

## Note

# Determination of Unsaturation in Polyepichlorohydrin by Near Infrared Spectra

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## 1 . Introduction

Synthetic highpolymers being imported are mainly classified into Chapter 39 or 40 of Customs Tariff Schedule in Japan, according to the Note 4(a) of Chapter 40 which, as one of the criteria, provides that polymers must contain double bonds with the possibility of being vulcanized with sulfur; and as for being referred to be rubbers, the vulcanized materials can be extended to over three times the original length without break and will return under one and half the original length after being extended twice the original length.

Such polymers as polybutadiene, poly (styrene - butadiene), poly (acrylonitrile - butadiene) and synthetic polyisoprene contain double bonds in their chains and usually are well vulcanized with sulfur to show rubber - like properties - in elongation and permanent set, for example - as recognized to meet the provision to be classified into Chapter 40 mentioned above.

On the contrary, poly (ethylene - propylene), poly - isobutene, poly (acrylic ester) and poly (propylene oxide) which are for use as rubbers usually contain quite a small amount of unsaturation such as ethylidene norbornene, isoprene and allyl glycidyl ether<sup>1)</sup> for sulfur vulcanization - up to several percent - which lead to difficulties to detect them. Among them the analysis of unsaturation for ethylene - propylene terpolymer and copolymer of isobutene - isoprene have studied by time averaging NMR, by iodine number, and poly (propylene oxide) by near infrared spectra.<sup>2),3),4),5),6)</sup>

Application of near infrared for the detection of unsaturation in such rubber - like materials have been tried by authors, and the good results are reported.<sup>6)</sup>

Polyepichlorohydrin, recently developed polymer for use as a synthetic rubber, contains allyl glycidyl ether as a moiety in most cases.

Therefore, as a model compound of copolymer of epichlorohydrin and allyl glycidyl ether, the mixture of polyepichlorohydrin and poly (allyl glycidyl ether) has been studied for the analysis of unsaturation by near infrared spectra, for the reason that it was difficult to obtain desirable copolymerization ratio.

In near infrared spectrum, the terminal vinyl group, - CH=CH<sub>2</sub>, shows absorption near 2.1 micron (4761 cm<sup>-1</sup>), 1.6 micron (5555cm<sup>-1</sup>), 1 micron (10000 cm<sup>-1</sup>) regions, assigned to combination, first and second overtone vibrations respectively.<sup>7)</sup> 1.6 micron band was considered to be the most suitable for the analysis of the terminal vinyl group because of low background and the least effects by neighboring CH absorption, and the linearity between molar concentrations of unsaturation and absorbance, in this experiment, was indicated satisfactorily.

## 2 . Experimental

### 2 . 1 Reagents

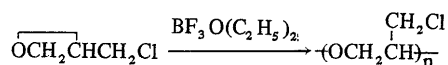
Epichlorohydrin  $\overline{\text{OCH}_2\text{CHCH}_2\text{Cl}}$ , allyl glycidyl ether  $\overline{\text{OCH}_2\text{CHCH}_2\text{OCH}_2\text{CH=CH}_2}$ , 1,2 - dichloroethane, boron trifluoride ethylether  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ ;  $\text{BF}_3$ , about 47%, carbon tetrachloride, chloroform were used without further purification.

### 2 . 2 Synthesis of polymers

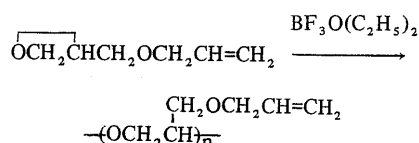
Polyepichlorohydrin was synthesized by following

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method.<sup>8)</sup> Monomeric epichlorohydrine (30g) was diluted with the same volume of dichloroethane and into which the boron trifluoride ethylether (1 ml) was added readily with stirring and dipping the flask in an ice - bucket in order to reduce the overheating by reaction for 30 minutes. Then, a small amount of ammonia solution was added as the termination agent. Reaction product was put on the water - bath to evaporate the dichloroethane. The final process was drying in the vacuum. The product was pale yellowish transparent paste.



