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Application News

Infrared Spectra of Polyvinyl Chloride

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User Benefits

- PVC can be qualitatively determined by checking specific peaks, and the presence of PVC can be confirmed even when the amount of additive is very large.
- Since PVC has few peaks in the fingerprint region, it is easy to qualitatively identify the additives contained in PVC.

■ Introduction

Polyvinyl chloride (PVC) is a synthetic thermoplastic polymer with excellent water resistance, acid resistance, alkali resistance, electrical nonconductivity, and flame resistance, and is used in a wide variety of applications, including film, synthetic leather, fibers, wire coating, rope, and toys, to name a few. Various types of additives such as plasticizers, stabilizers, and fillers can be added to this PVC resin, so that the final PVC product can be either rigid or soft, depending on the amount of plasticizer added. Various types of plasticizers, for example di-2-ethyl hexyl phthalate (dioctyl phthalate), have been added to PVC at concentrations higher than 10 % to produce soft PVC. Since PVC displays relatively weak infrared absorption, PVC that contains a large amount of phthalic ester is strongly affected by that substance, displaying an infrared spectrum which is more similar in shape to the phthalic ester than PVC. For this reason, many soft PVC samples have shown the similar type of infrared spectrum as the phthalic ester. However, due to concerns about the adverse health affects of these phthalic ester plasticizers, including their carcinogenicity, their application and content levels are regulated. Consequently, soft PVC containing various types of plasticizers instead of those containing phthalic esters are currently being marketed.

Since soft PVC containing a large amount of plasticizer displays an infrared spectrum that is greatly affected by the plasticizer, a variety of infrared spectral shapes are seen with soft PVC.

Here we introduce and discuss the infrared spectra of this type of soft PVC.

■ Infrared Spectra of Polyvinyl Chloride and Polyvinyl Chloride Containing Phthalic Ester

Fig. 1 and 2 show infrared spectra of PVC measured by the single-reflection ATR method, in which a diamond was used for the prism. The results of Fig. 1 were obtained from measurement of hard PVC which contained almost no plasticizer or other additives, while the results shown in Fig. 2 were obtained from measurement of soft PVC containing di-2-ethyl hexyl phthalate as the plasticizer. In addition, Fig. 3 shows the results of measurement of the infrared spectrum of di-2-ethyl hexyl phthalate using the same method. Comparing the infrared spectra of Fig. 1, 2, and 3, it is clear that the soft PVC measurement results are greatly different from the results of the hard PVC but are quite similar to the results obtained from measurement of di-2-ethyl hexyl phthalate. This is because the infrared spectrum of the phthalic ester is stronger than that of PVC. In the measurement results of the soft PVC, the peaks in the vicinities of 1425 cm^{-1}, 959 cm^{-1} and 610 cm^{-1} are peaks originating from the PVC, but when other additives such as calcium carbonate and silicate salt are also included as additives, the peaks near 1425 cm^{-1} and 959 cm^{-1} are overlapped and are therefore difficult to confirm. Therefore, in many infrared spectra of soft PVC, verification of PVC is accomplished using the C – Cl stretching vibration near 610 cm^{-1}.

However, depending on the detector and measurement method used, confirmation using the peak associated with the above C – Cl stretching vibration may not be possible due to the measurement wavenumber range being used. Even in that case, if the sample is soft PVC, it can be assumed to be such based on the similarity of the measurement results with that of phthalic ester. However, due to concern regarding the adverse health affects of some phthalic ester plasticizers, soft PVC containing plasticizers other than phthalic esters are appearing. An example of this is exemplified by the labeling of “Non-phthalic ester PVC” on toys and other articles.

