



PAPER AND FOIL CHARACTERISATION WITH FT-IR AND UV/VIS SPECTROSCOPY

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Abstract:

With the IR absorption spectroscopy, the structure of molecules can be identified. The identification can be quantitative as well as qualitative. UV/VIS spectroscopy enables the reflectance and transmittance measurements on solid or liquid materials. The application areas range from the surface characterisation of solids to the photometric analysis of turbid, colloidal, reflective, transparent and translucent samples. The main reason for the research was to examine classic and recycled papers, and classic and recycled polyethylene foils with spectroscopic instruments. The species of fillers and coatings in the paper samples were detected with the help of spectra, which were measured with a FT-IR spectrometer. Polyethylene foils spectra were recognized as low density polyethylenes. Additionally, the content of optical brighteners in the paper samples was detected from the reflectance measurements of a UV/VIS spectrometer. The foils had extremely low reflectance and extremely high transmittance in comparison with papers. Furthermore, small differences between classic and recycled materials are discussed in the article.

Keywords:

FT-IR spectroscopy, UV/VIS spectroscopy, paper, polyethylene foil, recycled material

1 INTRODUCTION

The molecule structure can be identified with infrared (IR) absorption spectroscopy quantitatively as well as qualitatively. The most useful for the analysis is the mid-IR spectra, i.e. the region from 4,000 to 400 cm^{-1} . The region from 4,000 to approximately 1,300 cm^{-1} is the region of functional groups. The absorption peaks within this region are closely related to the functional groups in molecules. The region from 1,300 to approximately 600 cm^{-1} is the fingerprint region. The absorption peaks in this region are closely related to the molecule structure of analytes [1, 2]. The IR absorption is analysed with the help of absorbance spectra in dependence of the wavenumber (cm^{-1}), observing the position, intensity (height), half-width and the shape of individual peaks. The peak position is the basic characteristic of vibration. It reveals an effective mass of group of vibrating atoms, the vibration geometry and coupling with the immediate surroundings, i.e. the vibrational species in the neighbourhood. A different position can indicate a different effective mass and/or different surroundings. A different force regarding the surroundings can, in general, cause minor differences (5–10 cm^{-1}); therefore, the latter are not a consequence of various functional groups; however, a shift in the peak position may indicate small changes in the vibrational group itself or in surrounding groups. The height of the peak presents strong, medium or weak vibrations, and the number of atom groups causing the vibrations. The peak width demonstrates the symmetry of vibrational species – crystalline or amorphous state, respectively, and the surroundings potential [3].



The ultraviolet/visible (UV/VIS) spectroscopy enables the measuring of reflectance and transmittance of solid or liquid materials. The measurements are performed using collimated beam; when it is detected in collimated form, specular reflectance or directional transmittance is measured. The integrating sphere enables the collecting of the light emerging from the sample in arbitrary direction; thus, the diffuse reflectance or diffuse transmittance could be obtained. Such analysis enables the surface characterisation of glossy or rough solids or the photometric analyses of turbid, colloidal, transparent and translucent samples in solid or liquid forms. Most common are the measurements of textiles, dyes, papers and glass. The spectra give information about electronic shells of the material in the investigated sample, which is of great importance in many applications in the material science and in several applications. The UV/VIS spectroscopy is used in the characterisation of solar cells, the analysis of security ink, specific measurements and analyses of colour, in the evaluation of differences between the specular and diffuse reflectance, in determining the dye concentration in textiles, determining food composition etc [4].

2 EXPERIMENTAL

The aim of the research was to study classic and recycled papers as well as classic and recycled polyethylene foils with FT-IR and UV-VIS spectrometers. The analysis was performed on the upper (A) and bottom (B) side of the following six samples: classic uncoated paper (S1), classic matte coated paper (S2), recycled uncoated paper (S3), recycled matte coated paper (S4), classic polyethylene foil (S5) and recycled polyethylene foil (S6).

The samples were measured with a FT-IR spectrometer, using the attenuated total reflectance (ATR) measuring cell. The ATR crystal of the applied cell was a diamond. All measurements were performed with the resolution of 4 cm^{-1} , obtaining absorbance spectra of all samples, for side A and B.

- Hardware: Spectrum GX, FT-IR System, PerkinElmer
- Software: Spectrum v 5.3.1
- ATR measuring cell, Golden Gate
- Database: Nicodom IR/NIR Libraries for polymers, fibres, dyes, pigments

Using the UV/VIS spectrometer, we measured the transmittance and reflectance values in the wavelength region 200–900 nm. The measurements of all samples were conducted in 10-nm steps, preparing 5 specimens for each sample, separately for side A and B, the average values of reflectance and transmittance of which was calculated with software.

