1 Introduction

Quite many organic polymers are being used in a variety of fields in our lives, thanks to their good abilities of electrical insulation, ease of molding, and other properties [1–3]. However, if organic polymers are used under a harsh environment or they are processed at high temperatures for a long time, degradation resulting from oxidation would occur [4, 5]. In many cases, antioxidants are added to polymeric insulating materials to suppress such oxidative degradation [6–10]. Here, a problem for users of polymeric insulation is that the details of antioxidant added to the polymer are seldom disclosed.

In recent years, terahertz (THz) waves, which are electromagnetic waves in a frequency range from 0.1 to 10 THz (333–333 cm$^{-1}$), have attracted much attention in many fields of research or industrial applications. THz waves are a part of far-infrared (FIR) waves, and they were a research tool or target of researchers in basic sciences even on early days such as the 1960s [11]. Since the generation and detection of THz waves has recently become much easier with the advent of related technologies, various applications of THz waves, for example, THz absorption spectroscopy have become industrially possible. Various pieces of valuable information on macroscopic molecular structures in inorganic and organic substances, such as lattice vibrations, intermolecular interactions, and skeletal oscillations, can be obtained by analysing THz absorption spectra [12–23].

However, this relatively new THz absorption spectroscopy has not yet been widely used compared to Fourier-transform mid-infrared absorption spectroscopy, although several challenging and advanced trials to use quantum chemical calculations for analysing THz absorption spectra have recently been conducted [24, 25].

As an instrumental analysis tool that typically uses frequencies from 3.0 to 18.0 THz (100–600 cm$^{-1}$), intermediate between the THz and the MIR frequency ranges, Fourier-transform far-infrared (FT-FIR) absorption spectroscopy can mainly provide useful information on skeletal vibrations [21, 23, 25, 26].

For antioxidants, spectroscopic analyses have not been performed so often in the THz and FIR frequency ranges, although several quantum chemical calculations have been conducted [27–29]. From such a background, we reported THz absorption spectra for low-density polyethylene (LDPE) sheets containing nine kinds of antioxidants in our previous paper [27]. Furthermore, we measured absorption spectra of three kinds of phenol-type antioxidants added in LDPE sheets in a broadband FIR range, including both ordinary FIR and THz frequencies [30], and tried to quantify their contents by partial least-squares (PLS) regression, a kind of chemometric multivariate analysis [31]. In this paper, we report similar broadband FIR absorption spectra measured for LDPE sheets containing the remaining six kinds of antioxidants and conduct PLS regression analyses.

2 Experimental method

2.1 Acquisition of absorption spectra

Six kinds of antioxidants, details and chemical structures of which are shown in Table 1 and Fig. 1, respectively, were used in this research. Many antioxidants possess very complicated chemical names. Therefore, their trade names or abbreviations are usually used.

Each antioxidant was added to the powder of LDPE up to contents of 0.1, 1.0, 5.0, and 10.0 wt%. After the powder with antioxidant was mixed as uniformly as possible, it was extruded at 200°C to the shape of a long tube with a diameter of ∼15 mm using a 15-mm twin-screw extruder. Then, the tube was cut into pellets. The pellets were pressed at 190°C for 5 min to the form of a sheet with a thickness of ∼1.9 mm by a hydraulic heating press (Daishin Machine). Similar sheets of LDPE, but with no additives, were also obtained.

Absorption spectra of these sheets were measured in a broadband FIR range from 0.5 to 18.0 THz (16.7–600 cm$^{-1}$) in a transmission mode using a THz time-domain spectrometer (THz-TDS, TAS7500TS, Advantest) and an FT-FIR absorption spectrometer (VIR-F, JASCO). The TAS7500TS spectrometer can measure the time-resolved changes in the intensity and phase of electric fields, transmitted through or reflected from a sample, in a frequency range from 0.5 to 5.0 THz (16.7–167 cm$^{-1}$). The method to obtain frequency-domain absorption spectra from time-domain spectra is basically the Fourier transform, of which the details are...
Several methods have been proposed for analysing many spectra. Among them, multiple regression, principal component regression (PCR), and PLS regression have been widely adopted in chemometrics [31–40].

