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The Use of the Spectrometric Technique FTIR-ATR to Examine the Polymers Surface

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Additional information is available at the end of the chapter

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1. Introduction

The development of material engineering is accompanied by a growing demand for routine, nondestructive techniques for material and product testing. These techniques are to be used for the assessment of chemical and physical structure of new materials as well as for a systematic control of their manufacturing processes. Nowadays nanotechnologies fulfill a particular role in creating new materials of nanometric dimensions. The products of nanotechnology are made in various forms, mostly such as coatings and fibers. Coatings are of great practical importance while deposited on conventional substrates, such as metals, ceramics and polymers to impart new functions, e.g. anticorrosive, reflexive, sensory properties, etc., to them. Coatings are mostly made of polymers and hence their functional properties and durability mainly depend on polymer chemical and supermolecular structure. The current control tests of the chemical properties and supermolecular characteristic of materials are carried out with the use of IR absorption spectroscopy. Currently, these are dedicated to test the surface of materials. This paper concerns the spectroscopic technique FTIR used to test the surface of polymeric materials and coatings formed on polymeric substrates. The general characteristics, advantages and drawbacks of this technique in testing polymer surfaces have been presented.

2. Technique of infrared absorption spectroscopy

Material testing by the technique of IR spectroscopy consists in making a spectrum of radiation energy absorbed by material molecules and interpreting the spectrum obtained. IR radiation within the wavelength range from 2.5 mm to 15 mm (the wave number from 4000 cm^{-1} to 666 cm^{-1}) is selectively absorbed by material molecules and converted into their oscillatory energy. The oscillations of molecules are of various characters, connected with their chemical structure, and depend on the type of bonds (frequency increases with

increasing bond energy), relative atomic weights (frequency decreases with increasing atomic weight), spatial position of atoms in a molecule, intra- and intermolecular interaction forces. During absorption, various vibration modes are generated that can be ranged with respect to energy in the following order: stretching vibration > bending vibration > oscillatory/torsional vibration. Vibration modes are active in IR only when the frequency of radiation coincides with the own frequency of molecule oscillation (resonance) and the dipole moments of molecules change in the same direction as the electric vector of IR radiation wave.

In the absorption spectroscopy techniques, IR radiation, after passing the material, where molecules selectively absorb radiation quanta, the absorption spectrum is recorded in the form of changes in the IR spectra radiation intensity as a function of radiation energy. The intensity of a beam after passing through sample (I), transmittance (T) or absorbance (A) is assumed as a measure of absorption. If the intensity of the primary incident beam on a sample is equal to I_0 , the relation between intensity, transmittance and absorbance is as follows: $T = I/I_0$, $A = \log(I_0/I) = -\log T$. Energy is expressed in eV, but mostly practical parameters such as IR radiation wavelength (λ , nm), wave number ($\nu=1/\lambda$, cm^{-1}) and radiation frequency (ν , Hz) are used to express energy.

Originally, tests and recording the IR radiation absorption spectra of samples were performed by means of two-beam diffraction spectrometers. Modern technical solutions of IR spectrometers consist in replacing the reticular monochromators with interferometers, which considerably increases the sensitivity of spectrometers (a high value of the signal to noise ratio is obtained), making it possible to shorten the spectrum recording and to obtain its good definition. Moreover, there occur the transformation and ordering of the interferogram obtained to the frequency domain by the use of Fourier Transform (FTIR). The high resolving power of spectrometer makes it possible to record complicated spectra of materials, spectra mixing, the distinction of band derived from crystalline and non-crystalline areas and performing static and dynamic tests.

The IR spectrometry technique can be used in two variants: transmission and reflection. The transmission version is used to test the effects of IR radiation absorption in the volume of sample. It is possible to test samples in any form: solid, liquid and gaseous with the use of an appropriate procedure. Gases and liquids are placed in special cuvettes with windows, made of transparent materials for IR radiation (e.g. ionic crystals: KBr, NaCl). The spectra of solids can be measured using previously prepared specimens on quartz plates, in a suspension in liquid paraffin or in the form of tablets made of KBr. If the object tested is sufficiently thin and transparent, its spectra are measured directly on a sample. The transmission technique cannot be used for materials that strongly absorb IR radiation and to test local areas of sample such as surface. In the sixties of the last century, the reflection variant was developed, so-called Attenuated Total Reflection (ATR), which makes it possible to test specific version of samples. The ATR-IR uses the phenomenon of a complete reflection during the transition of IR radiation from an optically denser medium (prism) to thinner medium (sample). A sample is placed on the IR-transparent prism surface with a refractive index being always higher than that of the sample (Figure 1). The radiation beam

is directed by one of the prism wall to the prism-sample interface at angle θ higher than the limiting. Under these conditions, a complete reflection occurs at the internal prism side and the beam reflected comes out through the second prism wall, where the beam intensity and absorption spectrum are recorded.

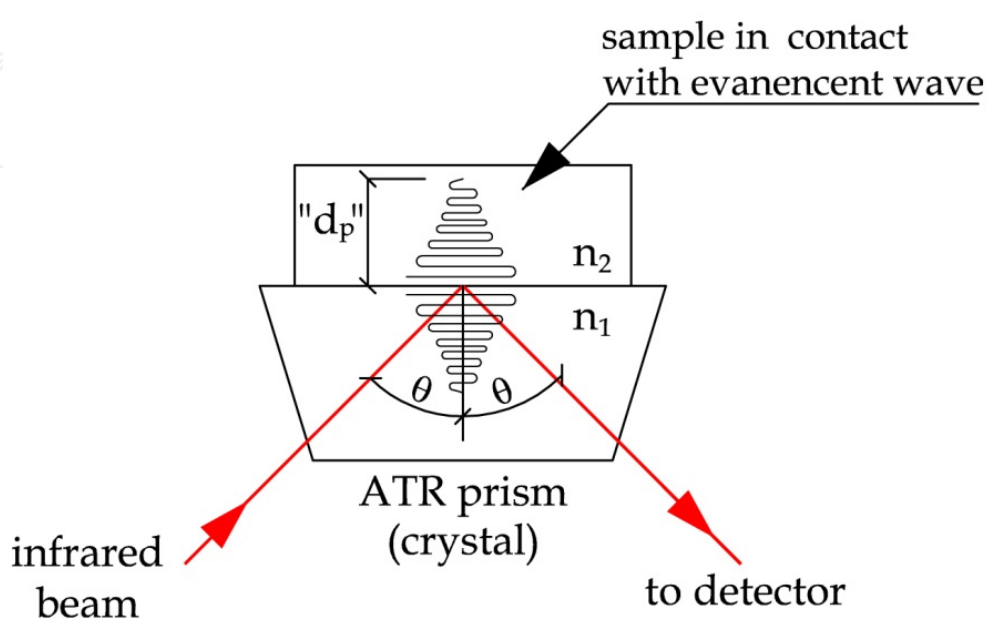


Figure 1. The schematic representation of infrared beam reflected on the crystal - sample interface in FTIR-ATR spectrometer. (on the base <http://www.sprpages.nl/SprTheory/SprTheory.htm>)

During the total internal reflection in the optically thinner medium (sample) is formed an electromagnetic wave, so-called evanescent wave that fulfills the condition of the continuity of electromagnetic field vectors at the interface of media with various wave refractive indices, n_1 and n_2 (Fornel, 2000). The IR evanescent wave has two wave vector components: parallel component to the interface of the contact between materials, under influence of which the wave propagates along surface resulting in the formation of so-called Goos-Hänchen's displacement (Goos&Hänchen, 1947), and perpendicular component, under the influence of which the wave propagates in the optically thinner medium in the direction perpendicular to the surface and exponentially disappears. The evanescent wave penetration depth, „dp”, in sample depends on the IR radiation wavelength (λ), incident angle, (θ), prism refractive index, (n_1), and sample refractive index in relation to the prism ($n_{2,1}$) and is expressed by the following equation (Dechant, 1972):

$$d_p = \frac{\lambda / n_1}{2\pi \sqrt{(\sin^2 \theta - n_{2,1}^2)}} \quad (1)$$

Along the path of IR evanescent wave the sample selectively absorbs energy to decrease the intensity of radiation. The weakened wave returns to the prism and then to an IR detector.

