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DSC and Two-dimensional Correlation Infrared Spectroscopy Studies of PA6/Montmorillonite Composite Fibres

Abstract
The majority of research on polymer/layered silicate nanocomposite (PLSN) has focused on molded bulk materials with very few recent studies reporting on the formation of PLSN fibres. Hence, more research needs to be conducted in this area in order to better understand the formation and properties of PLSN nanofibres. In this paper composite fibres of PA6, and organically modified montmorillonite (MMT) of the type Cloisite 15A , were formed from the melt by means of a laboratory spinning machine. Fibres were extruded from the melt at a temperature of 240 °C and spun at take up velocities of 1200, 860, 460 m/min and extrusion velocity of 26 m/min. For the investigations we selected four kinds of manufactured undrawn filaments with the following compositions (by weight): 100/0, 99/1, 98/2 and 95/5 PA6/MMT. The effect of the MMT filler on PA6 crystalline morphology was examined by Fourier transform infrared spectroscopy (FTIR), IR microspectrocopy and differential scanning calorimetry (DSC). Because all the types of the fibres studied displayed both α and γ crystals, FTIR spectra were performed in wavenumber regions consisting of characteristic bands of these two polymorphs as well as the Si-O stretching wavenumber region. Analysis of FTIR spectra was performed by means of two-dimensional (2D) correlation spectroscopy. This technique revealed the composition-induced structural changes in the PA6/MMT composite fibres in detail. It was found that the content of montmorillonite in the core is higher than in the skin of the fibre, suggesting that during the formation process of the PA6/MMT composite fibres, montmorillonite was pushed into the fibre core.

Key words: *2D correlation IR, polyamide 6, montmorillonite, composite fibres, DSC.*

■ Introduction

Polyamide 6 (PA6) is one of the most successful synthetic semicrystalline polymers because of its good physical properties and high resistance to a wide spectrum of fuels, oils and chemicals. This success is also due to the excellent fibre properties [1]. Applications of PA6 fibres largely fall into two classes: woven (e.g. in clothing textiles and carpets) and non-woven (e.g. in tyre reinforcement cord, ropes, fishing lines, sport rackets and dental floss). The mechanical and physical properties of PA6 fibres are controlled by their supermolecular structure, where finite sections of crystalline lamellae and amorphous polymer alternate throughout a lamellar stack. Polyamide 6 exhibits polymorphism, and the polymorph depends on the crystallization condition [2, 3]. The production of PA6 fibres has a tendency to promote the formation of the kinetically favoured γ phase over the thermodynamically stable α phase, but in the final fibre both phases are usually present.

In recent years, nanocomposites based on polyamide 6 matrix and layer silicate nanofillers, primarily PA6 – montmorillonite (MMT) clay nanocomposites, have aroused great interest due to splendid thermo-mechanical reinforcement at a temperature above that of the glass transition [4].

The majority of research on PA6/MMT composites has focused on molded bulk materials with very few recent studies on the formation of PA6/MMT fibres [5-7]. Hence, more research needs to be conducted in this area in order to better understand the formation and properties of these fibres.

In this study, nanocomposite fibres of polyamide-6 and organically modified montmorillonite of the type Cloisite 15A, were formed from the melt by means of a laboratory spinning machine. The aims of the study are the following: (1) to examine the dispersion of nanoclays in PA6/MMT composite fibres; (2) to investigate the influence of MMT content on the polymorphism of these fibres. It was found that the γ phase is readily formed in PA6/MMT clay nanocomposites. The relative fraction of α and γ phases is dependent on the layered silicate content because the clay surface induces the formation of the γ phase [8, 9].

In order to realize these aims, Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) were used. FTIR spectra were performed in wavenumber regions containing characteristic bands of both α and γ crystals as well as the Si-O stretching wavenumber region. Analysis of FTIR spectra was performed by means of two-

dimensional (2D) correlation spectroscopy [10, 11]. 2D correlation spectroscopy simplifies complex spectra consisting of many overlapped peaks and enhances spectral resolution by spreading peaks along the second dimension, enabling one to extract information that cannot be obtained from one-dimensional spectra. Of particular interest to us was the application of this technique to the study of PA6/MMT composite fibres.

