Confocal Micro-Raman Investigation of Multilayer Systems

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Summary: The modern technologies use many multilayer composites comprising the connection of different classes substrates: ceramics, metals, polymers, etc. In this work we focused our attention on an application of confocal micro-Raman spectroscopy to study the multilayer composites. Different multilayer model systems were used to check the role of the confocal mode. The problem of the transparency of layer, and their thickness were discussed. The procedure of determination of interfaces from so-called depth profiles and their first derivatives was also presented.

Introduction

The modern technologies often use complex materials (e.g. multilayer composites) comprising the connection of different classes substrates: ceramics, metals, polymers, etc. In such aspect, the special attention is focused on the interfaces. Direct investigation of the chemical and physical properties of the usually thin interface region (sometimes even monomolecular) separating two relatively thick layers of different materials is difficult. Commonly used mechanical measurements lead to destruction of the interface and generally give only information about the strength of adhesion. Modern techniques like AFM, ESCA, XPS give information about the structure and properties of surface, but do not offer possibilities of direct, *in situ*, characterisation of interfaces. The confocal micro-Raman spectroscopy is a non-destructive, fast analytical technique, and allows characterisation of sample interior.

Micro-Raman spectroscopy was known already in the middle 70-ties [1,2]. However fast development of this technique has been observed for last years, and has been induced by use of charge coupling detectors (CCD), powerful lasers and confocal microscope systems. According to the information provided by the producers the commercial contemporary Raman micro-spectrometers attain the spatial resolution $1\times1\times1.4$ μm [3].

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In this work we check the possibilities of the application of confocal micro-Raman spectroscopy to study multilayer polymer composites. The advantages and limitations of this technique will be discussed. Only few articles describing the investigation of polymer composites or blends by confocal micro-Raman spectroscopy can be found in literature [4-11]. It means that the opinion formulated in 1994 by Meier and Kip, that micro-Raman spectroscopy had not as yet been recognised widely enough despite its high potential application is still actual [6].

Experimental

Commercial polymer films investigations were carried out for laminates made of: polytetrafluoroethylene (PTFE) (20 μm thick) and poly(ethylene therephtalate) (PET) films (12, 16, 19, 22 and 68 μm thick). Polyethylene (PE) film (80 μm thick) was prepared from powder (Aldrich Chemical) by pressed. PTFE/PE and PE/PET composites were obtained by pressure welding of adequate polymer films. The composites of poly(acrylic acid) (pAA) and (2-hydroksypropyl)cellulose (HPC) (Aldrich Chemical) were prepared by drop casting of HPC (from chloroform) on pAA film obtained before by photopolymerisation.

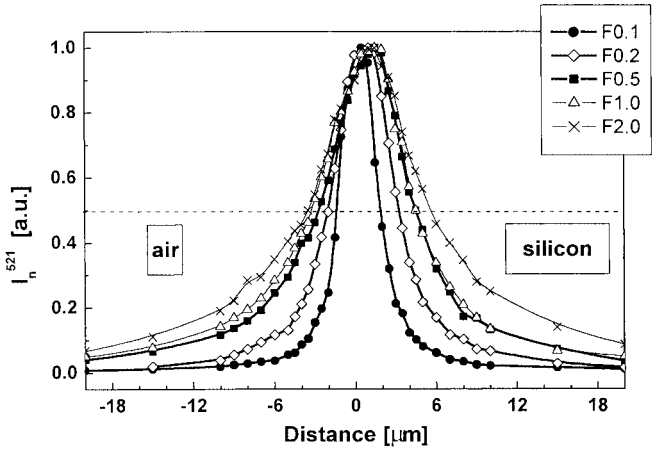
Micro-Raman investigations were performed using Raman spectrometer T-64000 Yobin-Yvon with the CCD detector and three gratings (1800 grooves/mm) monochromator. Spectrometer is equipped with Olympus microscope. Short-working-length objectives, 50× and 100×, with numerical apertures 0.75 and 0.9 respectively and five confocal pinholes (0.1, 0.2, 0.5, 1.0 and 2.0 mm) were used. As source of excitation light the LEXEL Ar (λ = 514.5 nm) laser was used.