- Hardware: Lambda 800 with PELA-1000 integrating sphere accessory, PerkinElmer
- Software: UV WinLab 6.0.2.0723

3 FT-IR SPECTROSCOPY

3.1 Database

The applied database detected calcium carbonate (CaCO_3) for classic as well as recycled uncoated paper (S1 and S3). It detected CaCO_3 only on side A of the paper, which most likely indicates that side B contains a smaller share of CaCO_3 . We were informed by the producers that they use CaCO_3 as the only filler in the production of classic and recycled uncoated paper. Due to the similarity of CaCO_3 with our uncoated papers, we compared their spectra. The peaks which are located in the same positions in the spectra of our samples at CaCO_3 positions indicated the CaCO_3 presence in uncoated papers (at 1420 , 870 and 710 cm^{-1}). It can also be found in the literature [5] that asymmetric stretching of the CO_3 group is detected in the paper spectrum at about 1425 cm^{-1} . The peaks at 870 and 710 cm^{-1}



are ascribed to the out-of-plane CO_3 bending vibration and the in-plane CO_2 bending vibration. All listed groups of molecules can be found in CaCO_3 .

For classic coated paper (S2), we obtained information from the producer that they also use CaCO_3 as a filler in the paper production. Moreover, for the coating, they use apart from CaCO_3 also kaolin as a pigment. The database listed in the first place kaolin and in the fifth place CaCO_3 for side A and B of the paper. Recycled coated paper (S4) contains CaCO_3 as a filler, while it contains apart from CaCO_3 for the coating also size and latex. The database lists in the first place CaCO_3 and slightly lower kaolin, which was not listed by the producers; nevertheless, the coating most likely contains a smaller amount of kaolin on both paper sides. We compared the spectra of coated papers with those of CaCO_3 and kaolin. Even here, the peaks are detected for the CaCO_3 content as at uncoated papers, while some of these peaks are less and some more distinctive. The peaks are located at 1800, 1400, 870 and 710 cm^{-1} . According to the literature [6], the CaCO_3 peaks which appear in the coated paper spectrum are to be located at the wavenumbers around 2550, 1800, 1500–1300 and 890 cm^{-1} . The latter also proved correct in our case, not exposing the peak at 2550 cm^{-1} for being so small (in our case it appears at 2510 cm^{-1}). Slightly more distinct are the peaks located in the same places as kaolin. The first three very distinct peaks are at 3690, 3650 and 3620 cm^{-1} , followed by the peaks at the wavenumbers 1400, 1090, 1030, 1010, 910, 790, 750, 700 and 540 cm^{-1} .

At classic and recycled polyethylene foils (S5 and S6), the database listed in the first place for both sides polyethylene of high density. If we compare the spectra of our polyethylene foils and the spectrum of polyethylene of high density, the peaks are undoubtedly located in the same places, i.e. at 2920, 2850, 1470, 1460, 730 and 720 cm^{-1} . The literature [7] which studies polyethylene by means of the FT-IR spectroscopy states that the peak at around 2919 cm^{-1} defines the CH_2 asymmetric stretching and at around 2851 cm^{-1} the CH_2 symmetric stretching. The peaks at 1473 and 1463 cm^{-1} are typical of the bending deformation of the CH_2 group. The literature mentions also slightly smaller intensities of the peak at 1377 cm^{-1} typical of the CH_3 symmetric deformation and at 1366 cm^{-1} which is typical of wagging deformation. The region from 731 to 720 cm^{-1} is ascribed to the rocking deformation.

3.2 Position, height and half-width of peaks

A substantially more precise analysis followed in the research, i.e. the analysis of our FT-IR spectra. We compared the recycled and non-recycled materials (side A and B), separately for uncoated papers, coated papers and foils. Using the program Spectrum, we defined the baseline for each spectrum individually and subtracted it from the spectrum. Figure 1 shows the spectra of classic uncoated paper for side A and B, and of the recycled uncoated paper for side A and B. In Figure 2, the spectra of classic and recycled coated paper are shown, separately for each side, whereas Figure 3 shows the spectra of classic and recycled polyethylene for both sides. It can be instantly noticed that the peak positions separately for uncoated papers, coated papers and polyethylene foils are almost identical, while they differ in their height ratios.

