Fluorescence Illuminator for Continuμm Infrared Microscope Reveal Detail of Contaminant Formations in Polypropylene Film

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Key Words

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Introduction

Polypropylene (PP) is a commonly occurring polymer used in a host of commercial products. When polymerizing sheets of PP from its monomer, defects are commonly introduced into the film. This can drastically affect the commercial value of the polymer film. Fourier transform infrared (FT-IR) micro-spectroscopy is a powerful technique for investigating many of these defects, allowing the manufacturer to modify the processing conditions to minimize such defects.

A common defect in polymer sheets is a formation referred to as a "fish-eye." Fish-eyes are circular blemishes or defects found on the surface of the polymer. The defects are the result of a contaminant particle, an unreacted starting material or a localized heterogeneity in the film. Once identified, the defects can often be controlled by altering the process conditions. FT-IR microspectroscopy has been successfully used to identify the contaminants and film heterogeneities that can lead to fish-eye formations[1].

One critical aspect of polymer defect analysis is the ability to visually locate the defect, which can appear similar to the surrounding polymer under standard microscope illumination. To locate defects for spectroscopic analysis, one must first use the enhancement techniques available on the Continuμm™ infrared (IR) microscope from Thermo Nicolet, to highlight important optical differences too subtle to see under normal brightfield illumination.

It is common in microscopy to encounter samples, such as the polymer films discussed here, where brightfield illumination does not sufficiently enhance the differences within the sample to allow the user to visually locate defects with confidence. Often, the color or transparency of the polymeric material is very similar to that of the features or defects, thereby requiring some other method of enhancement.

One example can be found in Polyethylene Terephthalate (PET), where the direction in which the polymer sheet is drawn across the processing machinery during fabrication, imparting different refractive index properties to the material. These properties depend on whether the polymer is used in an orientation that is parallel or perpendicular to the direction in which it was drawn. Under standard visual inspection, it is almost impossible to determine the direction in which the film was drawn or any local defects that may have resulted. However, when analyzed by polarized light, these features are easily determined. Differential Interference Contrast (DIC)[2] is a complex, but more powerful technique for highlighting subtle contrast differences in samples that are not oriented.

Even with polarization contrast enhancement techniques, it can still be difficult to locate the area of interest within the polymer sheet, thus another contrast-enhancement tool is fluorescence illumination[3]. The technique utilizes a high-intensity ultraviolet source to illuminate the sample, causing fluorescent emission. By placing a series of optical filters in the microscope, it is possible to preferentially select emission resulting from specific chemical environments in the sample. For many sample types, different regions of the sample give rise to different fluorescence profiles. This provides a mechanism for locating differences in the sample that are not visible under brightfield illumination[4].

In this note, a Thermo Nicolet Continuμm IR microscope, equipped with fluorescence illumination, was used to investigate fish-eye defects in PP film. Although the PP film did not indicate any fluorescence, defects within the films did cause most fish-eye formations to fluoresce.

Materials and Fish-eyes

PP is a widely used polymeric material that is used in a number of forms. In contrast to the transparent, rigid polymer films often used in packaging, the samples studied here were opaque, soft and elastic. These particular films also contained a number of fish-eye contaminants, making them ideal for the analysis at hand.

Figure 1a shows the visible light image of three fish-eyes in a region of the PP film, all of which appear very similar. However, under illumination with both the UV and the visible

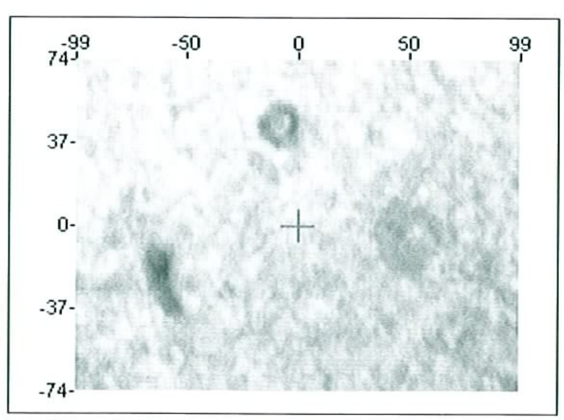

Figure 1a: Image of three fish-eyes under visible light illumination

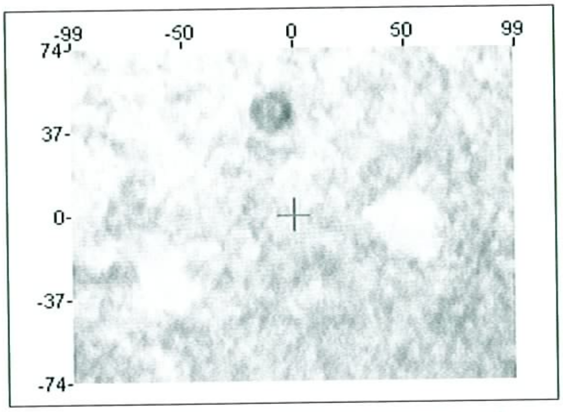

Figure 1b: Image of three fish-eyes under both visible light illumination and ultra-violet light

source, it is obvious that there are differences in the defects. Two of them gave rise to a different fluorescence emission than the third, as indicated by the lighter colored areas in Figure 1b.