Poly ( allyl glycidyl ether ) was synthesized as the same procedure mentioned above for polyepichlorohydrin - drin.



Two polymers were, then, mixed to prepare the various contents of unsaturation.

### 2 . 3 Measurements of near infrared

Near infrared spectra were run on near infrared instrument built in Shimadzu Multi - Purpose Spectrophotometer MPS - 50L. Of which light source is of tungsten lamp and the detector is of lead sulfide. Solution cells are made of quartz. Calibration for the near infrared was by the absorption of chloroform at 2.054 micron ( $4868\text{cm}^{-1}$ ), 1.862 micron ( $5317\text{cm}^{-1}$ ), 1.409 micron ( $7097\text{cm}^{-1}$ ) and 1.154 micron ( $8666\text{cm}^{-1}$ )<sup>9)</sup>. The normal operating setting were as follows; scanning time 20 minutes, signal response 2.

### 3 . Discussion

There are three characteristic aspects in the near infrared of which region is referred to as that between about 0.7 and 2.5 micron ( $13000$  and  $4000\text{cm}^{-1}$ ); (1) the strong energy from the light source emits with very low stray light as the tungsten lamp is used, (2) the lead sulfide detector is very sensitive, superior to a thermocouple and rapid responding, and yields large signals, (3)

quartz prism and gratings of high dispersion offer good resolution of spectrum, and accurate and long quartz cell for solution is available especially in the case of carbon tetrachloride which is non - polar and suitable for overall region for measurement eliminating the troublesome in quantitative analysis. These are very helpful when near infrared is applied to the analysis of small quantity of unsaturation.

The near infrared spectra of polyepichlorohydrin are shown in Fig.1 measured in 10% solution with carbon tetrachloride and without any diluent. The second overtone band by CH and CH<sub>2</sub> appeared at 1.1 micron region, OH or C - O - C overtone at 1.4 micron and CH overtone at 1.7 micron, C - C 1 overtone at 1.9 micron and CH combination band at 2.2 to 2.5 micron respectively.

The spectrum of a typical terminal unsaturation, poly (allyl glycidyl ether), in 10% solution with carbon tetrachloride is shown in Fig.2 in which the unsaturation bands at 1.6 and 2.1 micron, assigned to first overtone for the former and combination for the latter, appeared rather strongly but, in contrast, at 1.1 micron the weak band with second overtone of unsaturation appeared. Thus, 1.1 micron band was excluded from analysis of terminal unsaturation and the discussion was only limited to the first overtone band at 1.6 micron and the combination band at 2.1 micron region. When a small amount of unsaturation, as in Table, was added to polyepichlorohydrin and the mixture was diluted with carbon tetrachloride to 10% solution, it was almost impossible to detect the unsaturation. Accordingly, the spectra of mixtures were measured without any diluent using 1 cm - cell. In this case, even in the region of 1.6 micron, neighboring CH band were so strong that 1.6 micron band could not be avoidable from the interruption to some extent. 2.1 micron band was impossible to use for the detection by the interruption caused by the strong CH combination band, which left the possibility of offering good information when measured by the compensation method, which was not used in this experiment. In 1.6 micron region, although it was weak, but the absorption occurred apparently on the shoulder of the strong 1.7 micron band. The spectra in different concentration in the 1.6 region are shown in Fig.3

