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Studies on the Heterogeneity of Polymeric Systems by Vibrational Microscopy[1]

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Summary: Considerations on the measurement and characterisation of the heterogeneity of multiphase polymeric systems were discussed with examples from polymer blends and composites, in order to demonstrate how vibrational spectroscopy, and in particular IR microscopy, can provide important information on the type and level of heterogeneity of this type of material. Further, as examples of heterogeneity in multiphase systems, the composition of polyolefin blends, the structure of PP/nylon-6 blends, and the distribution of crystalline polymorphs in isotactic polypropylene was described, and polymorphic transitions in iPP were characterised by time-resolved IR microscopy.

Introduction

Undoubtedly the largest area in the design and development of new polymeric materials is that of multiphase systems, which includes polymer blends and composites along with homopolymer or copolymer systems that can present compositional, structural and/or morphological heterogeneity. The final properties of multiphase materials not only depends on the intrinsic properties of each component and its concentration, but also on the distribution of the components within the system, or in other words their degree of heterogeneity.

Broadly speaking, three types of heterogeneity can be encountered; compositional heterogeneity, structural heterogeneity and morphological heterogeneity. Although various physical and spectroscopic techniques can provide evidence for the heterogeneous nature of a given multiphase system, very few methods exist that allow one to assess the levels of heterogeneity of the system.

Vibrational spectroscopy is often used to characterise multiphase systems, and can provide detailed information on composition and structure. Infrared and Raman microscopy has also been used to study the characteristics of multiphase systems such as compositional variations [1-3], contaminants [4], polymer surfaces and interfaces [5,6]

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and structural and orientational variations [7,8], each providing very specific information. However, due to the heterogeneous nature of many materials one can often obtain misleading or non-representative information depending on how and where the spectra were recorded.

In this lecture, a series of factors that should be taken into consideration when using IR microscopy to evaluate the heterogeneous nature of multiphase systems is discussed, and a number of examples of the type of information available is given in order to illustrate the potential of this technique for assessing levels of heterogeneity.

Observation of heterogeneity

Vibrational spectroscopy is very sensitive to the heterogeneous nature of multiphase systems, however, this sensitivity depends on the scale of the measurement and the size of the heterogeneous domains in the sample.

We can often simply use band relationships in order to obtain information about the levels of heterogeneity and its distribution. By recording several spectra from different points on the sample we can identify a material as more or less heterogeneous compared to another sample by quantifying the differences between relative band intensities. For example, if we record the IR spectra from a polymer film composed of a relatively well-dispersed 2-component blend, and find that for a number of measurements at different positions on the film there is only a slight variation in the relative intensity of bands due to each component, for many purposes we might consider this sample as being homogeneous if the variation in the relative band intensities is no greater than 1-2%. However, in order to adopt this type of criteria we must consider the measurement scale. In the above case, we expect to illuminate between 5 – 10 mm of the sample in a standard IR sample area. However, if we measure the same sample in an IR microscope through a 25 μm aperture, the results will most probably be completely different.

We can illustrate this point with data obtained from a 70/30 wt% blend of poly(aryl ether ether ketone), PEEK and the thermotropic liquid crystal copolyester Vectra®. When we analyse a film prepared in a hot press using standard macroscopic IR sampling we observe a relatively homogeneous distribution of the components over the film. However, by recording the spectra in an infrared microscope through a 100 μm aperture we can observe that the relative intensity of the components is not homogeneous, see Figure 1. When the aperture size approaches the phase separated domain size observed in the optical microphotograh, we can observe details of the type of heterogeneity and its distribution over the area of the sample studied.

