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Raman Microspectroscopy of Polymeric Materials

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SUMMARY: Vibrational spectroscopy is an important tool to characterize polymeric materials. Confocal Raman Microspectroscopy allows to analyze micrometric areas and yields information about the chemical and physical parameters of polymers. The interpretation of the Raman spectra is usually related to the properties and processing. Thus, this non-destructive technique is appropriated to investigate the skin/core morphology of injection-molded semicrystalline polymers, blends, interface of composites, etc.

Introduction

Raman spectroscopy provides information about molecular composition, structure (configuration and conformation), orientation and morphology (i. e. amorphous or crystalline phase). This technique is based on the spectral distribution of inelastically scattered light and by coupling an optical microscope to a conventional Raman spectrometer, the technique becomes a microprobe with spatial resolution at about 1 μm. The dimension of the focal region (d) depends on the numerical aperture (NA) of the microscope objective and wavelength (λ) of the radiation ($d = 1.22\ \lambda/NA$)1).

Raman Microspectroscopy is a non-destructive technique that offers a unique combination of spatial resolution and chemical/physical characterization. It enables measurements of many chemical and physical properties, including chemical composition, molecular orientation, conformation, crystallinity, strain, temperature and so on.

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In a *Confocal Raman microscope* the laser beam is filtered by an illumination pinhole and the Raman light scattered by the sample is directed to an adjustable pinhole placed in the image plane of the microscope objective. This arrangement ensures that only light coming from the focal plane entirely reaches the detector while the one coming from upper and lower planes is partially attenuated. Hence, the depth resolution of the microscope is increased. The confocal microscope also offers improved lateral resolution compared with conventional microscopes. The use of very small pinhole (100 μm), typical values for NA and visible laser gives a spatial resolution of 1-2 μm and depth resolution of 2-4 μm[2]. *Confocal Raman Microspectroscopy* is appropriated to the structural analysis of very small areas, impurities, inhomogeneities, interface adhesion, interlayer diffusion, molecular orientation and local stress.

Polarized Raman Microspectroscopy can yield information on the molecular orientation distribution in polymer samples. Chain orientations can be detected by the analysis of the spectra with the polarized laser beam and the scattered light. The polarizing optical system normally used is shown in Figure 1.

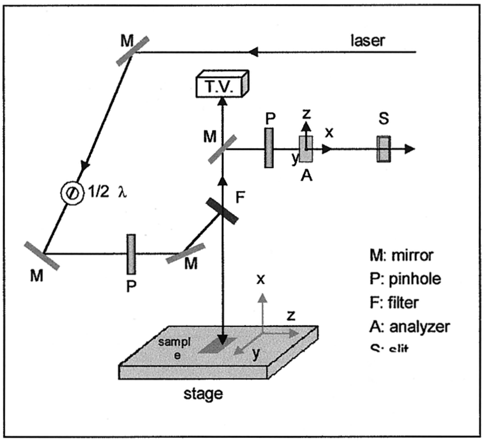

Figure 1. Optical system used for the polarized confocal micro-Raman measurements

Confocal Raman Microspectroscopy is also a widely used technique to analyze, map and image chemical and physical properties in one, two and three dimensions. The sample is usually placed on an automated xyz stage. Raman spectra at different points can be collected allowing the mapping of a selective area of the sample. In this way, full spectra can be carried out throughout a sample and properties can be reconstructed from the spectra and displayed as line, area or volume image3)

Raman Microspectroscopy has been used in a huge of works to characterize the influence of thermal treatments, stress process, degradation, etc. on the structure of polymers. Blends materials are also analyzed to get information of the immiscible components. Influence of the fillers in the polymer structure is also investigated with this technique. The properties of composites are mainly related to the interface fiber/matrix and the multilayer materials characteristics depend of the adhesion of the different components. *Confocal Raman Microspectroscopy* is a very useful technique to characterize the structural properties of the interface.