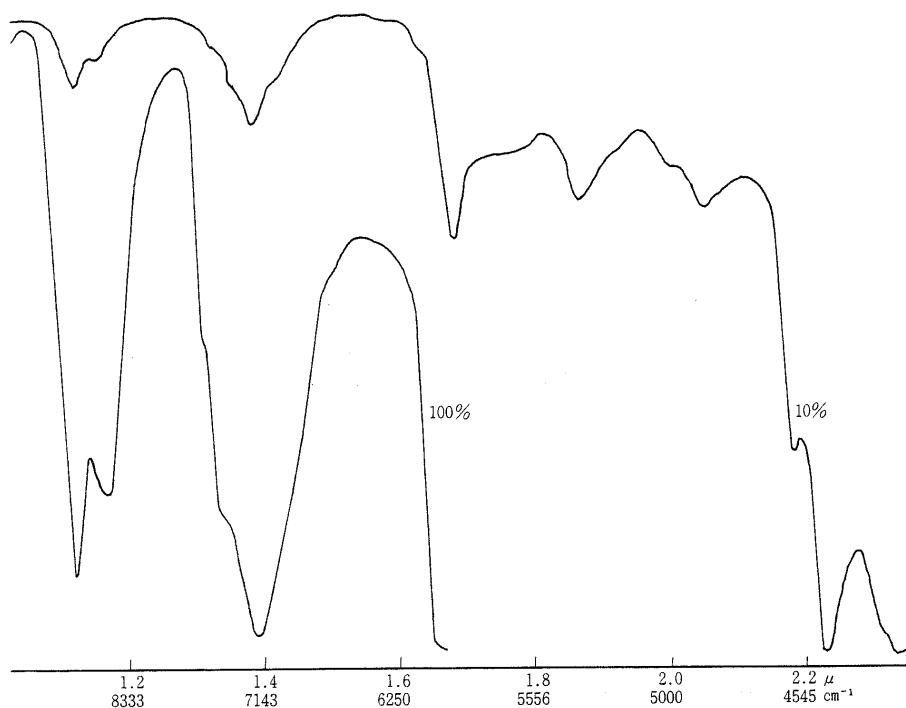


Fig.1 Near infrared spectra of polyepichlorohydrin

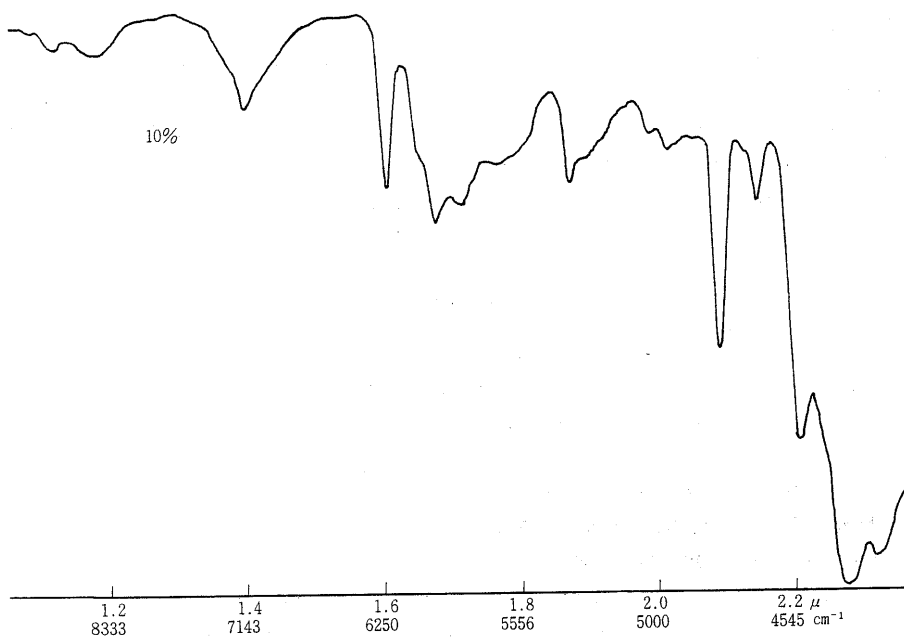


Fig.2 Near infrared spectrum of poly (allyl glycidyl ether)