2.2 Analysis of absorption spectra

Several methods have been proposed for analysing many spectra statistically. Among them, multiple regression, principal component regression (PCR), and PLS regression have been widely adopted in chemometrics [31–40].

The principle of PLS regression is schematically illustrated in Fig. 2 [32–34]. Here, we assume that we measured optical absorption at two wavelengths $\lambda_1$ and $\lambda_2$ for four samples that contain a certain impurity or additive with known contents. The four open circles in Fig. 2 represent the absorbance measured in the four samples. Here, $i$ in $x_i$ represents the sample number, while $j$ represents the wavelength. Namely, for sample 1, its absorbance values measured at the wavelengths $\lambda_1$ and $\lambda_2$ are represented as $x_{11}$ and $x_{12}$, respectively. The point $(x_{11}, x_{12})$ is plotted as shown in Fig. 2 by taking the absorbance at $\lambda_1$ on the $x_1$ axis and that at $\lambda_2$ on the $x_2$ axis. The value of $x_{ij}$ is called an explanatory variable. We have a total of eight explanatory variables in Fig. 2. On the other hand, the additive contents are objective variables. Here, we shift the average of the four open circles to the origin of the coordinates. Then, the four circles are moved to the positions shown by the four solid black circles. Now, we can draw the dashed red line by the least-squares approximation. This dashed line will be treated as a new coordinate axis $a$. In PLS regression, the axis $a$ is called a loading vector, and the projection of each black circle to the loading vector is score $t$. Since each score $t$ contains the information on the absorbance values of each sample at the two wavelengths, the loading vector $a$ can be used for further analysis.

In this study, the PLS regression method for a single-objective variable, PLS1 regression, was adopted using a software package (Origin® 2018b, LightStone). Here, the explanatory variables are all the absorption coefficients ($x_i$) measured with a resolution of 7.6 GHz in the case of the THz measurements and those measured with a resolution of 2 cm$^{-1}$ (60 GHz) in the case of the FT-FIR measurements, while the objective variables are the contents of antioxidant. Note that the THz or FIR spectrum measured in the sample with no antioxidant was not subtracted from the spectra of the samples with antioxidants for the chemometric approach, although such subtraction was made in the simple comparison of absorption intensities, which will be mentioned later in relation to Figs. 3 and 4.

3 Results

Figs. 5 and 6 show the absorption spectra in both the THz and the FIR ranges, respectively, measured for the sample sheets containing six kinds of antioxidants. The spectra are shown in the form of an absorption coefficient ($a$) in cm$^{-1}$. In both figures, (a) to (f) show the spectra of Nocrac 300, Nocrac NBC, DSTP, Nocrac DP, Nocrac 224, and Irgafos 168, respectively. The black solid line in each figure represents the spectrum observed in LDPE with no antioxidant, and it is the same in (a)–(f).

A tiny absorption peak, seen at $\sim$2 THz in Fig. 5, is known to be due to translational lattice vibrations of methylene groups [41]. Furthermore, the broad absorption seen in Fig. 6 at $\sim$550 cm$^{-1}$ in the sample with no antioxidant is due to amorphous parts in LDPE [42]. For quantifying the antioxidant contents by comparing the absorption intensities of the corresponding samples, the difference