There the system generates an FTIR-ATR absorption spectrum characteristic of the given sample. The FTIR-ATR absorption spectrum slightly differs from that obtained by the transmission method. The differences concern the intensity and frequency of absorption peaks characteristic of chemical groups in view of the phenomenon of reflection, e.g. Goos-Hänchen's displacement. Thus it is necessary to take corrective action that can be realized automatically. The penetration depth of IR beam can be controlled within some range by selecting an appropriate prism (selection of the refractive index) and the incident angle of beam. The commonly used prisms are made of diamond, germanium, silicon and ZnSe, whose refractive indices are equal to 2.4, 4.0, 3.4 and 2.4, respectively, and the beam penetration depths: 2.03 μm , 0.67 μm , 0.84 μm and 2.03 μm , respectively, at $\nu = 1000\text{ cm}^{-1}$ (Material Thermo Scientific Smart ITR). During testing sub-micrometric coating, the beam penetrates a higher depth than the coating depth and also passes to the substrate, on which the coating is deposited. The absorption spectrum then constitutes a superposition of the spectrum of coating material and substrate. In such cases, qualitative analysis is carried out, which takes into account the absorption spectrum of substrate.

The basic requirement for ATR technique is to place a sample in direct contact with the prism as only such conditions allow the IR evanescent wave to penetrate the sample surface layer. Moreover, there should be a considerable difference between the refractive indices of prism and sample to get the phenomenon of internal reflection occurred.

The drawback of ATR technique is a relatively low sensitivity and susceptibility to the effect of environmental conditions, which makes it necessary to calibrate the IR spectrum. Modern spectrometers have an option of automatic computer-aided spectrum correction. ATR technique has numerous advantages. FTIR-ATR shows the features of a routine method for testing the chemical and physical surface structure of materials such as polymers, films and membranes provided that these well adhere to the crystal. Tests with a modern instrumentation are characterized by a high reproducibility (better than 0.1%) (Urbanczyk, 1988). FTIR-ATR makes it possible to record spectra within a wider frequency range of IR radiation than transmission spectroscopy owing to the lack of limitations caused by the absorption of cuvette windows. An important advantage of this technique is the possibility of recording spectra *in situ* and *in vivo*, e.g. in testing biological objects and using it as a diagnostic tool in medicine.

In this work, the FTIR-ATR technique was used to analyze the surfaces of modified polymers and to test the polymeric layers deposited on substrates.

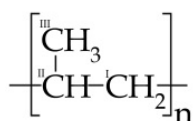
3. Examples of testing polymers by FTIR-ATR

Tests were carried out by means of a single-beam FTIR-Nicolet 6700 spectrometer from Thermo Scientific, equipped with a diamond crystal (refractive index $n = 2.4$). IR spectra were recorded as changes in absorption as a function of wave number ranging from 600 cm^{-1} to 4000 cm^{-1} . A DTGS KBR detector was used. The following measurement technical conditions were used: measurement recording accuracy - 4 cm^{-1} , mirror travel rate - 0.31 cm^{-1}/s , aperture - 50, minimal scans number - 32.

3.1. Assessment of the modification effects on the surface of polypropylene (PP) films and nonwovens

Polypropylene products are commonly used in commodity production due to their special chemical properties (resistance to organic and inorganic solvent, hydrophobic properties) and physical characteristics (lightness, mechanical strength, electro- and thermal insulating capabilities). In the methods of making products such as composites with the use of PP films or fibers as reinforcing components, a serious drawback of these materials is their low free surface energy, which results in weak molecular interactions between the composite components. The free energy of PP material surface can be increased by creating new functional chemical groups in the material surface layer. This task has been fulfilled by exploring different approaches such as chemical, electrochemical, physical and plasma methods. The effectiveness of the methods used was assessed by means of the FTIR-ATR technique.

The molecular structure of polypropylene is the same in the use of films and nonwovens products:



In one unit of PP molecule chain are three atoms of carbon, in the form of different groups: $-\text{CH}_2-$; $-\text{CH}-$; and $-\text{CH}_3$. Each of them is correlated in IR spectra with the suitable absorption peak by definite wavenumber values (Figure 2). The proper characteristic, concerning this correlation is presented in Table 1.

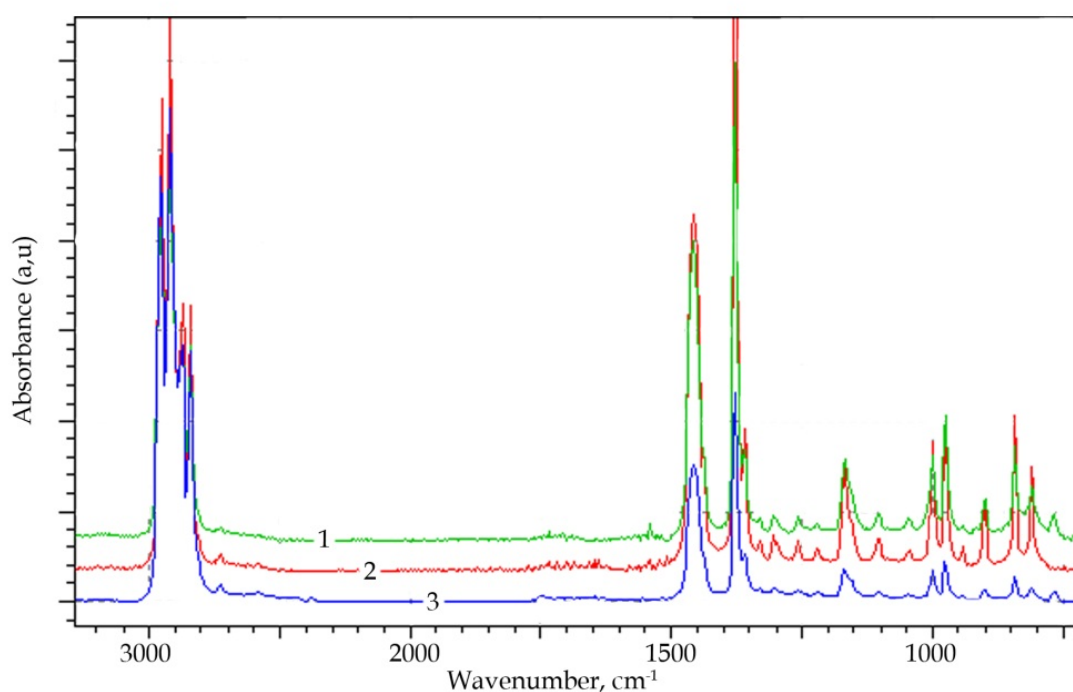


Figure 2. FTIR-ATR spectra of commercial PP films : non-oriented, non-crystalline PP Cast (Sample 1); bidirectionally oriented, crystalline PP AG (Sample 2) and PP nonwoven (Sample 3).

IR spectra of PP for film and nonwoven can differ between themselves only in defiles (the differences in shape and intensity of peaks), because in ATR technique, the contact of the samples with measure crystal, can be different for different structure of samples (film – continuous structure, nonwoven – porous structure). The explanation of this problems shown as an example at Figure 3.

Wave number, cm ⁻¹	Absorbing group and type of vibration
2916	va (CH ₂)
2959	va (CH ₃)
2881	vs (CH ₃)
2841	vs (CH ₂)
1460	δa (CH ₃)
1376	δs (CH ₃)
1357,	γw (CH ₂ - CH)
1328	γw (CH ₂ - CH)
1302, 1224, 941	Carbon lattice pulsation
1170, 1153	γw (CH ₃), δ (CH ₂), δ (CH)
975, 899,	γr (CH ₃), vr (CH ₂), vr (CH)
841, 810	γr (CH ₂), vr (CH), vr (CH ₃)
765	γw (CH ₂)

*) vs - stretching vibration symmetrical and va -asymmetrical, δs - deformation vibration symmetrical and δa – asymmetrical, γw - wagging vibration, γr – rocking vibration

Table 1. IR absorption bands of Polypropylene (Urbanczyk, 1988; Rau, 1963)