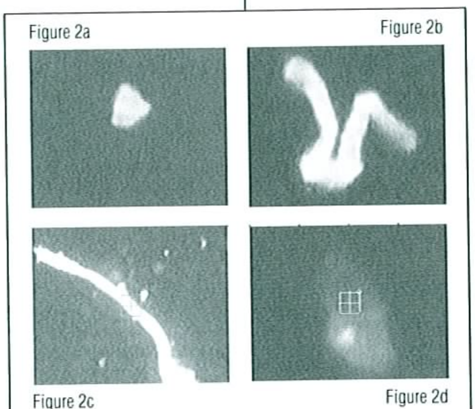

Figure 2: Examples of fluorescing materials found in PP film sample. Squares represent 20 x 20 micron areas

Other defects and irregularities were evident within the polymer under fluorescence illumination, as shown in Figure 2. Some of the apparent defects were flakes, as in Figure 2a, and ribbons in Figure 2b and filaments in Figure 2c. All gave strong, yet different colors of fluorescence emission. By contrast, the defect in Figure 2d demonstrated minimal fluorescence.

Spectra were collected using a Thermo Nicolet Nexus 670 FT-IR spectrometer. Figure 3 shows an IR spectrum of a non-fluorescing, fish-eye defect, along with a spectrum collected from the defect-free bulk PP film. There is an apparent difference in the intensity of the carbonyl stretch at 1746 cm^{-1} and the peak is slightly shifted from the 1734 cm^{-1} location of the pure polymer. This indicates that there are two different kinds of carbonyl compounds in this film.

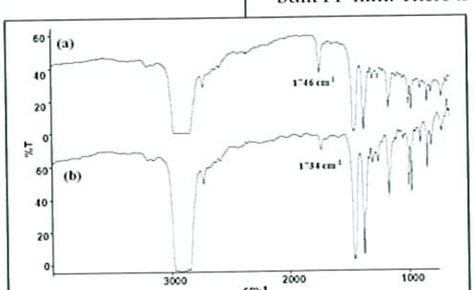

Figure 3: IR spectra of non-fluorescing fish eye (a) and normal part (b)

Similarly, spectra of the fluorescent fish-eye defects demonstrated significant differences associated with the amide structure. There were variations in the NH stretch bands at 3284 and 3073 cm^{-1} as well as the Amide-I and Amide-II bands at 1644 and 1536 cm^{-1} respectively[5].

In addition to the amide compound suggested by the previously described spectra, the IR spectrum of the flake, shown in Figure 2a, revealed strong bands at 1654 and 1548 cm^{-1}, is also indicative of an amide compound.

The ribbon material, which displayed strong fluorescence in Figure 2b, was identified as cellulose. The IR spectrum of the ribbon and the ribbon spectrum after subtraction of PP are shown in Figure 4. A spectrum of a standard cellulose sample is also shown in Figure 4d for comparison.

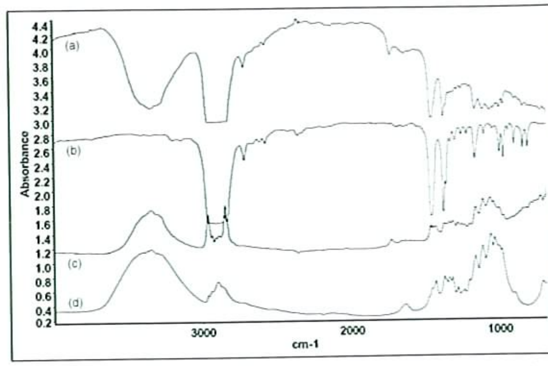

Figure 4: IR spectra of blue fluorescing ribbon (a), normal part of the PP film (b), ribbon after subtraction of PP film (c) and standard cellulose (d). Spectra (a) and (b) are presented in %T for interpretation purposes.

The ribbon material shown in Figure 2c exhibits a strong spectral band at 1733 cm^{-1}, as shown in 4a. Its position is the same as the band observed in the spectrum collected from the bulk portion of this film, but different from the one observed by the non-fluorescing fish eye. The large flake shown in Figure 2d seems to be non-fluorescing.

In Figure 2d, the weak fluorescence is believed to come from the surface, which is smeared with a fluorescing compound. The IR spectrum obtained from the material after subtraction of the PP spectrum displays features of the amide compound.

