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Quantitative Analysis of Functional Groups in HDPE Powder by DRIFT Spectroscopy

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Summary: FT-IR spectra of ethylene homopolymers and ethylene/1-hexene copolymers polymerized under different conditions were studied by transmission and diffuse reflection (DRIFT) spectroscopy. The absorbance spectra of film samples were compared with the DRIFT spectra of powders ground from the films. For determining the concentration of the methyl and unsaturated (vinyl, vinylidene and *trans*-vinylene) groups of polyethylene powders the DRIFT spectra were calibrated by comparing the IR intensities of the corresponding bands measured by the two methods. The results proved that the effect of differences in scattering of the polymer powder originating from the irregularity of the top surface, as well as the size and shape of the particles can be eliminated by the use of a proper internal standard. Linear correlation was established between the logarithms of the normalized intensities measured in absorbance and Kubelka-Munk units. In the case of polyethylene the selection of the internal reference band affects significantly the accuracy of the calibration due to the difference in the refractive indices of the crystalline and amorphous phases.

Keywords: diffuse reflection; DRIFT; FT-IR; polyethylene; transmission

Introduction

During the processing of polyethylene (PE) chemical reactions take place as an effect of heat, shear and oxygen resulting in some changes of the structure and the properties of the polymer. It was established that all the changes in the various characteristics of the polymer are related to each other.[1,2] A systematic study of the effects of multiple extrusion revealed that the mechanism of the chemical reactions taking place in the first extrusion of PE differs from that in the subsequent processing steps.[3] The chemical structure of the polymer was analyzed by

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Fourier Transform Infrared (FT-IR) Spectroscopy. For the determination of the number of the functional groups (methyl and unsaturated) in the nascent polymer powder Diffuse Reflection FT-IR (DRIFT) Spectroscopy was introduced. Initially the DRIFT spectra were evaluated by the method used for the absorbance spectra. The results were handled with care, as the necessity of calibration of the DRIFT spectra was obvious, because of the essential differences between the Kubelka-Munk theory applied to describe diffuse reflection and the Beer's law used in transmission spectroscopy.

According to the Kubelka-Munk theory the reflection characteristics are related to the ratio of the absorption to scattering coefficients:[4,5]

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{K}{S} = \frac{2.303\varepsilon C}{S} \qquad (1)$$

where R_∞ is the reflectance from a specimen of "infinite" thickness, i.e. a specimen sufficiently thick so that a further increase of the thickness does not change the reflectance; K is the absorption coefficient (twice the Beer's law absorption coefficient); S is the scattering coefficient of the sample; ε is the absorptivity; and C is the analyte concentration. Experiments showed that for finely ground powders 2 mm deep sample cups fulfil practically the criteria of infinite sample thickness.[6]

The scattering coefficient depends on particle size, shape, refractive index, and wavelength. If S is constant, then $F(R_\infty)$ (Kubelka-Munk units) should change linearly with concentration. Such situation is rarely achieved, but with a careful choice of the experimental conditions and calibration, DRIFT can give quantitative information over a limited range.[4]

The effects of sampling technique and measuring conditions on the reliability of quantitative analysis by DRIFT spectroscopy were studied on inorganic materials. It was established that the packing of the powder and the morphology of the top surface of the sample are two important parameters affecting the reproducibility of the diffuse reflectance measurement.[7] The optical or geometrical irregularities at the surface affect the overall reflectance and transmittance more than an identical perturbation in the bulk or at the bottom of the sample. For the quantitative analysis Boroumand et al.[7] suggested the normalization of the DRIFT spectra by using a reference, and emphasized the importance of the choice of this reference. Studying the IR spectra of quartz and calcite in spectroscopic grade KBr Krivácsy and Hlavay[6,8] showed that the relative standard deviation (RSD) in the DRIFT measurements is high, and depends on the intensities. The smaller the Kubelka-Munk values are the greater the RSD is. The reliability of the quantitative analysis can be improved by using the same reference for the calibration standards and the investigated samples. They found that the same level of reliability as in conventional pressed pellet transmission technique can be achieved by multiple calibration followed by reference reflectance correction.[9]

In macromolecular science the DRIFT technique was applied successfully to study the chemical modification of fibers cut into small pieces. Gulyás et al.[10] investigated carbon fibers subjected to electrochemical oxidation under a wide variety of conditions. Correlation was established between the concentration of certain functional groups on the surface identified by DRIFT and the strength of adhesion between the fiber and an epoxy matrix. Takács et al.[11-13] studied the changes in the chemical structure caused by alkali treatment and irradiation of cotton-cellulose fibers by DRIFT spectroscopy. They used internal standards for normalization of the characteristic bands. The results obtained from the DRIFT analysis correlate well with those of X-ray measurements.