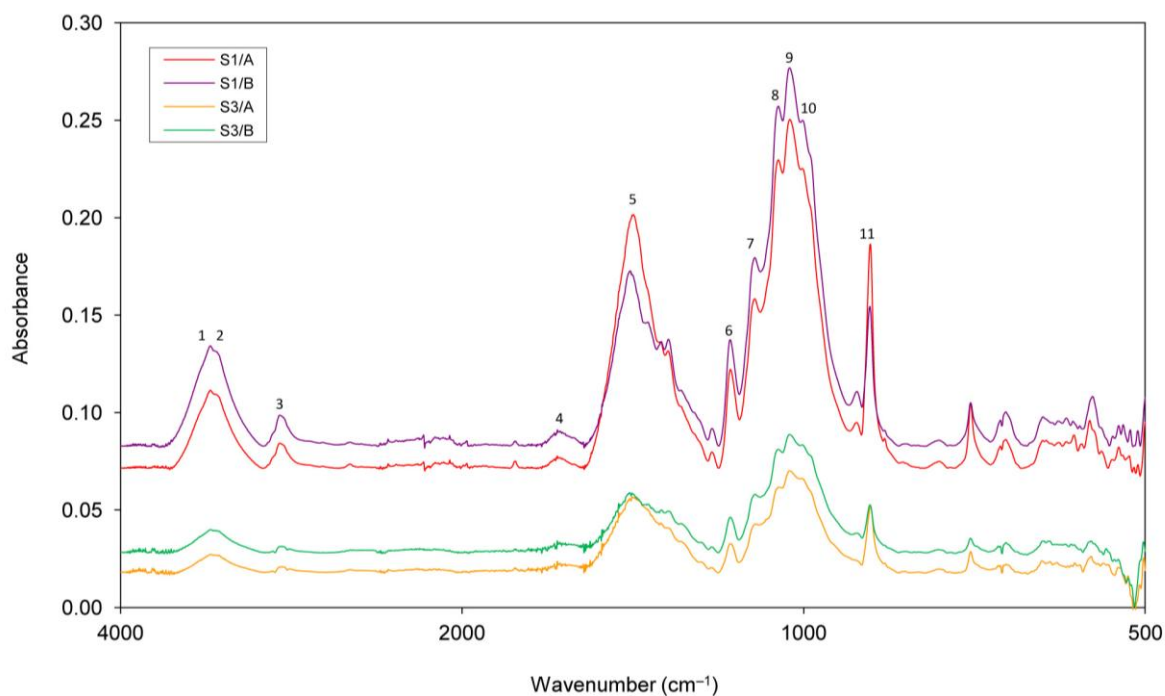


Figure 1: Spectra of classic (S1) and recycled (S3) uncoated papers for side A and B.