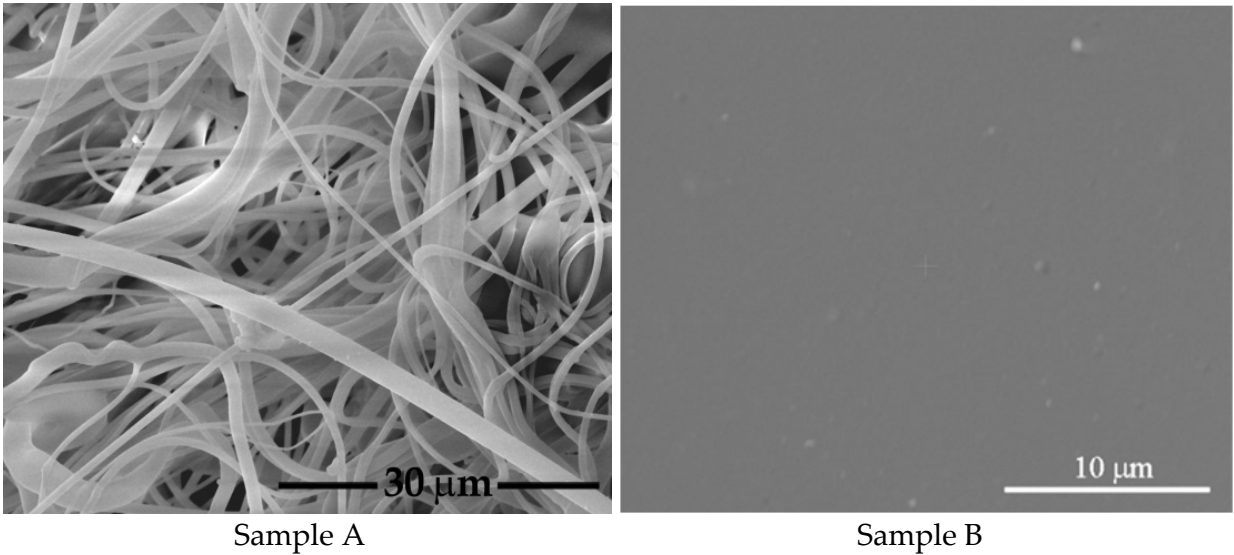


Figure 3. SEM images of type surface structure : PP nonwoven fabrics (Sample A), PP Cast film (Sample B)

3.1.1. Effects of PP film modification

Commercial PP, non-oriented, non-crystalline (PP Cast) and bidirectionally oriented, crystalline (PP-AG) films were modified in media of strong oxidants, such as: 3M nitric acid, 30% hydrogen peroxide, and a saturated solution of potassium dichromate in 70% sulfuric acid ($K_2Cr_2O_7 + H_2SO_4$). The electrochemical oxidation was carried out with the use of anolyte ($AgNO_3$ solution in nitric acid) and catholyte (nitric acid solution). The physical modification of PP was performed by means of a Xenotest apparatus, irradiating PP film with UV radiation according to EN ISO 105-B02:2006 (Urbaniak-Domagala, 2011). Plasma modification processes were carried out with the use of RF glow discharge of special gases under decreased pressure (Urbaniak-Domagala, 2011). Figures 4, 5 show the FTIR-ATR spectrograms of the PP film surfaces after oxidation compared with unmodified PP films. In the FTIR-ATR spectrograms of the PP film surface layer, one can observe absorption bands that are consistent with those of isotactic PP obtained by the authors mentioned in Table 1.

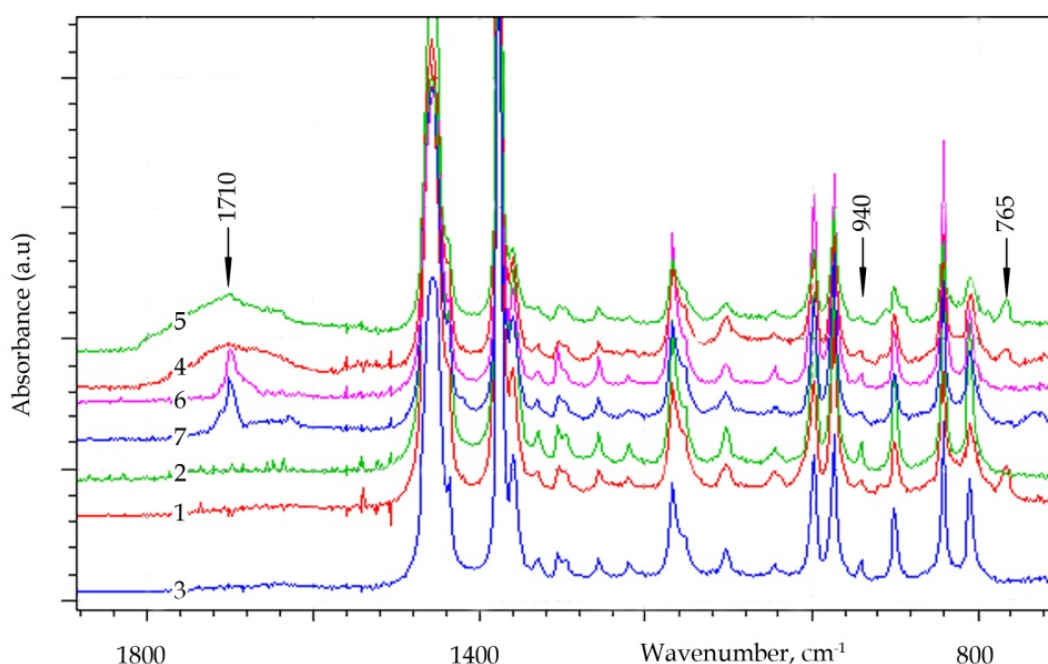


Figure 4. FTIR-ATR spectra of commercial PP films before and after oxidation. 1- PP Cast untreated, 2 - PP AG untreated. Samples 3÷7 PP Cast modified: by using electrochemical method, current intensity: 100 mA/cm², 30 min. (Sample 3), UV treatment (Xenotest) 170h (Sample 4), $K_2Cr_2O_7 + H_2SO_4$ solution at 70°C, 3 min. (Sample 5), 3M nitric acid at 20°C, 24 h (Sample 6), 30% hydrogen peroxide at 20°C, 1 h (Sample 7).

Moreover, the spectrograms of PP surface layer oxidized by chemical methods show a new absorption band within the wave number range of (1730 – 1680) cm⁻¹ that corresponds to a carbonyl group formed in a oxidizing medium as a results of the nucleophilic substitution of PP, mainly at the tertiary carbon atom: $-CH_2 - C < R H - CH_2 -$ (the substitution susceptibility of the tertiary, secondary and primary carbon is 7000: 1100: 1, respectively) (Wiberg & Eisenthal, 1964). The absorption maximum of carbonyl group is slightly shifted depending on the type of oxidizing medium.

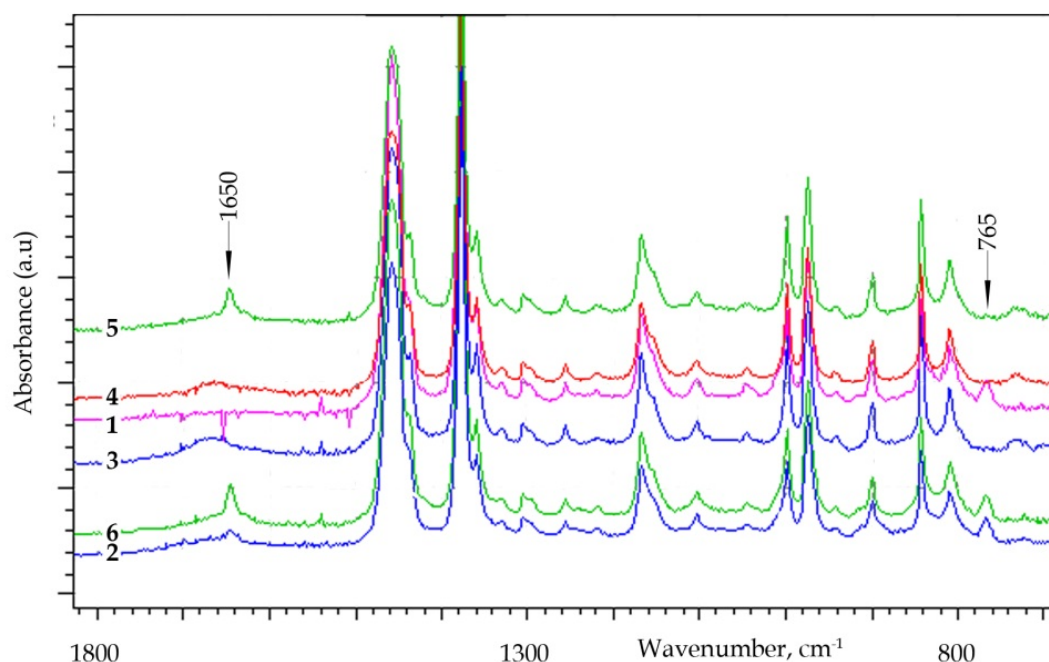


Figure 5. FTIR-ATR spectra of PP Cast films before and after plasma oxidation. Sample 1 - PP untreated, Sample 2. PP treated Ar plasma $p=0.05\text{Tr}$, power 300W, $t=10$ min., Sample 3 - PP treated Acetic Acid Vapour plasma: $p=0.05\text{Tr}$ 300W, $t=10$ min., Sample 4 - PP treated Water Vapour plasma: $p=0.05\text{Tr}$; 300W, 10min, Sample 5 - PP treated Air plasma: $p=0.05\text{Tr}$; 300W. $t=5$ min., Sample 6 - PP treated Air plasma: $p=0.05\text{Tr}$; 300W, $t=10$ min.

