Macromol. Symp. ***184****, 107–122 (2002)*

Structure of Polypropylene/ Polyethylene Blends Assessed by Polarised PA-FTIR Spectroscopy, Polarised FT Raman Spectroscopy and Confocal Raman Microscopy

Pavel Schmidt, Jiří Dybal, Jaroslav Ščudla, Miroslav Raab, Jaroslav Kratochvíl*
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague, Czech Republic

Klaus-Jochen Eichhorn
Institute of Polymer Research, Hohe Strasse 6, D-01069 Dresden, Germany

Sonia López Quintana, José María Pastor
Department of Physics of Condensed Matter, University of Valladolid, 47011 Valladolid, Spain

Summary: Physical structure and morphology of differently prepared and treated bulk specimens of isotactic polypropylene, linear polyethylene and their blend was studied by polarised FT Raman spectroscopy, polarised FTIR spectroscopy with photoacoustic detection, and by confocal Raman microscopy. The specimens differed in preparation technique, mechanical and thermal history. The orientation and reorientation of molecular chains of individual blend components, their crystallinity and the size and structure of the microdomains both in the skin and in the core of the specimens were correlated with the preparation conditions, mechanical treatment and thermal history. The possibilities and limitations of each method were discussed.

Introduction

It is known that mechanical properties of polyolefins strongly depend on their phase structure, crystallinity, chain orientation and microdomain structure resulting from their composition and processing history. Skin-core effects can also be important.

Potentials of the polarised Raman spectroscopy[1,2], polarised photoacoustic FTIR spectroscopy (PPA-FTIR)[3,4], and micro-Raman confocal imaging spectroscopy[5,6,7] for the investigation of various polymer systems have recently been demonstrated. The subject of the present contribution is a comparison of the information provided by these methods and evaluation of their advantages and limitations. The application of different methods to the same specimen allowed a complex characterisation of individual levels of the hierarchical structure. The specimens for spectroscopic investigations were prepared from standard bulk dumbbells used for measurements of the tensile mechanical properties.

CCC 1022-1360/00/$ 17.50+.50/0

Experimental Part

Materials and specimens: Isotactic polypropylene (PP) was MOSTEN 58412, high-density polyethylene (PE) was LITEN MB 62 (both polymers supplied by Chemopetrol, Czech Republic). The experimental model blend was prepared by mixing PP and PE pellets (weight ratio 50/50) in a Banbury mixer and then in a double-screw extruder. The standard dumbbell specimens were prepared by injection moulding. Processing conditions for the specimen preparation were described elsewhere8). The gauge length, width and thickness of the injection-moulded dumbbell specimens were 90, 10, and 4 mm, respectively. Such specimens were then drawn at 23 °C at a test speed of 20 mm.min^{-1} using an Instron 6025. The drawing was heterogeneous, i.e. concentrated in a sharp neck shoulder. The obtained draw ratio reached the value of 5.1. The cold-drawn specimens were exposed to annealing in a vacuum oven at 140 °C for 20 h and then slowly cooled down. Such an annealing led for the samples with PP to shrinkage with the resulting draw ratio of 4.6. At that temperature, the shape of the neat PE specimen was completely destroyed by melting. For comparison, macroscopically non-oriented specimens were prepared by pressing at a temperature of 220 °C.

Polarised FT Raman spectra were performed on a Bruker FT spectrometer IFS 55 equipped with a Raman module FRA 106 at 2 cm^{-1} resolution. The spectra were obtained using a 1064 nm diode-pumped Nd^{+}:YAG laser radiating a horizontally polarised beam of 500 mW. The measurements of both liquid heptane and non-oriented polyolefin samples showed that optical throughput of the spectrometer with the position of a horizontally transmitting analyser was 1.32times larger than for its position transmitting vertically. The measured spectra were corrected accordingly. All specimens were positioned with their largest planes perpendicular to the laser beam direction; the lengths of the dumbbells were oriented vertically, i.e. the direction of the injection moulding and drawing was perpendicular to the basic laser beam polarisation. The spectra were obtained in the back-scattered regime, in a series of four parallel or perpendicular combinations of positions of the half-wave plate and of the analyser with respect to injection moulding and drawing. During such a series, the intensity of the laser and the position of the specimens were sufficiently stable, so that the Raman intensities of different measurements in one series could be compared.

Polarised photoacoustic Fourier-transform infrared (PPA-FTIR) measurements were performed with an infrared spectrometer Bruker IFS66v/S using an MTEC 200 photoacoustic cell (Ames, Iowa). Experimental and theoretical details of this technique were described in our previous papers3,4). For measurements of the surface regions of the material, specimens of approximate dimensions of 8 × 4 × 2 mm were cut from the injection-moulded or cold-drawn specimens to fit into the cell holder. For measurement of PPA-FTIR spectra of inner portions of the specimens, the injection-moulded and the subsequently drawn specimens were cooled with liquid nitrogen and split into two halves along the injection and draw direction in the plane perpendicular to the wider side of the neck. The cleaved specimens had approximate dimensions of 4 × 2 × 2 mm. After inserting the cell holder with the specimen into the spectrometer, the cell was flushed with He for at least 1 h before the beginning of measurement. The spectral resolution was 4 cm^{-1}, a carbon-black standard was used as a reference. The infrared spectra were measured with a mirror frequency of 2.2 kHz, 1000 scans being accumulated. The direction of the specimen orientation coincided with the plane in which the infrared beam passed through the photoacoustic cell. A KRS-5 wire grid polariser (SPECAC) was placed immediately in front of the cell. Two successive measurements, with parallel ($\|$) and with perpendicular ($\perp$) polarisation of the electric vector with respect to the draw direction of the specimen, were performed.