The literature on the quantitative analysis of polyethylene (PE) powder by IR spectroscopy is extremely limited. Earlier Baker at al.[14] studied the chain branching of PE powder by using potassium bromide disc technique. They had to overcome several difficulties - like particles larger than 100 μm led to poor quality discs and inferior results - before obtaining results with a precision of 5-10 % and an accuracy of about 15 %. The DRIFT technique provides a relatively simple sampling method, even if several considerations have to be taken into account in the evaluation of the spectra. Hrebičík et al.[15] investigated the time dependent chemical changes of an ultra high molecular weight polyethylene (UHMWPE) besides rice and oats irradiated by gamma radiation. They used the DRIFT technique and discussed the changes observed in the carbonyl stretching region. The repeatability of the spectra caused the critical problem for them. The change of the carbonyl absorption of UHMWPE was followed by relating the log(1/R) value at 1739 to that at 1717 cm^{-1}, but no attempt was made for the complete quantitative evaluation of the spectra.

The aim of the present work was the development of a method for the quantitative analysis of the methyl and the unsaturated groups of polyethylene powder by DRIFT technique. An assortment of polyethylenes prepared by different catalysts under varying conditions was investigated. The samples were compression molded to films followed by grinding to powder. The DRIFT spectra were calibrated by comparing the intensities of the corresponding bands of the functional groups of the polymer determined from transmission and diffuse reflection spectra of the same material. In the quantitative evaluation of the DRIFT spectra the following considerations were taken into account:

1. The size of the primary powder particles (300 μm-1 mm) and the samples ground for the experiments is much larger than the wavelength of the analytic IR light (2.5-25 μm), therefore little or no wavelength dependence of scattering can be assumed.[16]
2. The light scattering coefficient is affected by the difference in refractive indices of the crystalline and the amorphous phases of the polymer.
3. As the size and shape of the powder particles investigated vary, the regularity and reproducibility of the macroscopic surface layer cannot be ensured.
4. The selection of an adequate reference band for normalization must be crucial in the calibration due to the conditions described.

Experimental

Materials

30 ethylene homopolymers and ethylene/1-hexene copolymers were investigated with different concentrations of methyl and unsaturated groups. Phillips, Ziegler-Natta and metallocene catalysts were used for the polymerization. The molecular weight and the concentration of the functional groups varied in wide ranges. The number of the methyl groups changed from 0.8 to 14 per 1000 carbon atoms, the vinyl content from 0.03 to 1.9, the vinylidene from 0.01 to 0.23, and the *trans*-vinylene from 0 to 0.1. For checking the reliability of the measuring technique and calculations one of the samples was investigated twice at different times (two independent sets of experiments).

Preparation of Samples

Films of 200-300 μm were compression molded from the different polymer powders and granules at 180 °C. Samples with a diameter of 22 mm were cut for transmission measurements. For the diffuse reflection measurements the films were cooled by liquid nitrogen then ground to powder. The powder was not sieved, and no further sample preparation was applied.

In separate sets of experiments the effect of particle size on the DRIFT spectra was investigated by using nascent PE powder samples taken from the polymerization reactor. Before the measurement the polymer powder was sieved into 4 fractions: >1 mm, 1 mm-800 μm, 800-500 μm and <500 μm. It was concluded that the effect of differences in the intensities originating from variations in particle size and packing can be eliminated by normalization with an appropriate internal reference band. It has to be noted that some spectral artifacts can be observed in the case of relatively large particles due to Fresnel reflection.[5] Therefore smaller particles are favorable. However, the quality of the spectrum of larger particles can also be improved by careful rearrangement of the sample in the holder.

Methods

Mattson Galaxy 3020 (*Unicam*) type FT-IR spectrophotometer equipped with a DTGS detector and controlled by the Enhanced FIRST™ FTIR software was used for the experiments. The spectra were measured in the range of 4000-400 cm^{-1} at a resolution of 2 cm^{-1}. In transmission mode 16 scans were accumulated. The DRIFT measurements were carried out with a Baseline Diffuse Reflectance Accessory (*Spectra-Tech*) using 128 scans. Some model experiments revealed that higher number of scans does not improve essentially the signal/noise ratio of the spectra.

For the diffuse reflection measurements the powder was placed into the sample holder then packed loosely by pressing with a flat object. Five parallel measurements were carried out in the case of both techniques. The averages of the peak and integrated intensity values were determined from the transmission and DRIFT spectra.

Results and Discussion

The intensity of the bands in the infrared spectra of polyethylene is strongly affected by the method of investigation, as it can be seen from Figure 1 where the transmission and reflection spectra of the same Phillips type PE are compared. The ratio of the crystalline to amorphous band intensities is much higher in the DRIFT spectrum than in the absorbance spectrum (e.g. CH_2 rocking bands at 730 and 720 cm^{-1}). This indicates that the selection of the reference band for normalization plays a very important role in the quantitative evaluation of the spectra.