The absorption band of carbonyl group in the PP spectrum is broad, which can indicate the presence of carbonyl group in various products of oxidation, such as aldehydes and ketones (Carlsson & Wiles, 1969): 1700 cm^{-1} absorption ($>\text{C} = \text{CH}-\text{CO}-\text{OH}$), 1710 cm^{-1} absorption ($-\text{CO}-\text{OH}$), 1715 cm^{-1} absorption ($>\text{C} = \text{O}$), 1718 cm^{-1} absorption ($-\text{CCH}_3-\text{CH}_2-\text{CO}-\text{CH}_2-\text{CH}_3$), 1726 cm^{-1} absorption ($-\text{CCH}_3-\text{CH}_2-\text{CO}-\text{CH}_3$).

The spectrogram of oriented and crystalline PP AG shows no absorption band of carbonyl group despite the fact that the determination of the contact angle of PP surface wetted with polar liquids indicated an increase in free energy (Urbaniak-Domagala, 2011). One may assume that the active center concentration is too low for the FTIR-ATR method. The spectrogram of PP oxidized by chemical methods also indicates changes in two bands at 940 cm^{-1} and 765 cm^{-1} (Figure 4).

The first one indicates the skeleton vibration of mer links with a relative phase shift of $2/3$, being mainly characteristic of the crystalline phase (Rau, 1963). In the case of PP AG film, this band is intensive, while in PP Cast, it decreases and after oxidation is absent, which can indicate that the PP surface layer becomes amorphous due to the oxidation process. The absorption band at 765 cm^{-1} is characteristic of non-crystalline PP, caused by the deformation vibration of methylene group ($-\text{CH}_2-$) (Kazicina.&Kupletska, 1976). This band is absent in the spectrogram of PP after oxidation, which can be due to the decrease in the number of methylene groups caused by the degradation of the polymer in its surface layer. This band is also absent in crystalline PP due to spherical limitations caused by a long-range order.

FTIR-ATR absorption spectra (Figure 5) present the chemical effects of plasma on PP film. The gases used in this process included: argon and air and vapors of acetic acid and water under optimal conditions of plasma treatment (time and power applied to the system).

The spectra of the plasma-treated PP film show a new absorption band within the range of wave numbers of $(1640 \div 1660) \text{ cm}^{-1}$, which can indicate the formation of carbonyl group, $>\text{C}=\text{O}$, (valence vibration) as well as $-\text{C}=\text{C}-$ groups (valence vibration) (Kazicina&Kupletska, 1976). The prolongation of plasma treatment and increase in power leads to the increase in the IR radiation intensity of the band of new functional groups. The position of IR absorption maximum slightly shifts depending on the plasma composition. These new active centers can be regarded as a result of PP surface oxidation with plasma particles. In the case of Ar plasma, the effect of surface functionalization can result from the so-called post-treatment process (Guruvenket et al, 2004). The results obtained indicate a particular activity of air plasma as oxidizing medium for polypropylene.

3.1.2. Effects of PP nonwovens modification

FTIR-ATR was also used to assess the effects of plasma-treated PP nonwovens. PP melt-blown nonwovens (surface weight: 80 g/m^2 , average thickness: 1.5 mm) made of PP fibers with an average thickness of $2.12 \text{ }\mu\text{m}$ were modified by means of synthetic air plasma to form chemically active centers on the PP fiber surface.

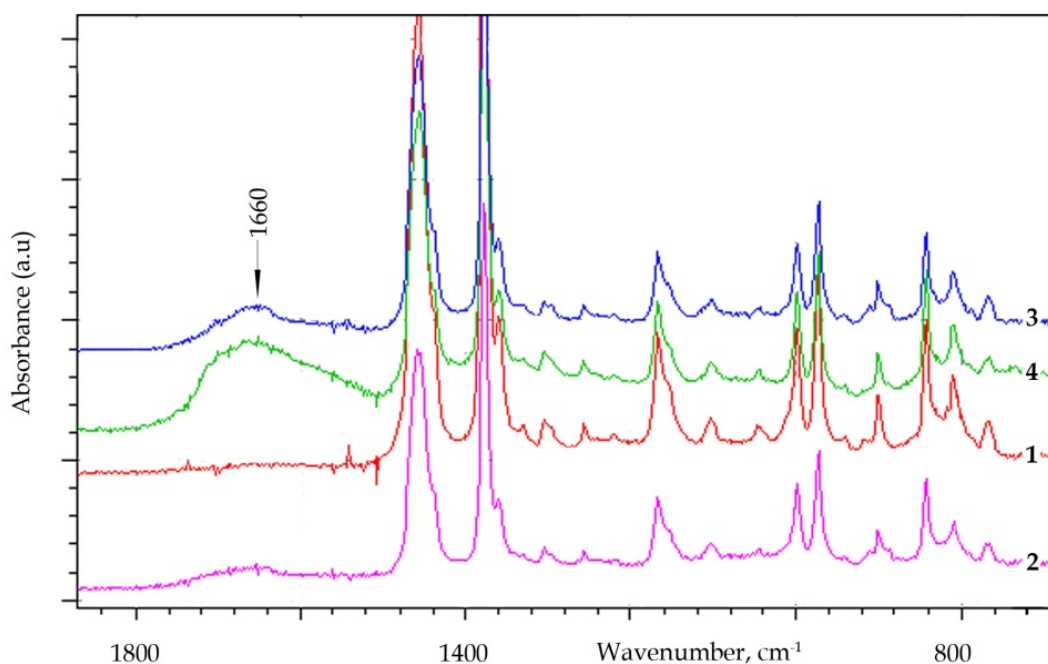


Figure 6. ATR IR spectra of PP nonwovens untreated (Sample 1) and air plasma treated, pressure 0.1Tr : Sample 2 - power 50W, time 5min. Sample 3- power 100W, time 5min., Sample 4 - power 100W, time 10min

The FTIR-ATR spectrogram of the air plasma-treated PP nonwoven shows two broad bands at 1660 cm^{-1} and 3320 cm^{-1} that indicate the formation of carbonyl group $>\text{C}=\text{O}$ and hydroxyl

group – OH (Kazicina.&Kupletska, 1976). One may assume that the air plasma oxidizes the fiber surface with the aid of reactive oxygen, peroxide and nitrogen groups that together with electrons react with the PP fiber surface causing not only the etching of surface layer but also its functionalization.

3.2. Polymeric coatings deposited on PP nonwovens

Nonwovens constitute a specific substrate for depositing thin polymeric layers. The nonwoven surface is developed to an extent dependent on the diameter of elementary fibers, density of their distribution and the formation technique used. The melt-blown PP nonwovens (see section 3.1.2.) were coated with thin layers of plasma polymers in a methane plasma and in hexamethyldisiloxane (HMDSO: $O-(Si-(CH_3)_2)$ vapors [Urbaniak-Domagala et al, 2010). As a result of this process, the nonwoven surface was covered with a plasma polymer layer with a thickness of about 100 nm. SEM photographs (Figure 7) indicate that the coating obtained shows a character of a continuous film fitted to the uneven nonwoven surface covering only the elementary fibers in the near-surface nonwoven layer.

