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Application News

Spectrophotometric Analysis No.A416

Analysis of Rubbers by FTIR
-Method to Remove Calcium Carbonate in Rubbers-

Calcium carbonate, a white-colored powder with the chemical formula $CaCO_3$, is widely used in many applications which can be found all around us. For instance, one of its most obvious applications is its use as the principal ingredient of chalk. However, calcium carbonate is also widely used in rubbers and plastics, paper and tooth powder, etc. as a filling material.

When measuring the infrared spectrum of rubber that contains calcium carbonate, a large calcium peak masks peaks originating from some of the rubber constituents, which could cause difficulties in qualitative analysis. Here we introduce a pretreatment method for removing the calcium carbonate from rubber that contains calcium carbonate.

■ Calcium Carbonate

Table 1 shows some of the properties of calcium carbonate.

Table 1 Properties of Calcium Carbonate[1)]

Crystal structure	Hexagonal structure, trimetric structure
Density	2.72 g/cm^3 (hexagonal structure) 2.95 g/cm^3 (trimetric structure)
Solubility	0.00134 g/water 100g(0 ˚C)

Calcium carbonate is poorly soluble in water, but when dissolved in acid, CO_2 is evolved[1)]. It reacts as follows when hydrochloric acid is used as the acid.

$$CaCO_3+2HCl \rightarrow CaCl_2+H_2O+CO_2 \quad \text{(Equation 1)}$$

Fig. 1 DuraSamplIR Ⅱ

■ Measurement Method

The infrared spectrum was measured using a single reflection ATR accessory (DuraSamplIR II). A photograph of the DuraSamplIR II is shown in Fig. 1, and the analytical conditions are shown in Table 2.

Table 2 Analytical Conditions

Resolution	: 4 cm^{-1}
Accumulation	: 45
Detector	: DLATGS

■ Spectrum of Calcium Carbonate

Fig. 2 shows an infrared spectrum of calcium carbonate measured using the single reflection ATR technique.

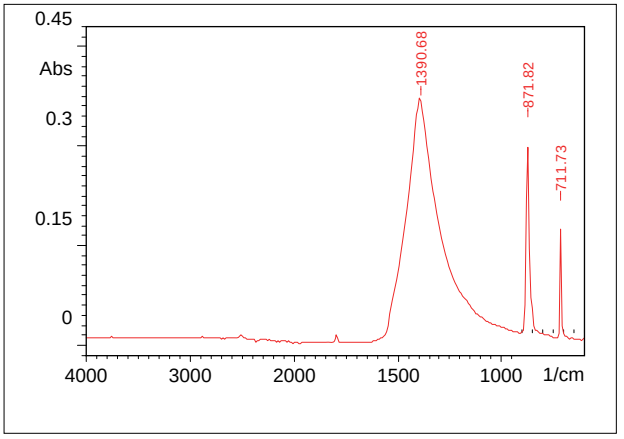

Fig. 2 Spectrum of Calcium Carbonate

Fig. 2 shows that there is broad absorption peak due to CO_3^{2-} in the region of 1390 cm^{-1}. In rubber that contains calcium carbonate, peaks originating from some of the rubber constituents are masked due to the calcium carbonate absorption, which might make it difficult to conduct qualitative analysis. In such scenario, removing the calcium carbonate peak will greatly facilitate qualitative analysis of the rubber components.

■ EPDM Rubber Containing $CaCO_3$

Here we used an ethylene-propylene-diene (EPDM) rubber sample containing calcium carbonate, talc, carboxylic acid ester, etc. The results, obtained using the single reflection ATR method, are shown in Fig. 3.

