Note

Determination of Monomer Unit Ratio in Copolymer by Infra−Red Spectrometry for Customs Purpose

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Measurements of absorbance ratio of CH bending vibration and C=O stretching vibration are one of the convenient methods for the determination of the monomer unit ratio of certain kinds of copolymers. Especially, in the case of ethylene−copolymer which contains C=O group, it is one of the most useful methods for customs purpose.

Using several kinds of ethylene-acrylic acid copolymers, the correlation between the absorbance of CH bending vibration and that of C=O stretching vibration was studied. It was a simple and quick method for determination of monomer units ratio for the customs laboratories to use the absorbance ratio of CH bending vibration and that of C=O stretching vibration in such copolymers.

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1 Introduction

According to the adoption the International Convention on the Harmonized Commodity Description and Coding System which declarations to customs are based on, it is clear that polymers or polymer blends in which any monomer contributes 95% or more by weight to the total polymer content are classified in “homopolymer”. And, polymers or polymer blends other than “homopolymer”, i.e. “copolymer” are classified in polymers of that comonomer which predominates by weight over every other single comonomer. Thus, it is very important for the customs to analyze what monomer unit ratio a copolymer or polymer blends contains.

The monomer unit ratio is well measured by the NMR or by the element analysis and so on. But, by the reason that these apparatus are not available for local customs laboratories, the most useful apparatus would be an infra-red spectrophotometer.

For determination of the monomer unit ratio in copoloymers or polymer blends, an infrared spectrometry has been hitherto employed[1]. Especially, in the case of ethylene-copolymer which contains C=O group, it would be one of the most useful method for the customs laboratories, because an absorption of the C=O group in the ethylene-copolymer in the range from 1, 600cm^{-1} to 1,800cm^{-1} is independent of other absorptions. For a part of the study on simple and quick determination of the monomer unit raio in copolymers or polymer blends for the customs laboratories, we tried to determine the acrylic acid

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content in ethylene-acrylic acid copolymer using the infrared spectrometory, and the results are reported herein.

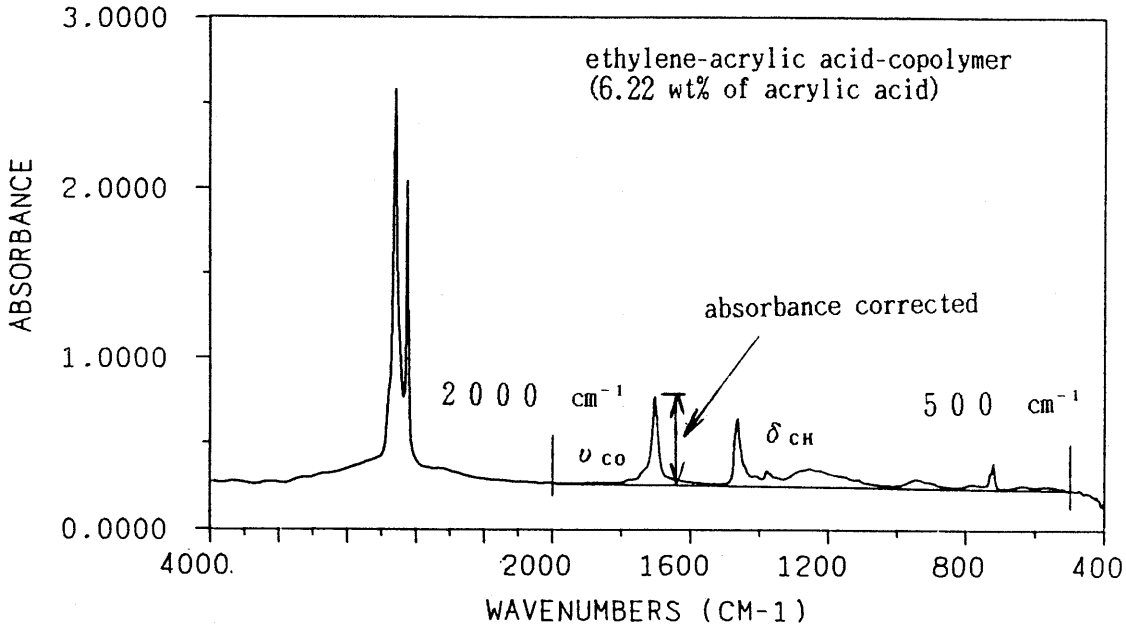
2 Experiments

2．1 Samples

Ethylene-acrylic acid copolymers manufactured by Aldorich Chemical Inc. and Scietific Polymer Products, Inc. were used. Furthermore, a variety of imported goods were used. The acrylic acid content of these copolymers were measured by the elemental analysis which were performed at the Laboratory of Yanagimoto Manufacturing Co.,using a Yanaco CHN coder Type MT—5.

