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The Application of Vibrational Spectroscopy in the Analysis of Ultra-High Molecular Weight Polyethylene for Knee and Hip Prosthetics

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Abstract

We systematically used infrared (IR) and Raman spectroscopy to study the structure of unprocessed and perturbed UHMWPE by □-irradiation. We tested the proposed methods on selected polymer samples with known structure. We used vibrational spectroscopy to analyse the chemical structure of two different types of UHMWPE with different molecular weight and density under the trade names GUR 1020 and GUR 1050. The samples were exposed to four different doses of γ-irradiation, which induces the cross-linking and oxidation of polyethylene chains. The showed results proved that vibration spectroscopy can be a fast, efficient, non-destructive and simple tool to characterize the oxidation and degree of crystallinity of UHMWPE, while the accuracy of determining the degree of cross-linking was omitted by the process of oxidation and band overlapping.

Keywords: UHMWPE; infrared spectroscopy; Raman spectroscopy; polymer crystallinity; cross-linking; oxidation.

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1. Introduction

The number of people with severe mobility problems due to various pathological conditions of the knee or hip is increasing dramatically. Generally, joint immobility due to age or injury can be satisfactorily corrected only by hip or knee replacement and the cost of such surgery can be extremely high. Therefore, it is very important that the artificial hip or knee joint is of the best quality to avoid further complications such as infections or mechanical damage to the materials used in the replaced joints. The weakest point in artificial joints is ultra-high molecular weight polyethylene (UHMWPE) [1-4], which is commonly used as a cup or liner material that slides over the metallic femoral head. Considering all chemical and mechanical properties, UHMWPE is currently the ideal polymer for this use [5]. However, any slight variation in the chemical structure of the polymer can result in a change in the mechanical behaviour of the replaced joint. Commercial production of UHMWPE is complex and involves several steps. This increases the margin of error, and the final product must be tested to determine whether it is suitable for further use in artificial joints. Therefore, we need a fast, accurate and non-destructive method to test the polymer. Since the mechanical properties of UHMWPE are closely related to its chemical composition [2,4,6], we decided to systematically use infrared (IR) and Raman spectroscopy to study the structure of UHMWPE. The vibrational spectrum contains all the information about the chemical structure, which can then be correlated with the mechanical properties. We have found suitable spectral parameters (frequencies and band shape of the corresponding bands in the vibrational spectra) that are sensitive to the degree of crystallinity, the degree of cross-linked chains, and the degree of oxidation. These properties of UHMWPE have been shown to be the most important in providing the required mechanical properties of the polymer.

Vibrational spectroscopy of polyethylene in all its forms is well documented. Infrared [7-13] and Raman spectroscopy [6,14,15] are widely used to determine the composition and conformation of polymers. The applicability of infrared spectroscopy is greatly enhanced by the use of the attenuated total reflection technique, which provides very high quality of the recorded spectra and high sensitivity. In addition, it provides effective quantitative analyses and requires no or only simple sample preparation. Raman spectroscopy, on the other hand, is more sensitive to the vibrations of the polymer constituents, such as CH, CH_2 and CH_3 stretching and deformation vibrations, and is therefore very well suited to follow the chemical changes of the polymer.

However, despite of a numerous spectroscopic studies, a complete and detailed structural study of the composition of UHMWPE is still lacking. In particular, one comparing the positive and negative effects of radiation irradiation. The □-irradiation-induced formation of a cross-linked structure of the polymer still needs spectroscopic characterization, just as the characterization of the oxidation product needs to be demonstrated by analysis of absorption infrared or Raman spectra. To obtain this information from vibrational spectra, we need accurately recorded and post-processed spectra from which these structural and analytical parameters can be retrieved.

Although polyethylene is a very simple molecule and consequently exhibits a fairly simple infrared or Raman spectrum, the presence of structural defects such as oxidation centres, cross-linking, or partial crystallinity of the sample can significantly complicate the interpretation of the vibrational bands. There are at least two reasons for

the increase in the complexity of the vibrational spectra. The first reason is related to the low concentration of the spices, which differ from the ordinary polyethylene sample, and the second reason is that the interferences described generally have little effect on the peak frequencies and/or band shapes, so that overlap can become a serious problem. These difficulties can be mitigated by using spectral post-processing techniques such as difference spectroscopy and band fitting modelling. Besides the overlapping, which can be considered as a serious limitation of the application of vibrational spectroscopy in the structural study of polyethylene, the homogeneity of the sample can be another limitation. By using ATR sampling techniques, only a small portion of the polymer surface is examined. If the sample is inhomogeneous, we can examine a very uncharacteristic part of the sample, and by analysing such spectra, we can partially draw wrong conclusions. To avoid misinterpretation of spectra from uncharacteristic areas, we need to check the homogeneity of the sample by sampling several different parts of the polymer surface.

In the present work, we used two types of commercially available UHMWPE with different molecular weights and densities. Both types of polyethylene are used in orthopaedic implants such as hips and knees. The cross-linking of the polymer was brought about by irradiation with □-rays, which also increase the defects due to oxidation and change the degree of crystallinity. Thus, irradiation gives us a partially cross-linked polymer with defects that significantly affect the mechanical properties of UHMWPE. The cross-linking makes the polymer more resistant to environmental influences, while the oxidation and the change in the degree of crystallinity reduce the mechanical strength of the polymer.