■ Experimental

Investigations were carried out for PA6/MMT filaments formed by means of a laboratory spinning machine. Commercial polyamide 6 Tarnamid T 27 and modified montmorillonite of type Cloisite 15A, produced by Southern Clay Product Ltd, were used. Fibres were extruded from the melt with a temperature of 240 °C and were spun at following take-up velocities: V_0 – gravity spun (26 m/min), V_2 = 460 m/min, V_4 = 860 m/min and V_6 = 1200 m/min, respectively. For the further investigations we selected four kinds of manufactured undrawn filaments with the following compositions (by weight): 100/0, 99/1, 98/2 and 95/5 PA6/MMT.

Thermal properties of the composite fibres investigated were determined with a TA Instruments Thermal Analysis System 5100 equipped with a MDSC Calorimeter 2920 and RCS cooling system. Measurements were performed in an atmosphere of nitrogen (flow 40 ml/min), using about 8 mg of samples contained in closed aluminum TA pans. The linear function of temperature change was used with a heating and cooling rate of 10 °C/min. Registration sensitivity was above 0.2 μW. Thermograms were evaluated by means of Universal V2.6D (TA Instruments) software. DSC curves were presented in a standard arrangement, illustrating the heat flow as the function of a sample temperature.

FTIR experiments were performed by means of a Thermo Nicolet Magna 860 FTIR spectrometer and a Thermo Nicolet Continuum Microscope coupled to a Thermo Nicolet 6700 spectrophotometer. The fibres were cut into 1 - 3 mm pieces, and next they were blended with powdered sodium chloride (spectr. grade). The samples were then pressed under 200 MPa to obtain a tablet. The tablet was placed in the spectrometer mea-

suring chamber, equipped with a mirror beam collimator (focused 16×) and IR microscope. As reference, a tablet made of NaCl (without fibres) was used. Spectra were obtained within the region of 4000 – 400 cm^{-1} with a spectral resolution of 4 cm^{-1}. 128 scans were coadded to ensure an acceptable signal-to-noise ratio. IR spectra were baseline-corrected and normalised to the same thickness, based on the 1170 cm^{-1} band of PA6. To obtain 2D spectra, Omnic ver. 7.3 software developed by Thermo Electron Corporation was used. An experimental matrix was formed from the original IR spectra, ordered in the direction of the

decreasing content of one of the fibre components, usually MMT. The average (or mean) spectrum of the spectra in the chosen set was then subtracted from each of the original spectra to obtain a set of "dynamic" difference spectra. Synchronous and asynchronous correlation spectra are then calculated from these dynamic spectra using the algorithm developed by Noda [5, 6].