2．2 Equipment and Measuring Points

The IR spectra were measured using a JEOL FT-IR spectrophotometer Type JIR-100. Absorbance at near 1,465cm^{-1} which assigned to CH bending vibration and that at near 1,705cm^{-1}, 705cm^{-1} which assigned to C=O stretching vibration were measured as key bands. And all of absorbances observed were corrected by baseline method which was drawn from 500cm^{-1} to 2,000cm^{-1} (see Fig. 1) [2].



F.1 Correlation of IR igspectra by base line

2．3 Preparation of Samples

The samples sandwiched between two 0.017mm aluminium foils were pressed into films at 140℃ and 5～10kg/cm2 using a Yorizane Press Manufacture molding test press Type YS—47. The sample films with aluminium foils were equiped withteflon-made sample holder (see Fig. 2). And aluminium foils were dissolved by 3N - HCl with care. But, for keeping the smoothness, it was necessary to retain the foils on the annular supporter.

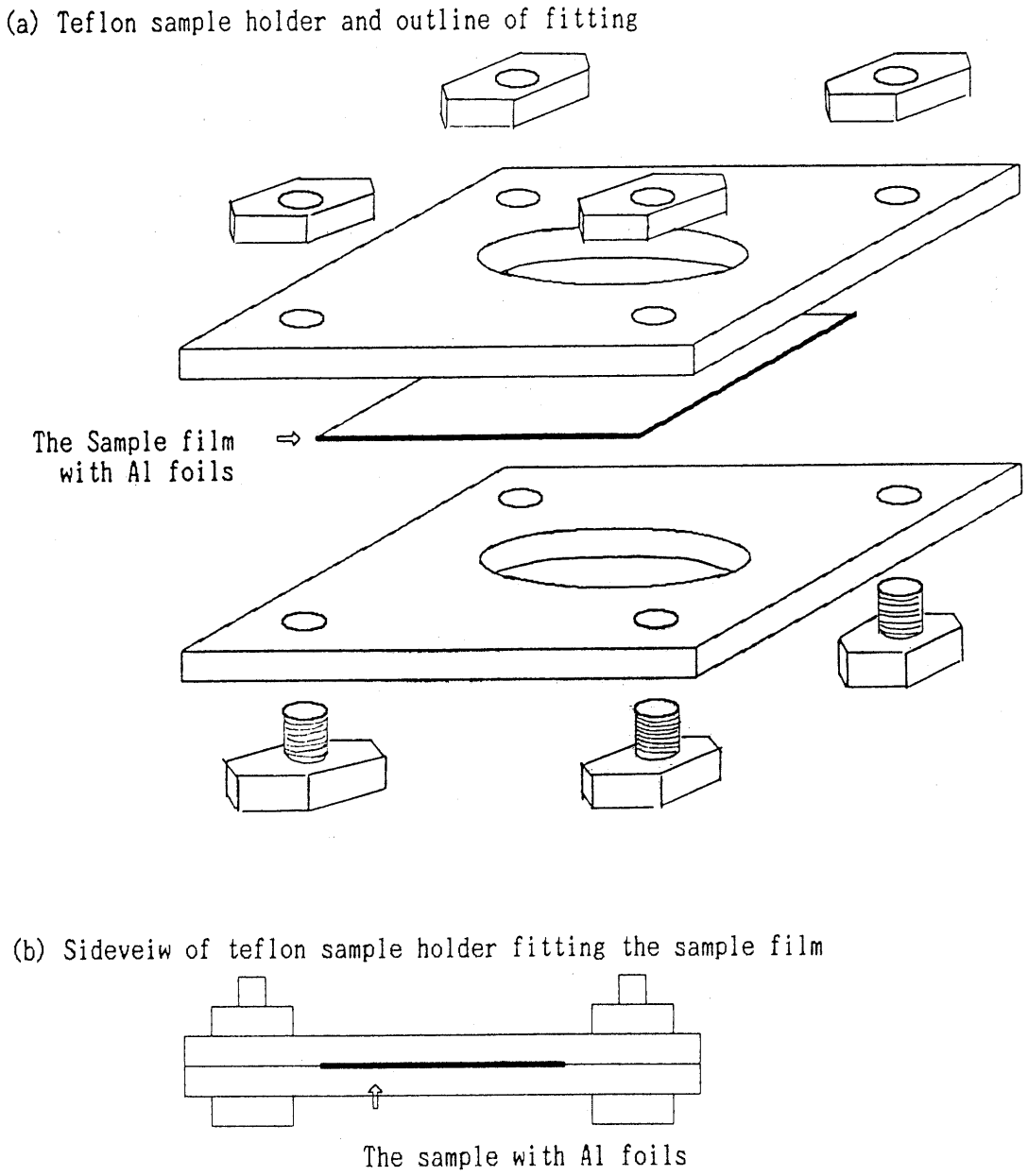