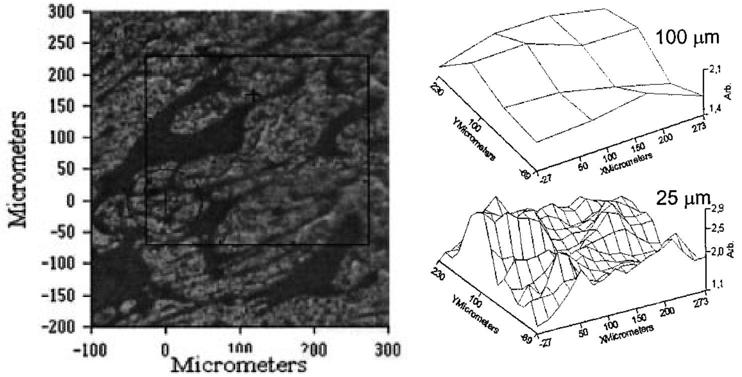


Figure 1. Optical microphotograph of a PEEK/Vectra® blend, and corresponding axonometric plots of the composition for 100 μm and 25 μm aperture sizes.

This type of observation raises a series of important considerations for the study of multiphase systems by vibrational microscopy.

Measurement of heterogeneity

A number of points should be taken into account when measuring the heterogeneity of a polymer system.

1. Sample preparation

A careful control of the thermal and mechanical history of the samples under study must be undertaken, in order that the data are comparable between samples. In this respect, uniform sample thickness is recommended in order to eliminate possible distribution variations in the thickness direction of the film. Further, since the processing conditions evidently condition the heterogeneity, the reproducibility of the sample preparation should be carefully considered.

2. Representative areas

In order to develop a useful analysis, representative areas of the sample should be selected. In this respect, the same criteria must be applied for their selection, which generally implies a careful optical inspection of the samples in order that any non-systematic variations, such as contaminants, are avoided. The larger the representative area, or the more numerous the areas included in the sample set, the better the analysis.

3. Selection of bands

In the first instance, the type of variation needs to be identified spectroscopically. In this respect, one should look for specific bands for each variable to be considered, if possible well separated and clearly differentiated from each other. Possible distortions in the data through variations in the spectral background and high spectral noise where very low band intensities are to be used should be taken into account. Finally, cooperative effects and perturbations should be carefully assessed, particularly where compositional, structural and morphological differences arise simultaneously and affect the relative intensities of the bands under consideration.

4. Mapping characteristics

The size of the sampled area is fundamental, since it defines both the measurement scale, and ultimately the limit of the detectable domain sizes, and the timescale. For example, "survey" maps of an area 10 x 10 cm^2 of a polymer film recording a spectrum every 10 mm in the IR sample area, or of an area of 10 x 10 mm^2 every 1 mm through a 100 μm aperture in an IR microscope, will generate 100 spectra. These maps may allow us to distinguish large domains. For the observation of intermediate domain sizes, we might consider a map of 1 x 1 mm^2 every 100 μm with a 100 μm aperture, giving us once again 100 spectra. In a typical modern microscope with a motorized stage and mapping software, this will take around 5 minutes. Sometimes simple line-scan surveys can give us some idea of the degree of variation in the parameter we are studying in a given direction, are less time consuming, and can provide some information on the size of the different domains. However, we may require higher spatial resolution in order to obtain information on the domains. It must be pointed out that, for example, a 1 mm x 1 mm map with a step size of 25 μm will produce 1600 spectra, and will take more than 5 hours to obtain! Thus, the study of smaller domain sizes is not only restricted by the spatial resolution of the microscope, around 10 μm at 1000 cm^{-1}, but also by the feasibility of the timescale of the measurement. The use of focal plane array detectors has greatly improved this situation by reducing significantly the measurement time [6,8-10], and directly providing an IR image of the area we wish to study, making this type of study more feasible at relatively high spatial resolution.

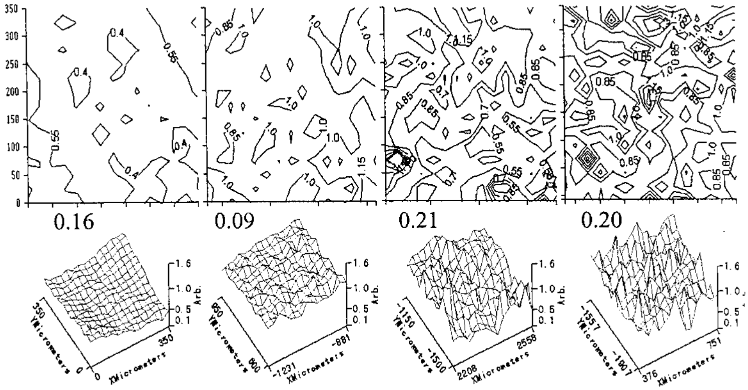
Types of heterogeneity

In order to illustrate the type of information available, examples are presented from each broad type of heterogeneity previously defined.