Intensities of both the FT Raman and infrared photoacoustic bands were evaluated by means of the OPUS software. The bands were separated when necessary.

Micro-Raman confocal measurements were performed with a confocal micro-Raman LABRAM equipment Dilor S.A. (Lille, France). This equipment uses a He-Ne laser beam operating at 632 nm, which supplies ca. 16 mW at the sample surface. The scattered light was detected with a CCD camera. Various pinhole apertures (normally 100 μm) and 300 grooves/mm grating were used. The spectral resolution was 4 cm^{-1}. The skin of the material was measured on the surface of the narrower parts of the test-pieces. For characterisation of the inner parts of the material, small pyramid-like pieces were cut from the centre of the dumbbell test pieces by ultrathin sectioning under liquid nitrogen, a technique used in sample preparation for electron microscopy. The size of upper plane of the pyramid used for the micro-Raman measurement was ~ 200 × 200 μm.

Point-by-point mappings were carried out using a motorised scanning stage controlled by the computer software LABSPEC (Dilor S.A.). For the formation of the composition images, the areas 15 × 15 μm with the distance between the points 0.5 μm were measured with the objective magnifying 100×. Chain orientation was estimated by measuring the samples in two mutually perpendicular positions so that the direction of injection moulding and drawing of the specimens were parallel (0^o) or perpendicular (90^o) to the polarisation of the laser beam. Neither a half-wave plate nor an analyser was used. The data were sampled with the objective magnifying 50× from the 100 × 100 μm squares in the steps of 10 or 20 μm. In such a relatively large area it was necessary to correct the focus manually.

DSC measurements were carried out on a Perkin Elmer Pyric 1 DSC apparatus. The values of 206 and 292 J/g were used as heats of fusion of 100% crystalline PP and PE, respectively.

Results

Polarised FT Raman spectra

For PP, the Raman bands at 809, 842, 1152 and 1168 cm^{-1} are the most characteristic of a directional ordering of the polymer chains$^{1)}$. Similarly for PE, the bands at 1062, 1130 and 1295 cm^{-1} are influenced by polarisation$^{2)}$. The oppositely polarised couple of polarisation arrangements A and B (A with both the laser polarisation and the analyser transmittance parallel to the injection and drawing directions, B with both the laser polarisation and the analyser transmittance perpendicular to them) appeared to reflect most sensitively the magnitude of orientation of polymeric materials.

As expected, no chain orientation was found in the pressed specimens – after normalisation to a constant optical throughput of the spectrometer, A and B spectra were identical.

The Raman spectra of differently treated neat polymers and of a blend of PP/PE 50/50 measured under the mentioned polarisation arrangements are shown in Fig. 1. As follows from the Figure, for the Raman bands of the injection-moulded specimens (for PP or for PE as neat polymers or components of the blend), no or a negligible band polarisation was found (see Fig. 1, curves a).

As a result of plastic drawing, the spectra of different polarisation markedly differed. A comparison of the curves b in Fig. 1 shows that for the oppositely polarised measurements A and B, differences in the intensities of the 809 and 842 cm^{-1} PP bands were higher for the neat PP than for the PP/PE blend. From the figure also follows that the Raman PE band at 1130 cm^{-1} seems to be influenced by the plastic drawing slightly more for neat PE than for the PP/PE blend.

Annealing of the drawn specimens at 140 °C had practically no influence on the intensities of the bands of the neat PP. On the other hand, the PP band intensities of the PP/PE blend changed: the difference between the oppositely polarised measurements increased for the bands at 809 and 1168 cm^{-1} and decreased for the band at 842 cm^{-1} (compare curves c with curves b).

The specimen of neat PE was melted during the annealing. Correspondingly, all the Raman anisotropy of the material was lost (see curve c of neat PE). On the other hand, some Raman