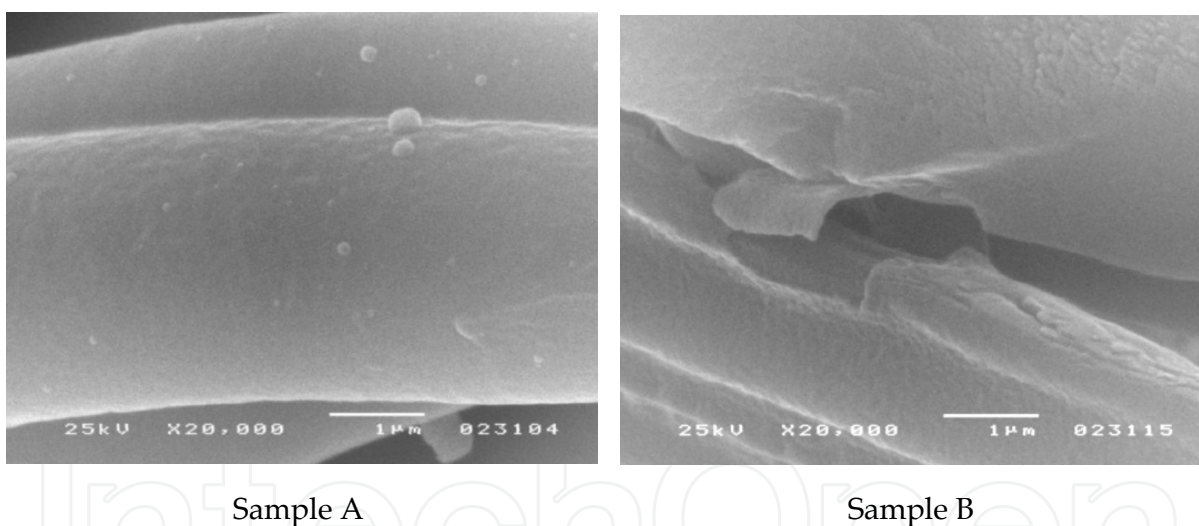


Figure 7. SEM images of PP fibers at nonwoven fabrics, treated methane plasma (Sample A), treated HMDSO plasma (Sample B). Plasma process time 10 min., pressure 0.05Tr, power 100W.

The FTIR-ATR spectrogram of the methane plasma-modified nonwoven surface (Figure 8) indicates that the layer chemical structure has a character of a hydrocarbon polymer as the PP substrate. The broad band with a maximal absorption at 1650 cm^{-1} can be assumed as a post-treatment effect (Guruvenket et al, 2004).

The IR-ATR spectrogram of the HMDSO plasma-modified nonwoven indicates that the layer deposited has a chemical structure of a $SiOC:H$ polymer (Creatore et al., 2002) and contains intensive absorption bands at 800 cm^{-1} , 841 cm^{-1} , 1040 cm^{-1} and 1256 cm^{-1} (Table 2) being characteristic of chemical groups containing silicon (Borvon et al., 2002).

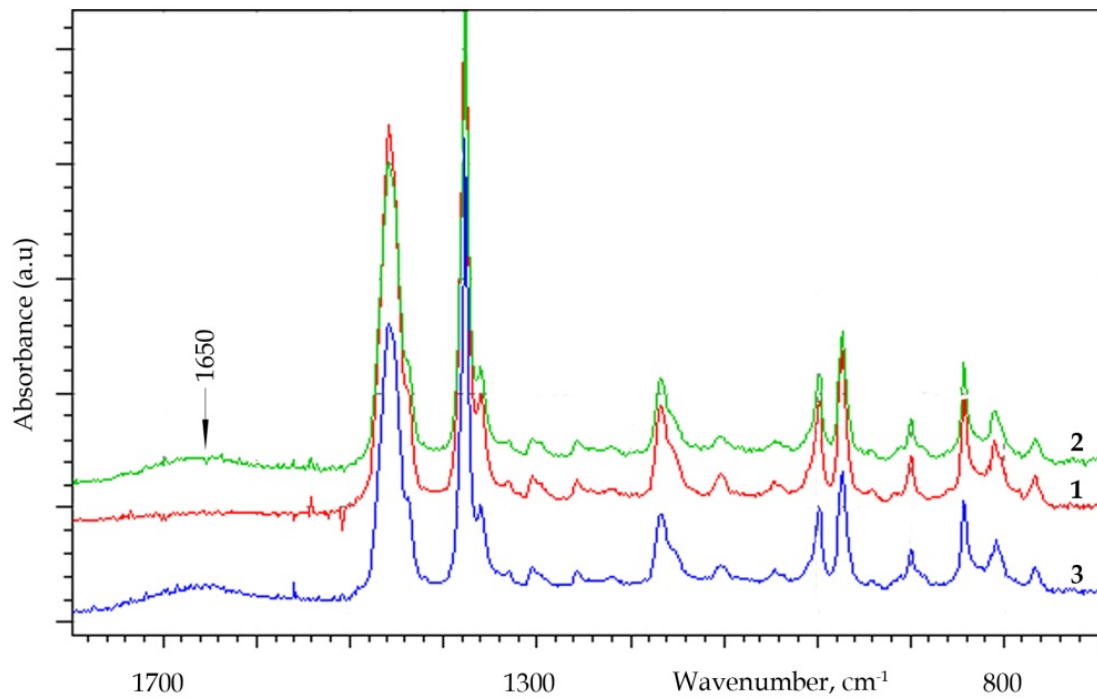


Figure 8. FTIR-ATR spectra of PP nonwoves. Sample 1- untreated, Sample 2 - methane plasma treated: power 25W, pressure 0.05Tr, Sample 3 - methane plasma treated: power 100W, pressure 0.05Tr.

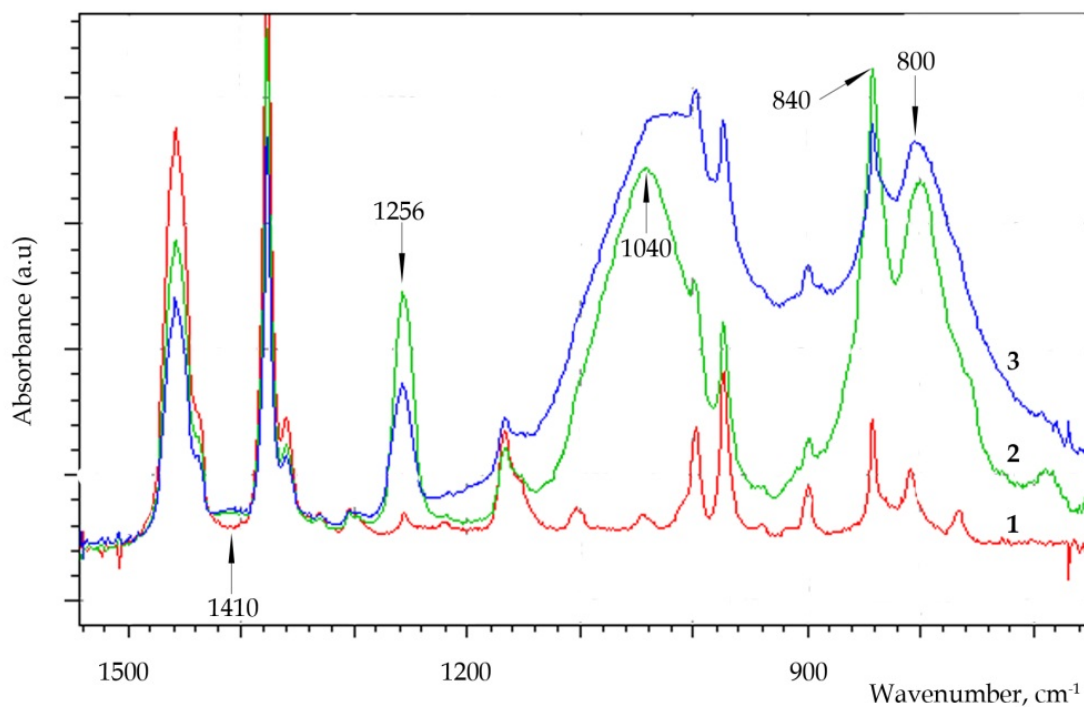


Figure 9. FTIR-ATR spectra of PP nonwoves. Sample 1 - untreated, Sample 2 - HMDSO plasma treated: power 25W, pressure 0.1Tr, Sample 3 - HMDSO plasma treated: power 100W, pressure 0.1Tr.

The assessment of the surface of samples was carried out in the diamond-sample system, in which the IR radiation beam penetrates the layer 2 μm in depth within the spectrum range discussed. The penetration depth of the IR radiation beam considerably exceeds the thickness of the p-HMDSO layer ($\sim 0.1 \mu\text{m}$), hence characteristic bands of PP substrate also occur in the absorption spectrum.