Determination of spatial resolution

The spatial resolution in micro-Raman spectroscopy depends not only on the characteristic of the apparatus, but also on optical properties (absorption, refraction, scattering) of investigated materials [7,12]. It is therefore very important to determine the spatial resolution of given apparatus using some well-known standard. As a reference material we used the silicon wafer. In the case of non-transparent samples like silicon situation is relatively clear because the light

can penetrate the samples at the distance not longer than the wavelength (c.a. 0.5 μm). In a case of multilayer systems the most important is to determine the spatial resolution along the axis perpendicular to the surface of sample (usually marked as Z axis), and only this problem will be considered.

Figure 1 presents the normalised Raman intensity of the fundamental silicon mode (I^{521}) as a function of the distance from the sample surface for different confocal diaphragms for the following parameters: excitation light wavelength 514.5 nm, power laser 200 mW, objective 100×. Distance is referred to the sample surface; negative values correspond to the air, positive, to the interior of the sample. The intensities of the I^{521} lines were normalised to the maximum value, which in a case of (non-transparent) silicon wafer was obtained for distance equal 0. The half width of obtained depth profiles (σ) can be used for a confocal system and simultaneously for spatial resolution evaluation [7,12] – see Figure 1. The best spatial resolution (σ = 3.0 ± 0.1 μm) obtained for the smallest confocal diaphragm (0.1 mm) is comparable to the resolution determined by other authors [7,8,10] in similar conditions.



Confocal diaphragm diameter [mm]	Spatial resolution σ [μm]
0.1	3.0 ± 0.1
0.2	5.1 ± 0.1
0.5	7.2 ± 0.2
1.0	7.7 ± 0.2
2.0	8.9 ± 0.2

Figure 1. Depth profiles of the silicon wafer obtained for fundamental silicon mode (521 cm^{-1}), for different confocal diaphragms. Negative values of distance correspond to the air, positive to the bulk of the sample.

Determination of the polymer film/air interfaces

Absorption and scattering of the excitation and scattered light can be a source of errors in depth profiles method applied to transparent layers. To demonstrate that five freestanding PET films with different thickness were used as model systems. The normalised Raman intensities of the PET characteristic peak 1610 cm^{-1} (I^{1610}) (vibration of the aromatic rings) as a function of distance from the sample surface are shown in Figure 2. Increase of the thickness of the film induces broadening, and shift of the depth profile, as expected. Contrary to the non-transparent materials (like silicon), maximum of the depth profile does not correspond to the sample surface. The half-width of the depth profiles is lower than the sample thickness. It means that neither the position of maximum, nor the broadness of the depth profiles can be used for determination of the interfaces of transparent films. Everall [13] presented depth profiles of similar asymmetric shape obtained for various polymer films. He has assigned this effect to different refractive indexes of the polymers and of air. To reduce this difference Everall has proposed to use immersion.

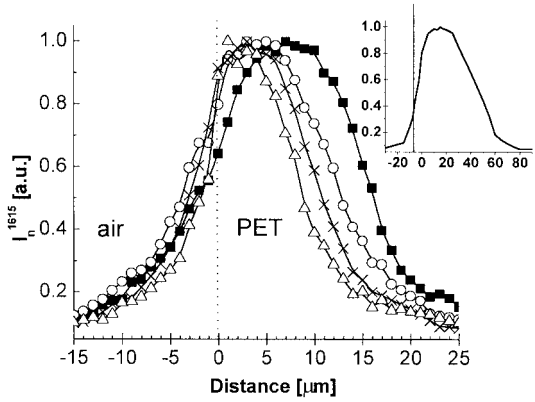


Figure 2. Depth profiles obtained for 1610 cm^{-1} band for PET freestanding films with different thickness: 12 μm - triangles, 16 μm - crosses, 19 μm - circles, 21 μm – squares, 68 μm - is presented in inset. Confocal diaphragm 0.1 mm.