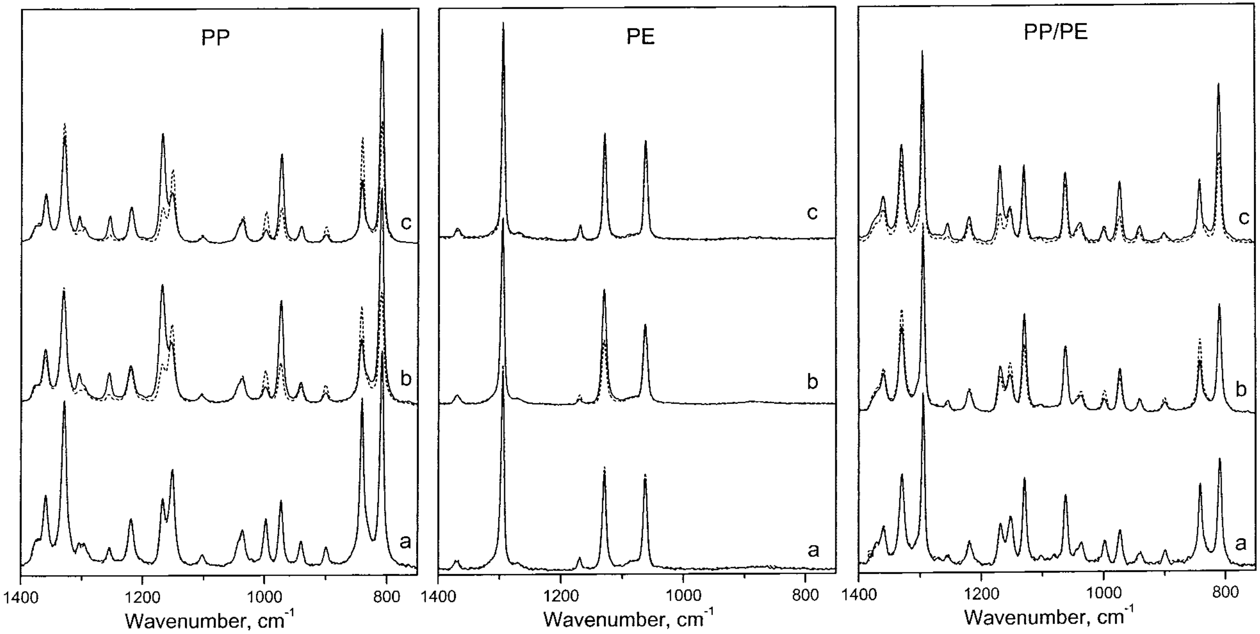

Fig. 1: Polarised FT Raman spectra of neat PP, neat PE and PP/PE 50/50 blend. (a) Injection-moulded, (b) drawn, (c) drawn and annealed; —— polarisation A, ------- polarisation B (see text).

anisotropy of the PE bands of the PP/PE specimen remained, nevertheless its character changed during the annealing. A comparison of the measurements A and B showed that the original polarisation difference of the band at 1130 cm^{-1} disappeared while a new slight polarisation difference for the bands at 1295 and 1062 cm^{-1} arose (Fig. 1, PP/PE blend, curves b and c).

Polarised PA FTIR spectra

Chain orientation

In the PA-FTIR spectroscopy, only a surface layer of the measured material, usually thinner than 20 μm, interacts with the infrared radiation. Consequently, the measurements on the surface of a dumbbell specimen give information about the skin of the material. To obtain information about the core, the middle part of the material was uncovered by splitting the specimen cooled under the liquid nitrogen into two halves.

The intensities of the polarised infrared bands at 998 and 973 cm^{-1} were shown to reflect the orientation of PP chains[9)]; similarly the intensities of the bands at 730 and 720 cm^{-1} were influenced by the orientation of the PE chains[10)]. Fig. 2 shows the PPA FTIR spectra of the middle parts (cores) of neat PP, neat PE and of a PP/PE 50/50 blend of differently prepared and treated specimens. In the figure, the orientation of the polymer chains is also characterised by the simplified orientation function f expressing the fraction of fully oriented chains[3,11)] The transition moment of the crystalline PP band at 998 cm^{-1} is parallel to the chain direction, while that of the crystalline PE band at 730 cm^{-1} is perpendicular. It follows from the figure that for the core of a neat injection-moulded PP, a slight orientation of PP chains could be seen (Fig. 2, neat PP, curve a). For the core of neat injection-moulded PE, only a negligible chain orientation can be estimated (Fig. 2, neat PE, curve a). The spectra suggest also a slight orientation for PE and PP chains in the injection-moulded specimens of the PP/PE 50/50 blend, respectively (Fig. 2, PP/PE blend, curve a).

On plastic drawing, the dichroism of the core PP bands substantially increases, suggesting a pronounced chain orientation. The increase is roughly identical for neat PP and for PP in the PP/PE blend. Also orientation of PE chains in the neat polymer and in the blend is similar (compare the respective curves b of Fig. 2).

After annealing of specimens at 140 °C, the dichroism of PP bands of neat PP and of PP in the blend slightly decreases or remains the same (Fig. 2, curves b, c). As expected, the neat PE specimen completely melted during annealing at 140 °C so that all the chain orientation was lost. On the other hand, after annealing at 140 °C and slow cooling of the drawn specimen of