Fig.2 Teflon sample holder

2. Results and Discussion

3.1 Relation between Absorbance and Absorbance Ratio

The infrared absorption spectra of four types of ethylene-acrylic acid copolymers were measured. The results with correlation[3] between absorbance ratio and absorbance at 1,465cm^{-1} are shown in Fig 3. It shows that the absorbance ratio was slightly related to the content of acrylic acid unit at highly acrylic acid contents. It indicates that two monomer units were not completely independent but merely related. Nevertheless, it would be negrigible for the customs analytical purpose, because low acrylic acid content were independent of absorabance.

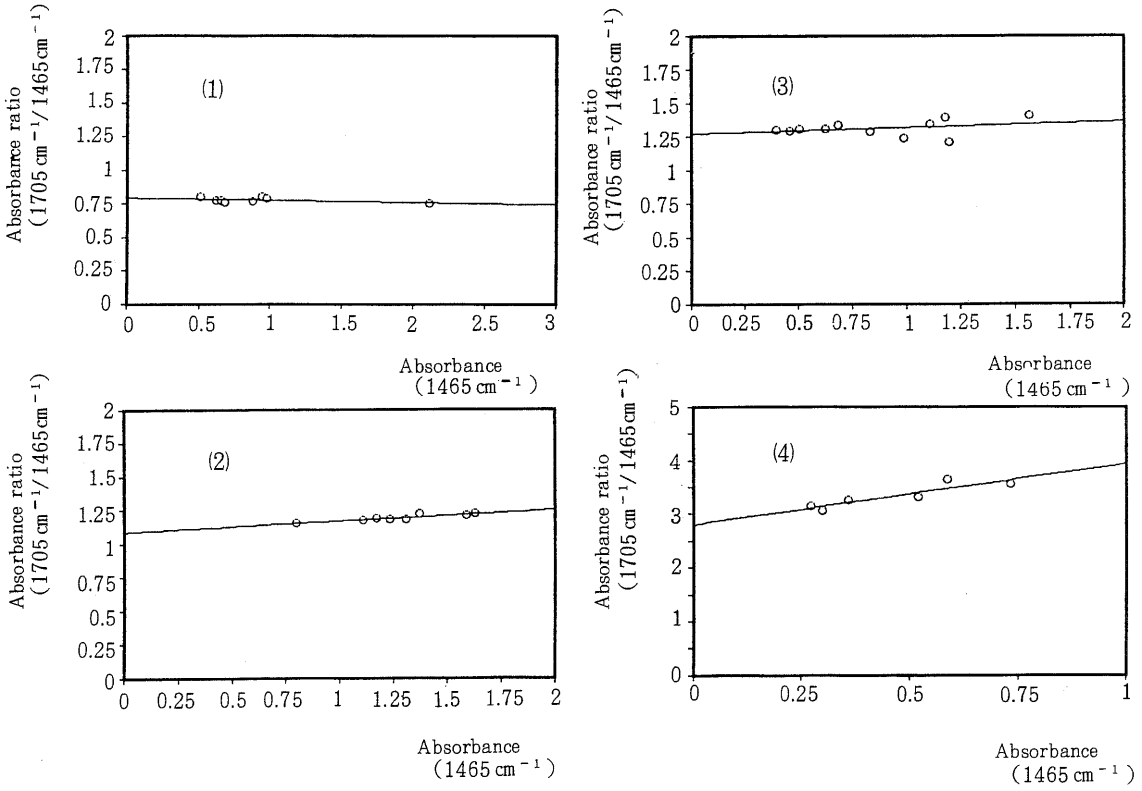


Fig.3 Relation between absorbance ratio and absorbance of various ethylene-actylic acid-copolymer:
(1)Acrylic acid content was 6.22wt%:
(2)Acrylic acid content was 8.88wt%:
(3)Acrylic acid content was 11.10wt%:
(4)Acrylic acid content was 20.53wt%.