We have found that the positions of the film surface correspond to some characteristic points on the first derivative of the depth profile curve, as illustrated in Figure 3. The maximum of the first derivative of the depth profile appears at the position of the front surface of the film. Position of the bottom surface can be determined as a point, at which the first derivative reaches constant values. It allows estimate the film thickness without the above described immersion procedure with quite good accuracy.

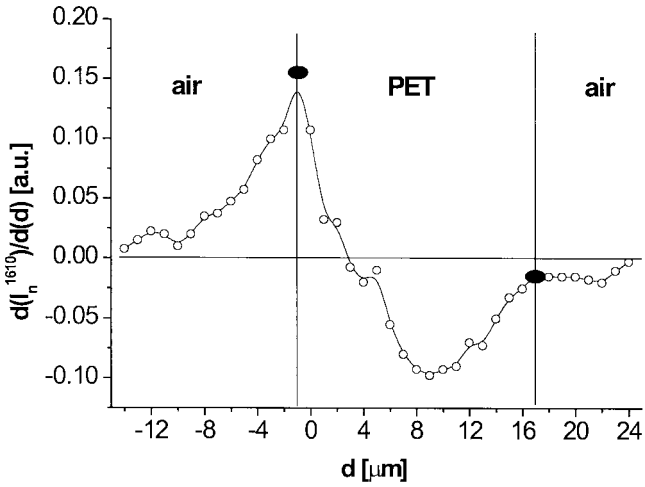


Figure 3. First derivative of depth profile (presented in Figure 2) for PET film with 16 μm of thickness.

Support effect

In order to evaluate an influence of the non-transparent support on the depth profile, the PET film 16 μm thick deposited on silicon wafer was investigated. The depth profiles of this system and freestanding PET film are compared in Figure 4a. In the case of PET/silicon system the maximum of the depth profile determined for the I^{1610} band is shifted corresponds approximately to centre of the polymer film. Figure 4b shows the first derivative of the depth profiles presented in Figure 4a. The maximum of both derivative curves corresponds to the front surface. In the case of the PET/silicon system the position of the bottom polymer film surface corresponds also to extreme (minimum) of the first derivative. It means that in the case of polymer film/reflecting support, the inflection points of the depth profile correspond to the positions of the front and bottom film surfaces.

Position of the PET/silicon interface can be also determined using the depth profile for the silicon fundamental mode (521 cm^{-1}). In this case position of the interface corresponds to maximum of the depth profile, similarly as it was for free silicon surface (c. f. Figure 1). It is worthy to notice that the above presented procedures of the determination of the polymer film interfaces were successfully applied also for other polymers, like PE or PTFE.

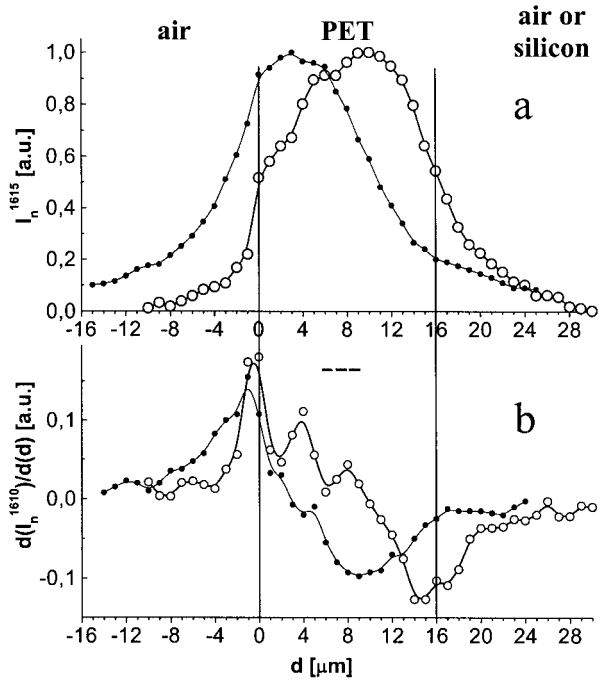


Figure 4. (a) Depth profiles obtained for 1610 cm^{-1} band for freestanding (full circles) and supported on silicon (open circles) PET films (16 μm thick); (b) their first derivatives. Confocal diaphragm 0.1 mm.