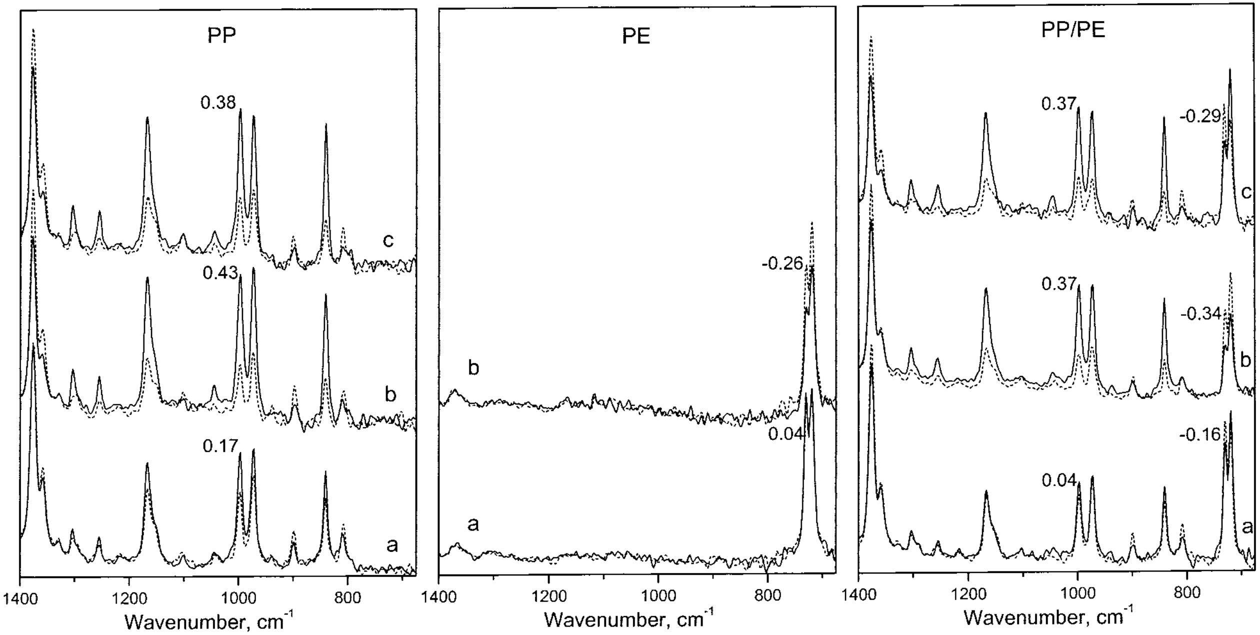

Fig. 2: Polarised PA FTIR spectra of the cores of neat PP, neat PE and PP/PE 50/50 blend. (a) Injection-moulded, (b) drawn, (c) drawn and annealed; —— parallel, ---- perpendicular polarisation. Negative signs added to the values of a simplified orientation function[3)] near the respective band express the perpendicular orientation of transition moment to the injection and drawing.

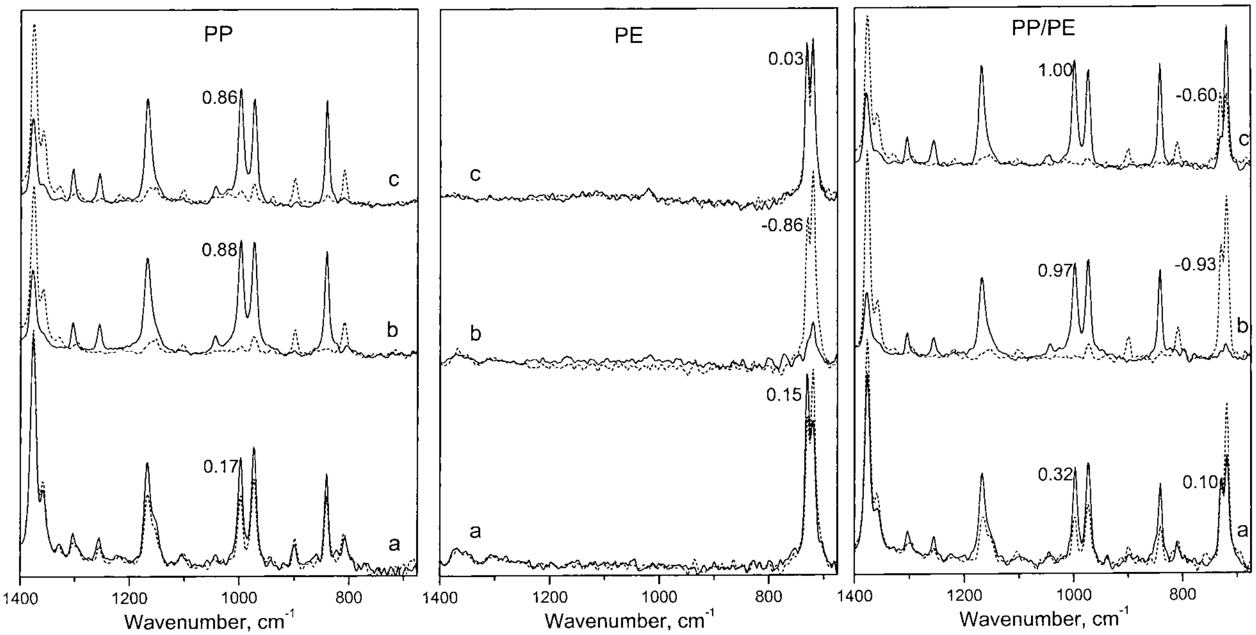

Fig. 3: Polarised PA FTIR spectra of the skins of neat PP, neat PE and PP/PE 50/50 blend. (a) Injection-moulded, (b) drawn, (c) drawn and annealed; —— parallel, ------- perpendicular polarisation. Negative signs added to the values of a simplified orientation function[3)] near the respective band express the perpendicular orientation of transition moment to the injection and drawing.

a PP/PE 50/50 blend, a striking change of infrared dichroisms occurred for the 730 cm^{-1} and 720 cm^{-1} PE bands: their polarisation dramatically changed into the opposite-one (Fig. 2, PP/PE blend, curve c). This effect was described in more detail in our previous study[4].