Selection of the Reference Band

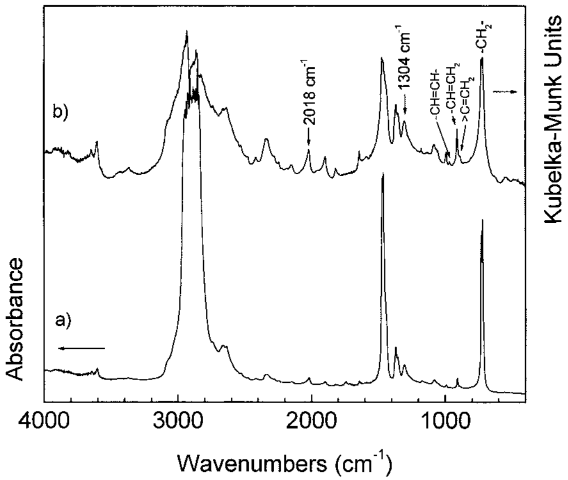

Fig. 1. FT-IR spectra of Phillips type ethylene/1-hexene copolymer measured in transmission (a) and diffuse reflection mode (b)

Two vibrational bands were selected for reference. The band at 2018 cm-1 is a combined overtone band, which originates from both the crystalline and the amorphous phases.[17] The band at 1304 cm^{-1} corresponds to the CH_2 wagging mode vibration in the disordered phase of

PE.[17-19] The ratio of the intensity at 2018 cm^{-1} (A_{2018}) to that at 1304 cm^{-1} (A_{1304}) is essentially larger in the DRIFT spectrum than in the transmission spectrum (Figure 1).

Correlation was established between the thickness of the film samples and the intensities of the selected reference bands measured in transmittance mode. Table 1 contains the calibration constants calculated by Equation (2) for both reference bands, and Figure 2 shows the relationship between A_{2018} and the film thickness.

$$A_{ref} = B \cdot l \qquad (2)$$

where A_{ref} is the absorbance of the reference band, l is the sample thickness measured (cm), and B is the proportionality factor.

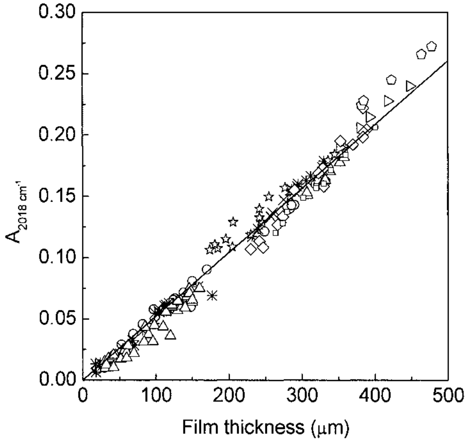

Fig. 2. Relationship between sample thickness and absorbance at 2018 cm^{-1} of different polyethylene types.

Table 1 reveals that the correlation of the film thickness with A_{2018} is closer than with A_{1304}. The reason is that the density of the polymer is affected by both the crystalline and disordered phases. However, the correlation coefficient for the amorphous band at 1304 cm^{-1} is also acceptable (>0.967).

Table 1. Calibration constants calculated for the correlation between the thickness of PE film and the FT-IR absorption intensities of two bands according to Equation (2).

Reference Band	B		Correlation Coefficient	Standard Deviation of Fitting	Number of Points
	Value	Standard Deviation			
A_{2018} [a)]	5.21	0.03	0.9916	0.0092	175
A_{1304} [b)]	6.24	0.06	0.9673	0.0192	174

[a)] Baseline between 2100-1980 cm^{-1}
[b)] Baseline between 1329-1275 cm^{-1}

Calibration for the Methyl Band

Willbourn[20] introduced a compensation method for the quantitative determination of the total number of chain branches in polyethylene from the methyl symmetrical deformation band around 1378 cm^{-1} in the absorbance spectra, which was later developed into a standard test method.[21] The position and the molar absorptivity of the methyl band at 1378 cm^{-1} varies with the length of the chain attached,[22-26] moreover the absorptivity depends also on the degree of crystallinity.[25] Nevertheless, the chemical changes of polyethylene during processing are well reflected in the modification of the intensity of this band.[1]

In the present work the intensity of the methyl symmetric deformation band around 1378 cm^{-1} (A_{1378}) was determined by the compensation method, i.e. subtracting the spectrum of a very high molecular weight linear polyethylene (M_n=130,000 g/mole) from that of the investigated sample (Figure 3). The absorbance spectra of the high molecular weight HDPE film were applied for compensation even in the case of DRIFT measurements, as it yielded difference spectra of better quality than the subtraction of DRIFT spectra. It is interesting to note that in their study of chain branching of polyethylene in KBr disc Baker at al.[14] also recommended a polymethylene film for the compensation instead of a disc.

The measured A_{1378} values were related to the intensities of the two reference bands (A_{2018} and A_{1304}), respectively, then the normalized intensities determined from the transmission and diffuse reflection spectra were plotted against each other. The correlation is non-linear, as it can be seen in Figure 4a where the A_{1378}/A_{1304} values are plotted. Linear correlation can be obtained in double logarithmic plots for both reference bands. Figure 4b illustrates the relationship in the case of normalization to A_{1304}.