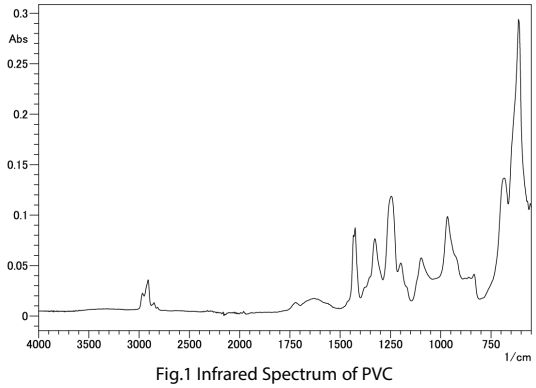

Fig.1 Infrared Spectrum of PVC

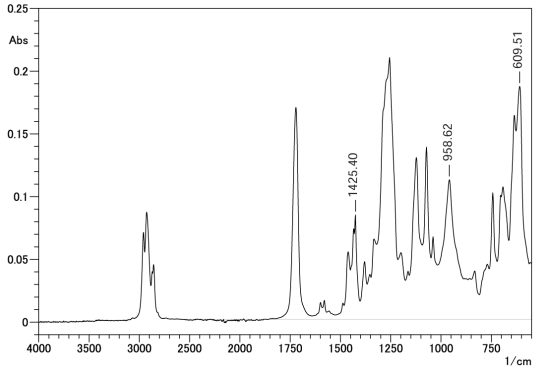

Fig.2 Infrared Spectrum of PVC Containing Di-2-Ethylhexyl Phthalate

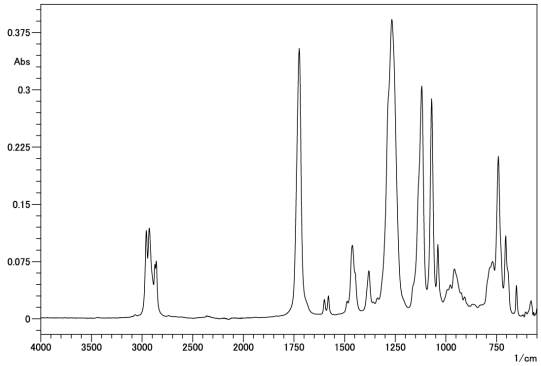

Fig.3 Infrared Spectrum of Di-2-Ethylhexyl Phthalate

■ Infrared Spectra of Polyvinyl Chloride Containing Plasticizers other than Phthalic Ester

Fig.4 shows infrared spectra of PVC products, such as toys, that contain plasticizers other than phthalic ester. Measurements were conducted by single reflection ATR using a diamond prism. The spectra of Fig. 4 are from soft PVC products containing as plasticizers, from the top spectrum downward, sulphonate phenyl ester, terephthalate ester, citrate ester, and adipate ester. The measurement results of Fig. 4 all show different spectral shapes, and further, it is clear that none of them are similar to the spectrum from hard PVC shown in Fig. 1. This is because the infrared absorption of these plasticizers is stronger than that of PVC, just as in the case of the phthalic ester. However, since the peak associated with the C – Cl stretching vibration near 610 cm^{-1} is visible in all of these spectra, PVC confirmation is possible. Thus, a variety of plasticizers other than the previously ubiquitous phthalic esters are now becoming prevalent, and accordingly, PVC products showing a great variety of infrared spectra are seen due to the differences in type and amounts used in the products. Therefore, the C – Cl stretching vibration near 610 cm^{-1} is important for the confirmation of PVC. The infrared spectra of the various PVCs shown in Fig. 4 are included in the standard library provided with the FTIR control software LabSolutions™ IR. Now, when this peak cannot be confirmed due to the measurement wavenumber range, analysis using the energy dispersive x-ray analysis instrument (EDX) introduced in Application News No. A406 "Analysis of Black Rubber Diaphragm by FTIR and EDX" is also effective.

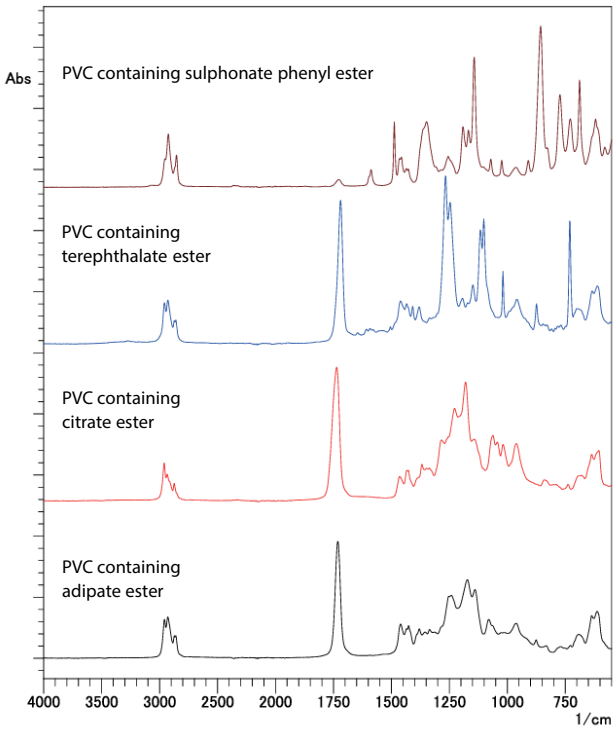

Fig.4 Infrared Spectra of Various PVC Products Containing Plasticizer

■ Conclusion

In this application, we analyzed PVC containing various plasticizers using the ATR method and demonstrated that the C-Cl stretching vibration near 610 cm^{-1} is important for identifying PVC. By checking the infrared spectrum using FTIR, it is possible to easily perform qualitative analysis of plasticizers used in soft PVC.

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QATR™-S Single - Reflection ATR Accessory

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This is a horizontal ATR with a single reflection. A prism with a diameter of 1.8 mm is placed horizontally, and the sample is pressed against the prism for measurement.
The prism is made of diamond and can measure spectra up to 400 cm^{-1} (broadband specification).
The clamp that holds the sample and prism in close contact has a built-in torque limiter, so there is no need to worry about damaging the prism by applying too much pressure.

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