Fig. 3 shows PPA-FTIR spectra of the surface (skin) of the same specimens. There is no difference between dichroism of the surface and of the inner part of injection-moulded neat PP; both in the skin and in the core, the injection-moulded neat PP exhibits a pronounced infrared anisotropy (compare curves a of neat PP in Fig. 3 and Fig. 2). The 720 and 730 cm^{-1} PE bands in the skins of injection-moulded neat PE and PP/PE blend show a pronounced dichroism (Fig. 3, curves a), with the relative intensities opposite to the specimens obtained by cold drawing.

For the skins of all the drawn materials, almost perfect suppression of intensities of the PPA FTIR bands both for PP and PE occurs for the position of the polariser opposite to that suitable for the maximum intensity (see Fig. 3, curves b). Consequently, also the dramatic change in the PE 730 and 720 cm^{-1} dichroism of the plastically drawn and subsequently annealed blend mentioned for the core is even more pronounced in the skin (compare b and c for PP/PE blend in Fig. 3).

Crystallinity

The spectral PPA FTIR information coming from the surface layer of the measured bulk material can be used also for discerning between the crystallinity of the polyolefin materials on the surface (skin) and, after baring the core, in its inner part. For the case of polypropylene, the infrared band at 998 cm^{-1} was assigned to the crystalline part, the band at 973 cm^{-1} both to the crystalline and amorphous part of the polymer[9,12)] For axial orientation, the structural factor $\mathbf{I = 1/3(I^0 + 2I^{90})}$, (where $\mathbf{I^0}$ and $\mathbf{I^{90}}$ are the intensities relating to the polariser transmitting parallel and perpendicularly to the injection and drawing direction), corresponds to a hypothetically isotropic material[13)]. The ratios of these factors for the 998 and 973 cm^{-1} PPA FTIR bands $\mathbf{I_{998}/I_{973}}$ were related to the mean crystallinity values of the specimens obtained by DSC. The estimated values of PP crystallinity in the skin and in the core are shown in Table 1. The mean DSC crystallinities increased both with drawing and with annealing and, accordingly, the intensity ratio $\mathbf{I_{998}/I_{973}}$ increased with such treatment. For the injection-moulded specimens, the crystallinity of the core was by 2–5% higher as compared with the skin. After drawing, this difference increased to 4–7%. After annealing the cold drawn specimen at 140 °C, the situation was reverse: for PP, the crystallinity of the core was about by 4% lower than that of the skin. For PE, the complex orientation and reorientation of the chains during the sample preparation and treatment[14,4] is probably the main obstacle for a similar infrared estimation of its crystallinity.

Table 1. Crystallinity of PP in neat PP specimen and in the PP/PE blend as assessed by DSC and PPA-FTIR

Sample	DSC Crystallinity (%)	PPA-FTIR			
		I_{998}/I_{973}		Crystallinity (%)	
		core	skin	core	skin
PP injected	43	0.826	0.782	48	46
PP cold-drawn	53	0.871	0.801	51	47
PP cold-drawn, annealed at 140 °C	57	0.908	0.985	53	57
PP/PE injected	42	0.879	0.790	51	46
PP/PE cold-drawn	52	0.923	0.798	54	47
PP/PE cold-drawn, annealed at 140 °C	61	0.943	1.012	55	59

Micro-Raman confocal spectra

Micro-Raman confocal spectroscopy affords information on a comparatively limited optical volume. With the objective magnifying 100×, it has the dimensions about 2 μm in diameter and 2 μm in depth; with the objective magnifying 50×, these dimensions are roughly double. The point-by-point mapping of the material was made both for the skin and, after removing the skin, for the core. During the micro-Raman confocal mapping, the overall intensity of the Raman signal depends strongly on focusation of the microscope and cannot be maintained stable for the measurements in different points. Consequently, only the ratios of intensities of the Raman bands measured on particular points of the material can be estimated.

Characterisation of chain orientation in different domains

The intensity ratio of the oppositely polarised PP Raman bands at 809 and 842 cm^{-1} can be used for characterisation of the chain orientation of PP chains in individual points. The same holds, to a smaller extent, also for characteristic bands of PE. In our preliminary micro-Raman confocal mappings, it was found that polyolefin materials in some cases contained domains of the dimensions of 15–50 μm; the intensity ratio of the oppositely polarised Raman bands between these domains considerably changed. Due to the fact it was decided to characterise the orientation of the materials by mapping squares of 100 × 100 μm in steps of 10 or 20 μm. The specimens were always oriented in two mutually perpendicular directions – parallel and perpendicular to the injection moulding or drawing with respect to the laser polarisation. For characterisation of mean orientation of the material in the measured surface layer, the mean spectra obtained by Dilor software as an average of the mapping of the chosen squares were used. In such a way, the micro-Raman confocal mean spectra of neat PP, neat PE and of a PP/PE blend of pressed specimens and of the core and skin of injection-moulded and drawn specimens were measured. As expected, in the pressed specimens, the mean spectra from the two opposite measurements were not discernible, and roughly the same happened for the core of injection-moulded specimens of neat PE and of the blend. The core of injection-moulded PP specimen showed quite pronounced orientation, and the same was right for the skins of both the neat polymers and of the blend. The drawn samples were substantially oriented – in the core, but especially in the skin. Spectra of some of the specimens evidenced a "chain orientation microstructure" – changes in orientation at different sites of a specimen. Examples of these situations are given in Fig. 4. Fig. 4a shows two mean spectra of the skin of drawn