### Table 1 Antioxidants used in this research

| Name       | Chemical name               | Category     | Chemical formula (molecular weight) | Density, g cm$^{-3}$ |
|------------|-----------------------------|--------------|-------------------------------------|---------------------|
| Nocrac 300 | 4,4′-thiobis(6-tert-butyl-m-cresol) | phenol, sulfur | C$_{22}$H$_{35}$O$_2$S (358)        | 1.06–1.12           |
| Nocrac NBC | nickel dibutyl-dithiocarbamate | amine        | C$_{18}$H$_{35}$N$_2$S$_4$ (467)   | 1.26                |
| DSTP       | diestyryl 3,3′'-thiodipropionate | amine      | C$_{42}$H$_{82}$O$_4$S (683)    | 1.03                |
| Nocrac DP  | N,N-di phenyl-p-phenylenediamine | amine  | C$_{18}$H$_{36}$N$_2$ (260)        | 1.20                |
| Irgafos 168| trioctyl di tert-butylphenylphosphate | phosphate | C$_{42}$H$_{90}$O$_3$P (646) | 1.02                |
in the absorption coefficient (Δα) was calculated by subtracting α of the sheet containing no antioxidants from α of the sheet containing each antioxidant. Figs. 3 and 4 show the spectra of Δαs in the THz and FIR frequency ranges, respectively, obtained for the sheets containing six kinds of antioxidants.

### 4 Discussion

It is indicated in Fig. 5 that α increases monotonically in the whole range from 0.5 to 5.0 THz in accordance with the increase in antioxidant content for all the six antioxidants. A similar increasing tendency is also seen in the whole FIR range from 100 to 600 cm⁻¹ in Fig. 6. In the absorption spectra, as shown in Fig. 6, it is obvious that several absorption peaks or bands due to the presence of antioxidant appear in the FIR range even in the samples containing 0.1 or 1.0 wt% of antioxidant. On the other hand, it is difficult in Fig. 5 to recognise the absorption specific to the antioxidant in the THz range when the content is as low as 1.0 wt% or less.

In Figs. 5b or 3b, the absorption at ∼2.2 THz increases in Nocrac NBC with the increase in its content. As mentioned above, a lattice mode of methylene groups is assigned to this absorption. Although Nocrac NBC does have methylene groups as shown in Fig. 1b, there seems no reason for the increase in the number of methylene groups in this antioxidant in a way that exceeds the increasing ratio of the antioxidant content. Regarding this, the reason for such a significant increase in absorption intensity is

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Fig. 3 Differences in the absorption coefficient from the pristine LDPE in the frequency range from 0.5 to 5.0 THz, measured for the samples containing six kinds of antioxidants with four different contents: 0.1, 1.0, 5.0, 10 wt% (a) Nocrac 300, (b) Nocrac NBC, (c) DSTP, (d) Nocrac DP, (e) Nocrac 224, (f) Irgafos 168

Fig. 4 Differences in the absorption coefficient from the pristine LDPE in the frequency range from 100 to 600 cm⁻¹, measured for the samples containing six kinds of antioxidants with four different contents: 0.1, 1.0, 5.0, 10 wt% (a) Nocrac 300, (b) Nocrac NBC, (c) DSTP, (d) Nocrac DP, (e) Nocrac 224, (f) Irgafos 168
unknown. As a possible reason, the quantum efficiency or the absorption intensity that is induced by a chain of methylene groups would be different in the two cases where the chain is short as in Nocrac NBC and long as in LDPE. It has been reported that a similar absorption peak at 2.2 THz is present in paraffins and that its intensity grows with the chain length [43].

In order to compare the absorption intensities among the six antioxidants, the $\Delta \alpha$ spectra in the THz range obtained for the samples containing the antioxidant with the content of 10 wt% are shown in Fig. 7a, while those obtained for the samples with the antioxidant content of 1.0 wt% are shown in Fig. 7b for the FIR range. To increase the visibility, the right ordinate is for DSTP in Fig. 7b, while the left one is for the others.

In Fig. 7b, several absorption peaks or bands that seem to originate in antioxidants are seen in the FIR range. For example, the absorption at 380 cm$^{-1}$ that appears in Nocrac NBC and DSTP is due to the in-plane bending vibrations of CCC, while the one at 575 cm$^{-1}$ appearing in Nocrac 300 and Irgafos 168 is attributable to the out-of-plane bending vibration of CC rings. However, in this FIR range, different antioxidants often exhibit their absorption at the same or similar wave numbers. Namely, the FIR spectroscopy is not simply superior to the THz spectroscopy as to the identification of antioxidants.