Wave number, cm^{-1}	Absorbing group and type of vibration
1410	vs (CH_3), va in $\text{Si}(\text{CH}_3)_x$
1256	νCH_x , $\delta (\text{CH}_3)$ in $\text{Si}(\text{CH}_3)_x$
1040	va (Si-O-Si)
840	$\nu \text{Si}(\text{CH}_3)_x$, $\gamma_r (\text{CH}_3)$ in $\text{Si}(\text{CH}_3)_3$
800	$\nu (\text{Si-O-Si})$, $\gamma_r (\text{CH}_3)$ in $\text{Si}(\text{CH}_3)_2$

*) vs - stretching vibration symmetrical and va -asymmetrical, δ - deformation vibration, γ_r – rocking vibration

Table 2. IR absorption bands of p-HMDSO plasma layers (Aumaille et al., 2002; Agres et al., 1996)

3.3. Testing polymeric coatings containing polypyrroles

Polypyrrole is a polymer widely used in commodity production owing to its high thermal stability, resistance to atmospheric conditions and biocompatibility. Its important advantages include electric properties. Using appropriate synthesis conditions, one can obtain electro-conductive, semi-conductive or electro-insulating polypyrroles. In view of processing difficulties, polypyrroles are produced directly on material surfaces in the form of coatings by “*in situ*” chemical, electrochemical or plasma methods. Moreover, polypyrroles are used to make composites as reinforcing and functional materials. In this work, the FTIR-ATR technique was used to monitor the results of polypyrrole synthesis by chemical and plasma methods and the preparation of pyrrole - containing composites.

3.3.1. Formation of latex-pyrrole composites

Polypyrrole (PPy) was used to make an electro-conductive composite as a backing of textile floor coverings (TFC). The TFC piles are fixed in a standard procedure with the use of dressing containing a synthetic rubber and vinyl-acrylic thickeners. The standard latex coating shows electro-insulating properties and impedes the leakage of static charges generated on the TFC pile during exploitation. A functional dressing was prepared to facilitate the leakage of static charges from TFC. PPy microspheres in the form of an aqueous dispersion, prepared by polymerization in an aqueous solution of ferric chloride, were added to an aqueous dispersion of butadiene-styrene-carboxyl copolymer (LBSK 4148) (Urbaniak-Domagala, 2005).

The dispersion components were intermixed by means of an ultrasonic stirrer and the resultant dressing was applied on the bottom of a raw TFC followed by the cross-linking process. The volume resistance tests of the latex-PPy coat confirmed its antistatic properties already with a 3% (by wt.) content of PPy in relation to the dry copolymer mass in the dressing.

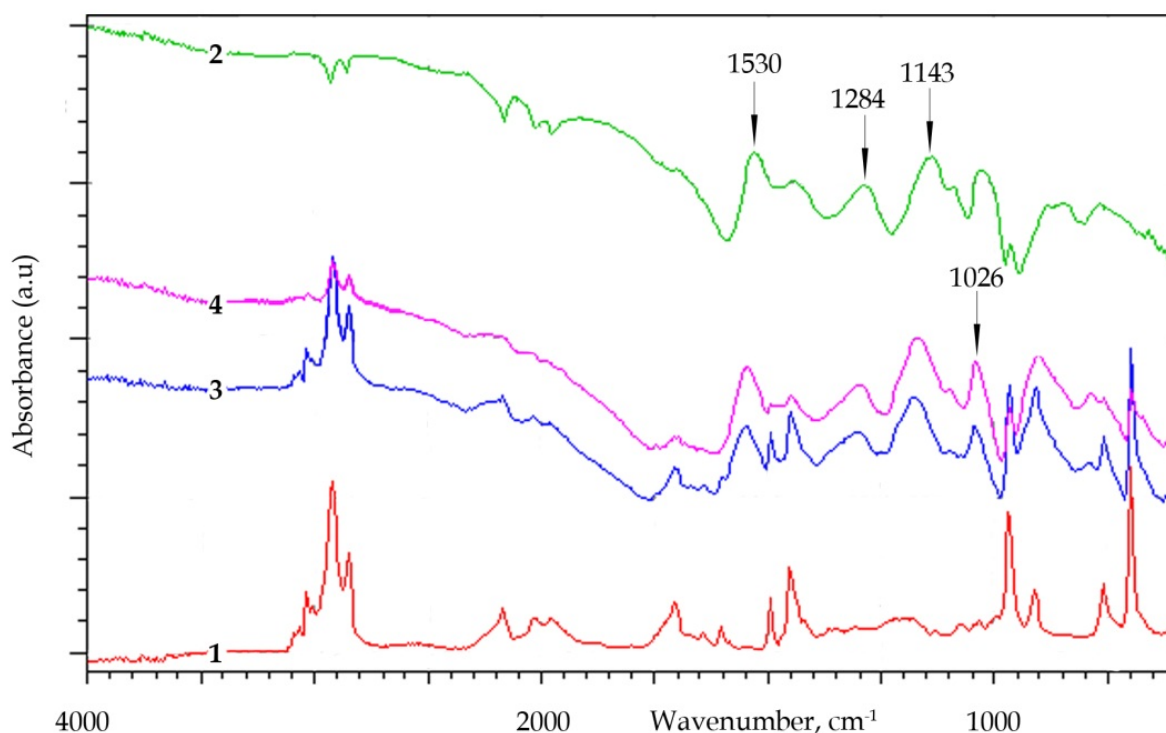


Figure 10. FTIR-ATR spectra pure latex LBSK 4148 (Sample 1), chemically synthesized polypyrrole (Sample 2), latex/PPy composite containing 2 wt% PPy (Sample 3), 3 wt% PPy (Sample 4)

The percolation of the coating electric conduction has a continuous character and the percolation threshold is relatively low. The coating formation on the TFC bottom was controlled by means of FTIR-ATR spectrometry

Changes in the IR radiation absorbance of the coatings were observed within the range from 600 cm^{-1} to 1700 cm^{-1} . Figure 10 shows the absorption spectra of pure LBSK 4148 latex (Sample 1), pure PPy (Sample 2) and two samples of LBSK-PPy composite containing 2% by wt. of PPy and 3% by wt. of PPy, respectively. The locations of absorption bands of LBSK, PPy and LBSK-PPy composite containing 3% by wt. of PPy are listed in Table 3.

The spectrum of LBSK indicates the presence of three types of butadiene isomeric units (1,4-cis, 1,4-trans and 1,2-vinyl), styrene PS and carboxyl (Molenda et al.,1998; Munteanu & Vasile, 2005) have carried out fundamental research of FT-IR spectra of butadiene-styrene copolymers with various structural arrangements (block and linear copolymers, block copolymers of the star type and statistic copolymers). The type of spectrum found for LBSK 4148 latex indicates the architecture of statistic copolymer. The spectrogram of the microspheres of chemically synthesized PPy (powder) indicates PPy rings in the polymer structure and groups connected with the ring being consistent with the results of authors (Eisazadeh, 2007; Cruz 1999; Ji-Ye Jin et al.,1991).

LBSK 4148		Chemically synthesized polypyrrole (PPy)		LBSK 4148/PPy
λ , cm^{-1}	Absorbing group and type of vibration	λ , cm^{-1}	Absorbing group and type of vibration	λ , cm^{-1}
-		659	$\delta(\text{C-N})$ out of plane ring	659
699, 758	$\delta(\text{CH})$ out of plane in the aromatic ring, PS units	-		699, 758
-		770	$\delta(\text{C-H})$ out of plane pyrrole ring, $\gamma(\text{NH}_2)$, $\nu(\text{C-N-C})$, $\delta(\text{C-N-C})$	790
911	$\delta(\text{CH})$ out of plane near the double bond of the vinyl-PB units	-		911
966	$\delta(\text{CH})$ out of plane near the double bond in trans-PB units	-		966
-		1026	$\delta(\text{N-H})$, $\delta(\text{C-H})$, pyrrole rings pulsation $\nu(\text{C-N})$ secondary amines	1040
-		1143	$\delta(\text{C-H})$	1170
-		1284	$\nu(\text{C-N})$ secondary amines, $\nu(\text{C-N})$ in pyrrole ring	1300
1451	$\delta(\text{CH})$ in cis-PB, trans-PB, vinyl-PB units	-		1451
1492	$\nu(\text{C=C})$ in aromatic ring PS units	-		-
-		1530	$\nu(\text{C=C})$ in pyrrole ring $\nu(\text{C=N})$ in pyrrole ring, pyrrole ring pulsation	1548
1600	$\nu(\text{C=C})$ in aromatic ring PS units	-		-
1638	$\nu(\text{C=C})$ PS units $\nu(\text{C=C})$ in vinyl-PB	-		-
1700	$\nu(\text{C=O})$	-		1700

Table 3. The FTIR absorption bands for latex LBSK 4148, chemically synthesized polypyrrole and LBSK 4148/PPy composite containing 3 wag.% PPy (Kazicina.&Kupletska, 1976, Molenda et al.,1998; Munteanu & Vasile, 2005; Bieliński et al., 2009; Eisazadeh, 2007; Cruz 1999; Ji-Ye Jin et al.,1991)

The spectrograms of LBSK-PPy composite samples indicate the superposition of characteristic bands of the composite components: PPy and latex. As the PPy content in the composite increases, one can observe an increase in the intensity of characteristic peaks of PPy, but the quantitative analysis of the composite is difficult to perform due to great differences in the absorbance of the composite components (latex is white, PPy is black). The band maxima shown by the PPy powder are delocalized in the spectrum of latex-PPy composite. The band indicating the pyrrole ring vibration at 1530cm^{-1} is shifted towards a higher frequency to 1548cm^{-1} . The bands of groups linked up to the pyrrole ring are also shifted: for CH deformation vibration (out of plane quinol PPy) from 1026cm^{-1} to 1040cm^{-1} , for C-N deformation vibration from 1143cm^{-1} to 1170cm^{-1} , and for the valence vibration of CN in pyrrole ring from 1284cm^{-1} to 1300cm^{-1} . The shifts of bands can be due to the scattering of IR radiation in the structure of PPy powder, but they can also indicate the occurrence of PPy - latex intermolecular

interactions, with which the oscillatory excitation of chemical groups in PPy requires a higher energy.