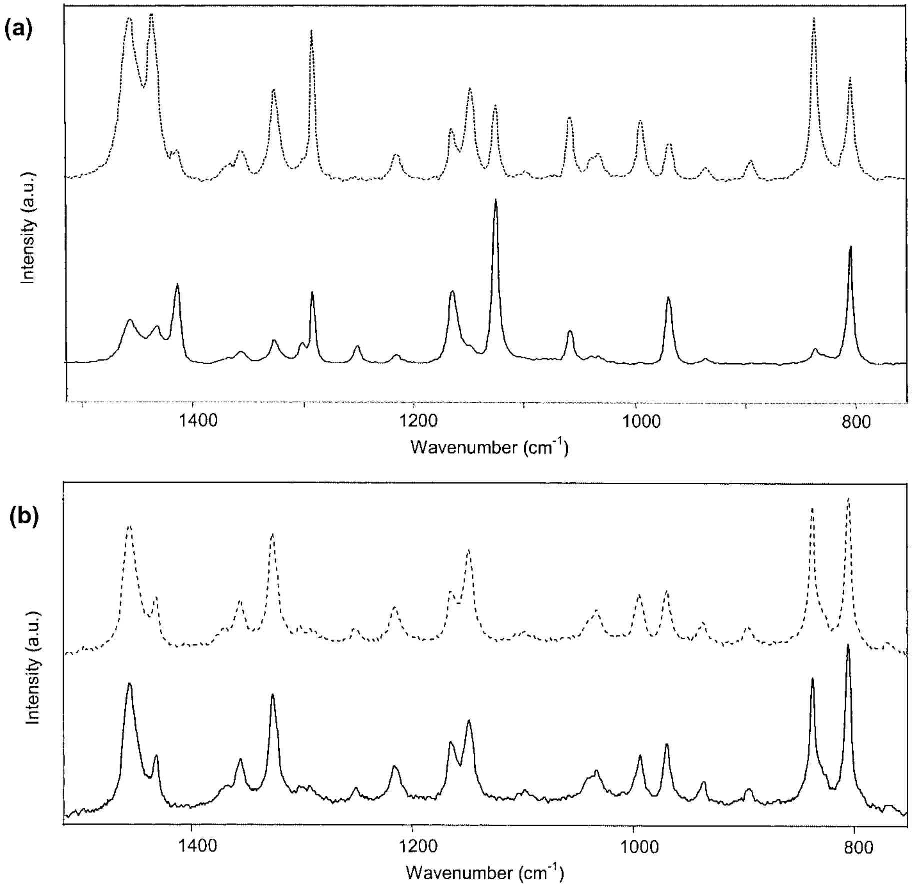

Fig. 4: Micro-Raman confocal spectroscopy – chain orientation. (a) Mean spectra of the skin of the drawn PP/PE blend; incident laser polarisation ―― parallel, ······ perpendicular with respect to drawing. (b) Spectra of the pressed neat PP found at different sites of the material.

oriented PP/PE blend, measured in two opposite directions. A very strong difference in the oppositely polarised bands is clearly seen. Fig. 4b presents two extreme spectra of a pressed non-oriented specimen of neat PP, found in the given square. This demonstrates fluctuation of orientation of polymer chains between individual microdomains.

Characterisation of size and shape of the domains with different composition

In a preliminary micro-Raman confocal examination of differently prepared specimens of the PP/PE 50/50 blend, the domains of PP or PE of a size of 2–5 μm were found. Therefore, the material was characterised by mapping the squares 15 × 15 μm, in the steps of 0.5 μm. The bands at 1330 and 1295 cm^{-1} were chosen for characterisation of domains of PP and PE, respectively.

Isotactic PP and high-density PE are immiscible; accordingly, only domains of practically neat PP and neat PE can exist in the blend. However, due to the final space resolution of the instrument (limited here to ~ 2 × 2 × 2 μm), the boundaries between the PP and PE domains