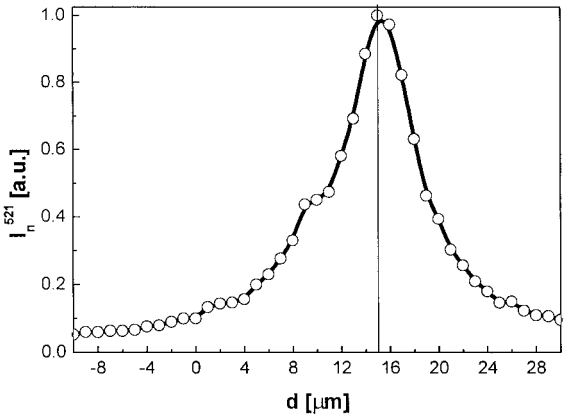


Figure 5. Depth profile for PET/silicon system obtained with the intensity of the silicon 521 cm^{-1} frequency. Confocal diaphragm 0.1 mm.

Polymer laminates

The PTFE/PE and PE/PET laminates were used as model systems. For such polymers weak interface interactions can be expected, what means that the shape and positions of Raman bands characteristics for these polymers should be not changed in the interface region. Depth profiles were obtained for the following peaks: 1130 cm^{-1} (skeletal mode) for PE, 732 cm^{-1} for PTFE (δ CF_2 modes) and 1610 cm^{-1} for PET (aromatic ring mode).

Figure 6 presents the 3-D representation of the Raman spectra of PTFE/PE system as a function of distance from the sample surface using two extreme confocal diaphragms. The depth profiles for 1130 cm^{-1} (PE peaks) and 732 cm^{-1} (PTFE peak) lines are shown in Figure 7a and their derivatives in Figure 7b. In the case of measurements realised with the smallest confocal pinhole inflection of the depth profile (maximum of respective first derivative) corresponds to the front surface of each polymer layer. For the measurements with the largest confocal pinhole (2 mm) obtained depth profiles are very broad, and only the position of the front surface of the first polymer film (PTFE) can be determined from the inflection point of the depth profile for 732 cm^{-1} PTFE peak.

In the case of laminate prepared from PE and PET (80 μm and 68 μm thick respectively) polymer films, depth profiles are relatively broad even for the smallest confocal diaphragm (0.1 mm) – see Figure 8. However analysis of the first derivatives of the depth profiles shows that positions of interfaces correspond also in these cases to the maxima of first derivatives.

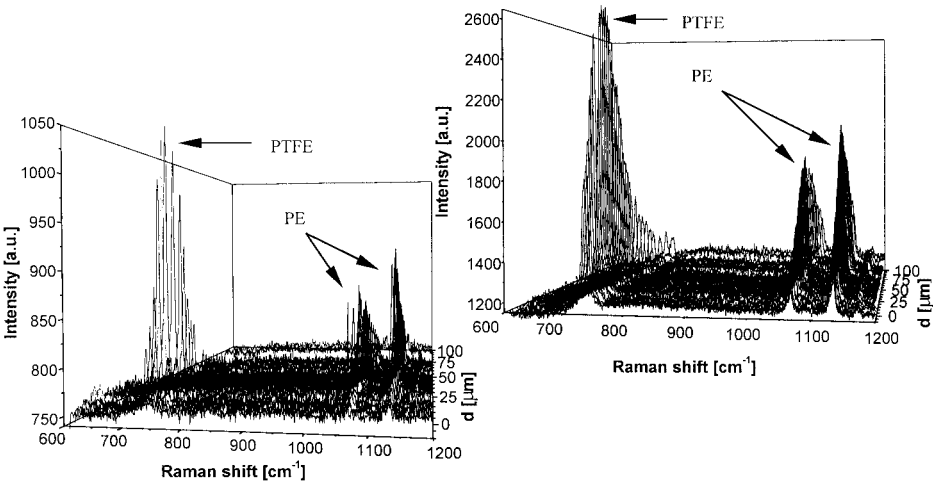


Figure 6. Pseudo 3-D representation of Raman spectra of the PTFE (20 μm)/PE (80 μm) system as a function of distance from the sample surface obtained for two different confocal diaphragms: 0.1 mm and 2.0 mm of diameter.