Compositional heterogeneity

Although functional group or band ratio mapping has been used for several years in order to study the composition of heterogeneous systems, such as fibre-reinforced composites [6], multilayer polymers [1,4] and polymer blends [2,3], little work has been applied to the determination of the levels of heterogeneity from the IR mapping data.

We are evaluating this possibility for a number of multiphase polymeric materials, including polyolefin blends based on an ethylene-propylene (EP) copolymer matrix and polyethylene (E) or ethylene-propylene elastomers (R) as the second component. In order to illustrate our strategy, the example given in Figure 2 shows a series of band ratio maps characteristic of the ethylene and propylene content of 4 blends comprising of block (bEP) or random (rEP) matrix with identical ethylene content blended with E or R, having an overall ethylene content of 28 ± 2%. The maps were recorded over an area of 350 x 350 μm^2 with a 25 μm square aperture.



(a) (b) (c) (d)

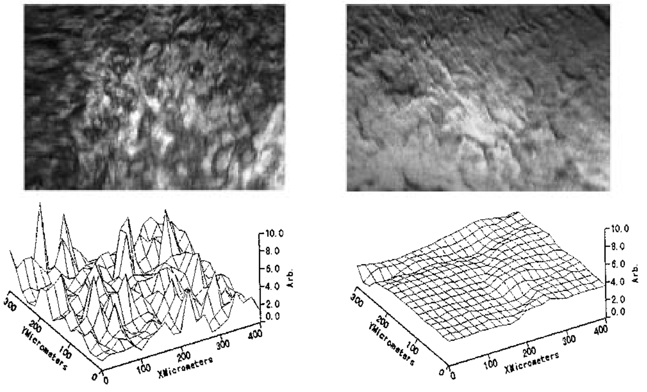
Figure 2. Contour maps and axonometric plots for the compositional heterogeneity of polyolefin blends, 350 x 350 μm^2 with 25 μm aperture: (a) bEP + PE, (b) bEP + R, (c) rEP + PE and (d) rEP + R. Values of f_H are given for each sample.

It can be observed from both the contour maps and the axonometric projections (each represented with the same z axis scales) that in general the blends with the block copolymer matrix appear to be less heterogeneous than those associated with the random copolymer matrix. In order to be able to correlate these results with, for example, optical and mechanical properties, we have attempted to use a numeric heterogeneity factor, f_H based on the standard deviation in the data normalised to the band ratio measured on the same film using macroscopic sampling, given in each curve.

The value of f_H is not sensitive to the type or size of domains observed, and can only give an overall value for the dispersion in the band ratios over the analysed area. It is, however, particularly sensitive to variations in the background such as interference fringes, and an example of this can be observed in the undulation in the map in Figure 2a, where a higher value of f_H is found for what appears to be a more homogeneous sample. When this occurs, we find that encapsulating the films in an IR window material such as KBr helps to reduce this problem. It is clear that a more sophisticated analysis of the topology is required, and is the subject of ongoing studies.