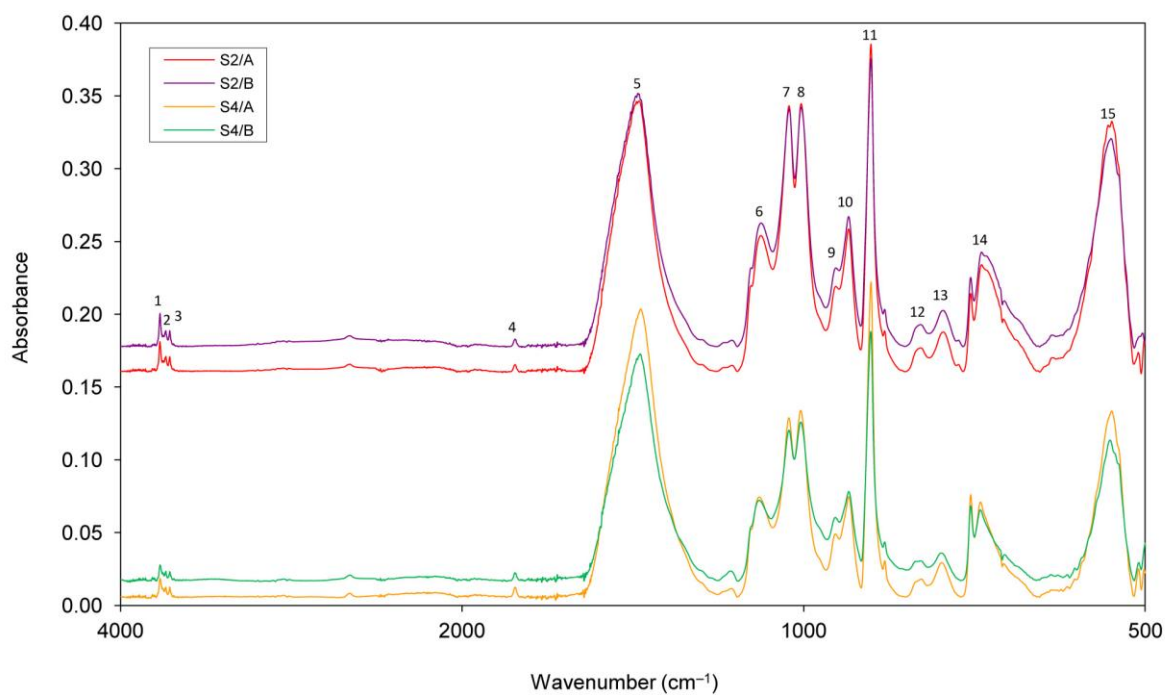


Figure 2: Spectra of classic (S2) and recycled (S4) coated papers for side A and B.

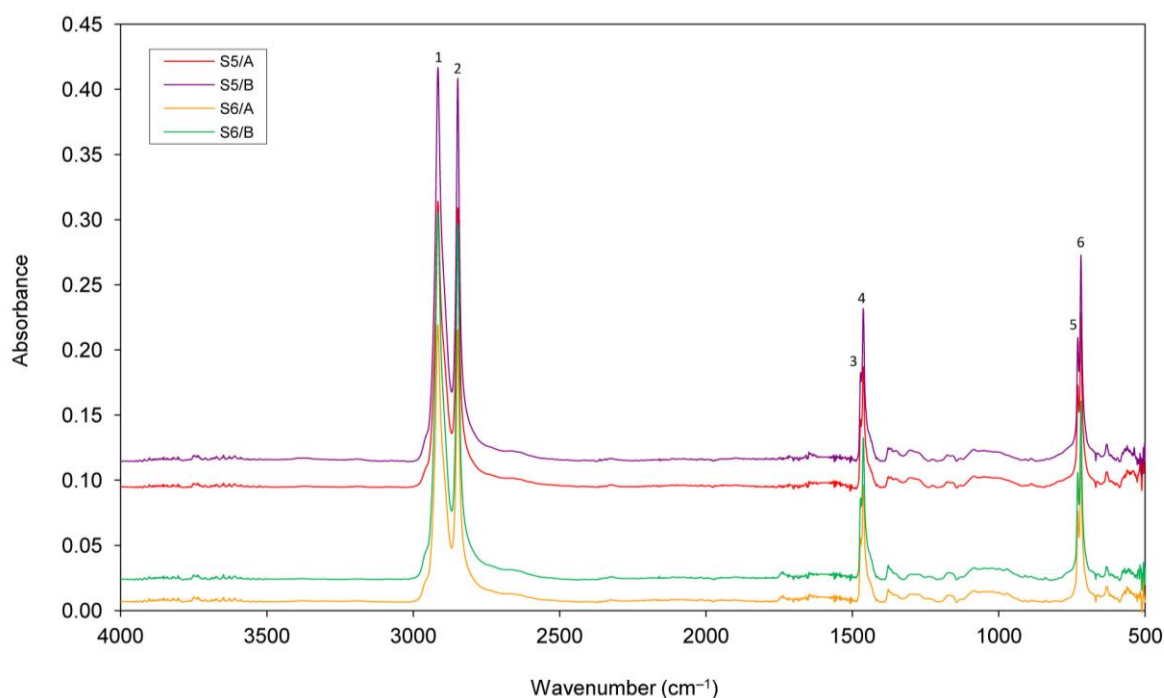


Figure 3: Spectra of classic (S5) and recycled (S6) polyethylene foils for side A and B.

We defined the position ν_0 (cm^{-1}), height I_0 and half-width hw (cm^{-1}) of individual peaks which are standing out the most. The data were inserted into Tables 1–3, separately for uncoated papers, coated papers and foils. Moreover, each of these tables was further divided into two parts. While the first part contains the peaks within the region of functional groups (from 4,000 to 1,300 cm^{-1}), the second part contains the peaks within the fingerprint region (from 1,300 to 600 cm^{-1}).