2. Materials and methods

The UHMWPEs we use have the commercial designations GUR 1020 and GUR 1050 (Orthoplastic, Lancashire, UK). The former has a density of 0.937 g/cm^3 and a molecular weight of 2000000 g/mol, and the latter has a density of 0.932 g/cm^{3}and a molecular weight of 5000000 g/mol. The samples were irradiated with □-radiation at 25 kGy, 50 kGy, 75 kGy, and 100 kGy in a research nuclear reactor TRIGA in Podgorica (Slovenia). Infrared spectra were measured using Bruker Vertex 80 and Alpha II spectrometers. The diamond cell (Specac) or a built-in ATR accessory (Alpha II) were used to measure the polymer samples. In general, 256 scans were averaged, with a nominal resolution of 2 cm^{-1}. All measurements were performed at room temperature. After and before each measurement, the background was checked to ensure that the results were as accurate and the graph as clear as possible. Raman spectra were measured using the Bruker Ram II system. We used the NIR laser with a wavelength of 1064 nm. In general, 256 scans were averaged with a nominal resolution of 2 cm^{-1}. All measurements were performed at room temperature. Comparison of the infrared spectra of different locations on the polymer surface shows that all samples were homogeneous before and after irradiation. Bruker Opus 7.1 software was used for spectral processing and band decomposition. Plots were drawn using Origin software. For band decomposition, we used a mixed model in which the band shape of the model band is approximated by the sum of the Lorentz and Gaussian functions. We intended to reduce the number of bands to a minimum number that would still provide good agreement with the experimental spectrum.

3. Results and discussion

3.1. Infrared measurements

The simplicity of the UHMWPE molecule is also reflected in the infrared spectrum, which is shown in Figures 1 A and B. For the assignment, we used the results of previous infrared studies of polyethylene [10]. The strongest bands in the high-frequency region belong to the CH_2 stretching vibrations, both antisymmetric and symmetric. In the fingerprint region, we found several bands belonging to different deformation modes, such as wagging and rocking. The polyethylene presented in Figure 1 is not completely crystalline, so we can also find bands belonging to deformation vibrations of polyethylene in the amorphous state. The occurrence of both types of polyethylene, leading to different values of wagging deformation, can be used to determine the degree of crystallinity. The CH_3 end group vibrations are very difficult to observe because the number of CH_3 groups is very small compared to the number of CH_2 groups. However, very efficient for determining the length of the CH_2 chains, which in turn correlates with the density of polyethylene, is the deformation mode of CH_3 at 1377 cm^{-1}. Comparing the intensity of this band with that of the CH_2 deformation at 1352 cm^{-1}, it is possible to determine whether the sample belongs to polyethylene with low density or to polyethylene with high density [8]. In the present spectrum, the intensity of the CH_3 deformation at 1377 cm^{-1} is so weak that it is completely overlapped by the stronger CH_2 deformation bands. This means that the aliphatic chains are very long, and this situation is characteristic of high density polyethylene. If the band at 1377 cm^{-1} is visible without the use of resolution enhancement techniques, the sample belongs to a class of polyethylene with very low density. Table 1 shows the frequencies of the infrared spectra for all stretchings and deformations of polyethylene.

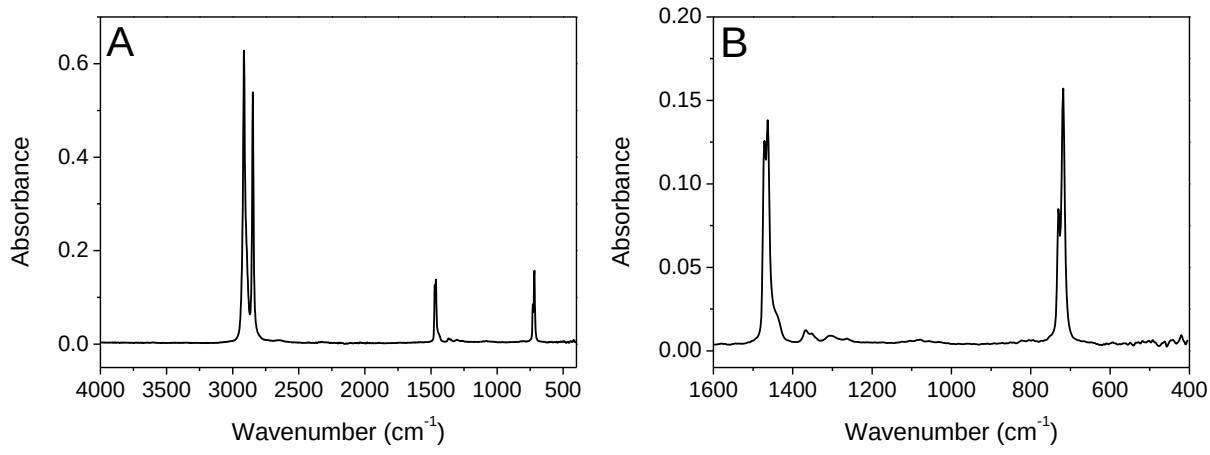


Figure 1: A) The infrared spectrum of commercial polyethylene. B) The fingerprint region of the polyethylene spectrum