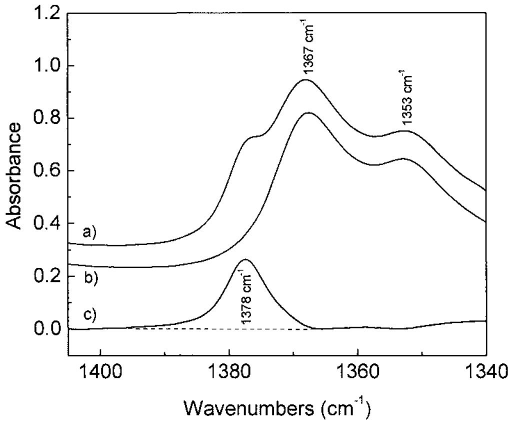

Fig. 3. Determination of the methyl absorption at 1378 cm^{-1} by compensation. Spectra of a) ethylene/1-hexene copolymer, b) reference HDPE, c) difference.

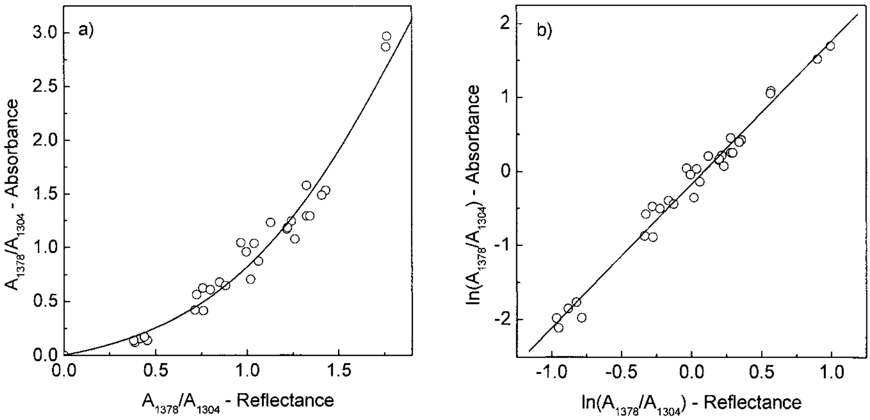

Fig. 4. Relationship between the normalized peak intensities of methyl group determined by DRIFT and transmission spectroscopy; a) linear plot, b) double logarithmic plot.

The relation between absorbance and Kubelka-Munk units can be expressed quantitatively by the following equation:

$$\ln\left(\frac{A_x}{A_{ref}}\right)_{abs} = C_1 + C_2 \cdot \ln\left(\frac{A_x}{A_{ref}}\right)_{refl} \qquad (3)$$

where A_x and A_{ref} are the peak intensities of the investigated and the reference bands, respectively. Subscript *abs* and *refl* refer to the absorbance and reflectance values, respectively. C_1 and C_2 are the calibration constants.

The normalization and correlation can be carried out also by the integrated intensities, which yield a relationship expressed by Equation (4):

$$\ln\left(\frac{I_x}{I_{ref}}\right)_{abs} = C_1' + C_2' \cdot \ln\left(\frac{I_x}{I_{ref}}\right)_{refl} \qquad (4)$$

where I_x and I_{ref} are the integrated intensities of the investigated and the reference bands, respectively. C_1' and C_2' are the calibration constants for the integrated intensities.

Table 2. Calibration constants calculated for the correlation between absorbance and Kubelka-Munk units according to Equations (3) and (4).

Investigated band	Reference band	C_1 and C_1'	C_2 and C_2'	Correlation Coefficient	Equation Nr.
A_{1378}	A_{1304}	-0.17 ± 0.03	1.94 ± 0.05	0.9894	3
A_{1378}	A_{2018}	1.50 ± 0.14	2.21 ± 0.16	0.9324	3
I_{1378}	I_{2018}	3.02 ± 0.35	2.12 ± 0.16	0.9243	4
A_{908}	A_{1304}	-0.85 ± 0.05	1.22 ± 0.05	0.9758	3
A_{908}	A_{2018}	0.15 ± 0.03	1.50 ± 0.03	0.9939	3
I_{908}	I_{2018}	0.36 ± 0.04	1.30 ± 0.03	0.9939	4
A_{890}	A_{2018}	-0.13 ± 0.08	1.13 ± 0.04	0.9799	3
I_{890}	I_{2018}	0.39 ± 0.16	1.18 ± 0.06	0.9704	4
A_{888}	A_{1304}	-1.09 ± 0.09	1.14 ± 0.06	0.9594	3
A_{888}	A_{2018}	-0.28 ± 0.08	1.12 ± 0.04	0.9816	3
A_{965}	A_{1304}	-1.18 ± 0.14	1.17 ± 0.06	0.9627	3
A_{965}	A_{2018}	0.06 ± 0.16	1.26 ± 0.06	0.9768	3
I_{965}	I_{2018}	0.31 ± 0.25	1.16 ± 0.06	0.9758	4

The calibration constants determined by Equations (3) and (4) for the methyl group intensities are given in Table 2. By comparing the correlation coefficients of the calculation we can conclude that the normalization to the band at 1304 cm^{-1} gives a better fit between the absorbance values and the Kubelka-Munk units than the use of the 2018 cm^{-1} reference band.