■ Results and discussion

The crystallization behaviour of the PA6/MMT composite fibres was investigated using the differential scanning
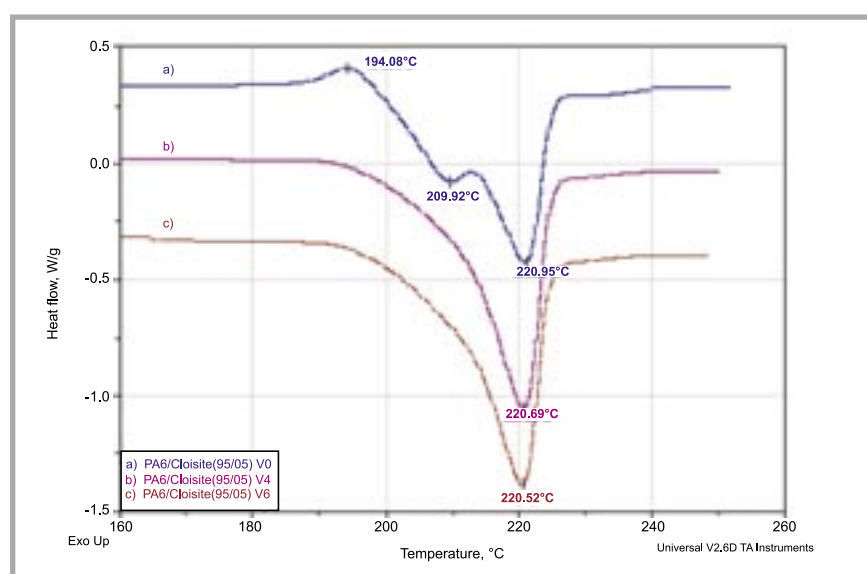
Figure 1. *DSC curves of 95/5 PA6/MMT fibres taken out with a velocity of 26 m/min (gravity spun), 860 m/min and 1200 m/min, respectively, in a temperature range of melting transition.*
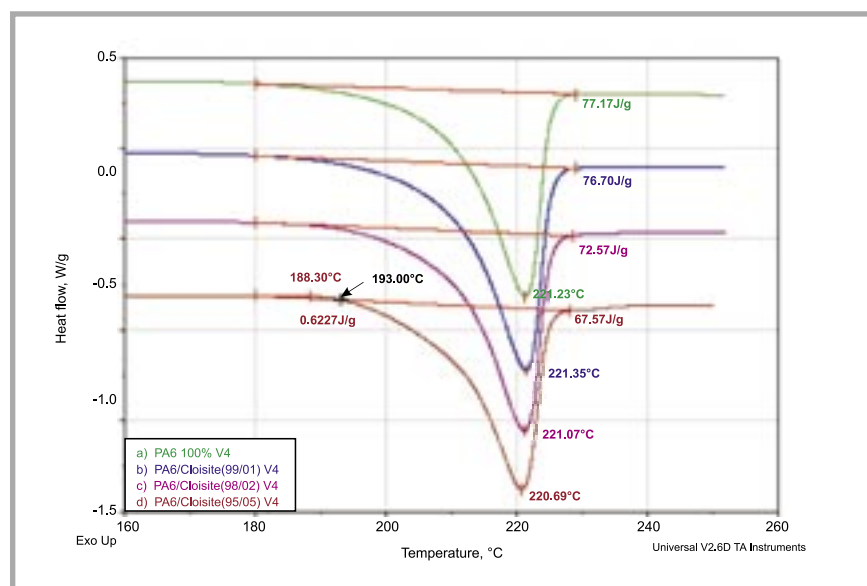

Figure 2. *Comparison of DSC curves registered during melting for PA6/MMT filaments spun with a take-up velocity of 860 m/min, containing various amounts of MMT modifier.*

calorimetry (DSC) method. DSC heating scans of fibres containing 5% MMT, formed at different take up velocities, are shown in Figure 1. The gravity spun fibres exhibited two endothermic peaks due to the melting of PA6 γ-form (209.9 °C) and α-form (220.6 °C), respectively. These effects are preceded by a small exothermic peak at 194.1 °C, which are connected with the recrystallization process. Figure 2 presents DSC heating scans of the composite fibres containing different amounts of montmorillonite. The pure PA6 fibres exhibited a melting point of 221.3 °C, whereas the composite fibres showed a slightly lower melting temperature of around 220 °C. The lower melting point observed for the composite fibres indicated that the PA6 crystals were less perfect in the composite fibres. In addition, the enthalpy of PA6 melting in composite fibres slightly decreased with increasing MMT content. For pure PA6 fibres the enthalpy is 77.2 J/g, and for PA6/MMT fibres containing 5% the MMT is equal to 67.7 J/g. Moreover, a wide exothermic peak at about 188 °C resulting from recrystallization was observed only for the composite fibres containing 5% clay modifier.

The FTIR spectra of 100% PA6 fibres and PA6/MMT fibres containing 5% MMT are presented in Figure 3. For a detailed assignment of the bands, corresponding second derivatives are also presented. The presence of γ crystals is evidenced by the dominant peaks at 976 cm^{-1} (CONH of γ crystal), 1122 cm^{-1} (C-C strech)and 1234 cm^{-1} (amide III and CH$_2$ wagging vibration). The α phase shows characteristic absorbance peaks at 929 cm^{-1}, 959 cm^{-1} (CONH of α crystal) and 1201 cm^{-1}. The exact assignments for some of these PA6 peaks are still debated in literature. The 1018 and 1046 cm^{-1} peaks can be solely attributed to the Si-O vibrations in montmorillonite since the only contribution from PA6 in this region is the small peak at about 1030 cm^{-1} which has a much lower intensity compared to the MMT peaks.