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Table 1: The assignment of the infrared bands in the spectrum of polyethylene [10,16]

Frequency [cm^{-1}]	***Mode***	***Remarks***
2914	$\nu_{as}CH_2$	crystalline
2848	$\nu_{s}CH_2$	crystalline
1471	δCH_2	crystalline
1463	δCH_2	crystalline
1367	$\omega_{w}CH_2$	crystalline
1352	$\omega_{w}CH_2$	amorphous
1306	$\omega_{w}CH_2$	amorphous
730	$\rho_{r}CH_2$	crystalline
719	$\rho_{r}CH_2$	crystalline

Notes: $\nu_{as,s}$ antisymmetric and symmetric stretching, δ deformation, ω_{w} wagging, ρ_{r} rocking;

3.2. Raman measurements

Similar to the infrared spectra of polyethylene, the symmetric and antisymmetric stretchings of the CH_2 groups are the most intense bands, located at 2881 cm^{-1} and 2847 cm^{-1}, respectively (Figure 2). The fingerprint region starts with a series of CH_2 deformation bands in the range between 1461 cm^{-1} and 1169 cm^{-1}. In addition to the symmetric deformation at 1439 cm^{-1} and 1416 cm^{-1}, also wagging, twisting and rocking bands are also present. Characteristic C-C bands can be observed only in the Raman spectra of polyethylene at 1129 cm^{-1}, 1079 cm^{-1} and 1062 cm^{-1}. The ratio between the intensities of the C-C and the CH_2 bands can be used to determine the degree of cross-linking of polyethylene. The Raman spectrum of polyethylene is shown in Figure 2, and the characteristic bands and their assignment are summarised in Table 2.

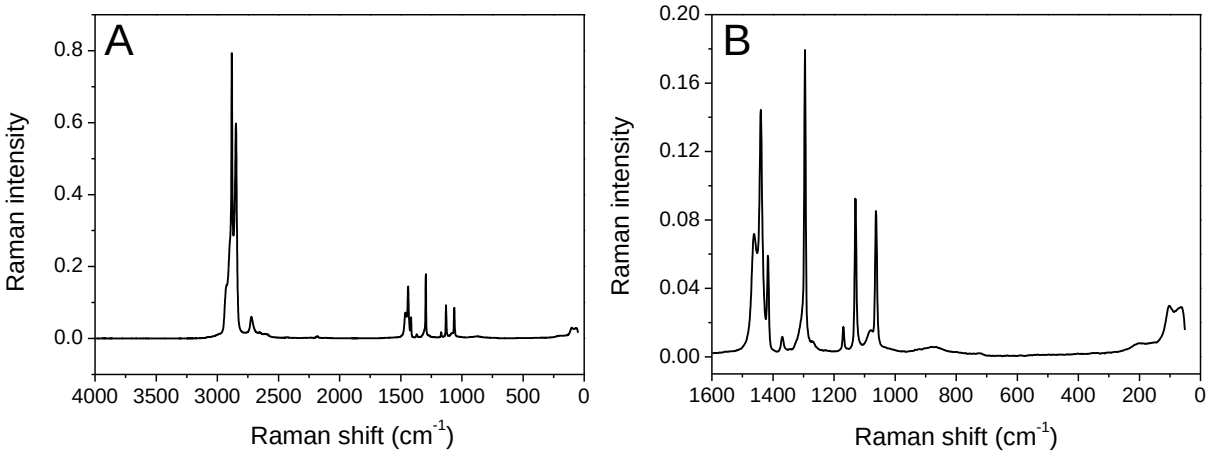


Figure 2: A) The Raman spectrum of commercial polyethylene. B) The fingerprint region of the polyethylene spectrum

Table 2: The assignment of the Raman bands in the spectrum of polyethylene [15,17,18]

Frequency [cm^{-1}]	***Mode***	***Remarks***
2881	ν_{as} CH_2	crystalline
2847	$\nu_s CH_2$	crystalline
1461	δCH_2	crystalline
1439	$\delta_s CH_2$	crystalline
1416	$\delta_s CH_2$	crystalline
1369	$\omega_w CH_2$	crystalline
1295	$\tau_t CH_2$	crystalline
1169	$\rho_r CH_2$	crystalline
1129	ν_sC-C	crystalline
1079	νC-C	amorphous
1062	ν_{as}C-C	crystalline

Note: τ_t twisting

The regions characteristic of the deformation modes are highly overlapped, so band fitting should be performed to accurately determine the band frequencies and intensities. An example of the application of this method is shown in Figure 3. It is obvious that the application of the model bands significantly improves the correct determination of the deformation band structure.

