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The Comparison and Matching of Low Density Polyethylene Plastic Bags by Infrared Spectroscopy

Low density polyethylene (LDPE) is by far the most common polymer film material. Bags and pouches made from LDPE are readily available and are being used as packaging by peddlers of illegal drugs and by other criminals. It is therefore important that an investigator have ways of comparing LDPE bags used in the commission of a crime with bags belonging to a suspect.

Weak to medium bands in the infrared spectra of comparatively thick films are commonly used for distinguishing between high and low density polyethylenes, but the differences between spectra are not generally sufficient to enable different LDPE resins to be distinguished from one another. This paper discusses the intensification of these weak infrared bands and shows there is sufficient difference in their shapes and relative intensities to use them for distinguishing between films made from different LDPE resins.

The infrared absorption spectrum is one of the few physical properties of LDPE that can be measured on a small piece of film, and it is one more characteristic, along with bag shape and size and manufacturing variables such as seals, knife cuts, and extrusion marks, that can be used for matching and comparing bags.

Method

Films of known LDPE resins were supplied by a film extruder, and bags were purchased in retail stores.

All spectra were recorded on a Perkin-Elmer Model 580 spectrophotometer with the integrated scan mode set at 2. Weak bands were intensified by using samples between 0.5 and 0.75 mm thick, 2× ordinate scale expansion, and additional noise filtering.

Samples were prepared from wads of LDPE film compressed into thick transparent films at a temperature somewhat lower than their melting point. Because the intensities of some of the absorption bands were influenced by the temperature the sample reached during preparation of the film, standard conditions were adopted. Wads were pressed for 1 min between the plungers of a 22-mm pelletizing die. The pressure was 49 kN (5000 kgf) initially but soon fell off as the wads were compressed. A pressure of 29 kN (3000 kgf) was sufficient with 13-mm plungers. The plungers were taken from an oven at 95°C and they sat in the die on a hot steel base. Sample films were stiff enough to be cut and wedged in a pellet holder placed at the focus of the sample beam.

It was difficult to press thick films when higher temperatures or pressures were used, but if the compressed film was too thick layers could be peeled off until the required thickness was obtained. For the purposes of illustration, the published spectra may have been made more intense than was necessary in practice.

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Interference fringes were eliminated by making the surfaces of the films uneven. This was done by placing the prepared sample film on a sheet of lead covered with aluminum foil and rolling a gear wheel first over one side of the film and then over the other. The gear came from an old spectrophotometer and had 72 teeth, 5 mm wide, around a circumference of 185 mm. It also helped if the sample film was evenly bowed towards the light source.

Results and Discussion

The spectrum of a thick sample made from a film of known resin appears in Fig. 1. This spectrum is shown here not because it is typical, but because it has most of the weak absorption bands observed in all the other spectra. The significance of the absorption bands can be discussed with reference to Fig. 1.

The spectra of all the polyethylenes studied were the same between 4000 and 1800 cm^{-1} , and this region has consequently been omitted in the remaining figures. Figures 2 to 6 are the spectra of LDPE bags, but any that are marked with an asterisk also resemble the spectra of samples prepared from films of known resins.

The spectra of films made from eleven commercial resins supplied by polymer manufacturers in Canada, Great Britain, Japan, and the U.S.A. were all different except two, and for these, the corresponding resins differed only in one of them having added slip and antiblocking agents. The spectrum of a reclaimed polymer had additional bands not found in the spectrum of the virgin resin.

Altogether, 29 packs of bags that had been produced in 16 different shapes and sizes by seven different bag makers were examined, and the infrared spectra of the polymer films from which the bags were made have been compared. Two different spectra of ethylene/vinyl acetate (EVA) copolymers (Fig. 2) and ten distinct homopolymer spectra (Fig. 3) were obtained. In addition, there were seven films in whose spectra were small but reproducible differences in the relative intensities of bands used for characterizing other films (for example, Fig. 4), making 19 different polymer spectra in all.

Five of the 19 polymer spectra were each associated with film from two different kinds of bag. This can be understood when it is known that a bag manufacturer may use the same kind of film or resin for making quite different kinds of bags, some of which may be sold by distributors under other brand names. Some extruders also supply film to other bag makers. The bags can still be distinguished by shape and size even though their spectra may be the same.