This technique has been also used to analyze thermoplastics reinforced by ceramic nanoparticles. The main problem of these nanocomposites is to get non-aggregated nanofillers in the matrix. However, a good interaction between matrix/nanoparticles is important to improve physical properties (permeability, tensile and flexural modulus, abrasive, stiffness, wear resistance, etc.). *Confocal Raman Microspectroscopy* has been used to detect structural perturbations around the nanoparticles as influence of the thermal treatments or injection process. These preliminary results show how the manufacture process induces a chain orientation on the matrix but different from the one produced around the nanoparticles

In this work, *Confocal Raman Microspectroscopy* has been used to investigate conformational changes of injection-molded semicrystalline PET parts, microdomains in two-phase structure blends of PC/PSAN and molecular orientation in transcrystalline structures of iPP.

Polymer characterization

A) Injection-molded PET

Uniaxial deformation4) or thermal treatments produce structural changes or chain orientation in most of the polymers, that could be monitored by vibrational spectroscopy. Micro-Raman technique allows to detect these changes in a very small area of the sample.

Because of the intrinsic characteristics of PET, either by thermal or mechanical modifications it is possible to obtain the polymer in amorphous or crystalline state5). Both orientation and crystallization mechanisms during the processing of material play a fundamental role, because properties of the end-use products are strongly influenced by structural characteristics.

Injection molding is one of the methods used for the processing of industrial parts of PET. During the injection process, the sample will be subjected to different temperatures and times of crystallization. This leads to a different crystallization throughout the whole volume and consequently to conformational changes that could be followed by means of spectroscopic techniques. So, the plastic injection molded parts generally show different microstructure on the surface (in contact with the mold walls in the injection machine) or inside the material. This skin/core structure can be optically observed by an optical microscope. Because of the high lateral and axial resolution of *Confocal Raman Microspectroscopy*, this technique allows to determine structural distribution on a cross section of the molded-injected sample. The structural characterization is based on the determination of the conformational distribution along the volume of the sample.

The intensity of Raman scattering by a functional group is proportional to its concentration. This relation is used for the determination of the relative concentration of polymers, which are present in several conformations. Raman bands situated at 998 cm^{-1} (assigned to a trans-conformation of the ethylene glycol segments) and 886 cm^{-1} (assigned to a gauche-conformation) are suitable for monitoring the conformational changes in annealed PET[6]. The Raman band at 793 cm^{-1} is used as a reference band. Changes in the relative intensities of the bands associated to both gauche (in the amorphous phase) and trans conformations (in both amorphous and crystalline phases) are observed when the spectra were collected along a cross section of the injection-molded sample[7]. In order to obtain a complete picture of isomer distributions in the injection-molded samples, spectroscopic results were correlated with DSC measurements. The combination of both techniques allows to separate the trans isomer into crystalline and amorphous trans isomer and detect its change along the injection-molded part. The complete picture of the individual isomer distribution versus the distance from the surface is shown in Figure 2. It can be observed that the injection-molded part shows: a mainly amorphous skin (of about 600-750 μm) and a more crystalline core. In the skin layer the crystalline trans isomer is estimated around 15 % increasing until about 40 % inside the material.

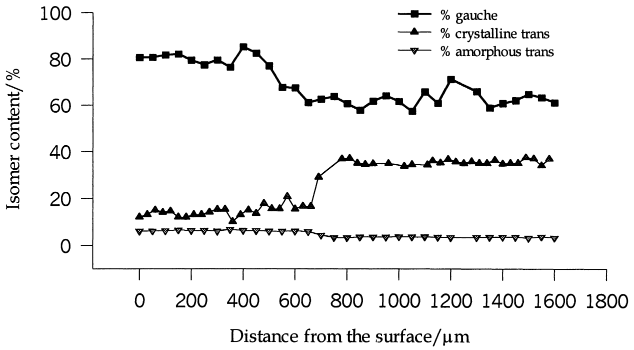

Figure 2. Distribution of rotational isomers in injection-molded semicrystalline PET as a function of the distance from the surface

B) Blends PC/PSAN

Partially miscible polymers form heterogeneous blends with microscopically distribution of the components. Physical properties of these blends are closely related to the composition, distribution, phases, etc. Thermal treatments or plastic deformation through the transformation of the microdomains can transform these properties. Confocal Raman Microspectroscopy is a useful tool to analyze microdomains in two-phase structure blends.

Bisphenol A polycarbonate (PC) and poly (styrene-co-acrylonitrile) (PSAN) are partially miscible polymers forming heterogeneous blends with a good adhesion at the formed interfaces, which ensures a good stress transmission between constituents during deformation up to fracture.