3.3.2. Synthesis of polypyrroles

Below are presented examples of using the FTIR-ATR technique to assess the progress in the synthesis of PPy. The polymerization of pyrrole was carried out by chemical and plasma methods. Thin layers of PPy were formed on the surface of a PP film by the *in situ* technique.

3.3.2.1. Chemical polymerization method

Polymer layers were formed by the polymerization of pyrrole according to the redox mechanism. Two media of pyrrole oxidation were used: an aqueous solution of ferric chloride and aqueous solution of ammonium sulfate with p-toluenesulfonic acid as dopant. Based on the FTIR-ATR spectrum of the polymer, its synthesis progress and chemical structure were characterized. Figure 11 shows examples of the spectra of PPy synthesized in both media for 2h and 5 h.

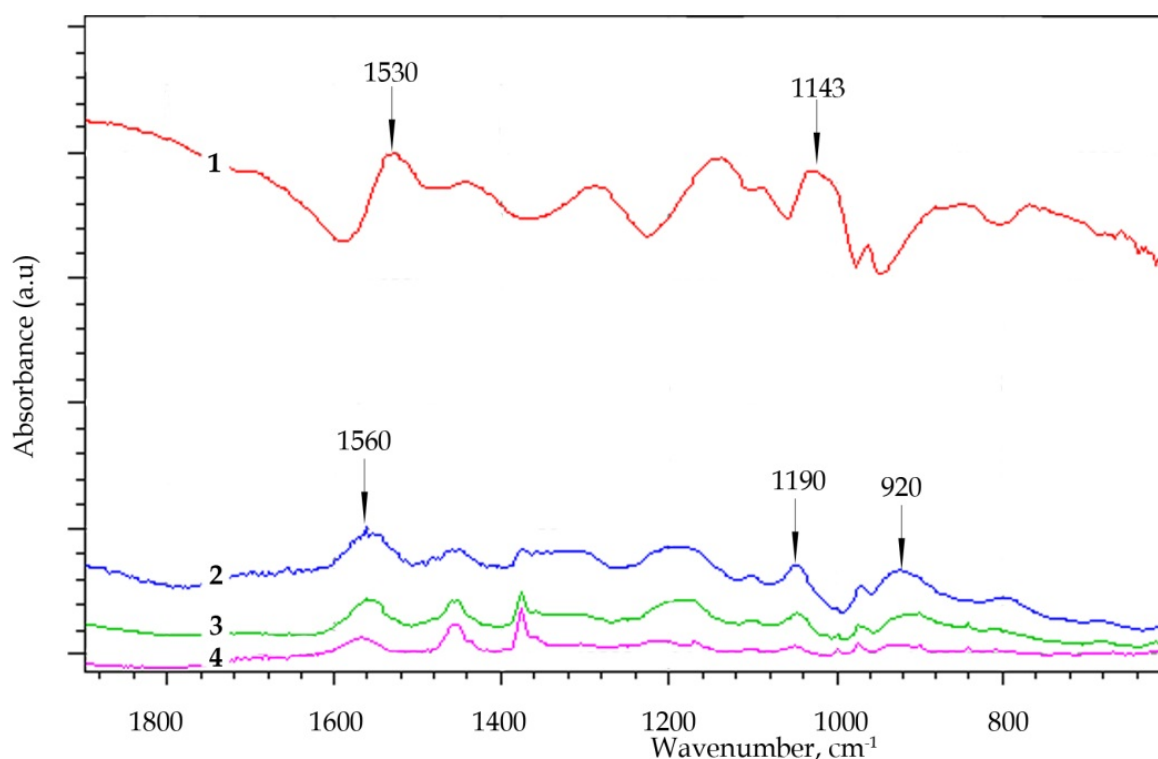


Figure 11. FTIR-ATR spectra chemically synthesized polypyrrole. Sample 1 - PPy powder (molar ratio of $\text{FeCl}_3:\text{Py}=2,3:1$) - polymerization time 5h; PPy layers on the polypropylene foil: Sample 2 – molar ratio of $\text{FeCl}_3:\text{Py}=2,3:1$, polymerization time 5h, Sample 3 – molar ratio of $\text{FeCl}_3:\text{Py}=2,3:1$, polymerization time 2h; Sample 4 – molar ratio of $(\text{NH}_4)_2\text{S}_2\text{O}_8:\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}:\text{Py}=0,2:0,25:1$, polymerization time 2h.

The spectra of PPy are recorded on the PP substrate. Owing to the low thickness of layers (0.1 - 1 μm), the spectrum additionally contains bands derived from the substrate. For comparison, the spectral characteristics of PPy synthesized in the form of powder were also presented. The absorption spectra of all the polymer samples within the wave number range of 600 cm^{-1} – 1800 cm^{-1} confirm the presence of pyrrole group (Table 3). The intensity of absorption bands increases with increasing polymerization time, which is due to the increased layer thickness. In the process of chemical synthesis, the aromatic character of pyrrole ring is maintained, which results in the formation of conjugated double bonds in the linear macromolecule chain. In the presence of admixtures intercalated to the system, the polymer is electro-conductive (incorporated dopants: Cl^- and $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$). The oxidized form of conductive PPy obtained shows a considerable absorption of IR radiation (black color of the polymer). The spectrogram of PPy synthesized with the use of two different oxidants shows no differences between the polymer chemical structures. Differences concern the progress rate of the synthesis: the higher intensity of pyrrole group bands in the polymer synthesized in the aqueous solution of ferric chloride indicates a higher polymerization rate, which is confirmed by the higher rate of layer building up.

3.3.2.2. Plasma polymerization method

Polymer synthesis performed in glow discharge of monomer vapors is a dry, ecological, energy- and material-saving process. The polymerization process is initiated by means of electrons and radicals formed in the gas discharge. The polymerization of pyrrole was carried out in a flow reactor, in glow discharge of the induction type by means of RF field 13.56 MHz (Urbaniak-Domagala, 2008). PP film substrate was centrally and axially placed on a glass carrier in the reactor. The film surface was preliminary purified by means of argon plasma followed by the deposition of the plasma polymer. The FTIR-ATR technique was used to examine the effect of process parameters, such as deposition time, pressure in the reactor and power input to the reactor, on the chemical structure of plasma polymer. In order to impart semi-conductive properties, the plasma PPy was doped after the deposition process by two methods: *in situ* in the reactor in glow discharge of the vapors of organic iodine compounds, and *ex situ* after removal from the reactor in crystalline iodine vapors.

