diatoms.

Microscopic Raman Spectrometry

Numerous studies have measured normal Raman spectra of various inorganic compounds. Some compounds are summarized in the spectroscopic literature, and discrimination by consulting a database seems possible (7,8). However, because a small amount of antiblocking agents is contained in each polyethylene film, it is necessary to control the optical alignment, apply the laser to a single particle, and make visual observations and measurements (6).

Figure 5 shows the focusing areas of the micro-Raman spectra of films containing various antiblocking agents: (i) synthesized silica (F412-1), (ii) natural silica (F019), (iii) aluminosilicate (CL1083), (iv) talc (F1920), and (v) calcium sulfate (LF440HB). We confirmed that the focusing area is large enough to obtain Raman spectra covering the fingerprint range of each antiblocking agent without hiding that of the polyethylene between about 1000 and 1400 per cm.

In Fig. 6, the micro-Raman spectra of the films containing antiblocking agents are shown. As a reference, the spectra of the antiblocking agents alone are also shown in the same figure. It is possible to distinguish among the inorganic compounds that were used by employing pattern analysis of the spectra in the fingerprint range of the agents. For the silica sample, the Raman peaks assigned to $E(t) + E(1)$ at 128 per cm, A_1 at 205 per cm, and A_1 at 463 per cm were observed clearly, as shown in Fig. 6a (9). Similarly, each major peak was observed in the fingerprint range for the other samples, as shown in Table 1 (10–15). This result suggests that micro-Raman spectroscopy can be applied to the discrimination of polyethylene films containing antiblocking agents, because most inorganic compounds that are used as antiblocking agents appear as oxides under nondestructive spectroscopic analysis. As described in the previous section on OM analysis, several samples could not be discriminated. The discrimination among F1920, F019, F022, F023, F222, and F522 and between FS153 and 0238H was successfully performed using micro-Raman spectroscopy by the assignment of chemical bonds in each sample.

However, it was impossible to discriminate among samples F019, F022, F023, F222, and F522, in which natural silica powder was dispersed, using OM image analysis and Raman spectroscopy. Further analysis using other methods concerning the properties of the polyethylene resin, such as thermal analysis, or those of

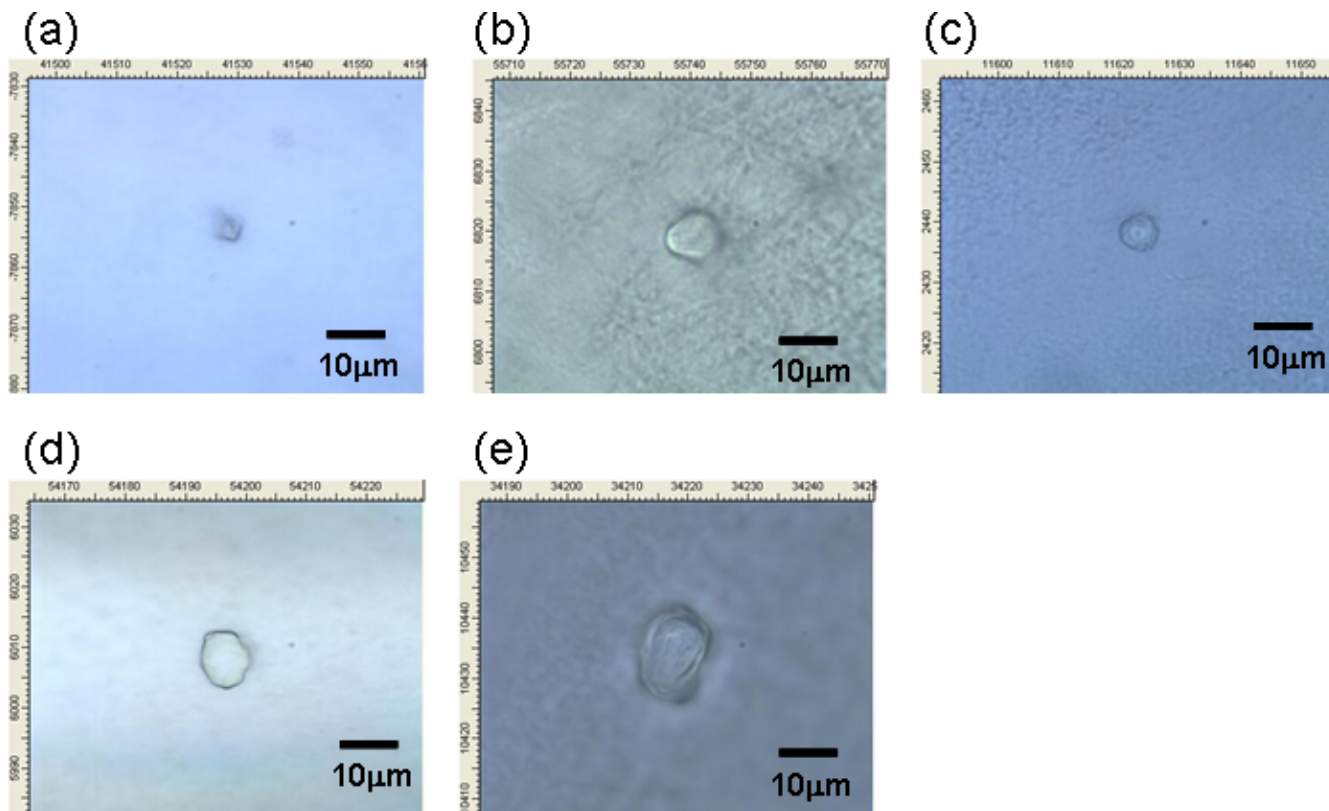


FIG. 5—Microscopic view image of antiblocking agent for Raman spectra measurement of polyethylene films containing antiblocking agents; (a) F412-1 (silica), (b) F019 (natural silica), (c) CL1083 (aluminosilicate), (d) F1920 (talc), and (e) LF440HB (CaSO_4).