3.2 Relation between Absorbance Ratio and Monomer Unit Content

The relation of absorbance ratio which were extrapolated to zero of absorbance at 1,465cm^{-1} to monomer unit ratio is shown in Fig. 4. By the method of least squares,the following formula between absorbance ratio and monomer unit ratio was obtained[3].

$$A_0=\frac{C_a}{0.002913\times C_a+0.091981\times(100-C_a)}\cdots\text{Eq.1}$$

where A_0 shows the absorbance ratio extrapolated to

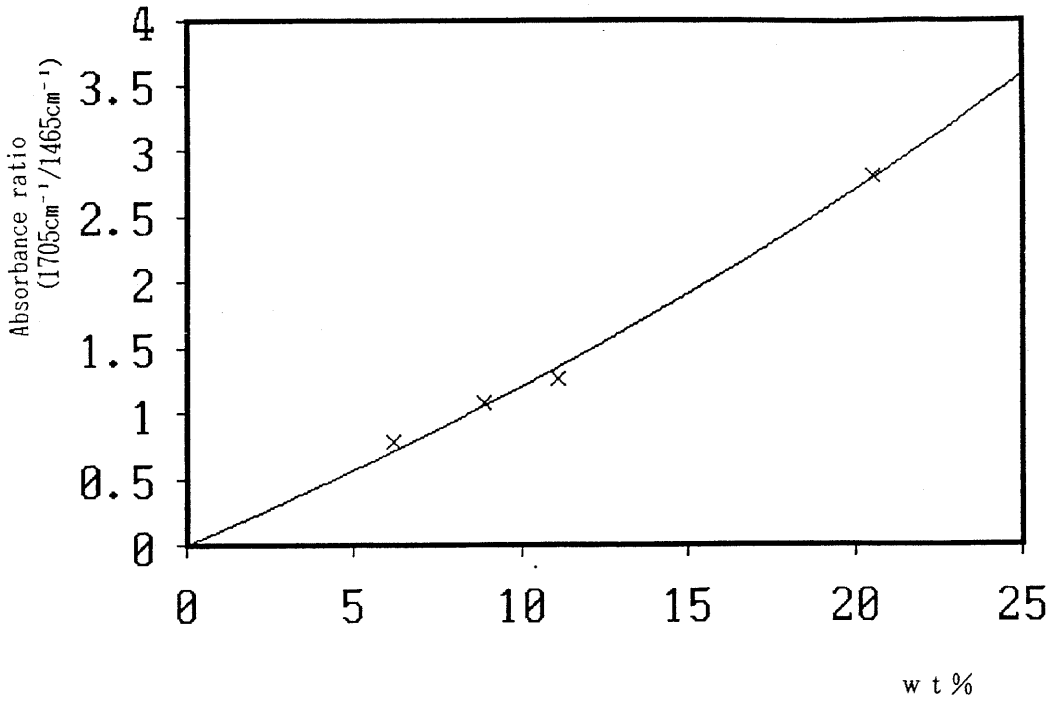


Fig.4 Relation between absorbance ratio and acrylic acid contant in various ethylene-acrylic acid-copolymer