Figure 12 shows the FTIR spectra of the plasma polymer within the range of (600-1850) cm^{-1} . The spectrogram shows the superposition of the absorption bands of plasma polymer (thickness 0.3 μm) and PP substrate. The broad band at (1500 – 1800) cm^{-1} indicates different structure of plasma PPy compared to that of PPy synthesized by the chemical method. This band points to a possible occurrence of primary and secondary amines, secondary amides (Kazicina.&Kupletska, 1976), and carbonyl groups (Ji-Ye Jin et al.,1991) in the polymer. The broad absorption band of the polymer indicates a complex absorption caused by the products of broken pyrrole rings that initiate the branching and cross-linking of the polymer followed by various substitutions. Thus the plasma spectrograms can show secondary and tertiary amines that complicate the absorption in this range. Moreover, one cannot exclude the occurrence of the band at 1710 cm^{-1} that, according to authors (Ji-Ye Jin et al.,1991) indicates the presence of carbonyl groups. This band is often observed in neutral or weakly doped forms of PPy, mainly due to their susceptibility to oxidation in air. The spectrum of

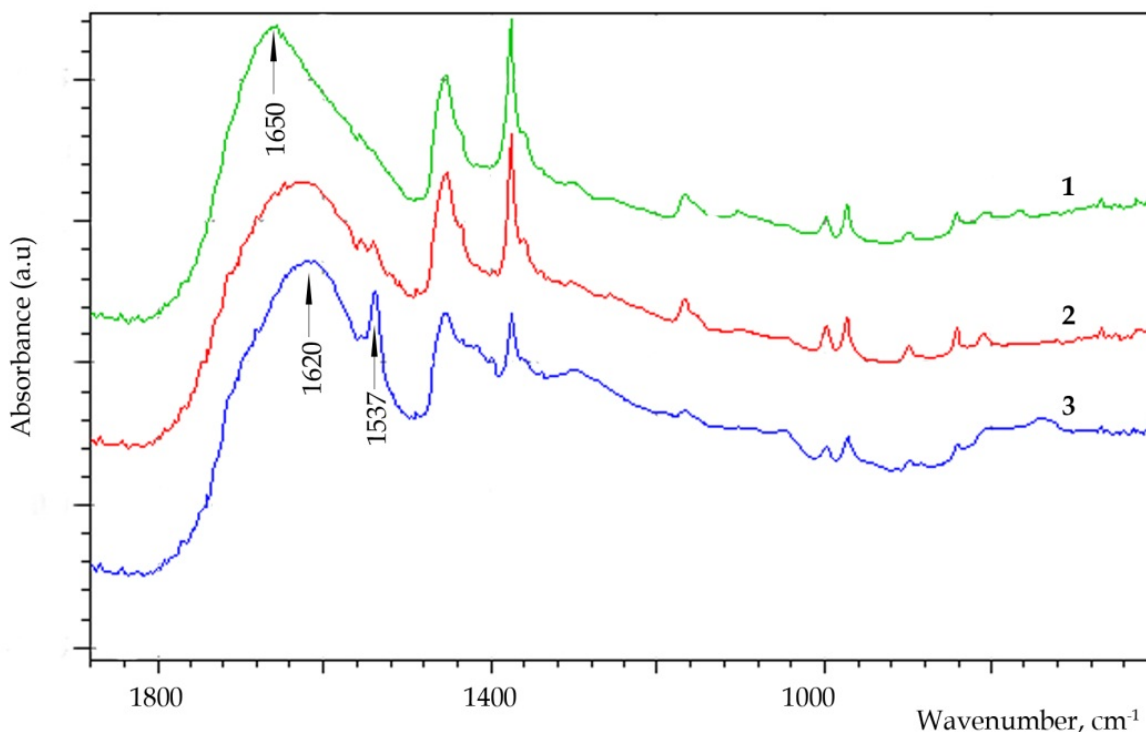


Figure 12. FTIR-ATR spectra plasma synthesized polypyrrole, pyrrole plasma: 50W, 10min, $p=0,05\text{Tr}$. Sample 1-polymer without dopand, Sample 2 - polymer dopanded at plasma CH_2J_2 : 25W, 30min., $p=0,05\text{Tr}$, Sample 3- polymer dopanded at J_2 vapours, 30min

the polymer doped with iodine vapors contains an additional band at 1537cm^{-1} , induced by the vibration of pyrrole ring, especially intensive in the polymer doped with crystalline iodine vapors. (Groenewoud et al. 2002) observed an increase in the intensity of peak 1520cm^{-1} under the influence of iodine vapors, which is connected with the formation of a new $\text{CH}_2=\text{J}$ group in the reaction of iodine with radicals present in the surface layer of the plasma polymer.

The spectrum of the plasma polymer synthesized in the presence of nitrogen as a carrier of pyrrole proves how significant is the influence exerted by the process gas on the chemical polymer structure. This is particularly evident in the polymer synthesized for a longer time (the spectrum of polymer after a 1 h process – Figure 13). The FTIR-ATR spectrum of the plasma PPy at $(500-1000)\text{cm}^{-1}$ contains numerous bands with a high absorption intensity that indicate the presence of primary amines (Kazicina.&Kupletska, 1976), and products of substituting chemical groups that were additionally formed in the polymer under the influence of the nitrogen plasma.

The absorption spectra obtained by the FTIR-ATR technique identify the chemical structure of PPy coatings and the structural changes that appear during changing the process parameters, such as pressure, power, type of doping agents, method of incorporating doping agents and the presence of process gas.

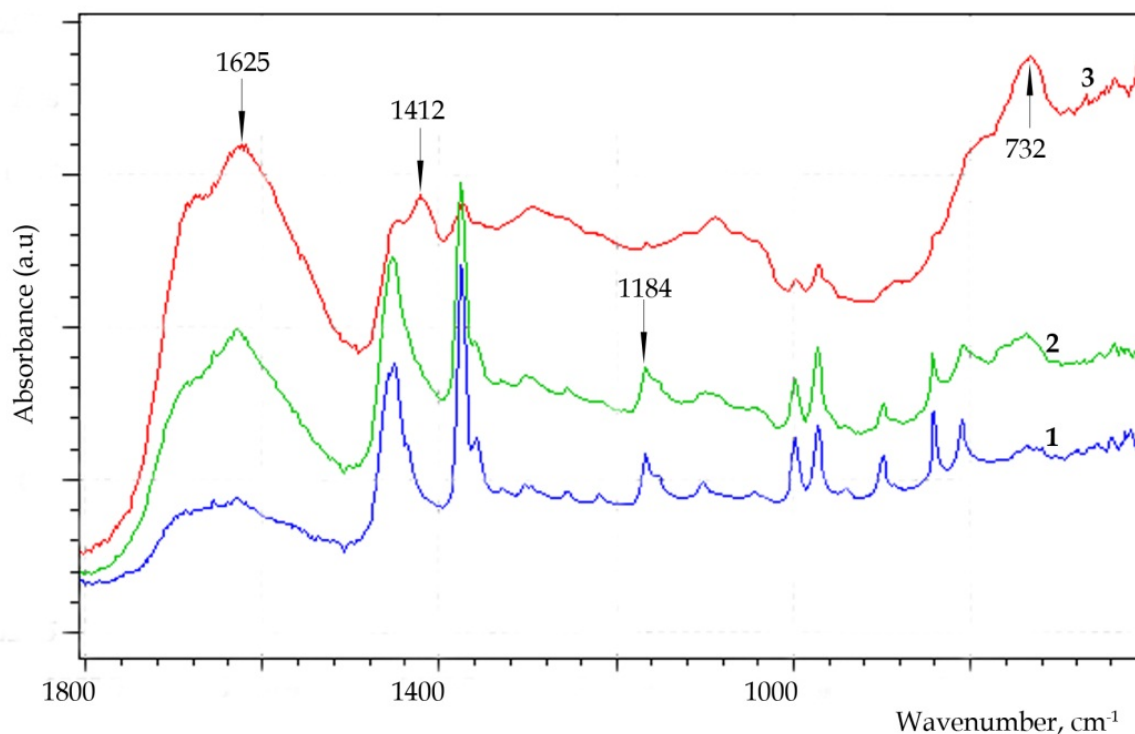


Figure 13. FTIR-ATR spectra plasma synthesized polypyrrole without dopands. Sample 1- plasma pyrrole 0,1Tr 10W, 15min, without processing gas, Sample 2- processing gas N₂ and pyrrole p= 0,15Tr. 10W, 15min. Sample 3 - processing gas N₂ and pyrrole p=0,15Tr 10W, 60min

4. Conclusions

The FTIR-ATR technique makes it possible to examine polymers in a simple, fast procedure avoiding sample destruction. It creates many opportunities for application to the chemical identification of the surface layer of polymers and thin polymeric layers. The analyses of test results of thin layers deposited on polymeric substrates can have rather qualitative character due to the penetration reach of the IR radiation beam being greater than the layer thickness. The examples of PP modification processes and deposition of coatings on polymeric substrates presented confirm that the FTIR-ATR method can be helpful in the examinations of the following:

- the chemical structure of the polymer surface layer and changes in the layer structure caused by the effects of chemical agents and electrochemical factors, UV radiation and low temperature plasma on polymers;
- the chemical structure of polymeric coatings deposited on substrates by chemical and plasma methods;
- the dependence of the chemical structure of polymeric coatings on the parameters of technological process.

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