This result confirms that the deformation band around 1378 cm^{-1} originates intrinsically from the methyl groups in the amorphous phase of the polymer.[17]

For checking the reliability of Equation (3) the methyl concentrations of the samples were calculated from both the transmission and the reflection (transformed Kubelka-Munk units) spectra. For calibration ^{13}C NMR method was used. The concentrations are compared in Figure 5. The deviation of the data determined by the two methods is less than 25 %, which can be considered satisfactory. The scatter of the values originates from different sources. It is affected by the precision of spectrum compensation, the chemical heterogeneity of the polymers (RSD ~5 %), the sensitivity of the deformation band at 1378 cm^{-1} to the structure of the polymer chain, as well as the optical and geometrical irregularities of the polymer powders investigated (RSD ~10%).

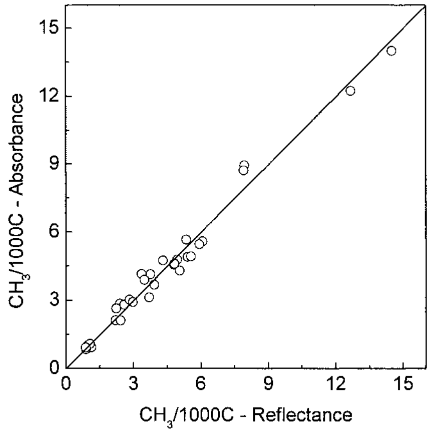

Fig. 5. Correlation between the methyl group concentrations derived from DRIFT and transmission spectra (normalization to the peak intensity of the reference band at 1304 cm^{-1}).

Calibration for the Vinyl Band

Except for some PE samples investigated, the bands of the vinyl and vinylidene groups overlap. For the determination of the concentrations of these unsaturated groups first the bands at 908 cm^{-1} [vibration of vinyl group[27]] and 890 cm^{-1} [vibrations of vinylidene group and butyl branches[28]] were separated by curve fitting (Figure 6).

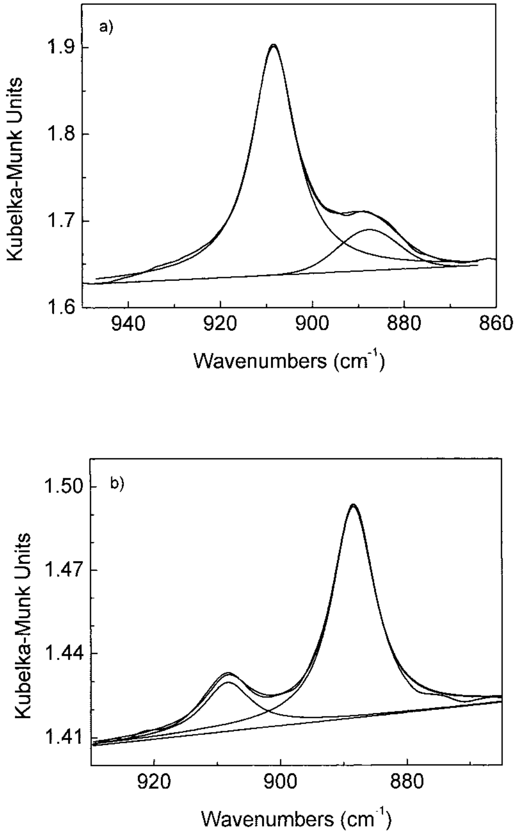

Fig. 6. Separation of the bands of vinyl and vinylidene groups by curve fitting. Spectra of a) Phillips type PE, b) metallocene PE.

In the next step the intensities at 908 cm^{-1} measured in transmission and diffuse reflection modes were normalized to the reference bands and plotted against each other. Similarly to the methyl vibration, non-linear correlation was obtained which could be linearized by double logarithmic representation. The calibration constants calculated by Equations (3) and (4) are summarized in Table 2. Comparing the correlation coefficients of the calculation we can conclude that the peak intensities and the integrated intensities normalized to the band at

2018 cm^{-1} yield similar accuracy and closer correlation than the use of the A_{1304} reference. The relationship between the A_{908}/A_{2018} relative intensities determined from the transmission and the DRIFT spectra is shown in Figure 7.