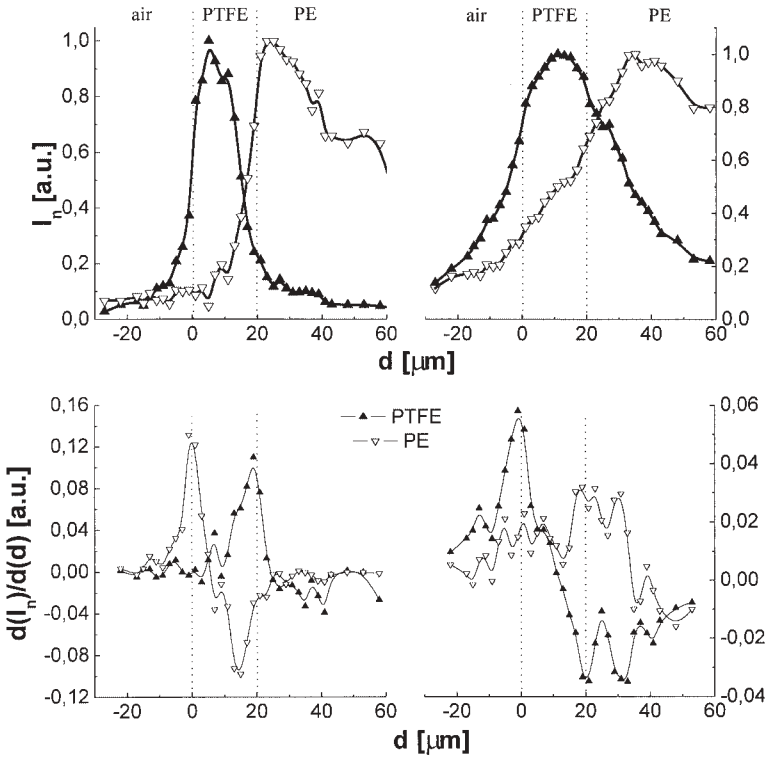


Figure 7. (a) Depth profiles of the PTFE (20 μm)/PE (80 μm) system obtained for two different confocal diaphragms (0.1 mm and 2.0 mm) for 1130 cm^{-1} (PE peak) and 732 cm^{-1} (PTFE peak); (b) and their first derivatives.

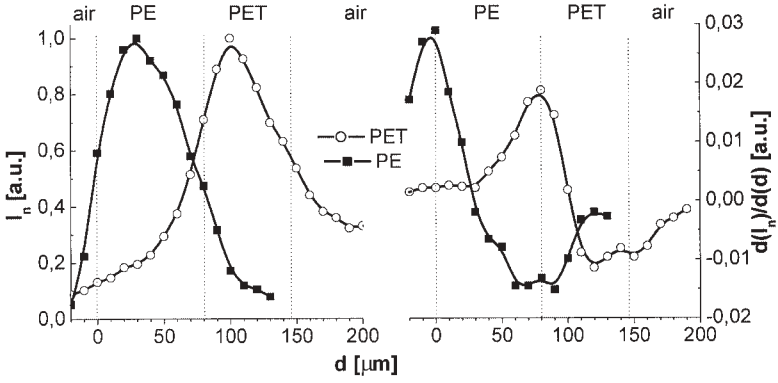


Figure 8. Depth profiles of the PE (80 μm)/PET (68 μm) composite obtained for 1130 cm^{-1} (PE peak) and 1610 cm^{-1} (PET peak). Confocal diaphragm 0.1 mm.

Polymer laminate with strong interface interaction

The pAA/HPC laminate was used as model for characterisation of the intermolecular interactions in anisotropic blends prepared from these components. Such blends have been extensively investigated by us recently [14-16].