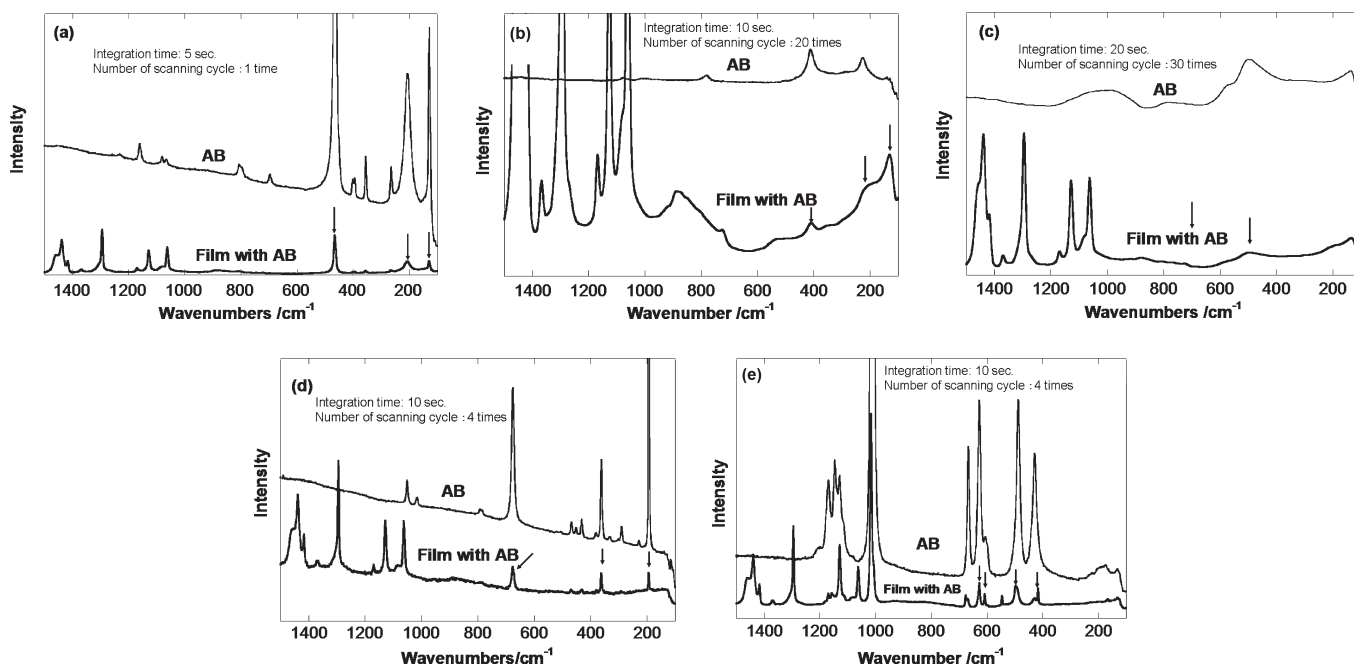


FIG. 6—Raman spectra of polyethylene films containing antiblocking agents (Film with AB) and the powder of the original antiblocking agents (AB). Kinds of films and contained antiblocking agents: (a) F412-1 (silica). Assignments of vibrational modes indicated by arrows are shown in Table 1. (b) F019 (natural silica). Assignments of vibrational modes indicated by arrows are shown in Table 1. (c) CL1083 (aluminosilicate). Assignments of vibrational modes indicated by arrows are shown in Table 1. (d) F1920 (talc). Assignments of vibrational modes indicated by arrows are shown in Table 1. (e) LF440HB (CaSO_4). Assignments of vibrational modes indicated by arrows are shown in Table 1.

additives such as antioxidant, anti-rip, and antistatic agents may be necessary for discrimination among film materials from the same manufacturer that contain the same antiblocking agent.

Conclusions

OM, SEM-EDX, and micro-Raman spectroscopic analyses were applied to polyethylene films to discriminate transparent plastic bags made of commercially available LDPE and LLDPE films. Antiblocking agents were observed easily by OM. By controlling the optical alignment, Raman spectra of inorganic compounds used in antiblocking agents in the films were obtained. The films were classified and discriminated using the composition of the antiblocking agents as determined by microscopic Raman spectrometry and SEM-EDX elemental analysis. Furthermore, films containing the same type of antiblocking agent can be discriminated by particle size if it differs significantly by using OM. This should be useful in forensic discrimination of plastic bags. Other additives such as antioxidant, anti-rip, and antistatic agents are used in plastic bags. It might also be useful to consider how to identify such additives for future research.

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