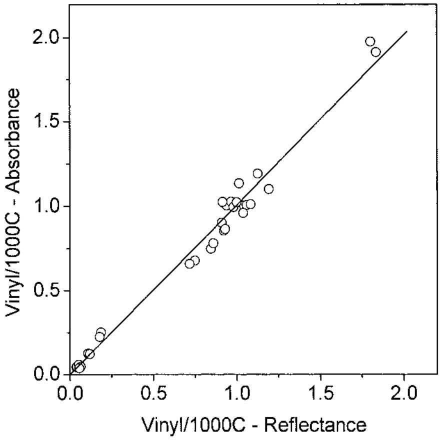

Fig. 7. Double logarithmic plot of the normalized peak intensities of vinyl group determined from DRIFT and transmission spectra.

The concentration of the vinyl group was calculated from both the absorbance values and the transformed Kubelka-Munk units normalized to the 2018 cm^{-1} reference band by Equations (5) and (6) using the absorptivity of 123 $cm^2/mmol$ given by de Kock and Hol.(29) The sample thickness was substituted by Equation (2).

$$n_{vinyl} = \frac{0.593}{\rho}\left(\frac{A_{908}}{A_{2018}}\right)_{abs} \tag{5}$$

$$n_{vinyl} = \frac{1.5}{\rho}\left(\frac{I_{908}}{I_{2018}}\right)_{abs} \tag{6}$$

where n_{vinyl} is the number of vinyl groups per 1000 carbon atoms; and ρ is the density of the sample.

The deviation between the vinyl concentrations derived from the peak intensities and the integrated intensities, respectively, in the transmission and reflection spectra is less than 20 %. The most reliable calibration of the Kubelka-Munk units is provided by the I_{908}/I_{2018} integrated intensity ratios (Figure 8).

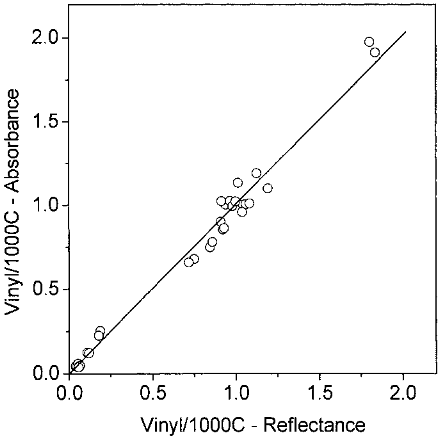

Fig. 8. Correlation between the vinyl group concentrations derived from DRIFT and transmission spectra (normalization to the integrated intensity of the reference band at 2018 cm^{-1}).

Calibration for the Vinylidene Band

The concentration of the vinylidene group can be obtained from the intensity of the band at 890 cm^{-1} (A_{890}), which is an overlap of the vinylidene band at 888 cm^{-1} and the 895 cm^{-1} band originating predominantly from butyl branches.[28,30] For the determination of the vinylidene concentration from the transmission spectrum of PE Lomonte[28] developed a calculation method. According to that the intensity of the butyl branch can be derived from the absorbance of the CH_3 group at 1378 cm^{-1} (A_{1378}). Considering the overlap of the two bands at 888 cm^{-1} the peak intensity of the vinylidene absorption (A_{888}) can be calculated by the following equation:

$$A_{888} = A_{890} - 0.85 \cdot \frac{A_{1378}}{28.9} \tag{7}$$

After separation of the bands at 908 and 890 cm^{-1} according to Figure 6 the intensity of the vinylidene group was calculated by Equation (7), as the overlapping bands of the vinylidene group and the butyl branch cannot be separated reliably by curve fitting. In the evaluation of the DRIFT spectra the question arose whether the ratio of the methyl intensities at 1378 and 895 cm^{-1} are similar in the transmission and reflection spectra. For the resolution two calculation methods were applied:

1. The intensity of the band at 890 cm^{-1} measured in Kubelka-Munk units was calibrated according to the absorbance values, then A_{888} was calculated by Equation (7).
2. First the intensity of the 888 cm^{-1} band was derived from the reflection spectra by Equation (7), then the calibration was carried out for the Kubelka-Munk units.

Both reference bands (2018 cm^{-1} and 1304 cm^{-1}) were tried for the calibration. Linear relationship was obtained between the logarithms of the normalized values determined from the transmission and reflection spectra in all cases. Figure 9a illustrates the double logarithmic correlation of the A_{888}/A_{2018} normalized peak intensities (method 2). From the results given in Table 2 the following conclusions can be drawn:

1. The calibration with the reference band at 2018 cm^{-1} results in better correlation than the normalization to the 1304 cm^{-1} band.
2. Calculation method 2 gives closer correlation between the absorbance values and the Kubelka-Munk units than method 1.
3. The integrated intensities do not provide higher correlation coefficient than the peak intensities.

Figure 9b reveals that the A_{888}/A_{2018} normalized intensities determined from the transmission and reflection spectra by method 2 relate close to linearly in the concentration range investigated. The correlation can be described by Equation (8):

$$\left(\frac{A_{888}}{A_{2018}}\right)_{abs} = C''\cdot\left(\frac{A_{888}}{A_{2018}}\right)_{refl} \qquad (8)$$

where the value of the proportionality factor C'' is 0.61 ± 0.02, and the correlation coefficient of the fitting $R = 0.9754$.