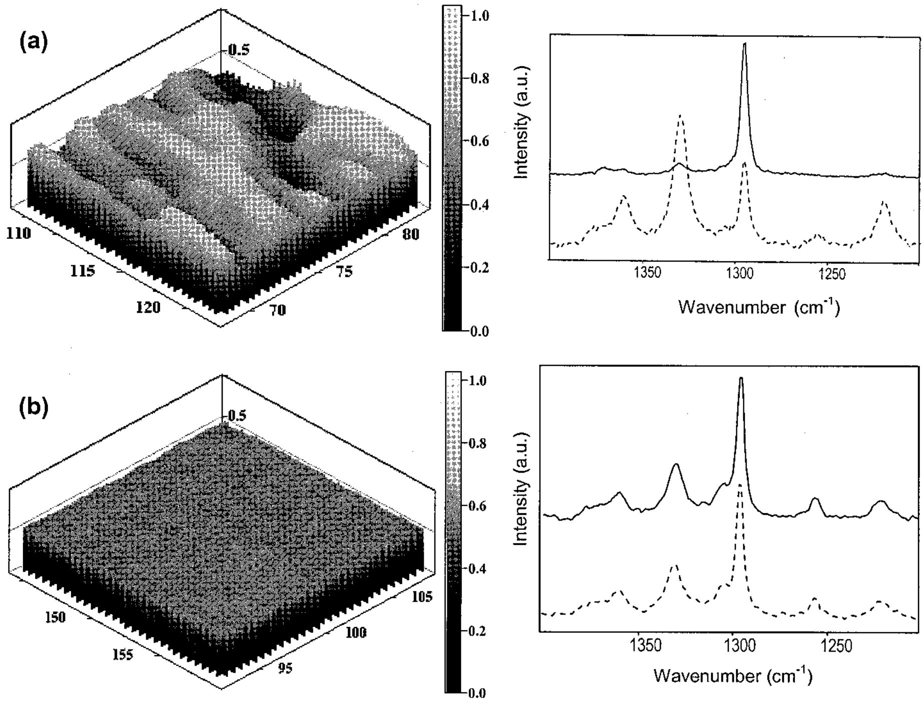

Fig. 5: Micro-Raman confocal spectroscopy – composition structure. Injection moulded PP/PE blend, three-dimensional images, —— PP-richest and ------ PP-poorest spectra correspond to maxima and minima of the images: (a) core, (b) skin.

are not sharp in the measured image. With the laser beam focused on the centre of a sufficiently large domain, the spectrometer should record the presence of individual polymer only. The smaller the polymer domains are, the more Raman intensity from the second polymer comes to the detector and the lower are the composition differences between the spectra taken at different points of the material. The domains of PP or PE smaller than 1 μm cannot be discerned by the micro-Raman confocal method at all.

Fig. 5a shows a three-dimensional micro-Raman confocal image of the inner part (core) of a PP/PE blend specimen, prepared by injection moulding. The intensity along the vertical axis reflects here an average content of PP in the particular measured position. In addition, two extreme Raman spectra extracted from the image, corresponding to the "PP-rich" and "PP-poor" locations are shown. On the surface of this specimen (skin), the domains are much less discernible (Fig. 5b). They are much smaller than in the core, which simultaneously causes lower differences in the intensity shown in the vertical axis of the image. The spectra extracted from the slightly "PP richer" and "PP poorer" locations of the skin are almost identical.

Comparison of individual spectral methods

FT Raman spectroscopy using an Nd^+:YAG laser as the source of excitation is now available in a number of spectroscopic laboratories. As the near-infrared laser beam penetrates into the bulk of the material, this simple method apparently would seem to be promising for the estimation of a mean value of polymer chain orientation. Nevertheless, the authors1,2) warned that scrambling of the excitation and Raman beams on the optical inhomogeneities could lead to false values of the intensities of the polarised Raman bands. These inhomogeneities differ for different samples and, moreover, they can change during the sample treatment. Compared with the conclusions made from two other spectral methods, the differences between the spectra taken with the polarisation arrangement A and B decreased both for the injection moulded and for the drawn specimens because of scrambling. As the blend specimens were more turbid than the neat polymers, their scrambling was higher. On annealing, the blend specimen became optically clearer4), which again increased the differences between the A and B method of polarisation measurements of the PP bands. The intensities of the Raman bands can be also influenced by crystallinity1,2). Taking all that into consideration, structural interpretation of the Raman results shown in Fig. 1 should be very careful.

Nevertheless, a structurally interesting effect for the drawn blend specimens annealed to 140 °C was discovered from the polarised FT Raman measurements. The loss of the original polarisation difference of the band at 1130 cm^{-1} found simultaneously with an appearance of new polarisations for the bands at 1295 and 1062 cm^{-1} demonstrates that, after melting the PE embedded inside of the PP matrix, a reorientation of PE chains proceeds. The band at 1130 cm^{-1} belongs to symmetry species A_g and both the bands at 1295 and 1062 cm^{-1} are composed of a pair of modes of the B_{2g} and B_{3g} classes[1,2)]. Therefore, the observed changes in the Raman polarisation support the evidence obtained recently by PPA FTIR and X-ray[4)] that the PE crystallites originally oriented with the *c*-axis (chain direction) parallel to the drawing are reoriented after annealing so that the *c* and *a* axes are perpendicular to the original draw direction.

Generally, polarised FT Raman spectra are a simple and versatile method of rough estimation of mean orientation of the polymer chains in specimens, both for neat polyolefins and for blends. Considering the obtained results with a sufficient criticism, new structural effects can be discovered.

PPA FTIR spectra take information from the surface layer of the measured materials and, unlike polarised Raman spectra, are not sensitive to optical inhomogeneities. This gives sufficient confidence to the results.