With a more detailed overview of Table 1, it can be established that regarding the peak position, samples S1 and S3 differ slightly more only in the position of peak 3 (C–H vibrations [1, 8]). S1 has by 13 and 12 cm^{-1} , respectively, higher wavenumber value than S3, which could be attributed only to different potential energy of atoms as a consequence of various surroundings. Regarding the peak height, Figure 1 and Table 1 demonstrate that all peaks of S1 are higher than those of S3, in some places more and in some less, which may indicate its higher density of molecular groups. However, the effect could also be a consequence of a different contact of the sample with the ATR crystal at the measurements due to unequal surface roughness, or different pressure applied when measuring. Only at peak 4 (C=C, C=O, C=N vibrations [1, 8], water molecules vibrations [9]), it can be said that the heights are comparable. Comparing only side A and B, the differences are more substantial at peak 5 and 11 of both samples, i.e. S1 and S3. Since these are the peaks typical of CaCO_3 , it can be said that side A of samples S1 and S3 has a higher content of CaCO_3 than side B. The difference in the peak width is bigger only at peaks 1 and 2, where S1 on side B has by 10 cm^{-1} greater width than on side A. Furthermore, S1 on side B has by 13 cm^{-1} greater width than S3. Larger width means lower density of molecular groups bonded in the same manner or in the same effective surroundings, i.e. less symmetry of the local environment. A note is in place here, namely that a slightly higher difference in the width could be a consequence of overlapping peaks. In the region around 1000 cm^{-1} , we register more vibrations (stretching and deformations) of more groups: C–O–C, C–O, C–C, C–N. These groups are located in cellulose fibres. As this is a mixture of more substances, more peaks appear; thus the overlapping into a wide absorption band. This is a consequence of the vibration of more groups in variable molecular surroundings, which cause distinctive peaks shift and widen. The asymmetric stretching of the C–O–C groups is caused by the peak at 1160 cm^{-1} , whereas the stretching of C–O in



cellulose/hemicellulose molecules is caused by the peaks at 1104 and 1028 cm^{-1} . The strongest peak at 1028 cm^{-1} is accompanied by two distinct peaks at 1051 and 1002 cm^{-1} [5].

Table 1: Position (ν_0), height (I_0) and half-width (hw) of individual peaks of classic (S1) and recycled (S3) uncoated paper for side A and B.

	Peak 1			Peak 2			Peak 3		Peak 4		Peak 5	
	ν_0 (cm^{-1})	I_0		ν_0 (cm^{-1})	I_0	hw (cm^{-1})	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0
S1/A	3333	0.040		3296	0.038	256*	2898	0.012	1649	0.006	1412	0.130
S1/B	3332	0.051		3295	0.049	266*	2899	0.016	1648	0.008	1421	0.090
S3/A	3332	0.009		3292	0.009	258*	2885	0.003	1649	0.006	1417	0.039
S3/B	3332	0.012		3293	0.011	253*	2887	0.003	1649	0.006	1423	0.031

	Peak 6			Peak 7		Peak 8		Peak 9		Peak 10		Peak 11		
	ν_0 (cm^{-1})	I_0	hw (cm^{-1})	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	hw (cm^{-1})
S1/A	1160	0.051	30	1104	0.087	1052	0.158	1028	0.179	1003	0.154	873	0.115	14
S1/B	1161	0.055	30	1104	0.097	1053	0.174	1029	0.194	1002	0.167	874	0.072	14
S3/A	1160	0.015	25	1102	0.025	1051	0.044	1029	0.052	1003	0.048	873	0.034	15
S3/B	1160	0.018	26	1103	0.030	1053	0.053	1029	0.061	1002	0.055	874	0.024	16

* Half-width listed at peak 2 is actually half-width of peaks 1 and 2.

At a more exact overview of Table 2, it can be instantly noticed that the differences in the position, height and half-width of peaks S2 and S4 are smaller than those for S1 and S3. At peak 5 between samples S2 and S4, the difference in the position is slightly bigger (the corresponding peak shifts by 7 cm^{-1} for side A and B), as well as in the half-width (S4 has by 6 cm^{-1} bigger width on side A). Bigger differences in the peak height between side A and B of both samples (cf. Figure 2 and Table 2) appear at peaks 5, 7, 8, 11 and 15 (sides A have higher values), and between samples S2 and S4 at the height of peaks 7, 8 and 15 (S2 has higher values). The results show that side A has in comparison with side B higher kaolin and CaCO_3 content, and S2 compared to S4 higher kaolin content.

Table 2: Position (ν_0), height (I_0) and half-width (hw) of individual peaks of classic (S2) and recycled (S4) coated paper for side A and B.