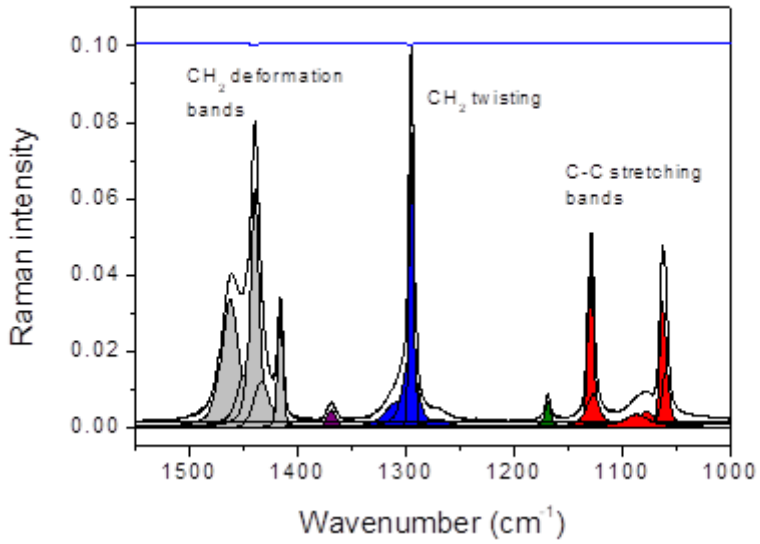


Figure 3: Fitting of the model bands in the experimental spectrum in the range of CH_2 deformations and C-C stretchings. The grey bands belong to deformation modes, blue to CH_2 twisting and rec to C-C stretching modes. The upper blue line is the difference between the calculated and recorded spectra

The upper blue line is the difference spectrum between the experimental spectrum and the calculated spectrum. The bands are approximated by a mixture of Lorentz and Gaussian band shapes.

3.3. The effects of crystallinity, presence of oxidized species and polymer cross-linking on infrared and Raman spectra of UHMWPE

The degree of crystallinity can be determined from either the infrared or Raman spectra. However, for simplicity, we will use the infrared spectra to determine crystallinity. In general, the sample polyethylene consists of a mixture of polyethylene chains arranged in the trans crystalline phase and an amorphous part with gauche defects. The deformation bands at 1471 cm^{-1} and 1463 cm^{-1} and the rocking bands at 730 cm^{-1} and 711 cm^{-1} (Figure 4) are a doublet of the deformation or rocking mode, which splits due to the different environment of the vibrating CH_2 groups [11,16].

It is known that the doublets observed in the infrared in deformation and rocking region result from a factor group splitting due to the packing of two polymer chains per unit cell of an orthorhombic lattice. The setting angle between the planes defined by the trans planar C-C chain frameworks in the lattice is close to 42°, which sets the theoretical ratio between the intensities in the doublet to a value of 1.233 [16]. However, the gauche defects enhance the intensity of the two low-frequency components. Thus, the complete expression for the determination of the amorphous fraction in the polyethylene sample (x^{am}) is expressed by the following equations:

$$\frac{I_a}{I_b^{cr}} = 1.23$$

$$I_b^{am} = I_b - I_b^{cr} = I_b - \left(\frac{I_a}{1.23}\right)$$

$$x^{am}(\%) = \frac{100 I_b^{am}}{I_a + I_b} = \frac{100\left(I_b - \left(\frac{I_a}{1.23}\right)\right)}{I_a + I_b}$$

The first expression represents the ratio between peaks A and B in the case of the pure crystalline phase. From two other equations, the ratio of the amorphous phase can be calculated. This procedure was used in the calculation of the amorphous phase as a function of the irradiation of the sample for both GUR 1020 and GUR 1050. The results are shown in Figure 5. We use the intensities of the CH_2 rocking splitting bands because they are farther apart than the corresponding deformation pair. A larger frequency difference and narrower bands ensure a more accurate determination of peak intensities.

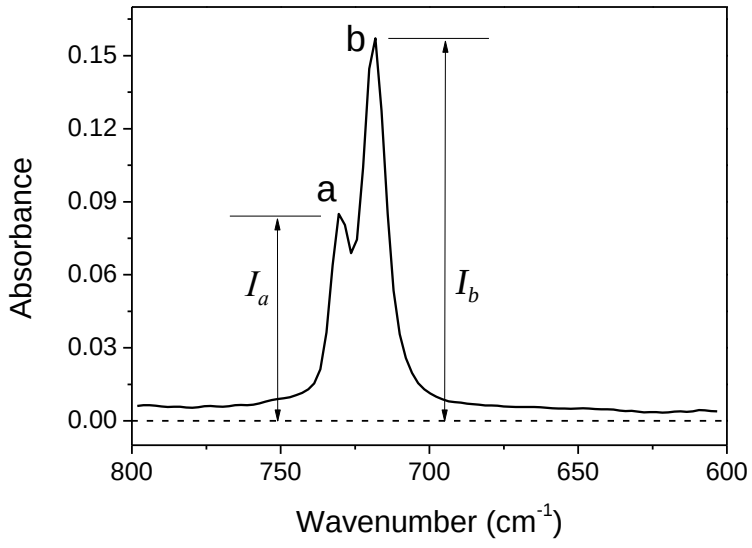


Figure 4: Definition of band intensities of CH_2 rocking mode

It is obvious from the Figure 5 that the amount of amorphous UHMWPE increases with irradiance. As we will see later, γ-irradiation significantly changes the structure of the polymer. It also induces the cross-linking mechanism and initiates oxidation processes. These structural changes correspondingly alter the degree of crystallinity. The proportion of amorphous polymer is already high in the original polymers before irradiation. In GUR 1020 it reaches 36 % and in GUR 1050 38 %.