The most useful result from this study has been the surprising discovery that different resins may be used at different times for making the same kind of bag. Seven packs of

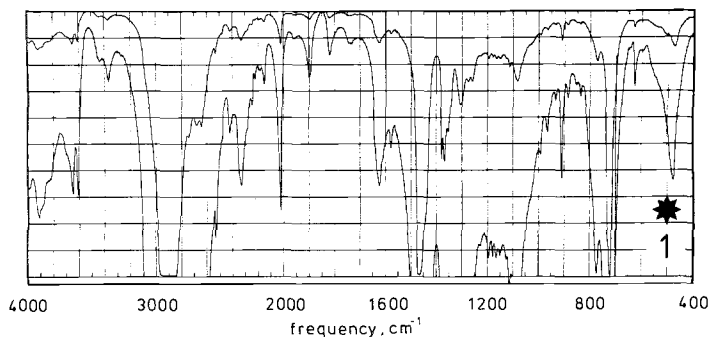


FIG. 1—*Spectrum of a thick sample of a LDPE film.*

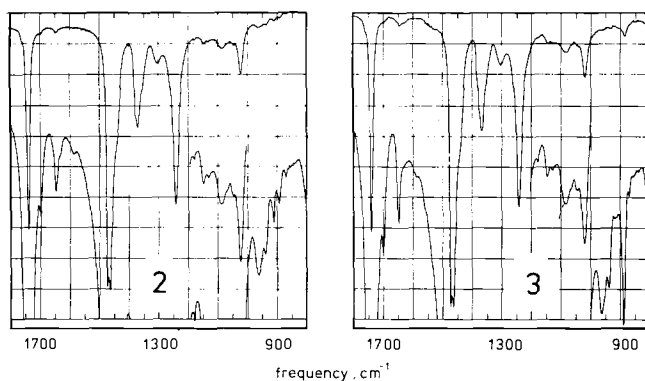


FIG. 2—Spectra of bags made from different ethylene/vinyl acetate copolymers.

one product were purchased during the same week in and about the same city, and their spectra showed that three distinct polymer resins had been used (Fig. 5). Two packs of each of seven other products were purchased in different stores, three months apart, and with only one of these products it was not possible to distinguish the films used in each of the two packs.

Bags from the same pack all had exactly the same spectrum except for one brand of tear-off bags; with these, not only were two packs purchased at different times found to have different spectra, but in both packs there were also steady changes of spectra as bags taken in succession from a roll were investigated (Fig. 6). The irregularity arises from the appearance of bands at 1122 and 1729 cm^{-1} and is probably the result of uneven distribution of an ester-type material.

It is understandable that LDPE resins that provide different film properties have different infrared spectra because the crystallinity or density, tensile strength, and melt viscosity of the polymer are determined by the type of chain branching produced by a given set of polymerization conditions. Small saturated and unsaturated branches and different chain conformations account for many of the weak infrared bands that are useful for characterizing LDPE resins. Fortunately, there are only a few strong bands in the infrared spectra of polyethylenes, and it is possible to intensify weak bands without losing them under stronger absorption bands.

Referring to Fig. 1, strong bands between 4000 and 1800 cm^{-1} arise from C—H stretching modes, and the remaining bands are mainly overtones and combinations. The relative intensities of the bands at 3608, 2330, 2024, and 1897 cm^{-1} depend on the method of sample preparation. The bands at 3608, 2330, and 1897 cm^{-1} are relatively stronger in the spectrum of an unchanged film or of a sample prepared from a melt than they are in the spectrum of a sample prepared by the method described, while the band at 2024 cm^{-1} is relatively stronger when the films have been pressed at a temperature below their melting point. The intensity changes brought about by the sample preparation are the result of partial orientation of the molecules when films are pressed while they are still solid, since the bands have the same opposite dichroism when an oriented film is examined in polarized infrared [1].

In the region from 1800 to 1600 cm^{-1} , —C=C— and —C=O groups absorb. The ester —C=O of EVA polymers absorbs strongly at 1742 cm^{-1} and the spectra of some of the other LDPE resins have quite strong bands at about the same frequency.

The greatest differences between minor bands in the spectra of LDPE resins are found between 1600 and 400 cm^{-1} . Fortunately, the shapes and relative intensities of weak bands in this region are almost independent of the method used for preparing samples.