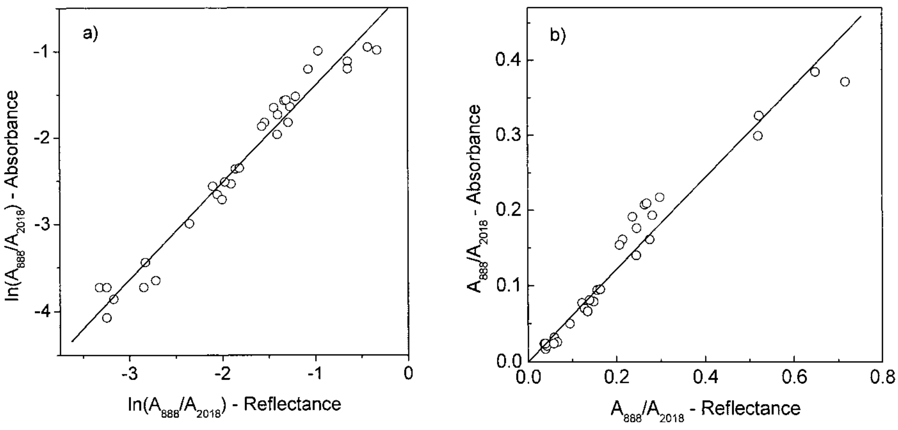

Fig. 9. Correlation between the normalized peak intensities of vinylidene group determined by DRIFT and trasmission spectroscopy; a) double logarithmic plot, b) linear plot.

The linear relationship between the absorbance and reflectance values shown in Figure 9b means, that the intensity of the vinylidene group is determined primarily by the absorption coefficient and affected less by the scattering coefficient of the sample.

The concentration of the vinylidene group was calculated from the transmission and the calibrated reflection spectra using the absorptivity given by de Kock and Hol.[29] Except for some samples the comparison reveled less than 20 % deviation between the concentrations determined by the two methods. The larger relative errors obtained for some samples originate mainly from the complex procedure used for the determination of the concentration of the vinylidene group.

Calibration for the Trans-vinylene Band

The *trans*-vinylene group of PE gives a vibration band at 965 cm^{-1}, which is well separated from the out-of-plane vibration bands of the vinyl group at 908 and 990 cm^{-1}.[27,29] The correlation between the normalized band intensities (reference bands at 2018 and 1304 cm^{-1}) determined from the transmission and reflection spectra is non-linear. Linear relationship can be obtained in double logarithmic representation also for this vibration. The calibration constants calculated are listed in Table 2, while Figure 10 shows the comparison of the A_{965}/A_{2018} normalized intensities derived from the DRIFT and transmission spectra. The correlation coefficient of the fit is larger in the case of the 2018 cm^{-1} reference band than for the normalization to the band at 1304 cm^{-1}. The peak intensities and integrated intensities yield correspondences of similar reliability.

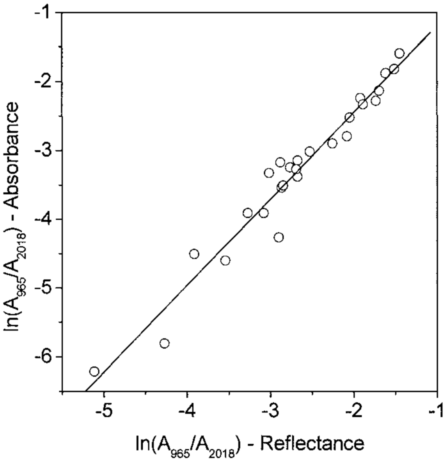

Fig. 10. Double logarithmic plot of the normalized peak intensities of *trans*-vinylene group determined from DRIFT and transmission spectra.

The concentration of the *trans*-vinylene group was calculated from the absorbance and calibrated reflectance values according to Reference 29. Except for the very low concentrations (<0.005 *trans*-vinylene/1000C) the deviation of the data determined by the two methods is less than 20 %.

Conclusions

Comparison of the transmission and reflection spectra of ethylene homopolymers and ethylene/1-hexene copolymers of different chemical structure revealed that the DRIFT technique can be applied successfully for the quantitative measurement of the functional (methyl and unsaturated) groups in polyethylene powder samples. The normalized intensities determined from the transmission and reflection spectra correlate linearly in double logarithmic plots. The relationship between the normalized intensities measured in Kubelka-Munk units by DRIFT technique (R_n) and in absorbance values by transmission method (A_n) can be described by the following empirical equation:

$$A_n = a \cdot R_n^b \qquad (9)$$

where a and b are constants characteristic for the investigated band.