	Peak 1		Peak 2		Peak 3		Peak 4			Peak 5		
	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	hw (cm^{-1})	ν_0 (cm^{-1})	I_0	hw (cm^{-1})
S2/A	3693	0.021	3649	0.011	3621	0.010	1797	0.005	11	1398	0.186	129
S2/B	3692	0.023	3649	0.011	3621	0.011	1797	0.005	12	1400	0.174	128
S4/A	3692	0.013	3649	0.007	3620	0.007	1797	0.007	12	1391	0.198	135
S4/B	3692	0.011	3649	0.007	3620	0.006	1797	0.006	12	1393	0.156	131

	Peak 6		Peak 7		Peak 8		Peak 9		Peak 10		Peak 11		
	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	hw (cm^{-1})
S2/A	1091	0.093	1030	0.182	1005	0.184	937	0.059	913	0.098	872	0.225	14
S2/B	1090	0.085	1030	0.163	1005	0.164	937	0.054	913	0.089	872	0.198	14
S4/A	1094	0.069	1030	0.123	1006	0.128	938	0.043	912	0.069	872	0.216	13
S4/B	1094	0.055	1030	0.104	1006	0.109	937	0.044	912	0.061	872	0.172	14

	Peak 12		Peak 13		Peak 14		Peak 15		
	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0	hw (cm^{-1})
S2/A	789	0.016	753	0.027	697	0.073	535	0.172	34
S2/B	789	0.015	753	0.025	697	0.065	536	0.143	34
S4/A	788	0.012	756	0.023	698	0.065	535	0.128	31
S4/B	789	0.014	756	0.019	698	0.049	537	0.097	31



The differences in Table 3 among individual peaks in the spectra of samples S5 and S6, and between side A and B are extremely small. The differences are perceived merely at the height of peak 1 and 2 between side A and B, where both S5 and S6 have higher peak height values for side B than side A (the differences range between 0.064 and 0.082 absorbance units). The results indicate higher content of C–H and O–H groups [1] on sides B of polyethylene foils. The literature [7] mentions a group of slightly smaller peaks which were not taken into consideration in this study. These are the peaks between our peak 4 and 5, which are located between 1380 and 1360 cm^{-1} . With them, three most important types of commercial polyethylene can be determined, i.e. high density polyethylene (HDPE), low density polyethylene (LDPE) or linear low density polyethylene (LLDPE). If the peak at 1377 cm^{-1} (peak I) is higher than the peak at around 1366 cm^{-1} (peak II), we speak of low density polyethylene. If peak I is smaller, we speak of linear low density polyethylene. When peak I is in comparison with peak II barely noticeable, we speak of high density polyethylene. As peak I was higher at our samples, it can be said that we are talking about low density polyethylene, this peak being more distinct and higher, respectively, at sample S6 than at S5.

Table 3: Position (ν_0), height (I_0) and half-width (hw) of individual peaks of classic (S5) and recycled (S6) polyethylene foil for side A and B.

	Peak 1			Peak 2			Peak 3		Peak 4	
	ν_0 (cm^{-1})	I_0	hw (cm^{-1})	ν_0 (cm^{-1})	I_0	hw (cm^{-1})	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0
S5/A	2916	0.220	30	2848	0.215	15	1472	0.052	1463	0.092
S5/B	2916	0.302	28	2848	0.294	14	1472	0.068	1463	0.117
S6/A	2916	0.213	31	2848	0.209	14	1472	0.049	1463	0.090
S6/B	2916	0.282	29	2848	0.273	14	1472	0.062	1463	0.109

	Peak 5		Peak 6	
	ν_0 (cm^{-1})	I_0	ν_0 (cm^{-1})	I_0
S5/A	730	0.079	719	0.134
S5/B	730	0.095	719	0.158
S6/A	730	0.070	719	0.121
S6/B	730	0.082	719	0.137

4 UV/VIS SPECTROSCOPY

Figure 4 shows the reflectance of all our samples in dependence of the wavelengths. Particularly interesting are the reflectance values of uncoated papers, the values of which exceed 100%. This is a typical phenomenon of papers which contain optical brighteners, due to which paper emits light even more in the UV spectral region. The phenomenon is the strongest at classic uncoated paper (S1), where the maximum reflectance value equals 250%. The phenomenon is smaller, yet still noticeable at recycled uncoated paper (S3) on side B, the reflectance value being 120%. The coating on paper partially suppresses the effect of brighteners, thus it is less distinct or not noticeable at all. In our case, the reflectance values of coated papers are lower than 100%, despite containing optical brighteners. Classic papers have in the UV and visible spectral region higher reflectance values than recycled papers. The reflectance values of polyethylene foils are lower due to higher transmittance. In the UV spectral region, they amount to around 20%, whereas they lower to 10% in the visible spectral region. Classic foil (S5) displays slightly higher reflectance value in the UV spectral region than recycled foil (S6).

