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Application News

Spectrophotometric Analysis No.A413

Analysis of Black Rubber by FTIR and Thermogravimetry

In Application News No. A406, we introduced the analysis of a black rubber diaphragm by FTIR and EDX, and in Application News No. 304, we introduced the analysis of rubber by the single reflection ATR method using FTIR. ATR measurement is easy to conduct, and accordingly, it is used to analyze a variety of samples. In particular, this method is widely used for analysis of rubber-related samples. However, as touched upon in the above-mentioned Application News articles, carbon black is added to many rubber products as a reinforcing agent, and this carbon black has a large effect on measurement results.
Here we introduce an analysis of black rubber with added carbon black, focusing on the amount of carbon black that was added.

■ ATR Spectra of Black Rubber Measured with a ZnSe Prism

Various types of measurement accessories are commercially available for attenuated total reflection (ATR) measurement, and one of those that is widely used is the single reflection accessory, which facilitates qualitative analysis of small solid samples. Here, we conducted measurements using the MIRacle single reflection ATR accessory, with a 45˚ angle of incidence. The samples consisted of NBR (acrylonitrile butadiene rubber) containing different amounts of carbon black. The measurement results obtained using a ZnSe prism with a refractive index of 2.4 are shown in Fig. 1. The quantities of carbon black were 1, 10, 20, 30, 40 and 50 wt%, as indicated starting from the lower spectrum in Fig. 1.

NBR is a substance that displays a nitrile group-associated C≡N stretch in the vicinity of 2240 cm^{-1}, and a C=C-H bend due to the butadiene trans-vinylene group in the vicinity of 966 cm^{-1}. These peaks are clearly seen in the carbon black 1 wt% and 10 wt% spectra shown in Fig. 1.

However, as the amount of added carbon black increases, baseline rise and peak distortion are accordingly accentuated.

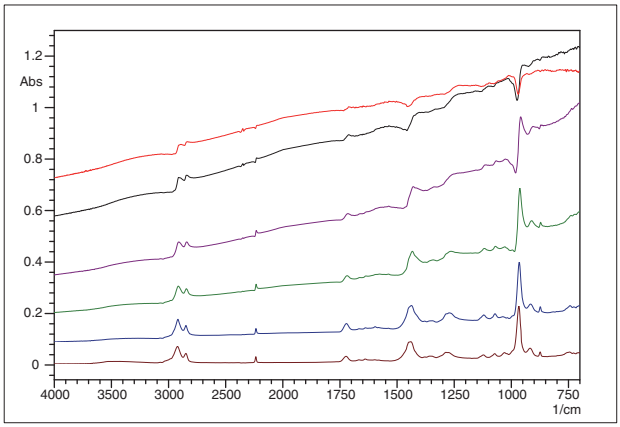

Fig.1 ATR Spectra of NBR Measured with a ZnSe Prism Carbon Black Content from Lower Spectrum: 1, 10, 20, 30, 40 and 50 wt%

Not only does carbon black display absorption throughout the entire infrared wavenumber region, it also has the effect of raising the refractive index of samples, so as the amount of added carbon black increases, there is a corresponding rise in the refractive index of the sample. As a result, as the total reflection condition cannot be met, and changes to the baseline and peak shape occur. In addition, when the carbon black content reaches 40 wt% and 50 wt% at the top of Fig. 1, the peak direction is reversed, so qualitative information is not easily obtained from these spectra.

■ ATR Spectra of Black Rubber Measured with a Ge Prism

Next, the same samples were measured using the MIRacle single reflection ATR accessory, this time with a Ge prism having a refractive index of 4.0. The measurement results are shown in Fig. 2. Using the Ge prism, the baseline rise and distorted peak shapes are seen similarly as in Fig. 1, but the degree is smaller, and the carbon black 50 wt% measurement result clearly shows the CaN stretch and the C=C-H bend.

Table 1 Analytical Conditions of FTIR

Analytical instrument	: IRAffinity-1, MIRacle (ZnSe prism and Ge prism)
Resolution	: 4 cm^{-1}
Accumulation	: 40
Apodization	: Happ-Genzel
Detector	: DLATGS

Fig. 3 plots the position of the peak corresponding to the C=C-H bend with respect to the amount of added carbon black in order to evaluate the change in peak shape (peak shift) due to carbon black. This plot shows the results of measurement of NBR samples containing carbon black at 24 different concentrations. It is clear from the results that there is a sudden peak position shift at a carbon black content of 30 wt% when the ZnSe prism is used. On the other hand, when the Ge prism is used, there is only about a 6 cm^{-1} shift between the 1 wt% and 50 wt% content values.

These results indicate that when conducting ATR measurement of NBR containing carbon black, there is a big change in the measurement result at a carbon black content boundary of about 30 wt% when a ZnSe prism having a 2.4 refractive index is used, while in the case of a Ge prism with a 4.0 refractive index, the measurement result remains about the same up to carbon black content of about 50 wt%.