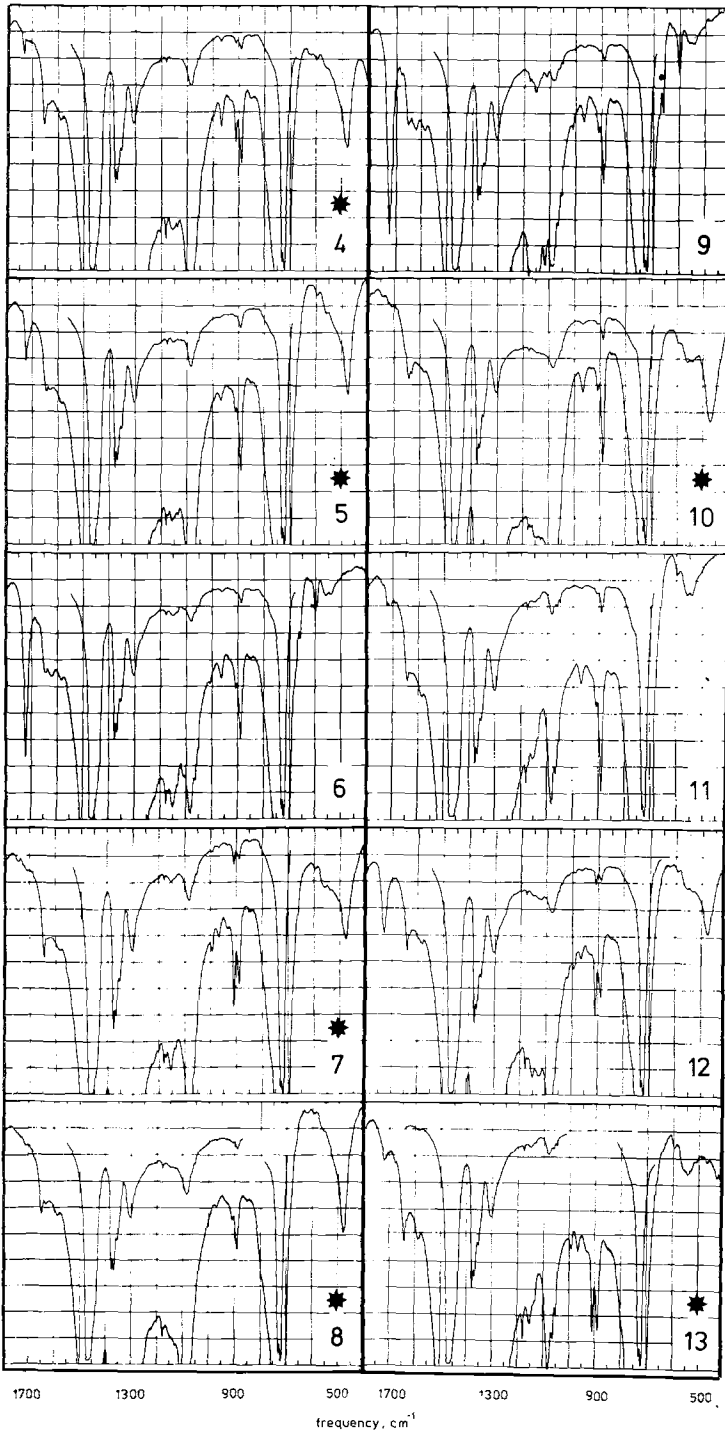


FIG. 3—Spectra of bags made from different LDPE resins.

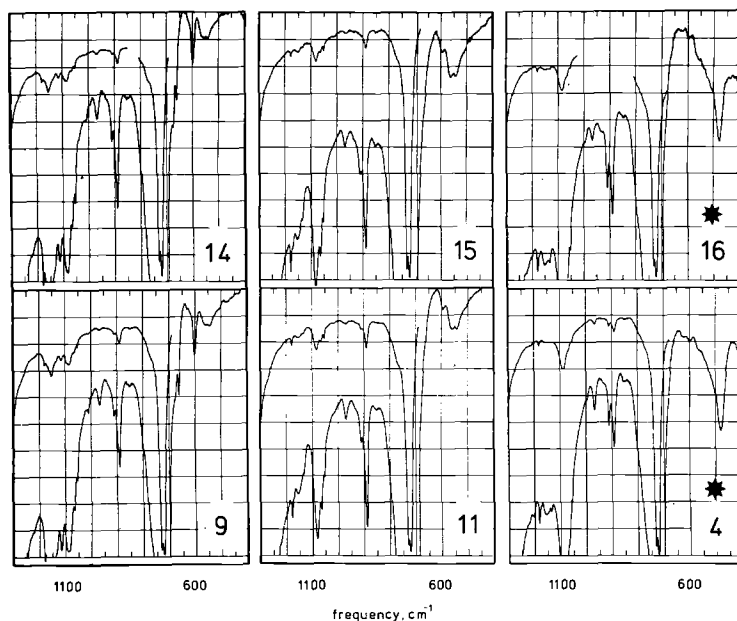


FIG. 4—Examples of differences of relative intensities in the spectra of polyethylene bags.