Discussion

From the observed frequencies of the carbonyl stretching vibrations, 1733 and 1744 cm^{-1}, one can deduce that there are two kinds of carbonyl compounds in this sample. The polymer additive seems to be the compound that displays the 1733 cm^{-1} band. Two kinds of amide-type compounds also exist. One fluoresces and one does not. In addition to these compounds, some contaminants (such as cellulose, kaolinite, calcium carbonate and an unknown compound displaying a nitrile band) exist. Moreover, the carbonyl compound used as the additive was found isolated from the film as a melt-type, non-fluorescing portion as mentioned above. Therefore, nine different compounds were found to be either film contaminants or deposits isolated from the film. The carbonyl compound with the 1744 cm^{-1} band shows a faint brown color and seems to be a foreign compound.

An area map was collected from the section on the film with the non-fluorescing circular fish eye shown in Figure 6. The top map shows an intensity plot of the carbonyl group, and the bottom map shows an intensity plot for the CH_2 rocking vibration. Note that the positions coincide exactly in the two maps. Therefore, it is safe to conclude that the fish eye contains a compound with a carbonyl group and a functional group responsible for a long CH_2 chain rocking at 720 cm^{-1}. The compound in the circular fish eye is attributed to one of the long chain esters, which are known PP additives. (However, this is not the additive previously mentioned.)

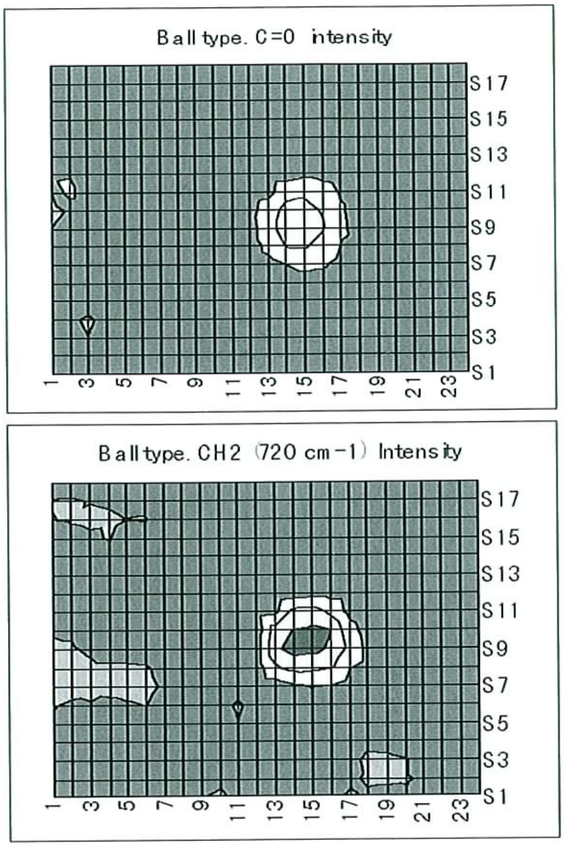

Figure 6: Mapping of non-fluorescing, circular fish-eyes. Maps based on the intensity of carbonyl group (top) and CH_2 rocking vibration (bottom)

It is well known that some amide compounds, such as Erucamide [6] and long-chain amides, are used as additives in PP. However, the spectral features of the amide compounds observed in this study are quite different from the features that would be expected from these additives. The spectra indicate that these amide compounds could be identified as some type of polyamide such as nylon. Although these compounds differ in the nature of their fluorescence, the IR spectra look similar. This indicates that some portion of the nylon was processed in a way that had substantial contact with a compound that would cause it to exhibit a yellow fluorescence. The other portion was in contact with a non-fluorescing compound.

If this is the case, the PP melted in the tank was not uniform. Therefore, the film was made inhomogeneous. In addition, the question still exists whether the nylon was intended to be in the film or whether it was a contaminant. If these materials were intended, the observation of cellulose flakes, kaolinite and other such particles indicate the dispersion of these compounds in the melted PP was less than perfect. The fact that the carbonyl compound serving as the additive is isolated, implies that the melting of the starting materials was not complete when the film was made. If these materials were not intended, and are considered to be contaminants, the system's cleaning is likely to have been inadequate.

Summary

Contrast enhancement technique can assist IR microspectroscopists in locating positions on their samples for single-point observation, IR mapping and IR imaging. The PP film discussed in this application note has shown numerous irregularities. Some of the portions discussed in this note could not have been easily located and isolated with visual observations. By utilizing the Continuμm microscope's fluorescence illumination, the identification of two similar-looking fish-eyes could be deduced. Using the various colors of fluorescence as a guide, many foreign materials deposited in the PP were found.

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