On the other hand, the absorption specific to each antioxidant appears in the THz range as shown in Fig. 7a, although this is the case only in the spectra of the high-content samples. For example,
an absorption peak appears ~1.6 THz in both Nocrac NBC and Nocrac DP, but only Nocrac NBC shows its specific absorption peak ~2.2 THz. These results indicate that the identification of antioxidants can be made possible by the THz spectroscopy in the case where it is difficult by the FIR spectroscopy. However, as mentioned above, regarding the spectra shown in Figs. 5 and 3, the identification and quantification are not easy by a simple comparison of the spectral shapes and heights, especially for the practically important antioxidant content of 1.0 wt% or less.

As a summary of the aforementioned results, it is difficult to identify and quantify the antioxidant by the simple observation of the spectra in both the THz and the FIR ranges. As a possible solution to this issue, we analysed the spectra by the PLS1 regression. Here, for both the THz-TDS and the FT-FIR ranges, the spectra of α shown in Figs. 5 and 6, namely the spectra without doing the subtraction of the LDPE spectrum, were analysed. The results are shown in Fig. 8. Here, using the values listed in Table 1 and 0.92 g cm$^{-3}$ as the densities of six antioxidants and LDPE, respectively, the unit of antioxidant content was converted to kg m$^{-3}$ from wt% for all the abscissae in Fig. 8. The density of 1.09 g cm$^{-3}$, which is the average of the values listed in Table 1, is used for Nocrac 300. In addition, the vertical axis is the antioxidant content estimated by the PLS1 regression.

We showed that the PLS1 regression gives good estimation for the contents of three phenol-type antioxidants in our preceding research [31]. Therefore, for all the nine kinds of antioxidants that are available for us, it is clearly shown that the antioxidant can be identified and its content can be estimated quite accurately by analysing THz and FIR spectra using chemometrics, without obtaining the spectra of the difference in absorbance (Δα).

Furthermore, as mentioned above, the PLS1 regression uses the entire spectra, not limited to few peaks and their vicinities. Therefore, its accuracy should be very high. Rather, the most

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**Fig. 7** Differences in absorption coefficient from the pristine LDPE measured for the samples containing six kinds of antioxidants. (a) 0.5–5.0 THz for the 10 wt% samples, (b) 100–600 cm$^{-1}$ for the 1.0 wt% samples: Nocrac 300, Nocrac NBC, DSTP, Nocrac DP, Nocrac 224, Irgafos 168. In (b), the right ordinate is for DSTP, while the left one is for the others

(a) THz range, (b) FIR range

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**Fig. 8** Comparisons of the antioxidant contents added experimentally and estimated by the PLS1 regression in the THz range (—) and the FIR range (---).

Note that the blue symbols and the blue lines for the FIR range are intentionally shifted vertically by 20 kg m$^{-3}$

(a) Nocrac 300, (b) Nocrac NBC, (c) DSTP, (d) Nocrac DP, (e) Nocrac 224, (f) Irgafos 168

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doubtful point in this study should be the difference in antioxidant content between the value actually present in each sample and the one we think we added. In addition, the samples used in this research are relatively thick (~1.9 mm). Because of this, the absorption could be beyond the dynamic range of the spectrometers at certain wave numbers, especially in Figs. 6d and e for the samples of 10 wt%. On the other hand, several peaks found at lower concentrations would not be resolved well. Taking account of these points, the relatively low values of $R^2$ such as 0.982 and 0.973 shown in Fig. 8 do not necessarily mean the low reliability of estimation. This in turn indicates the robustness of chemometrics.