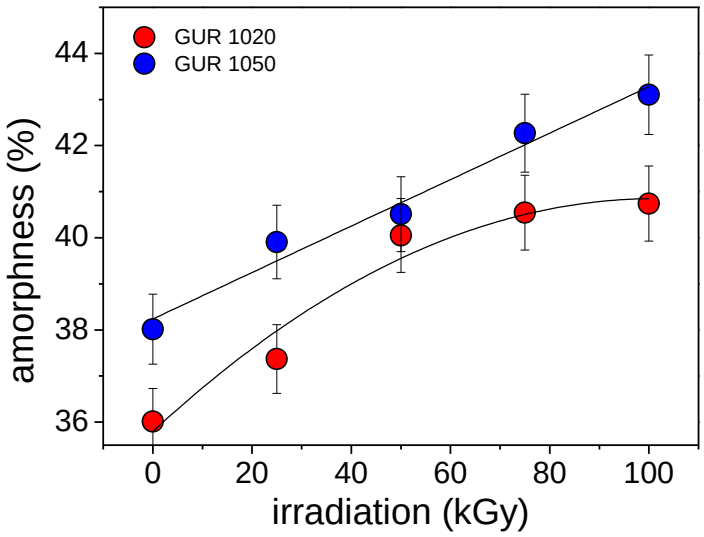


Figure 5: Calculated amorphous fraction in the GUR 1020 and GUR 1050 as a function of □-irradiation power

Through irradiation, the percentage of the amorphous phase increases gradually and reaches a value of almost 41% (GUR 1020) and 43% (GUR 1050) at the end of the 100kGy irradiation. The differences between the two polymers are not significant, although the relationship between the amorphousness and the irradiation level is almost linear in the case of GUR 1050, while for GUR 1020 at higher doses the response deviates slightly from linearity.

The properties of polymers, and UHMWPE in particular, are based on the long molecular chains, and anything that bend or/and breaks these chains has a very strong effect on the polymer mechanical properties. One of these processes is the oxidation process. The oxidized UHMWPE generally becomes brittle and is therefore not suitable for use in arthroscopy. The energy for the formation of free radicals can come from the reaction of impurities (peroxides), mechanical breaking of the chain and irradiation with high energy (UV, □-rays and electron beams) [19-22]. Therefore, the formation or presence of free radicals shortens the chain length and triggers an oxidation process that can be monitored by infrared spectroscopy. The most common method to accelerate the oxidation process is the application of □-rays.

We used the same samples as in the case of studying amorphness of the polymer, i.e. GUR 1020 and GUR 1050, respectively. Since the concentration level of oxidative species was expected to be small, we used difference spectroscopy, where two spectra (perturbed and unperturbed) are simply subtracted from each other. All spectral features that are the same in both spectra are eliminated. In a difference spectrum, only the bands that are exclusively present in one or the other spectrum remain.

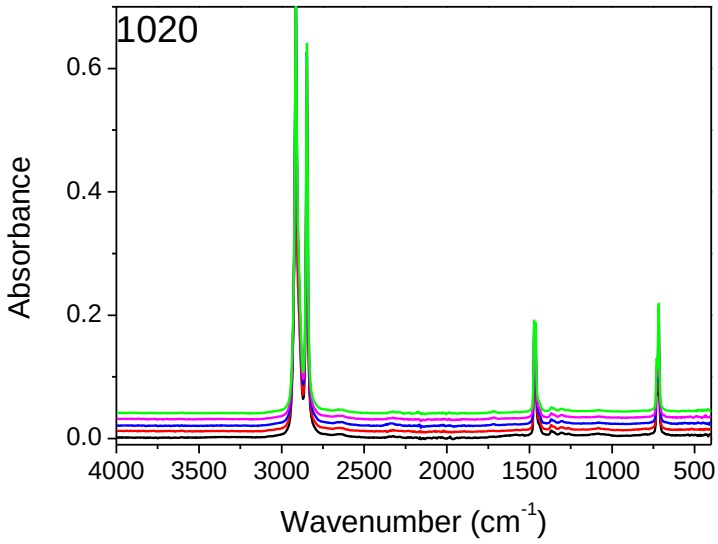


Figure 6: Infrared spectra of GUR 1020 exposed to □-irradiation. From bottom to top: 0 kGy, 25 kGy, 50 kGy, 75kGy, and 100 kGy