Figure 4 shows FTIR spectra and their second derivatives collected in the region of 1800 – 1400 cm^{-1} for the same fibres. It shows amide II mode in PA6 containing α and γ crystal phases. For α crystals the frequency of the amide II mode is 1548 cm^{-1}, whereas for γ crystals it is 1562 cm^{-1}. It is worth noting that both peaks are shifted in PA6/MMT composite fibres in comparison to that of
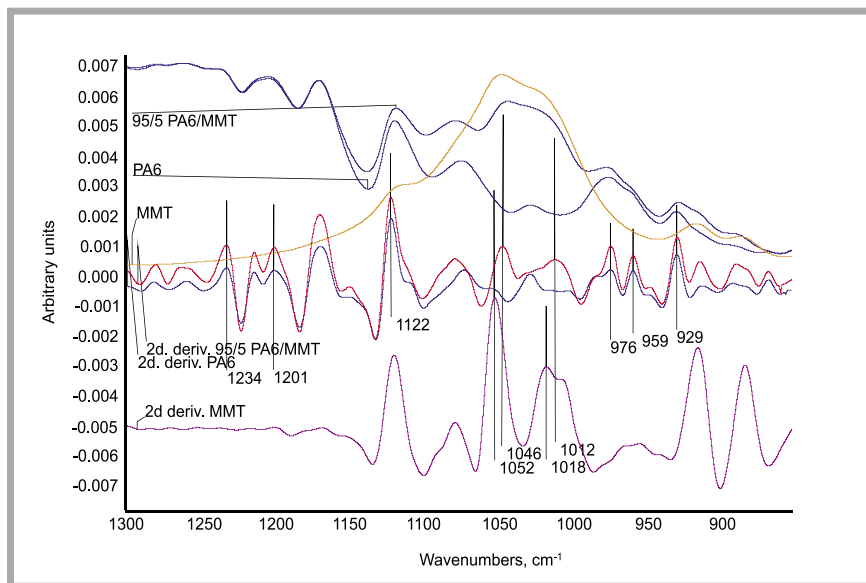
Figure 3. *FTIR spectra and their second derivatives collected in the region of 1300 - 800 cm^{-1} of pure PA6 and 95/5 PA6/MMT fibres.*
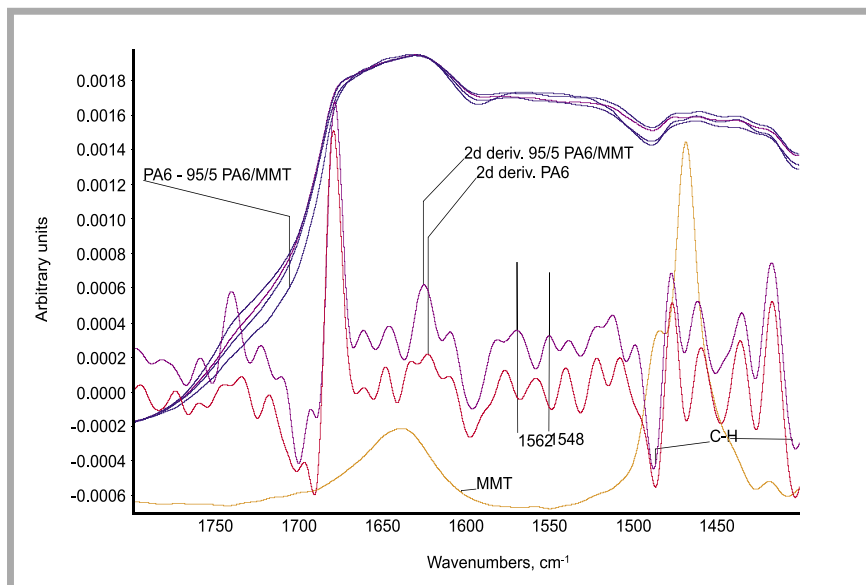

Figure 4. *FTIR spectra and their second derivatives collected in the region of 1800 – 1400 cm^{-1} of pure PA6 and 95/5PA6/MMT fibres, respectively.*

pure PA6 fibres, indicating the effect of montmorillonite on the C-N vibration in PA6 macromolecular chains.