5 Conclusion
Absorption spectroscopic measurements were conducted in both THz and FIR frequency ranges for LDPE sheets containing six kinds of antioxidants with various contents from 0 to 10 wt%. The following important findings have been obtained:

(i) There are several absorption peaks or bands that increase monotonically in both THz and FIR frequency ranges. Therefore, we can identify the six antioxidants by paying attention to the spectra of the difference in the absorption coefficient from the pristine LDPE.

(ii) When two or more antioxidants have similar structures, their FTR spectra are often similar. In such cases, if THz spectroscopy gives different spectra, we can identify them. We have confirmed this for Norac NBC and DSTP.

(iii) The identification and quantification of antioxidant can be done more accurately by analysing the THz and FTR spectra using the PLS regression.

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7 References
[1] Zhang, D.L., Zha, J.W., Li, C.Q., et al.: ‘High thermal conductivity and excellent electrical insulation performance in double-percolated three-phase polymer nanocomposites’, Compos. Sci. Technol., 2017, 144, (26), pp. 36–42.
[2] Andrichsch, T., Vaughan, A., Stevens, G.C.: ‘Novel insulation materials for high voltage cable systems’, IEEE Electr. Insul. Mag., 2017, 33, (4), pp. 27–35.
[3] Huang, X., Fan, Y., Zhang, J., et al.: ‘Polypropylene based thermoplastic polymers for potential recyclable HVDC cable insulation applications’, IEEE Trans. Dielectr. Electr. Insul., 2017, 24, (3), pp. 1446–1456.
[4] Balasooriya, W., Schrittesser, B., Pinter, G., et al.: ‘Induced material degradation of elastomers in harsh environments’, Polym. Test., 2018, 69, pp. 107–115.
[5] Johnson, L.M., Ledet, E., Huffman, N.D., et al.: ‘Controlled degradation of disulphide-based epoxy thermostets for extreme environments’, Polymer, 2015, 64, (1), pp. 84–92.
[6] Wang, X., Wang, B., Song, L., et al.: ‘Antioxidant behavior of a novel sulfur-bearing hindered phenolic antioxidant with a high molecular weight in polypropylene’, Polym. Degrad. Stab., 2013, 98, (9), pp. 1945–1951.
[7] Zhang, X., Yang, Y.H., Song, Y., et al.: ‘Influence of binary combined systems of antioxidants on the stabilization of peroxide-cured low-density polyethylene’, J. Appl. Polym. Sci., 2012, 126, (6), pp. 1885–1894.
[8] Bollbukh, Y., Kuzema, P., Tertykh, V., et al.: ‘Thermal degradation of polyethylene containing antioxidant and hydrophilic/hydrophobic silica’, J. Therm. Anal. Calorim., 2008, 94, (3), pp. 727–736.
[9] Liu, S., Veseys, S.W., Fifield, L.S., et al.: ‘Quantitative analysis of changes in antioxidant in crosslinked polyethylene (XLPE) cable insulation material exposed to heat and gamma radiation’, Polym. Degrad. Stab., 2018, 156, pp. 252–258.
[10] Seguchi, T., Tamura, K., Kudoh, H., et al.: ‘Degradation of cable insulation material by accelerated thermal radiation combined ageing’, IEEE Trans. Dielectr. Electr. Insul., 2015, 22, (6), pp. 1397–1406.
[11] Itoh, K., Nakahara, T., Oya, M., et al.: ‘Far-infrared spectra of polylalaines with α-helical and β-sheet structures’, Biopolym., 1968, 6, (12), pp. 1759–1766.
[12] Azeaynagi, C., Kaneko, T., Ohki, Y.: ‘Terahertz spectroscopic analysis of crystal growth in polymers’, Jpn. J. Appl. Phys., 2018, 57, (5), pp. 053002–053004.
[13] Azeaynagi, C., Ohki, Y.: ‘Terahertz spectroscopic estimation of crystallinity of polystyrene sulfide’, J. Appl. Polym. Sci., 2018, 135, (27), pp. 46427–464210.