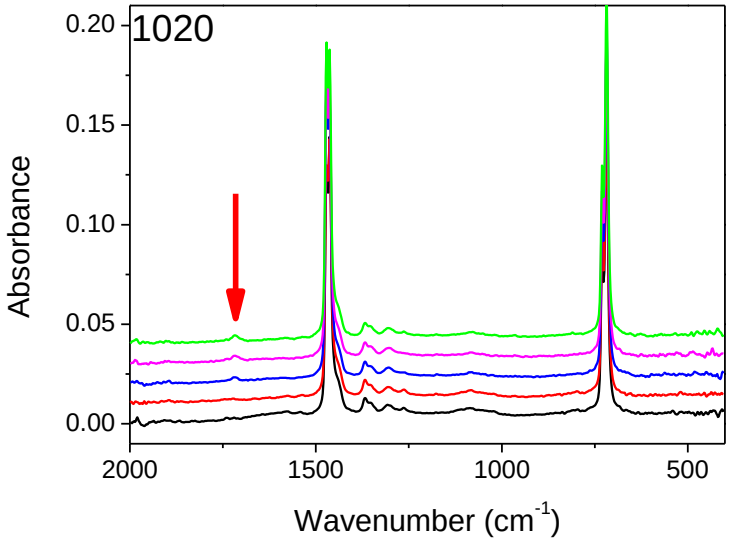


Figure 7: Extended infrared region GUR 1020 exposed to □-irradiation. From bottom to top: 0 kGy, 25 kGy, 50 kGy, 75kGy and 100 kGy. An arrow indicates the changes in the carbonyl region

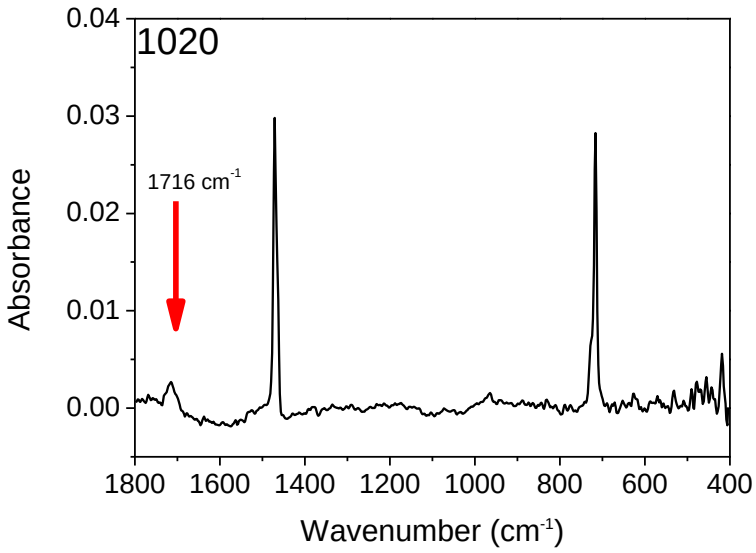


Figure 8: The difference spectrum (100 kGy - 0 kGy)

Figure 6 shows the infrared spectra of GUR 1020 exposed to different level of irradiation. It is obvious that the effects due to the formation of oxidation species are not visible in the original spectra. However, the difference spectrum shown in Figure 7 is more promising. Namely, the arrow points to the band characteristic of the C=O stretching mode [11], which was obviously caused by the irradiation that initiated degradation of the aliphatic chains. Moreover, the remaining narrow bands at lower wavenumbers indicate the change in the degree of crystallinity after irradiation. Both bands reflect the change in band intensity of the deformation and rocking doublet studied in the previous chapter.

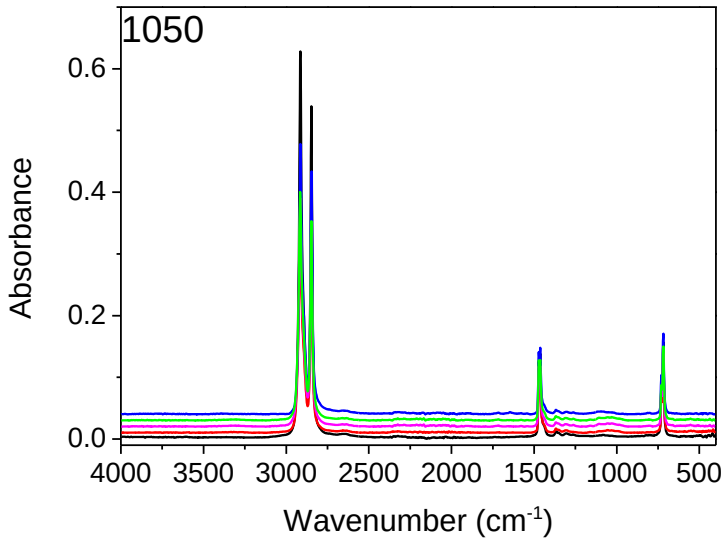


Figure 9: Infrared spectra of GUR 1050 exposed to □-irradiation. From bottom to top: 0 kGy, 25 kGy, 50 kGy, 75kGy and 100 kGy

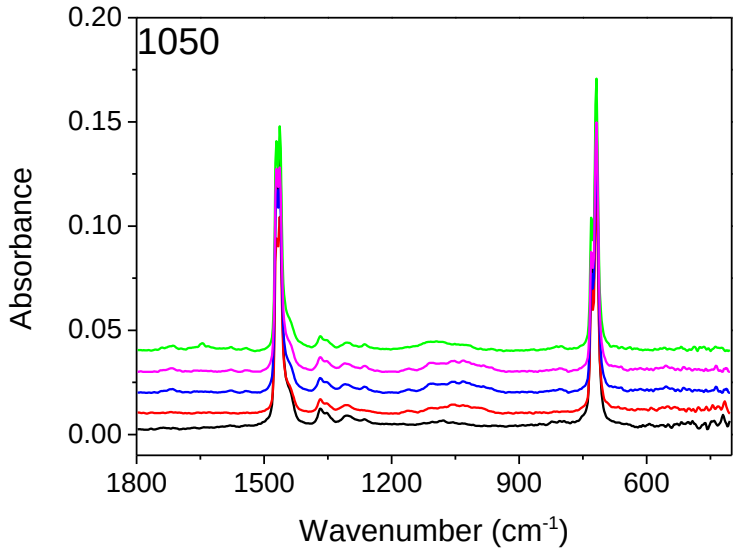


Figure 10: Extended infrared region UHMWPE exposed to □-irradiation**.** From bottom to top: 0 kGy, 25 kGy, 50 kGy, 75kGy, and 100 kGy

