NONDESTRUCTIVE ESTIMATION OF SAPONIFICATION DEGREE USING FT-IR/ATR DEPTH PROFILING METHOD

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Abstract - Concentration depth profiling of functional groups using FT-IR/ATR spectroscopy was applied to nondestructive determination of saponification degree in diacetyl cellulose films. Saponification degree was also determined destructively by neutralization titration and micro FT-IR. The results obtained showed good agreement. This method would be applicable to other nondestructive analyses of organic compounds.

Key words FT-IR/ATR, depth profiling, saponification degree

Depth distribution of chemical species within the range of a few micrometers from a sample surface has become important in many technological fields. Some destructive methods are available, but there are some cases in which nondestructive methods including electron and photon spectroscopies are desirable. Among them Fourier transform infrared attenuated total reflection (FT-IR/ATR) spectroscopy has proved to be a powerful tool for obtaining information about the sample surface[1]. With this method the concentration depth profiles have been determined[2], but the propriety of the depth profiles obtained was not discussed and practical applications of this approach were not reported. Here, we apply this method to the nondestructive estimation of the saponification degree in diacetyl cellulose (DAC) films. Saponification degree is also determined destructively by neutralization titration and by micro FT-IR. On the basis of these results we discuss the applicability of FT-IR/ATR to such kinds of nondestructive estimation.

EXPERIMENTAL

Samples Sample films consisted of a surface DAC layer, varying in saponification degree, and a substrate layer of polyethylene terephthalate (PET). Thickness of the DAC layer was 6-8 μm . This DAC layer was saponified by spreading a methanol solution of sodium hydroxide over its surface. Unsaponified sample was prepared separately as a blank.

FT-IR/ATR Measurements ATR spectra were measured on the JASCO VTT-8 FT-IR spectrometer with a mercury-cadmium-telluride (MCT) detector at a

resolution of 4cm^{-1} . The ATR accessory consisted of the commercial ATR attachment (JASCO ATR-500/V) and the goniometer unit. The incident angle was varied from 41° to 60° by one degree increments and twenty spectra were recorded for each sample. Critical angle in this experiment was calculated as about 38.7° .

Micro FT-IR Measurements The sample film was microtomed obliquely at a small angle ($4-9^\circ$) to enlarge the DAC layer and the sample cross-section was kept at a 0.5-1.0 μm thickness to prevent detector saturation. All measurements of micro FT-IR spectra were made on the JEOL JIR-100 spectrometer with the JEOL IR-MAU110 micro IR unit. A MCT detector was used. Resolution was 8cm^{-1} and 200 scans were made.

Neutralization Titration A film sample 30 mm x 30 mm was sliced off and

left in 10 ml of acetone and 15 ml of a 0.1N NaOH solution for about an hour at room temperature. After 15 ml of a 0.1N HCl solution was added, the neutralization titration was carried out with a 0.01N NaOH solution using phenolphthalein as indicator.

RESULTS AND DISCUSSIONS

The ATR spectra of two kinds of DAC films measured at the incident angle of 45° are shown in Fig. 1. The

characteristic peak near 1735 cm⁻¹ was assigned to $\nu(\text{C=O})$ of the acetyl groups. This peak was used as a key band for depth profile analysis. To discuss saponification degree, normalized absorbance R is defined as the absorbance ratio of the saponified film to the unsaponified film and written as [2]

$$R = (2/dp) \int_0^\infty G(z) \exp(-2z/dp) dz, \quad (1)$$

where dp and $G(z)$ denote penetration depth [1] and concentration ratio of the acetyl groups in the saponified film to that in the unsaponified film, respectively. If the reaction rate of saponification is assumed to be determined by diffusion, the concentration profile $G(z)$ is written using a parameter l as

$$G(z) = \text{erf}(z/l), \quad (2)$$

where $\text{erf}(z/l)$ is Gauss error function. The optimum value of l , l_{opt} , was determined by substituting Eq. (2) into Eq. (1) iteratively for different l values. The value of l_{opt} in this experiment was got as 2.0. Good agreement was seen between depth profiles obtained from FT-IR/ATR and micro FT-IR. Using these depth profiles the values of saponification degree K as a whole film were calculated from

$$K = \left(1 - \frac{\int_0^d G(z) dz}{l \times d} \right) \times 100, \quad (3)$$

where d was thickness of the DAC layer. The calculated K values are listed in Table 1 together with the results obtained from the neutralization titration. The relatively large range of K values obtained from the neutralization titration was considered to be caused by the small amount of acetyl groups contained in such a thin DAC layer. The K values obtained from these three methods were considered to almost agree with one another, within the experimental errors. This fact showed that FT-IR/ATR can estimate the amount of surface functional groups distributed nonuniformly in the depth direction. For more precise estimations, a strict theoretical treatment including the effect of absorption should be developed.

TABLE 1. Comparison of the K values obtained from the three methods.

Method	K value(%)
FT-IR/ATR	14
Micro FT-IR	11-17
Neutralization Titration	11-25

Fig. 1 ATR spectra of the DAC films for different saponification degrees.

REFERENCES

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