Figure 5 shows a synchronous 2D correlation spectrum for the samples containing 1, 2 and 5 wt% MMT in the region of 1800 – 850 cm^{-1}. Synchronous 2D spectra $\Phi(\nu_1, \nu_2)$ represent the overall similarity of responses measured at two separate spectral variables ν_1 and ν_2, for a given external variable, such as the content of MMT. Autopeaks at diagonal positions represent the extent of changes in spectral signals induced by changes in MMT content. Cross-peaks at off-

diagonal positions represent simultaneous changes in signals at two different spectral variables, suggesting a coupled or related origin of intensity variation, as the content of MMT is varied. If the sign of a cross-peak is positive, the spectral intensities measured at the corresponding two spectral variables are either increasing or decreasing together. If negative, on the other hand, one is increasing while the other is decreasing. In Figure 5A, two strong, overlapping autopeaks are observed at 1018 and 1046 cm^{-1}. Their appearance is expected because they reflect the increase of MMT content in fibres. As shown in Figure 5A, several
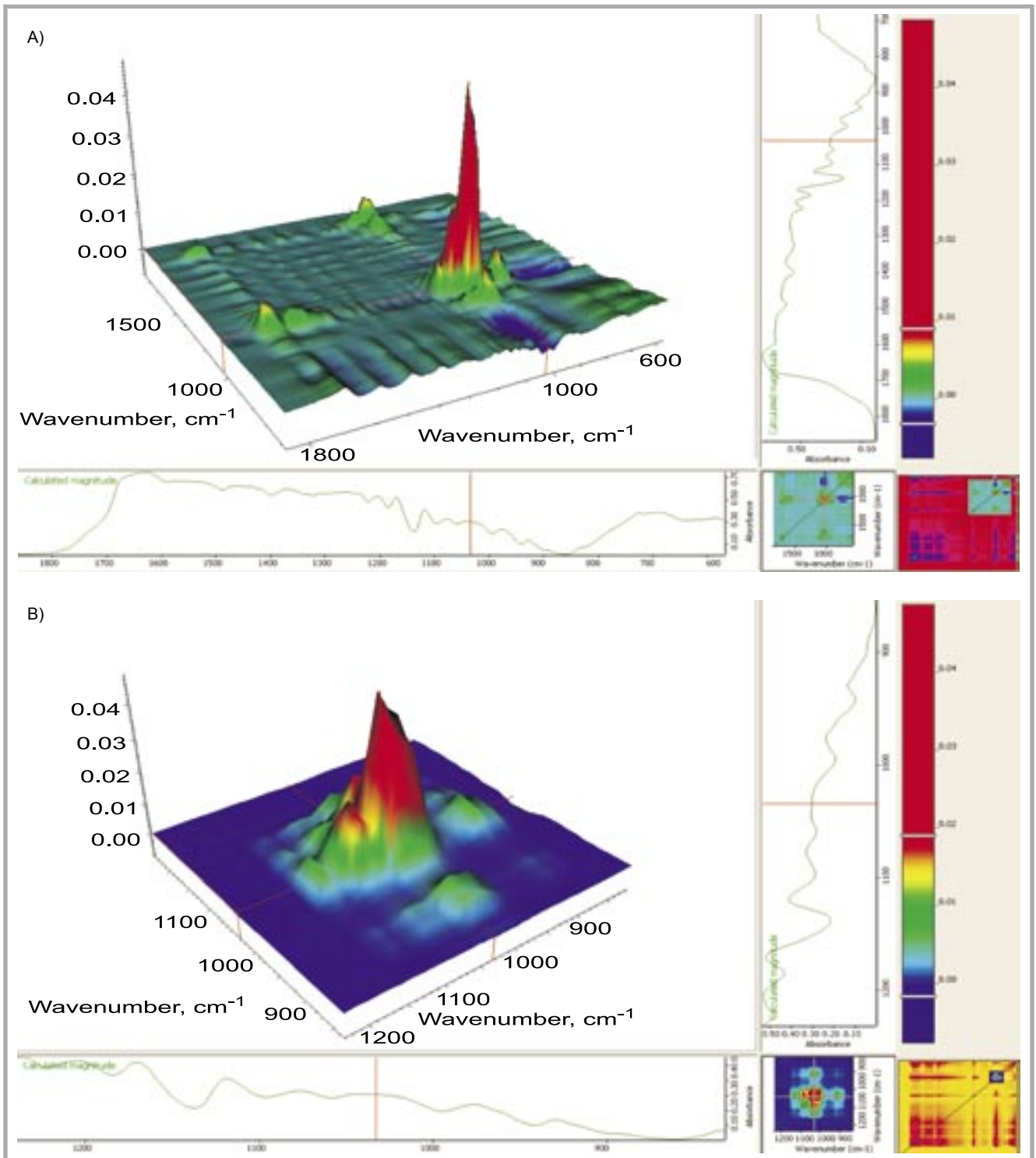
***Figure 5.*** *Synchronous 2D plots in the region of 1800 – 850 cm⁻¹ (A) and in the region of 1150 – 900 cm⁻¹ (B) of the data obtained from composite fibres of compositions (by weight): 100/0, 99/1, 98/2 95/5 PA6/MMT.*