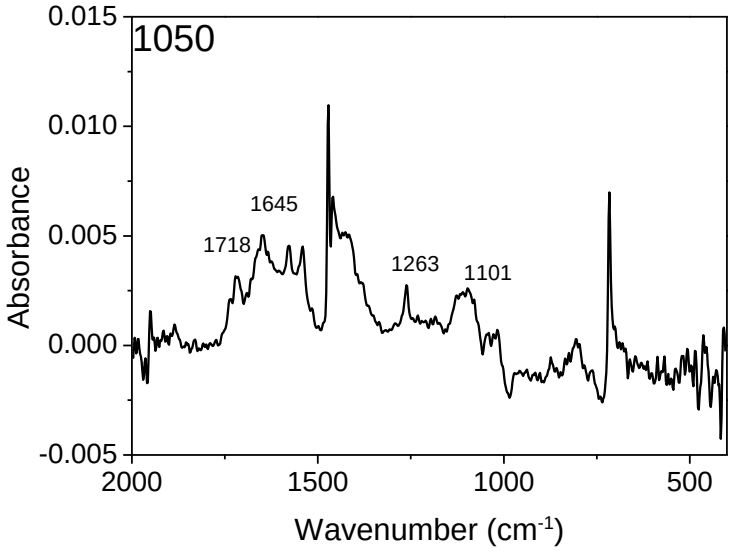


Figure 11: The difference spectrum of sample GUR 1050 irradiated with 100kGy and native 1050

As shown in Figure 11, the difference spectrum between irradiated GUR 1050 and native GUR 1050 is richer compared to previously used GUR 1020. Similarly to 1020 sample, we found narrow bands located at positions of CH_2 deformation and CH_2 rocking, which correspond to change in crystallinity. The band near 1718 cm^{-1} also appeared and it is ascribed to the vibration of C=O group [11]. However the bands near 1645 cm^{-1}, 1263 cm^{-1} and 1101 cm^{-1} are unique. The first two can be attributed to the symmetric and antisymmetric stretching vibration COO^- group [11], while the origin of the later band may be attributed to C-O stretchings.

Cross-linking of polymers is another process which can be in general initiated by the □-irradiation. During the cross-linking process, the nearby molecules start to chemically bond to each other. That means that the complete chemical structure is changed in that meaner that new groups appear. For detection the level of cross-linking we applied Raman spectroscopy, which is more suitable for detection of the C-C stretching and CH_2 deformation bands since the cross-linking increases the number of C-C bonds and decreases the number of CH_2 groups.

The hypothesis is that by measuring the intensities of CH_2 and C-C stretching bands in Raman spectra it is possible to detect the groups which are characteristic for cross-linking of polyethylene. Such fragment should belong to carbons with 3 or 4 bonds attached directly to other carbon atoms. Since the expected differences will be small and the overlapping of the bands of interest is high we should analyze the fitted spectra with model bands. The components used in the calculations are presented in Table 4.

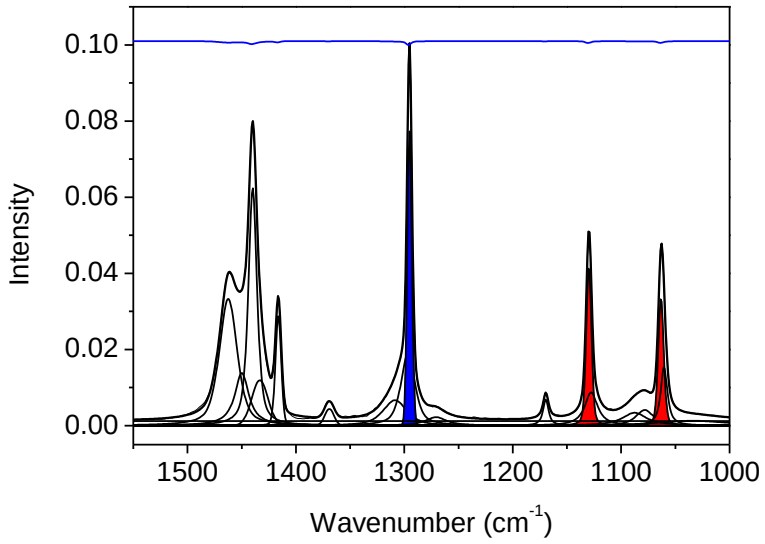


Figure 12: The bands used for determination of the cross-linking ratio. CH_2 deformation is colored blue and C-C stretching red

Table 3: Band intensities used in the calculation of cross-linking as a function of irradiation dose