Structural heterogeneity

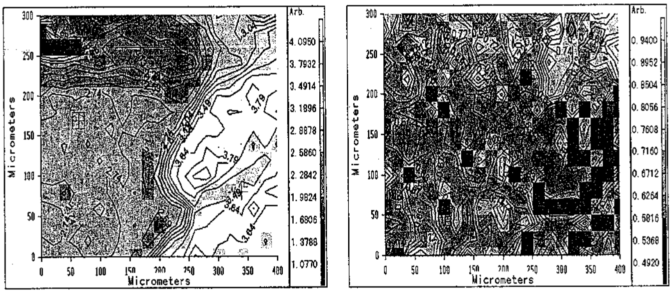
The example in Figure 3 illustrates how we can use IR band ratio mapping to obtain information not only on the heterogeneity of the system, but also on the structural differences between functionalised and non-functionalised polymer blends. The images in the upper part of the figure correspond to the optical photomicrographs of a 70/30 wt% blend of polypropylene (PP) and nylon-6 (N6), with and without a functionalised PP based on maleic anhydride, details of which are given elsewhere [11].



(a) (b)

Figure 3. Optical microphotographs and IR axonometric plots for PP / Nylon-6 (a) non-compatibilised and (b) compatibilised blends, using the band relationship 1642/1460 cm^{-1}.

It can be clearly observed that the introduction of the compatibilising agent improves the dispersion of the components, and better adhesion between the phases gives rise to an improved melt viscosity which is indicative of compatibilisation of the blends [12]. The IR band ratio maps represent the integrated intensity of the amide I carbonyl band of N6 versus the CH_2 deformations of PP for a film prepared in a hot press, recorded over an area of 200 x 200 μm^2 with a 20 μm aperture. The axonometric projections clearly reflect the improved homogeneity of the samples, but they also can provide us with more information on the system, such as the relative increase in the number of amide groups as a result of the chemical reaction that occurs between the amide and the maleic anhydride units [13,14]. Grey-scale contour maps, such as that in Figure 4a, provide us with information on the chemical structure distribution in the compatibilisation process. Further, since the compatibilisation process also affects the crystallisation behaviour, using a simple band ratio indicative of crystallinity, one is able to follow the variations in crystallinity over the area analysed. In the case of PP, using the band ratio 998 / 973 cm^{-1} [15] we can clearly observe a reduction in the crystallinity in the areas where the sample is more compatibilised, see Figure 4b, it has been shown previously [11].



(a) (b)

Figure 4. Grey-scale contour maps for a 70/30 wt% PP/Nylon 6 blend, (a) compatibilisation map (1642/1460 cm^{-1}), and (b) crystallinity map (998 / 973 cm^{-1}).

Morphological heterogeneity

In the final example, we consider the crystalline morphology in a homopolymer, isotactic polypropylene (iPP). It is well known that iPP exhibits four crystalline polymorphs, depending on the thermomechanical history of the samples or the addition of nucleating additives [16]. Recently we have demonstrated that it is possible to characterise the crystalline morphology of a sample with both α-iPP and β-iPP spherulitic structure through the differences between the IR spectra, as can be observed in Figure 5 [17]. We have observed [18] that some band ratios in bulk IR measurements can be associated with the relative amounts of each polymorph calculated from x-ray diffraction data using either the method of Turner-Jones [19], or that reported more recently by Zhou [20]. These differences have allowed us to map the polymorphic distribution in iPP films as a function of the type and amount of β-nucleating agent and the thermal history.

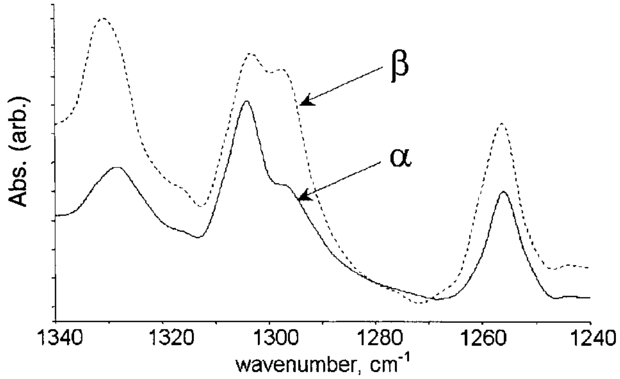


Figure 5. IR spectra recorded from α- and β- spherulites in an isothermally crystallised sample of iPP. The Spectra are normalised on the intensity of 1168 cm^{-1} band.