Carboxylic groups situated along the chain of pAA are ably to form hydrogen bonds leading to different supramolecular structures listed in Table 1. Hydrogen bonds change the vibration of the carbonyl groups engaged in their formation, and the position of the Raman bands related to these structures are known – see Table 1. Our earlier studies show that pAA forms different supramolecular structures in bulk and in composites: in pure pAA the cyclic dimers dominates, while in the composites the intermolecular HPC – pAA hydrogen bonds are preferred [14].

It is necessary to remark that in the case of Raman spectra of HPC and pAA the bands correspond to the both components overlap except of the 1600 – 1800 cm^{-1} range containing no lines originating from HPC [14]. The stretching C=O bands present in this range can be used for analysis of the supramolecular structures of pAA. However, an overlap of all HPC lines with pAA peaks in other ranges of the spectrum makes difficult determination of the changes of concentration in laminate along the Z axis. Therefore, to determine the concentration of the components we have used the ratio of the intensity of the 2865 cm^{-1} to 2930 cm^{-1} peaks ($R=I^{2865}/I^{2930}$) – see inset in Figure 9. R equal 1 corresponds to pure HPC, while R equal 0.2 corresponds to pure pAA. Analysis of the variation of R with distance allows to distinguish three zones in the laminate: first one close to the surface rich in HPC, second (above 6 μm) rich in pAA, and the interface between them.

Table 1. Raman bands for the C=O groups forming different supramolecular structures of pAA.

Raman shift [cm^{-1}]	Supramolecular structure of pAA
1660	Cyclic dimers
1680	Intramolecular hydrogen bonds
1695	Linear oligomers – „inner" groups
1715	Linear oligomers – „terminal" groups
1730	Intermolecular HPC – pAA hydrogen bonds
1745	Free COOH groups

The analysis of the 1600 – 1800 cm^{-1} range of Raman spectrum yield more information about the interface zone. Changes of band shape of stretching mode of the C=O groups are visible in the interface zone. The 1600 – 1800 cm^{-1} range for zone rich in HPC shows the presence of pAA molecules; moreover for the zone rich in pAA the spectra are characteristic for blends with small amount of HPC, not for bulk pAA. It means that the macromolecules of components penetrate the neighbouring layer.

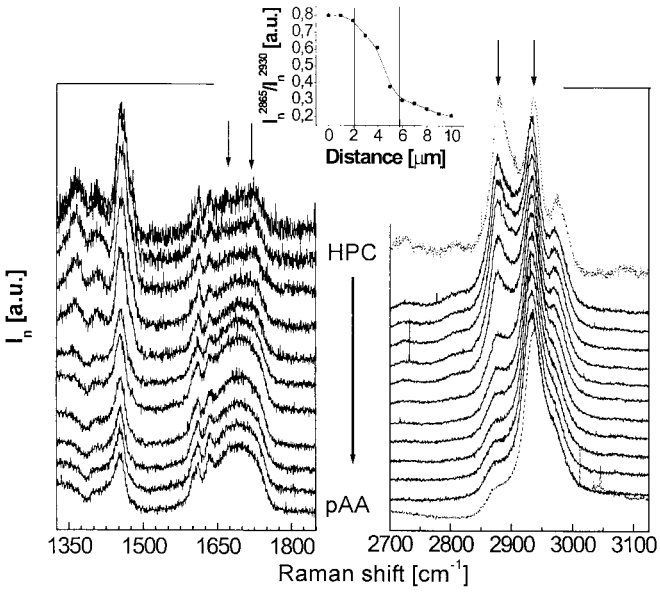


Figure 9. Raman spectra of HPC/pAA laminate recorded at different distance from the surface (step 1 μm). Insert presents $R=I^{2865}/I^{2930}$ vs. distance from surface.

Conclusions

The presented results demonstrate that analysis of the depth profiles makes possible determination of the interfaces position in polymer laminates with good accuracy, even without immersion procedure. Micro-Raman investigations of the HPC/pAA laminate demonstrate the diffusion of the macromolecules of both components to the neighbouring phase. The changes of the supramolecular structure of pAA were observed in each zone.

Acknowledgements

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