	GUR 1020				*GUR 1050*			
Irrad. kGy	*δ CH_2 1295 cm^{-1}*	*ν C-C 1130 cm^{-1}*	*ν C-C 1080 cm^{-1}*	*Ratio*	*δ CH_2 1295 cm^{-1}*	*ν C-C 1130 cm^{-1}*	*ν C-C 1080 cm^{-1}*	*Ratio*
0	12.91	11.46	11.01	1.15	13.17	11.49	9.58	1.25
25	12.89	10.96	10.29	1.21	13.00	9.43	9.01	1.41
50	12.63	9.87	10.31	1.25	13.20	9.71	8.82	1.43
75	12.67	10.25	9.74	1.27	13.08	9.58	8.61	1.44
100	11.75	8.64	7.31	1.47	12.72	8.69	8.72	1.46

Note: The ratio was calculated as $2*INT_{CH2}/(INT1_{C-C}+INT2_{C-C})$.

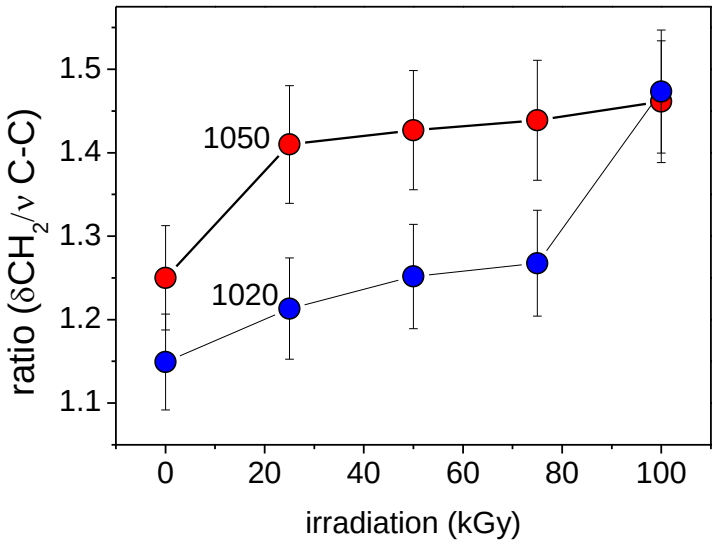


Figure 13: The calculated ratio from band intensities of CH_2 deformation mode and C-C stretching mode

The calculated ratio is shown in Figure 13. It is similar for both types of UHMWPE with different density. Both plots can be interpreted as decreases in the intensities of C-C stretching, which at first sight contradicts our expectations. Considering the expected new groups that should appear as a consequence of irradiation, there should be more C-C bonds and less CH_2 groups in cross-linked UHMWPE as a consequence of irradiation. In addition, the effect should occur to a greater extent at higher irradiation doses. The only explanation is that the expected C-C bond in the structures shown above has stretching bands with different frequencies. This would mean that the C-C stretching band originating from the $-H_2C-CH_2$ fragments loses intensity. New C-C bands should appear in the region around 1250 cm^{-1}, but they are not easy to detect because they have low intensity and overlap with the CH_2 bands. The comparison between the spectra of n-pentane, isopentane and tetramethylmethane confirms our assumption [23]. Another problem is also the oxidation of UHMWPE, which significantly changes the UHMWPE structure and thus also affects the number of C-C bonds and CH_2 groups.

4. Conclusions

In this study, we used vibrational spectroscopy to monitor the structure of native and stressed UHMWPE. We used two industrial grades of UHMWPE with different chain length and slightly different density. We demonstrated that we could analyse any structural deviations caused by γ-irradiation, which is mainly used to increase polymer cross-linking. Moreover, the same type of irradiation was also used to mimic the aging of the polymer.

The presented study shows that the application of vibrational spectroscopy is on the one hand a very simple, but on the other hand an efficient analytical tool that can serve as a method of choice for the determination of basic polymer properties, which in turn can be correlated with the mechanical properties of UHMWPE. We have successfully exploited all the advantages of the ATR method, which ensures rapid and accurate probing of polymer materials. In addition, we have shown that information about the highly overlapping bands can be

obtained by appropriate post-processing of the vibrational spectra. And this kind of information is crucial for structural characterization.

We have studied three properties of the polymer that directly affect the shape of the infrared or Raman spectra: crystallinity, oxidation damage, and cross-linking of the polymer chains. The applicability of the proposed methods was tested on two different types of polyethylene, GUR 1020 and 1050, which differ in the length of the polymer chains. We used time-varying □-irradiation to induce oxidation stress and cross-linking. We succeeded in determining the crystallinity of the polymer and the oxidation processes very efficiently, but the determination of the degree of cross-linked chains partially failed. The reason for this failure was the overexpression of the oxidation processes in the vibrational spectra, which successfully covered the spectral changes expected for the formation of cross-linked species. Thus, oxidation products are a serious limitation of vibrational spectroscopy for determining the degree of cross-linking in the polymer. But, by assigning the bands in the difference spectra of treated and untreated GUR 1020 and 1050, we were able to detect the presence of various groups such as C=O, COO^- and C-O, the presence of which indicates the oxidation processes in the polymer.

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Conflicts of interest

The authors declare no conflict of interest.

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