As the amorphous and the crystalline phases of the polymer have different refractive indices, the selection of the internal reference band used for normalization affects strongly the accuracy of the calibration of the reflection spectra. Two internal reference bands were selected for the calibration, one of them (at 1304 cm^{-1}) originating from the amorphous phase of the polymer and the other (at 2018 cm^{-1}) affected by both phases. For the methyl groups the normalization to the amorphous CH_2 vibration at 1304 cm^{-1} yields more reliable calibration. On the other hand, for the calculation of the concentrations of the unsaturated groups the combined overtone band at 2018 cm^{-1} can be used with higher accuracy as an internal standard.

The precision of the concentration values of the functional groups determined from the reflection spectra is around 20-25 % or better, which can be considered satisfactory when the difficulties in sampling and calculations are considered.

One of the most important conclusions of the present work is that the use of an appropriate internal standard for normalization of the reflection spectra can eliminate the effects of differences in scattering caused by the irregularity of the polymer powder and the variations in the investigated surface layer.

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[1] E. Epacher, E. Fekete, M. Gahleiter, B. Pukánszky, *Polym. Degrad. Stab.* **1999**, *63*, 489.
[2] E. Epacher, E. Fekete, M. Gahleiter, B. Pukánszky, *Polym. Degrad. Stab.* **1999**, *63*, 499.
[3] E. Epacher, J. Tolvéth, K. Stoll, B. Pukánszky, *J. Appl. Polym. Sci.* **1999**, *74*, 1596.
[4] A. Garton, *"Infrared Spectroscopy of Polymer Blends, Composites and Surfaces"*, Hanser, Munich 1992, p. 107.
[5] J. P. Blitz, in *"Modern Techniques in Applied Molecular Spectroscopy"*, F. M. Mirabella, Ed., John Wiley & Sons, New York 1998, p. 185.
[6] Z. Krivácsy, J. Hlavay, *Talanta* **1994,** *41*, 1143.
[7] F. Boroumand, H. van den Bergh, J. E. Moser, **1994**, *Anal. Chem. 66*, 2260.
[8] Z. Krivácsy, J. Hlavay, *Magy. Kém. Folyórat* **1995**, *101*, 47.
[9] Z. Krivácsy, J. Hlavay, *Talanta 42*, **1995**, 613.
[10] J. Gulyás, E. Földes, A. Lázár, B. Pukánszky, *Composites: Part A* **2001**, *32*, 353.
[11] E. Takács, L. Wojnárovits, Cs. Földváry, P. Hargittai, J. Borsa, I. Sajó, *Res. Chem. Intermed.* **2001,** *27*, 837.
[12] J. Borsa, T. Tóth, E. Takács, P. Hargittai, *Radiat. Phys. Chem.* **2003**, in press.
[13] T. Tóth, J. Borsa, E. Takács, *Radiat. Phys. Chem.* **2003**, in press.
[14] C. Baker, P. David, W. F. Maddams, *Makromol. Chem.* **1979**, *180*, 975.
[15] M. Hrebičík, M. Suchánek, K. Volka, P. Novák, C. N. G. Scotter, *J. Molecular Structure*, **1995**, *347*, 485.
[16] R. W. Duerst, M. D. Duerst, W. L. Stebbings, in *"Modern Techniques in Applied Molecular Spectroscopy"*, F. M. Mirabella, Ed., John Wiley & Sons, New York 1998, p. 11.
[17] S. Krimm, **1960**, *Fortschr. Hochpolym.-Forsch*, *2*, 51.
[18] S. Krimm, *Phys. Rev.* **1954**, *94*, 1426.
[19] S. Krimm, C. Y. Liang, G. B. B. M. Sutherland, *J. Chem. Phys.* **1956**, *25*, 549.
[20] A. H. Willbourn, *J. Polym. Sci.* **1959**, *34*, 569.
[21] ASTM D 2238-68 (Reapproved 1979). *"Absorbance of polyethylene due to methyl groups at 1378 cm^{-1}"*.
[22] D. L. Wood, J. P. Luongo, *Modern Plastics*, **1961**, (*March*), 132.
[23] C. Baker, W. F. Maddams, G. S. Park, B. Robertson, *Makromol. Chem.* **1973**, *165*, 321.
[24] T. Usami, S. Takayama, *Polym. J.* **1984**, *16*, 731.
[25] A. Solti, D. O. Hummel, P. Simak, *Makromol. Chem., Macromol. Symp.* **1986**, *5*, 105.
[26] G. C. Pandey, *Process Control Quality* **1995**, *7*, 173.
[27] G. Socrates, *"Infrared Characteristic Group Frequencies"*, John Wiley & Sons, Chichester 1980.
[28] J. N. Lomonte, *Anal. Chem.* **1962**, *34*, 129.
[29] R. J. de Kock, P. A. H. M. Hol, *J. Polym. Sci. B, Polym. Lett.* **1964**, *2*, 339.
[30] J. P. Blitz, D. C. McFaddin, *J. Appl. Polym. Sci.* **1994**, *51*, 13.