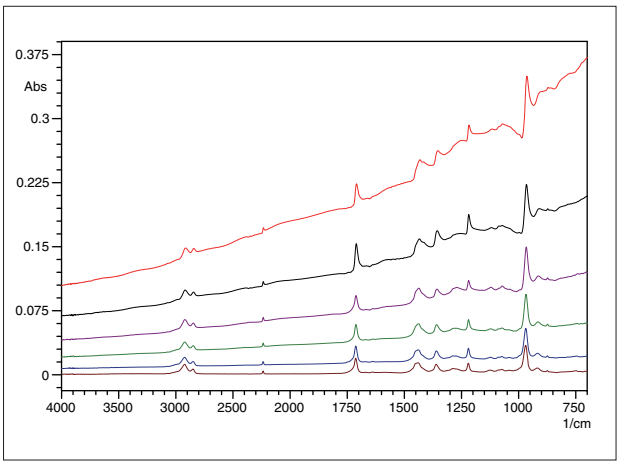

Fig.2 ATR Spectra of NBR Measured with a Ge Prism Carbon Black Content from Lower Spectrum: 1, 10, 20, 30, 40 and 50 wt%

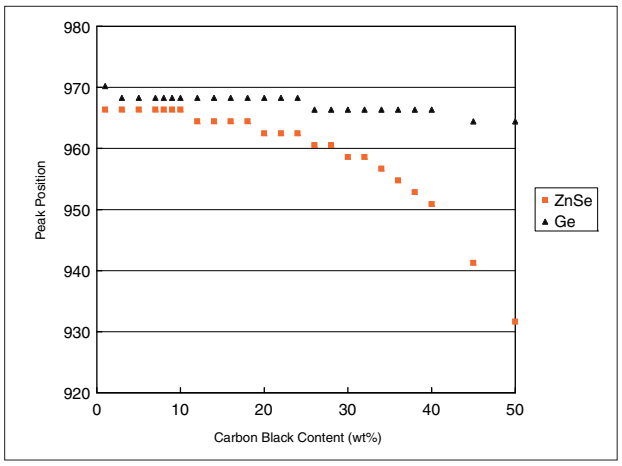

Fig.3 Relation Between the Peak Position of Trans-Vinylene and the Carbon Black Content

■ Determination of Carbon Black by Thermogravimetry

The results shown in Fig. 1 - 3 demonstrate that the ATR spectrum changes depending on the amount of added carbon black. Therefore, the amount of the carbon black in a sample can theoretically be determined from the change in its spectrum. However, not only does this method require that measurement be conducted beforehand on samples containing different levels of carbon black, considering the possibility that the difference in degree might also be attributed to the type of rubber, it would also be necessary to investigate the effects of other additives beforehand, thereby severely limiting the range in which this approach could be used.

Typical methods of measuring the amount of added carbon black in rubber include pyrolysis, chemical decomposition, and thermal analysis, and here we introduce the thermal analysis method, which features easy operation and requires almost no preparation.

In thermal analysis, the loss in weight due to combustion of the carbon black is obtained by TG (thermogravimetric measurement). Fig. 4 shows the results of measurement of NBR (carbon black content 40 wt%). The sample is first heated in a nitrogen environment to a temperature of 700 ˚C to decompose rubber components (organic substances) other than carbon black.

Then, the temperature is lowered to 400 ˚C while maintaining the nitrogen environment, at which time the environment is switched to air (oxygen), and reheating is conducted. As a result, a weight reduction due to combustion of the carbon black in air is observed, and the amount of added carbon black is determined from the rate of weight loss. From the rate of weight loss indicated in Fig. 4, the amount of carbon black in the measured sample is determined to be 38.9 %. This method is effective for quantitation of carbon black in many types of rubber and polymer materials

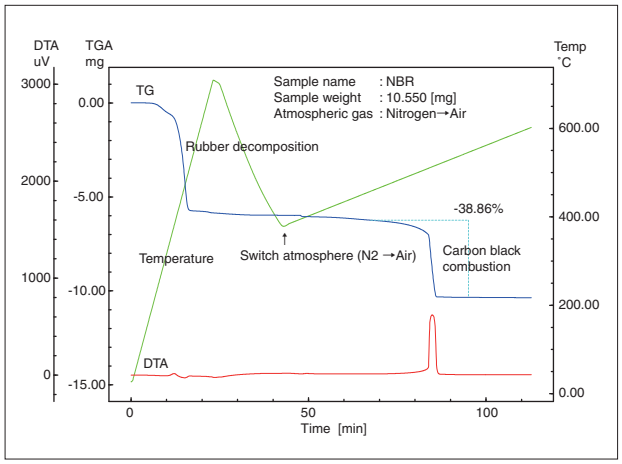

Fig.4 Quantitation of Carbon Black by Thermogravimetry

NOTES:
✻This Application News has been produced and edited using information that was available when the data was acquired for each article. This Application News is subject to revision without prior notice.

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Printed in Japan 3295-09905-10A-IK