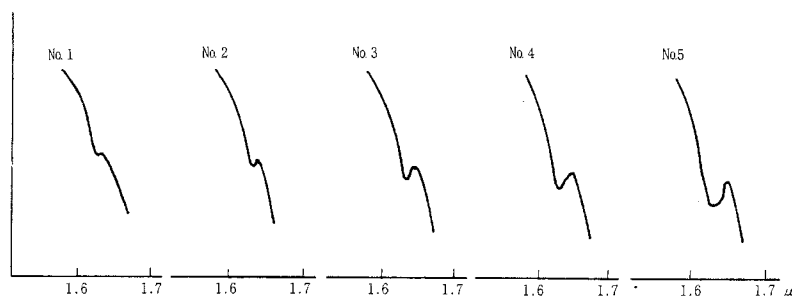


Fig.3 Near infrared spectra of polyepichlorohydrin and Poly (allyl glycidyl ether) mixtures in the region of 1.6  $\mu$

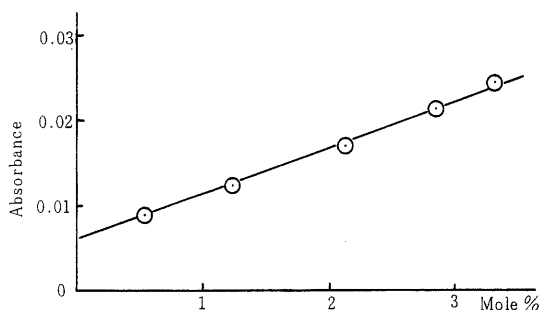


Fig.4 Absorbance at 1.6  $\mu$  vs molar concentration

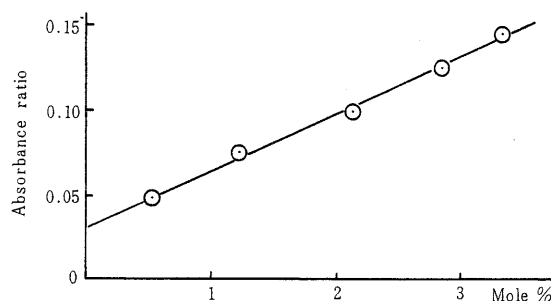


Fig.5 Absorbance ratio (1.6/1.5  $\mu$ ) vs molar concentration

In the calculation of absorbance of 1.6 micron, for the unsaturation, and 1.1 micron, for the CH overtone band, the base line method was applied. The results are summarized in Table. 1.1 micron band was constant in intensity and showed no change during measurements at all. The plot between the absorbance of 1.6 micron and molar concentration is shown in Fig. 4. Another plot

between the absorbance ratio (1.6/1.15  $\mu$ ) and molar concentration is shown in Fig.5.

These indicate good linearity and imply the possibility of applying to the quantitative analysis, that is, the detection of small amount of unsaturation in epichlorohydrin rubber by this near infrared method will give good result.

#### References

- 1) Kanbara, Kawasaki et al.: "Synthetic Rubber Handbook", 424, Asakura Publishing Co. (1969).
- 2) T.S.Lee, I.M.Kolthoff, E.Johnson : *Anal. Chem.*, **22**, 995 (1950).
- 3) R.Hamk : *Kautsuk und Gummi*, **18**, 295 (1965).
- 4) P.R.Swell : *J.Polymer Sci A - 1*, **6**, 2425 (1968).
- 5) Hung Yu Chen : *Polymer Letters*, **5**, 501 (1967).
- 6) Shimada, Mizuki, Fujita : This Report, No.13, 75 (1973).
- 7) R.F.Goddu : *Anal. Chem.*, **29**, 1790 (1957).
- 8) Z.T.Ossefort, W.M.Veroven : *I&EC Product Research and Development*, **6**, 12 (1967).
- 9) D.O.Hummel: "Atlas der Kunststoff - Analyse", Band 1, 48 Carl Hanser Verlag (1968).