PC/PSAN blends can be formed with different percentages of the individual polymers. For the Raman study, the bands at 887 cm^{-1} and 1002 cm^{-1} were selected as the most characteristic bands of PC and PSAN respectively. The high spatial resolution of the *Confocal Raman Microspectroscopy* technique let us follow the distribution of regions with different chemical composition (domains rich in PC or PSAN) in the cross section of the samples. A 20x20 point rectangular area was mapped on an isotropic area (5 x 5 μm), so 400 Raman spectra were obtained. The Raman spectra for each individual sample point was processed in order to obtain the desired spectral Raman image, also called a Raman map. The ratio I_{887}/I_{1002} was used for the construction of the Raman images to show composition changes in the mapped regions. The pseudo 3-D representation of the Raman image of a isotropic zone in a 50/50 PC/PSAN blend is shown in Figure 3a, in which the PC domains distribution is easily observed. However, the magnified 2D representation of a part of the image (Figure 3b) reveals the possibility of a more complex compositional structure of the material: inside a PC domain, some very small domains rich in PSAN seem to exist.

Raman mapping of these materials after plastic deformation shows that the domains are markedly prolonged in the direction of uniaxial deformation8). The behavior of the PC/PSAN blends with respect to the changes in chain orientations occurs during injection molding and results a substantially oriented PC chains in the plastic deformation process; on the other hand, PSAN, despite marked elongation of the microdomains, attains only a slight chain orientation8).

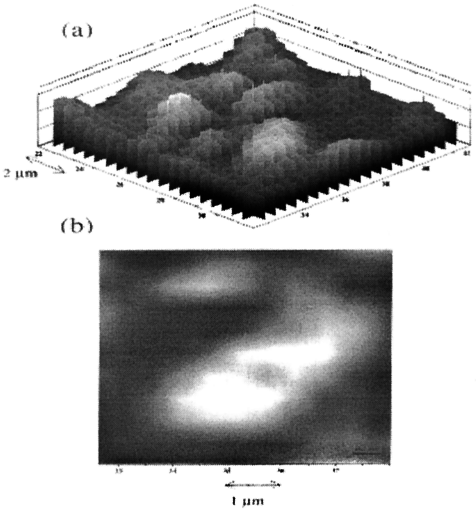

Figure 3. (a) 3D representation of the spectral image of an isotropic region of 50/50 PC/PSAN blend; intensity (the vertical axis) is proportional to the I_{887}/I_{1002} ratio in the respective point of the specimen; (b) 2D magnified representation of the spectral image of a part of the same region, showing its complex structure; increasing PC/PSAN ratio is represented by increasing whiteness of the picture. (From ref. 8)

C) iPP / PET fiber composites

Polymeric composites have been developed for highly advanced performance materials. The role of the interface in a composite system is important not only to understand the multicomponent materials, but also to improve the mechanical and physical performance of composite materials. In this kind of materials, the interface acts transmitting a stress from one phase to another phase. The efficiency of this stress transfer is dependent on the nature of composite interface.

The studies of molecular microstructure of interfaces in composites will lead to a better understanding in the relationship between interfacial structure and mechanical properties of multicomponent materials. Confocal micro-Raman spectroscopy which have been used to characterize materials can also be used as a non-destructive technique to measure the structure of the interface fiber/matrix9), or measure directly stress or strain in the reinforcing fibres10).

The processing of isotactic Polypropylene (iPP)/glass fiber or organic fiber composites modifies to a great extent the behavior of the polymer during crystallization because of the role of nucleating agents played by fibrous fillers, the pre-impregnated agents and the presence of shear stress. These particular conditions are able to promote the appearance of a transcrystalline phase in the vicinity of the fibers. The multiplication of the number of nuclei of heterogeneous crystallization prevents a three-dimensional spherulitic development of the lamellae. Thus, spherulite growth is constrained to develop in only one direction, which is normal to the filler surface. This phenomenon, known as transcrystallinity, typically takes place during the crystallization from the melt of many thermoplastic polymers in the presence of fibers, e. g. organic fibers. (Figure 4).