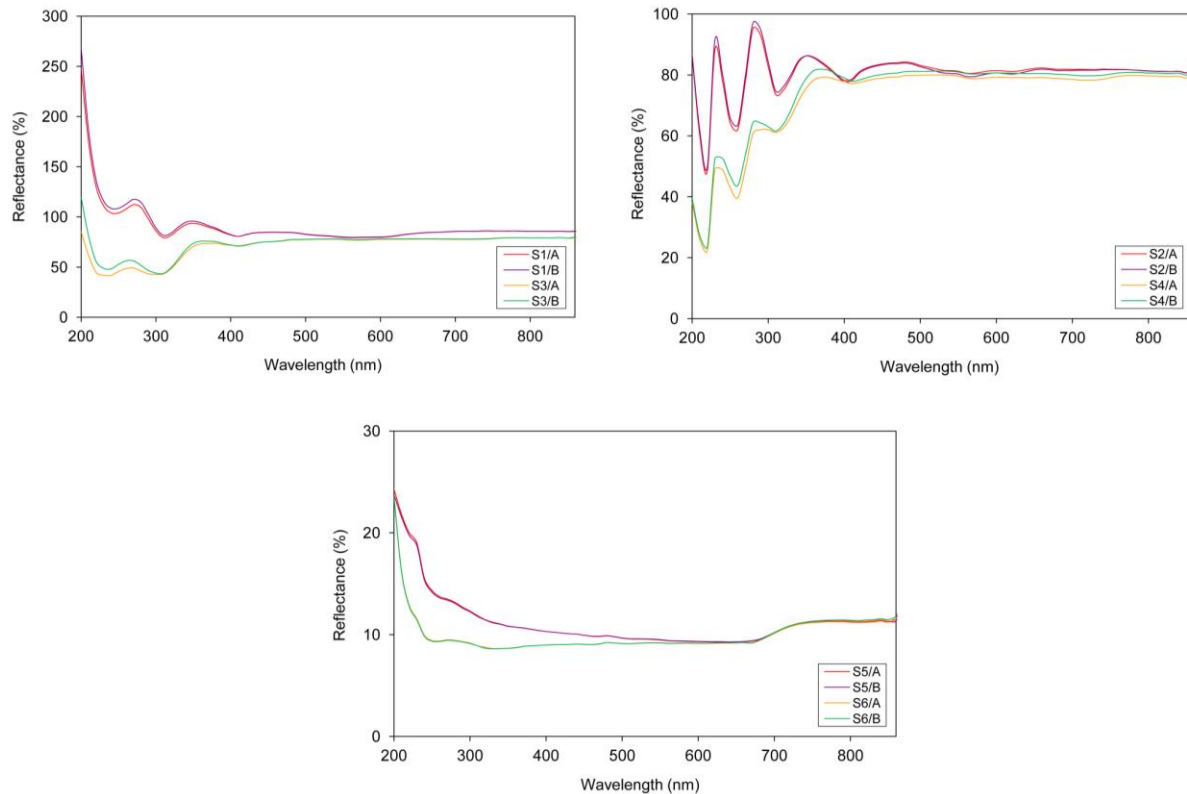


Figure 4: *Reflectance spectra for uncoated papers, coated papers and polyethylene foils.*

Apart from reflectance, we also measured the transmittance values of our samples (cf. Figure 5). The transmittance of recycled uncoated paper (S3) is in the UV spectral region smaller, while it increases in the visible region and is higher than classic uncoated paper (S1). At coated papers, by increasing the wavelength, transmittance increases as well. Classic coated paper (S2) has higher transmittance than recycled coated paper (S4) throughout the whole UV and visible spectrum. Polyethylene foils have high transmittance. Classic foil (S5) has 90% transmittance in the whole observed spectral region, except at 200 nm, where transmittance decreases to 60%. The transmittance of recycled foil (S6) exponentially increases from the UV to visible spectrum from 7% to 90%. The differences between the transmittance values for side A and B of papers and foils are extremely small.