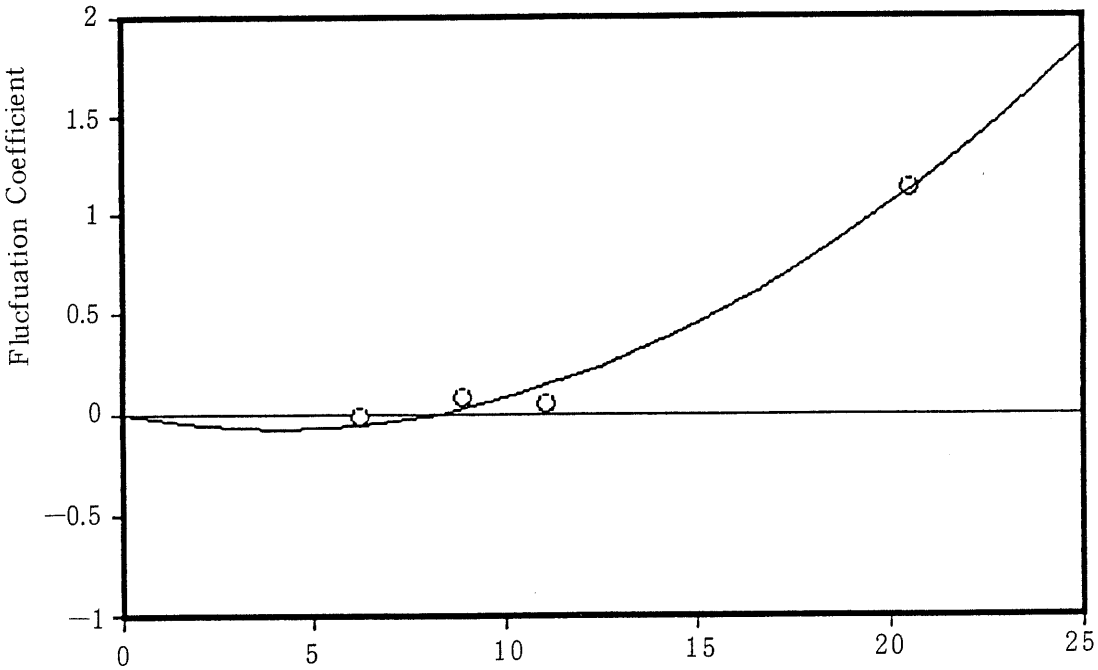


Fig.5 Relation between fluctuation coefficient on absorbance and acrylic acid contant in various ethylene—acrylic acid-copolymer

zero and C_a shows wt% of acrylic acid unit in an ethylene－acrylic acid－copolymer. Eq. 1 can be arranged as follows：

$$C_a = \frac{9.1981 \times A_0}{1 + 0.08970 \times A_0} \cdots\cdots\cdots\cdots \text{Eq. 2}$$

Considering the fluctuation of absorbance, if a quadratic equation was used for approximation, the following formula is obatained (see Fig. 5). In equations of the relation between absorbance ratio and absorbance at 1,465cm^{-1} in each ethylene-acrylic acid copolymers.

$$A_R = \frac{C_a}{0.002913 \times C_a - 0.091981 \times (100 - C_a)} + 0.004456 \times A^2 - 0.03682 + A \cdots\cdots\cdots \text{Eq. 3}$$

wher A shows the absorbance at 1,465cm^{-1} which was correlated using base line and A_R shows the observed absorbance ratio.

3．3 Repeatability

By means of measuring the same sample several times, the reproducibility was observed. The results are shown in Table 1.

Table 1　Repeatability of measurements

Test No.	Absorbance ratio (1705cm^{-1}/1464cm^{-1})
1	0.7765
2	0.7843
3	0.7801
4	0.7803
5	0.7847
Average	0.7812
Standard deviation	0.003392

Note：Ethylene-acrylic acid copolmer containing 6.22% of acylic acid was used.

3．4 Confidential Interval

The standard deviation of difference between data obtained and the value calculated by Eq.2 or Eq.3 were computed. And assuming that confidence intervals were three times the standard deviation, the following observations on ethylene-acrylic acid-copolymers which contain low acrylic acid were obtained.

(1) When absorbance were corrected using extrapolation, if the acrylic acid content falls within the range of 3.09wt% to 6.91wt% in measurement, it is necessary to determine acrylic acid content using other method, i.e. the NMR the elemental analysis and so on.

(2) When Eq.3 is used for correction, if the acrylic acid content falls within the range of 2.61wt% to 7.39wt%, it is necessary to determine acrylic acid content using other method.

4 Conclusion

It was recognized that as a rapid and convenient method for determination of monomer unit ratio for the customs laboratories, it is recommended to use the ratio of absorbance of CH bending vibration and that of C=O stretching vibration in ethylene－acrylic acid－copolymers with low acrylic acid content, But, if the result measured falls within the range of 2wt% to 8wt% of acrylic acid content, other analytical method, i.e. the NMR, the elemental analysis and so on becomes necessary.

References

1） E. Oyama. et al：This journal 2, 63（1966）
2）“ Sekigaikyushusupekutoruno ”, by M. Tanaka. et al：Hirokawa Publishing Co., Bunkyo—ku, Tokyo, pp.238—240, 1964
3） ibid ., pp.22—226