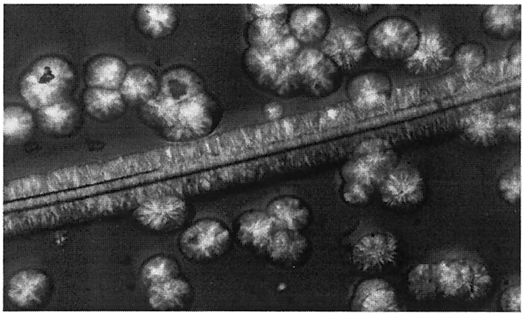

Figure 4. Polarized optical micrograph of iPP/PET fiber, showing the transcrystalline region around the fiber.

Transcrystalline layers around uncoated PET fibers are formed by the α crystalline modification of iPP. Molecular orientation of this iPP-transcrystalline phase was analyzed by *Confocal Polarized Raman Microspectroscopy.* The Raman bands of uniaxially oriented iPP can be classified into three groups: those polarized in a parallel direction with respect to the molecular chain (type $A_{||}$), perpendicular ($A_{\perp}$) and unpolarized bands (E). The Raman bands detected at 809, 973 and 1167 cm^{-1} have been proposed for the study of molecular orientation in uniaxially oriented iPP$^{11)}$. Bands situated at 841, 997 and 1151 cm^{-1} were found no sensitive to the polarization conditions. Information on the orientation of the polypropylene chains on the transcrystalline phase has been obtained by collecting Raman spectra under the parallel/parallel polarization condition and subsequent calculation of the ratio of the area under the Raman band at 809 cm^{-1} and 841cm^{-1}. Alternatively, the ratios A(973 cm^{-1})/A(997cm^{-1}) and A(1167 cm^{-1})/A(1151cm^{-1}) have been used.

Figure 5 shows a scheme of a 12x12 point rectangular area that was mapped on a transcrystalline area (60x40 μm^2) with *Confocal Polarized Raman Microspectroscopy*. The above ratios were used for the construction of Raman images to show orientation changes in the mapped regions. The 3-D representation of the Raman image monitored by the ratio A(973 cm^{-1})/A(997cm^{-1}) and for $X(ZZ)\overline{X}$ polarization geometry is shown in Figure 6. Arrows indicate preferential orientation.

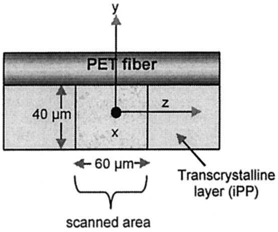

Figure 5. Scheme of the scanned area on the transcrystalline layer

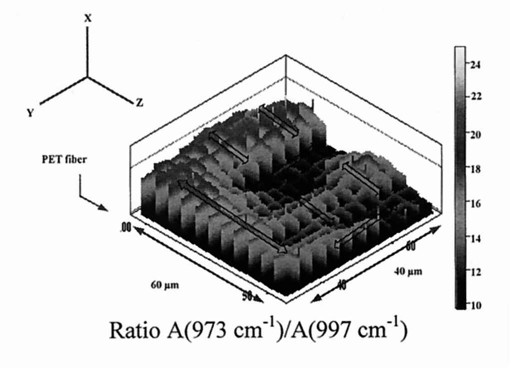

Figure 6. Pseudo 3D Raman image of the transcrystalline layer around uncoated PET fibers (From ref. 9).

From the analysis of the Raman image, it is observed that next to the fiber surface, the molecular chains are preferably oriented parallel to the fiber axis. In contrast, above a distance of approximately 10 μm from the fiber surface, molecular orientation in both parallel and perpendicular directions is observed. These results indicate the presence of two sets of oriented lamellae in the transcrystalline region: lamellae with the chain axis parallel to the fiber surface and lamellae with the chains perpendicular to the substrate surface. This lamellar branching found in the analyzed transcrystalline zone is in agreement with the so-called cross-hatch structure of lamellae(12).

Transcrystallinity around coated PET fibers in iPP matrix is also analyzed in a similar way. The Confocal Polarized MicroRaman measurements show the presence of β-transcrystalline phase for the iPP and no lamellar branching structure has been detected.

Conclusion

Confocal Raman Microspectroscopy has now become a micro analytical technique for both research and industrial applications. This technique can be used to determine properties of polymers in very small areas, blends, and composites. Data carried out from this technique allows to establish the relationship between the microstructural characteristics and properties of polymeric materials

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