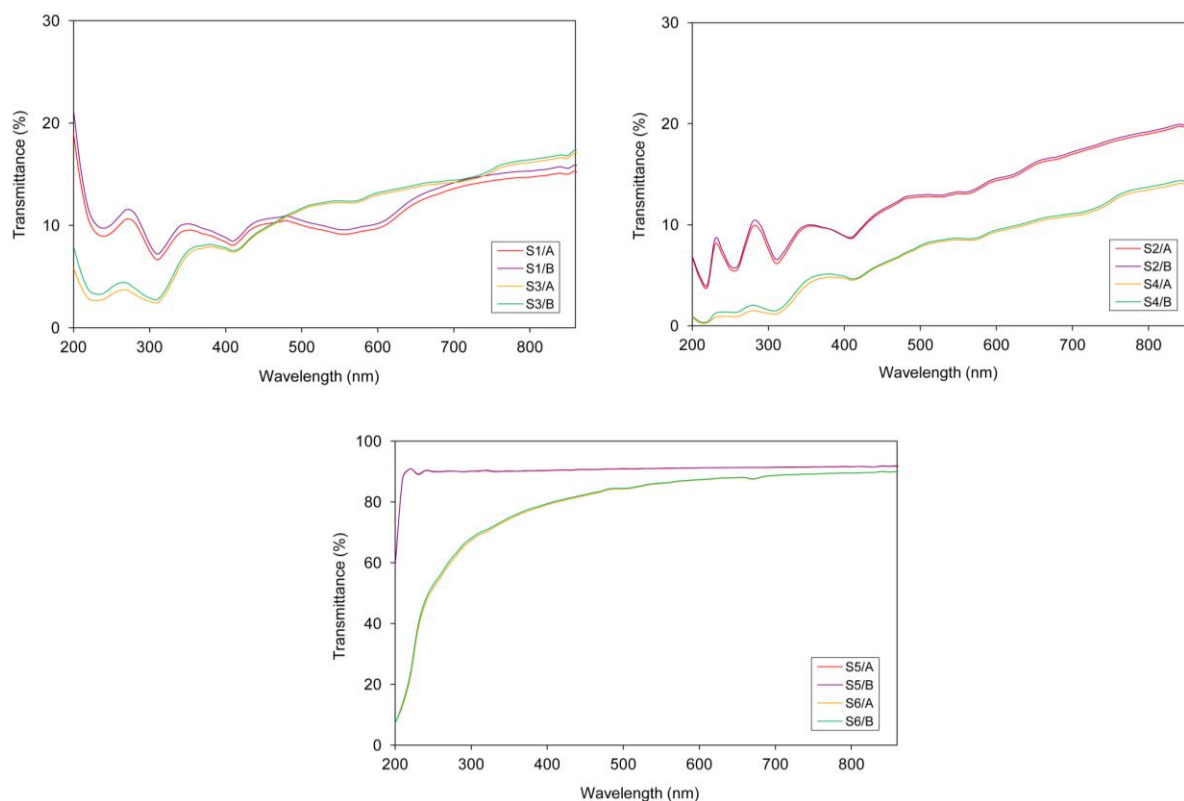


Figure 5: *Transmittance spectra for uncoated papers, coated papers and polyethylene foils.*

5 CONCLUSIONS

With the help of FT-IR-ATR spectra, we detected the content of calcium carbonate in all papers, and at coated papers, also the content of kaolin. With an exacted analysis, we established that classic uncoated papers have in comparison with recycled uncoated papers higher density of molecular groups in the whole region. Coated papers showed smaller differences. We found out that the surface of classic coated paper contains more kaolin than the surface of recycled coated paper. From the spectra of polyethylene foils, we established that we have samples of low density polyethylene (LDPE).

With a UV/VIS spectrometer, we detected in the measured reflectance the content of optical brighteners in the paper samples, due to which paper additionally emits light in the UV spectral region which gives higher reflectance in the blue region and therefore a whiter surface appearance. The reflectance values in the UV and visible spectral region were higher at classic materials in comparison with the recycled ones. Compared to papers, foils had extremely low reflectance and very high transmittance.

Acknowledgements

This work was supported by the Slovenian Research Agency (Project BI-HU/10-11-013). The authors would like to thank the paper manufacturer Papirnica Vevče for providing some paper samples. S. G. thanks the Ministry of Higher Education, Science and Technology for the PhD grant.



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