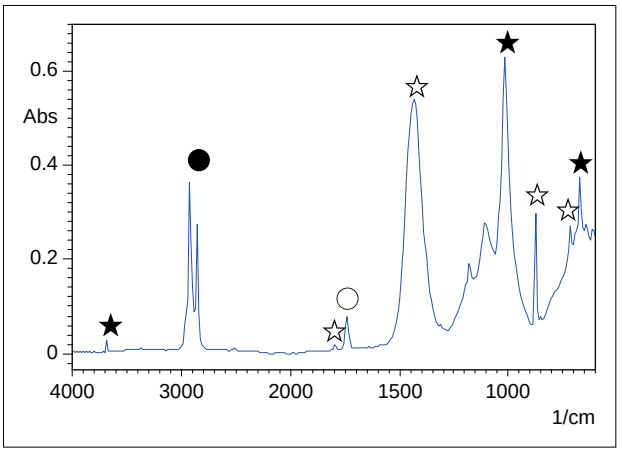

Fig.3 Spectrum of EPDM Containing Calcium Carbonate

The various symbols used in Fig. 3 indicate the peaks associated with calcium carbonate (☆), talc (★), carboxylic acid ester (○) and EPDM (●), respectively. EPDM, a synthetic rubber consisting of hydrocarbons, displays a peak in the region of 3000 – 2800 cm^{-1} attributed to a C-H bond stretch and a peak in the region of 1500 – 1300 cm^{-1} due to a C-H bend. However, no peak associated with the EPDM C-H bend is evident due to the broad absorption peak of calcium carbonate CO_3^{2-}.
In order to eliminate the CO_3^{2-} the sample was treated with hydrochloric acid for 10 minutes, after which the spectrum was measured again. The corresponding spectrum is shown in Fig. 4 (Note: Be careful to thoroughly rinse off all hydrochloric acid from the rubber sample following the hydrochloric acid treatment).

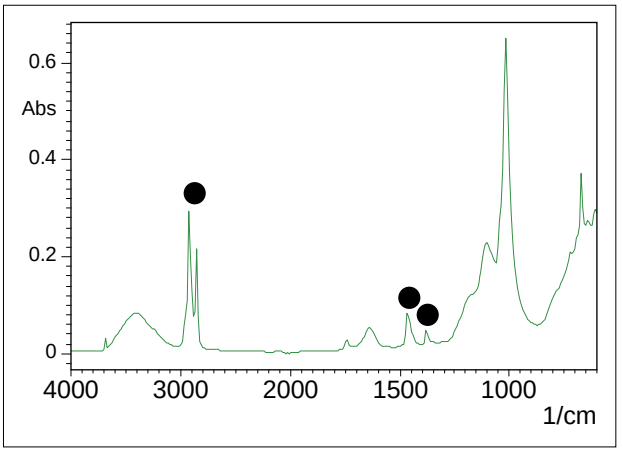

Fig. 4 Spectrum of EPDM After Reaction of Calcium Carbonate with Hydrochloric Acid

In Fig. 4, it is seen that the peaks associated with calcium carbonate have disappeared following reaction with the hydrochloric acid, and the peaks due to the C-H bend of EPDM are clearly seen in the vicinities of 1460 cm^{-1} and 1380 cm^{-1}. This is due to the conversion of calcium carbonate into calcium chloride according to the chemical reaction of Equation 1, above.
On the other hand, in Fig. 4 additional peaks are observed around 3400 cm^{-1} and 1650 cm^{-1}. These peaks were assumed to be due to water remaining as a result of incomplete drying of the rinsed sample following the hydrochloric acid reaction. To verify this, we dried the post-processed sample, and conducted the measurements at various stages of drying. The obtained spectra are shown in Fig. 5. The spectra were measured at 1, 5 and 10 minutes into the drying process.

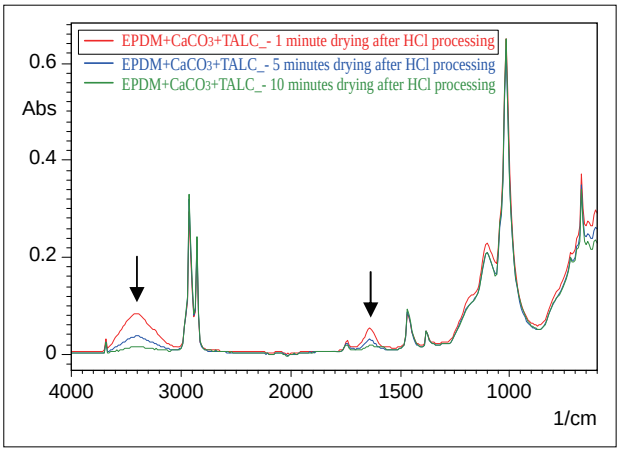

Fig.5 Spectra of EPDM after Drying

From Fig. 5, it is clear that the water-associated peaks seen in Fig. 4 gradually disappeared during the drying process.

Thus, calcium carbonate peaks can be eliminated from the infrared spectrum of rubber samples pre-treated with hydrochloric acid. However, since strong acid is used in this pretreatment procedure, due care must be exercised.

References

1) Physics and Chemistry Dictionary, Iwanami Shoten, Publishers

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