Strong and medium bands arising from methylene bending, wagging, and rocking modes are common to all the samples, but the shapes of the expanded spectra are mainly determined by the relative intensities of four groups of weak bands: a sharp band at 1180 cm^{-1} assigned to a $-\text{CH}_2-$ wagging mode; sharp bands near 900 cm^{-1} , which are the well-known C—H deformation vibrations of the olefinic side chains: vinyl $-\text{CH}=\text{CH}_2$ at 888 cm^{-1} , vinylidene $\text{RR}'\text{C}=\text{CH}_2$ at 908 and 990 cm^{-1} , and the trans double bond at 964 cm^{-1} ; and broad bands at 1150 and 1080 cm^{-1} , which have been described as composites of overlapping C—C stretch and $-\text{CH}_2-$ wagging and twisting modes [2]. A methyl rocking mode could also contribute to the absorption band at 890 cm^{-1} [2].

Still weaker bands, superimposed on the other weak bands between 1200 and 700 cm^{-1} , have been assigned to absorption by $-\text{CH}_2-$ wagging, twisting, and rocking modes, often doubled by the presence together of ordered and disordered molecular arrangements and by the effects of chain conformations [2]. In Fig. 1, these weak bands appear to form a regular band progression.

Other weak bands at 600 , 550 , and 475 cm^{-1} are sometimes useful for resin identification. These bands have appeared in published spectra but have not been assigned [1]. In the spectra of EVA resins there is a distinctive C—O stretching absorption at 1241 cm^{-1} . Ethyl side chains are associated with a band at 770 cm^{-1} [3], but only in Fig. 1 is there a band at this frequency.

The concentration of additives in LDPE films is generally too low to affect the spectrum. The spectra of opaque films and printed bags have strong pigment absorption superimposed on the polyethylene spectrum.

The full value of the method for forensic comparison lies in the discovery that different batches of the same product may have different spectra. This could come about through resin manufacturers blending their output to maintain uniform rheological properties, but it is more likely the result of film extruders changing resins between batches.

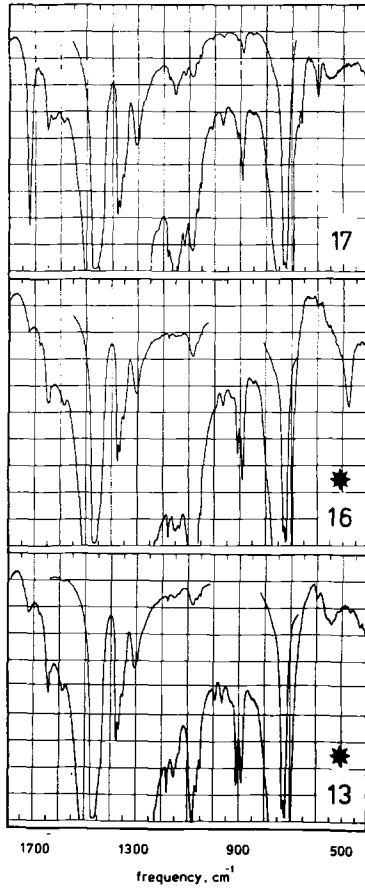


FIG. 5—Spectra of bags from different packs of the same product.

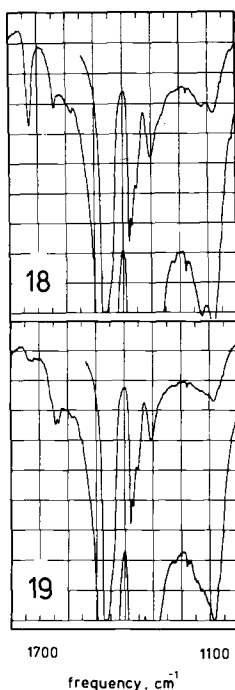


FIG. 6—Spectra of Bag 1 and Bag 7 from the same roll of tear-off bags.

Summary

The comparison and matching of low density polyethylene bags has been discussed and a method described that makes use of the frequencies, shapes, and relative intensities of weak infrared absorption bands to match and identify LDPE films. Since it has been found that different batches of the same bag or film may be made from different LDPE resins, the method has forensic applications.

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