As an example, Figure 6a shows a polarised light micrograph of an area of a film with 250 ppm pimelic acid as a β-nucleating agent, dynamically crystallised at a cooling rate of 20°C/min, where we can clearly observe the different crystalline forms, since β-iPP is characterised by a much higher birefringence [16]. We have recorded spectra through a 25 μm aperture over an area of 250 x 250 μm^2 marked on the image, and constructed a grey-scale contour map using as an example the band ratio 1330 / 1168 cm^{-1}. We can clearly distinguish between the α-rich and β-rich areas of the sample. On the other hand, Figure 6b shows the case for 1000 ppm pimelic acid, where a much more homogeneous distribution is observed in both the polarised optical micrograph and the grey-scale contour map. Further, Figure 6c shows the spectra obtained from the positions marked α and β in Figure 6a, and those obtained from several positions on the sample in Figure 6b, given in Figure 6d, clearly demonstrate the improved homogeneity of the system.

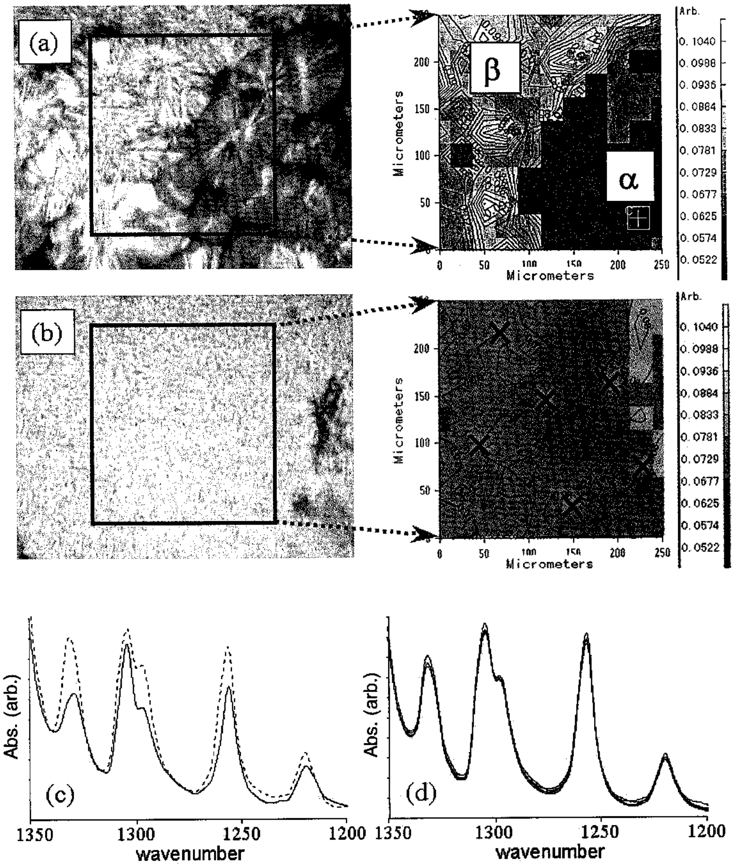


Figure 6. Polymorphic distribution in iPP. Polarised optical micrographs and grey-scale contour maps for samples with (a) 250 ppm, and (b) 1000 ppm of β-nucleating agent. Spectra recorded for (c) α-rich area (continuous line), and β-rich area (dotted line) in sample (a), and (d) at the positions marked X in sample (b). The spectra are normalised on the intensity of the 1168 cm^{-1} band.

Using the same type of band relationships in samples with a high proportion of β-iPP, we have also been able to follow polymorphic phase transitions as a function of temperature in KBr encapsulated films with IR microscopy using time-resolved software and a programmable hot stage. Figure 7 shows the β – α phase transition, which we observe at around 160°C, followed by the melting of the α phase at around 180°C, which correlates very well with previously obtained x-ray, DSC and TOA data [21].