positive cross-peaks are also detected among the bands of PA6 γ phase at 976, 1122, 1562 cm⁻¹ and the MMT bands at 1018, 1046 cm⁻¹. This result strongly suggests that the intensities of γ phase bands change simultaneously in the same direction with an increase in the concentration of montmorillonite in fibres. Figure 5B additionally shows that the MMT bands at 1018and 1046 cm⁻¹ have weak

but positive correlation with the bands at 929, 959 and 1201 cm⁻¹ arising from the PA6 α phase. Summarising, 2D correlation spectroscopy reveals a distinct influence of the montmorillonite content on the crystalline phases of PA6 in the composite fibres investigated.

In order to determine the distribution of MMT layers in PA6/MMT composite

fibres, we used an IR microscope "Continuum" which enables an execution of IR spectra at different points across a fibre axis (Figure 6). Figure 7 presents FTIR spectra of the PA6/MMT fibre containing 5% MMT in the region consisting of bands at 1018 and 1046 cm⁻¹, which are attributed to montmorillonite. The intensities of these bands in a skin of fibre are clearly greater than in a fibre
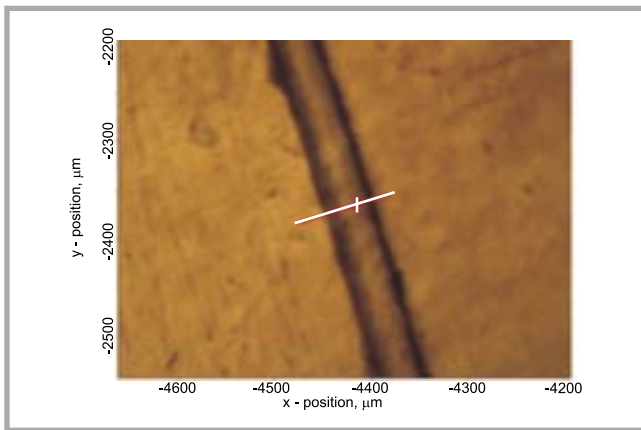
Figure 6. *Photo of the 95/5 PA6/MMT fibre taken by means of a "Continuum" IR microscope. The line indicates the scanning direction for preparing the spectrum map from Figure 8.*
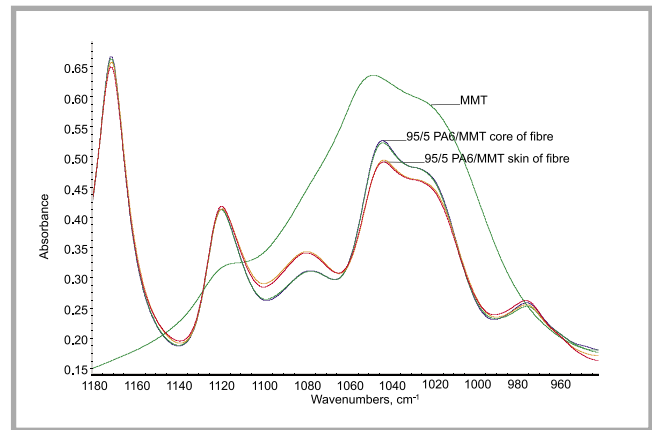
Figure 7. *FTIR spectra of the 95/5 PA6/MMT fibre obtained by means of a "Continuum" IR microscope in the region of 1180 – 950 cm⁻¹.*