It follows from the spectra shown in Figs. 2 and 3 and in accordance with Refs[13,14)] that injection moulding causes some small orientation of the PP chains parallel to the flow direction, whereas the PE chains are oriented perpendicularly to it. These effects hold both for the neat polymers and for the blend. During plastic deformation, the parallel orientation of PP chains increased and also the previously perpendicular or randomly oriented PE chains changed their orientation into mostly parallel direction. PE chains in the solid PP matrix of the blend, after melting and recrystallisation, changed their direction dramatically: they reoriented again prevailingly perpendicularly with respect to the drawing direction. This effect discussed in more detail earlier[4] was also reflected by the polarised Raman spectra described above. For the skin of specimens, probably as a result of a faster cooling of the material during solidification, these dichroic effects of the infrared bands are much more pronounced than for the core.

The relative intensities of the infrared bands characteristic of the crystalline part of PP were frequently used for estimating the PP crystallinity[12)]. We have shown that the PPA FTIR spectra could also be used for a comparison of the skin and core in this respect. The lower values of crystallinity found for the skins of non-annealed specimens can then be explained (similarly to the higher chain orientation in the skin) by faster cooling of the material on the surface during injection moulding. On annealing followed by slow cooling, crystallisation of the polymer continues and higher crystallinity values of PP are reached for the skin than for the core.

Of the spectroscopic methods discussed here, the PPA FTIR is the most suitable for a quantitative discerning of skin and core concerning the chain orientation and crystallinity.

Micro-Raman confocal spectroscopy made with the He–Ne laser yields information from the volumes of the order of several micrometers – both in the diameter and in penetration depth. The unfavourable scrambling effect found in the macro-Raman measurement is almost eliminated here. Then, as a result of chain orientation, the measured Raman bands of the skins of drawn samples show very high polarisation. The measurements done at different sites of a specimen showed in some cases the existence of micro-regions of a size ~10–50 μm differing in chain orientation. The mean micro-Raman spectra taken from an area of 100 μm × 100 μm confirmed the results of PPA-FTIR spectra, namely the fact that the chain orientation is much higher on the surface than in the inner part of both the injection-moulded and of the drawn blend specimens.

In the PP/PE blend, the micro-Raman confocal spectra were able to discern very successfully microdomains of PP and PE. It was found that the inner part of the material prepared by injection moulding contained polymer microdomains of size 2–5 μm. Such relatively large domains were formed as a consequence of separate coalescence of PP and PE drops in the material, which remained in the melted state for a longer time. The dispersion of the components in the more rapidly cooled surface was much finer.

Considering the time-consuming character of micro-Raman confocal spectroscopy, a preliminary characterisation of the material under study by at least one of the above-mentioned method is desirable. However, the spatial resolution of this method is impressive and its ability to correlate morphology with chemical composition or structure is more or less unique.

Acknowledgements

The authors are greatly indebted to the Grant Agency of the Czech Republic (grants nos. 106/97/1071, 203/97/0539), to the Grant Agency of the Academy of Sciences of the Czech Republic (grants nos. KSK4050111, A4050904) and to CICYT (MAT1999-1029) for financial support. Thanks are due to Mrs. G. Adam, IPF Dresden, and Mrs. M. Brunclíková, IMC Prague, for very helpful technical assistance.

References

1. M. Arrubarrena de Baez, P.J. Hendra, M. Judkins, *Spectrochim. Acta A* **51**, 2117 (1995)
2. P.A. Bentley, P.J. Hendra, *Spectrochim. Acta A* **51,** 2125 (1995)
3. P. Schmidt, M. Raab, J. Kolařík, K.J. Eichhorn, *Polym. Test.* **19**, 205 (2000)
4. P. Schmidt, J. Baldrian, J. Ščudla, J. Dybal, M. Raab, K.J. Eichhorn, *Polymer* **42**, 5321 (2001)
5. L. Markwort, B. Kip, *J. Appl. Polym. Sci* **61**, 231 (1996)
6. M.R. Fernandez, J.C. Merino, M.I. Gobernado-Mitre, J.M. Pastor, *Appl. Spectrosc.* **54**, 1105 (2000)
7. P. Schmidt, J. Kolařík, F. Lednický, J. Dybal, J.M. Lagarón, J.M. Pastor *Polymer* **41**, 4267 (2001)
8. M. Raab, J. Kotek, J. Baldrian, W. Grellmann, *J. Appl. Polym. Sci.* **69**, 2255 (1998)
9. Y. Kobayashi, S. Okajima, A. Narita, *J. Appl. Polym. Sci.* **11**, 2515 (1967)
10. R. S. Stein, G.B.M.M. Sutherland, *J. Chem. Phys.* **23**, 734 (1955)
11. R.D.B. Fraser, *J.Chem.Phys.* **29**, 1428 (1958)
12. J.P. Luongo, *J. Appl. Polym. Sci* **3,** 302 (1960)
13. J.L. Koenig, S.W. Cornell, D.E. Wittenhafer, *J. Polym. Sci. Part A2,* 301 (1967)
14. R. Kaiser, *Kolloid-Z*. **152**, 8 (1957)