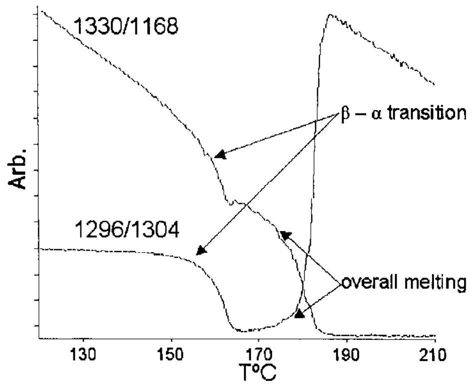


Figure 7. Observation of polymorphic transitions in iPP by following the variations in the relative band intensities shown using time-resolved IR microscopy measurements, at a heating rate of 1°C/min.

Closing remarks

IR microscopy is a powerful tool for the characterisation of heterogeneity in multiphase polymer systems. Carefully applied, it is capable of providing detailed information on the heterogeneous nature of the systems under study, and the appropriate methodology can provide useful parameters for the design, development and control of multiphase polymeric materials.

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References

[1] J. L. Koenig, *"Microspectroscopic imaging of polymers"*, American Chemical Society, Washington D.C. 1998

[2] A. Garton, D. N. Batchelder, C. Cheng, *Appl. Spectrosc.* **1993**, *47*, 922

[3] L. Markwort, B. Kip, *J. Appl. Polym. Sci.* **1996**, *61*, 231

[4] H. J. Humecki, in *"Infrared Microspectroscopy. Theory and Applications"*, R. G. Messerschmidt, M. A. Harthcock (eds.), Marcel Decker, New York 1988

[5] C. Sammon, C. Mura, P. Eaton, J. Yarwood, *Analusis* **2000**, *28*, 30

[6] A.M. Mavrich, H. Ishida, J. L. Koenig, *Appl. Spectrosc.* **1995**, *49*, 149

[7] J. M. Chalmers, N. J. Everall, K. Hewitson, M. A. Chesters, M. Pearson, A. Grady, B. Ruzicka, *Analyst* **1998**, *123*, 579

[8] J. M. Chalmers, N. J. Everall, *Analusis* **2000**, *28*, 53

[9] E. N. Lewis, L. H. Kidder, J. F. Arrens, M. C. Peck, I. W. Levin, *Appl. Spectrosc.* **1997**, *51*, 563

[10] R. Bhargava, B. G. Wall, J. L. Koenig, *Appl. Spectrosc.* **2000**, *54*, 470

[11] C. Marco, G. Ellis, M. A. Gómez, J. G. Fatou, J. M. Arribas, I. Campoy, A. Fontecha, *J. Appl. Polym. Sci.* **1997**, *65*, 2665

[12] I. Campoy, J. M. Arribas, M. A. M. Zaporta, C. Marco, M. A. Gómez, J. G. Fatou, *Eur. Polym. J.* **1995**, *31*, 475

[13] F. Ide, A. Hasegawa, *J. Appl. Polym. Sci.* **1974**, *18*, 963

[14] I. Grof, O. Durcova, M. Jambrich, *Coll. Polym. Sci.* **1992**, *22*, 270

[15] R. G. Quynn, J. L. Riley, D. A. Young, H. D. Noether, *J. Appl. Polym. Sci.* **1959**, *2*, 166

[16] J. Karger-Kocsis (ed.) *"Polypropylene. Structure, blends and composites. I. Structure and morphology"*, Chapman & Hall, London 1995

[17] G. Ellis, M. A. Gómez, C. Marco, *Int. J. Vibr. Spec.*, [www.ijvs.com] **2001**, *5(4)*, 7

[18] G. Ellis, M. A. Gómez, C. Marco, C. Blancas, unpublished results.

[19] A. Turner-Jones, J. M. Aizlewood, D. R. Beckett, *Makromol. Chem.* **1964**, *75*, 134

[20] G. Zhou, Z. He, J. Yu, Z. Han, G. Shi, *Makromol. Chem.* **1986**, *187*, 633

[21] C. Marco, M. A. Gómez, G. Ellis, J. M. Arribas, *J. Appl. Polym. Sci.* **2001**, in press.