core. These differences indicate that the content of montmorillonite in the core is higher than in the skin of the fibre, suggesting that during the formation process of the PA6/MMT composite fibres, montmorillonite is pushed into the fibre core. The distribution of montmorillonite is also visible on the spectrum map (Figure 8) obtained for the same fibre by means of a "Continuum" IR microscope in the direction perpendicular to the axis of the fibre. Differences in absorbances of 1018 and 1046 cm⁻¹ bands indicate a fluctuation of montmorillonite content in the fibre.

■ Conclusions

PA6/MMT composite fibres using different contents of organo-clay were successfully prepared by melt extrusion. The effect of the MMT filler on PA6 crystalline morphology in terms of clay dispersion was studied by means of DSC measurements, 2D FTIR correlation spectroscopy and IR microspectroscopy. The following conclusions have been reached:

1) The 2D FTIR correlation spectroscopy technique revealed the composition-induced structural changes in the PA6/MMT composite fibres in detail. Positive correlation peaks at off-diagonal positions appear between bands arising from PA6 α and γ polymorphs and bands attributed to montmorillonite, showing a distinct influence of this layer silicate on the crystalline phases of PA6 in the composite fibres investigated.

2) The marked differences in the band intensities at 1018 and 1046 cm⁻¹ between the skin and core regions of composite fibres indicates that a content of montmorillonite in the core is higher than in the skin of the individual fibres.

3) DSC measurements showed that MMT-filled fibres have less perfect crystals than those in unfilled PA6 fibres.

This paper has demonstrated the potential of 2D FTIR correlation spectroscopy in the study of compositional-induced structural changes in clay-polymer nanocomposites.

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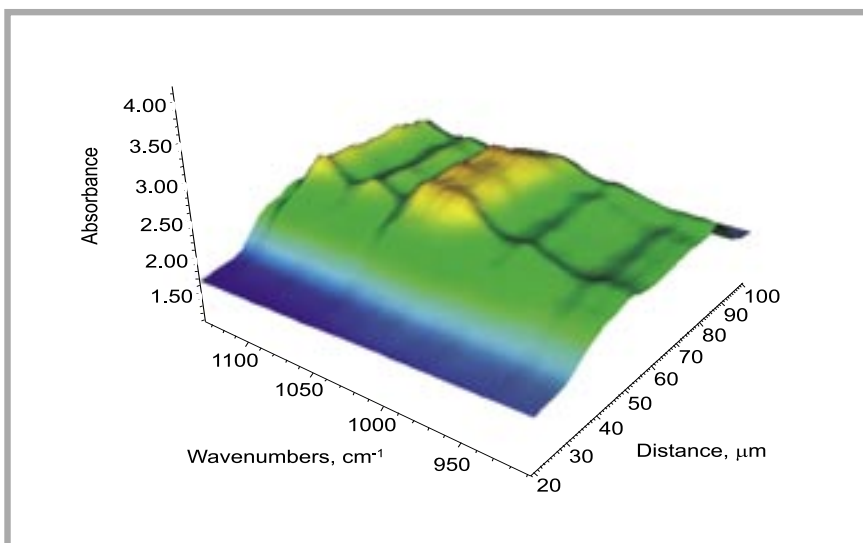
Figure 8. *The spectrum map obtained perpendicular to an axis of the 95/5 PA6/MMT fibre. Differences in absorbances of 1018 and 1046 cm⁻¹ bands indicate a fluctuation of montmorillonite content in the fibre.*