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Damage of polymers studied by micro-Fourier Transform Raman spectroscopy

T. Jawhari*, J. C. Merino, J. M. Pastor**

Física Materia Condensada, Facultad de Ciencias/ETSII, Universidad de Valladolid, Valladolid, Spain

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SUMMARY

The potential of the micro-Fourier Transform Raman tool in examining specific localized regions in polymeric materials with some degree of fluorescence when analyzed by conventional Raman spectroscopy is examined. Analysis of characteristic bands of the vibrational spectra obtained in a small area damaged by a visible and NIR laser beam in commercial Polyethylene Terephthalate (PET) shows a different conformer ratio than that observed in a non irradiated zone.

INTRODUCTION

Over the last few years (1-10) an increasingly large number of analytical studies were carried out using the near infrared Fourier Transform (NIR-FT) Raman method as a consequence of the continuous progress made in instrumentation (11-19). The great interest for the NIR-FT-Raman tool among the spectroscopic community once the instrument was commercially available, i.e. near the end of the 80's, is mainly due to the fact that NIR-FT-Raman spectroscopy has eliminated most of the problems associated with fluorescence. For example, in the field of polymers, conventional Raman analyses of polymeric materials with a visible excitation source often show the presence of a large background due to fluorescing particles. This fluorescence effect, which is often derived from impurities present in polymeric materials or by degradation process, strongly interferes with the Raman scattering and as a result it limits the vibrational analysis of the material.

The coupling of a microscopic system to the NIR-FT Raman instrument will enable to record Raman spectra with a higher spatial resolution and take profit of the capabilities of the FT-Raman technique. The advantages that such attracting system would offer to the spectroscopist in the field of microanalysis has brought early interest in examining the feasibility of FT-Raman microspectroscopy. As early as 1988, two research groups (20-21) proposed and built two different micro-NIR-FT-Raman systems in order to explore the capabilities and limitations of FT-Raman microspectroscopy. These preliminary works (20-23) permitted to demonstrate the feasibility of the micro-FT-Raman technique when combined with a NIR source.

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* *Present address:* Serveis Científico-Tècnics, Universitat de Barcelona, Barcelona, Spain

** Corresponding author

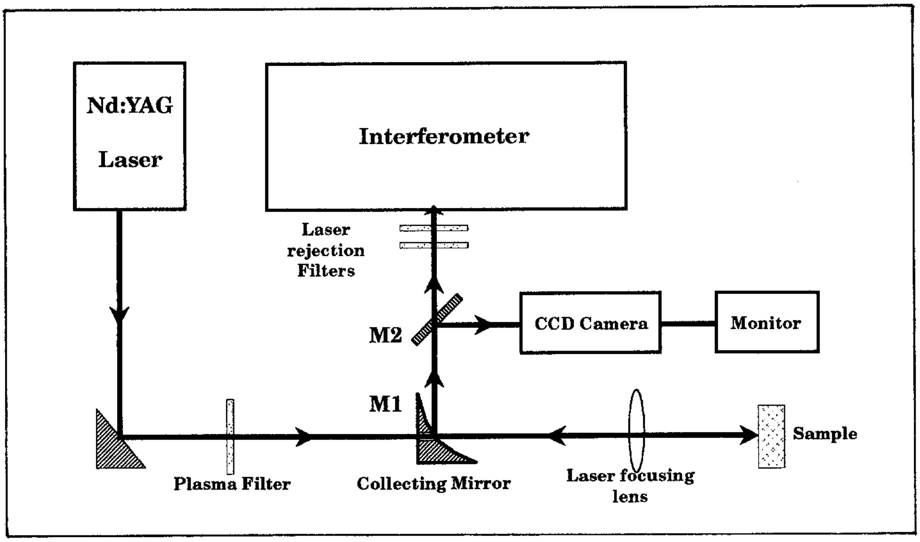

Figure 1. Schematic diagram of the micro-FT-Raman instrument.

In a previous work (24-28) we showed the capability of the micro Raman technique for the structural analysis of microdeformations in polymeric materials. We extended these studies to other kind of deformations on other polymers, but the presence of fluorescence on the spectra hindered the research. The main purpose of the work here presented is to examine the potential of micro-FT Raman spectroscopy when analyzing microstructural changes in some localized regions as well as defects, impurities and damages in materials showing some degree of fluorescence. This technique can be of great interest when studying industrial polymeric materials since they are usually mixed with all kinds of additives such as colorants, stabilizers, antioxidants, lubricants, flame retarders, etc., which make quite impossible the detection of the Raman signal in the visible spectrum. A structural analysis of a small area of Polyethylene Terephthalate damaged by laser beam irradiation is presented.

INSTRUMENTATION

The instrument used in this work is a commercial Bomem (series MB 155) and it consists of a FT-Raman compartment attached to the Michelson MB 155 FT-IR spectrometer which allows to carry out both FT-Raman and FTIR analyses. The schematic diagram of the micro-system is given in figure 1. Excitation for FT-Raman experiments was obtained with a near infrared diode pumped solid state (Nd^{3+}:YAG) laser operating at 1.06 μm. The laser used here, a Laser Diode-LDP 1000 series, provides up to 2 W of power (TEM_{OO}). The beam of approximately 2 mm diameter is focused by a lens (f/2.5) onto the sample. The spot size obtained at the sample is of the order of 20 μm. The backscattered light is collected by an ellipsoidal mirror M_1 which is then directed to the interferometer, and finally detected by a thermoelectrically cooled InGaAs detector. A small mirror M_2 can be added on the path of the scattered beam after the collecting mirror M_1 in order to deviate some of the radiation to the CCD video camera that permits simultaneous visualization of the sample and the laser spot. Plasma filters are placed near the laser output to eliminate the plasma lines emitted by the Nd^{3+}:YAG laser. Furthermore, two dielectric filters are used in order to avoid intense laser reflections and Rayleigh scattering reaching the detector. The combination of the high rejection laser filters and the cooled InGaAs detector allow to record Raman spectra between 200 to 3350 cm^{-1}. A He-Ne rejection filter is also added in the infrared sample compartment in order to cut off the radiation provided by the He-Ne laser of the interferometer.

In the macro-configuration, the high focusing lens situated between the ellipsoidal mirror and the sample is removed and replaced by a lens situated just after the plasma filter. The spot size produced at the sample with macro-geometry is of the order of 200 μm. The spectra presented in this work were recorded at 4 cm^{-1} resolution with a laser power at the sample varying between 100 and 600 mW. The spectra illustrated here were not corrected for instrumental response.

RESULTS AND DISCUSSION

First, it must be noted that one of the main features of the instrument when used in the micro-Raman mode is the good reliability shown even when run over large periods of time. The performance of the micro-FT Raman tool used here was found to be quite satisfying when compared to the macro-FT-Raman instrument. This can be tested in a bulky brown coloured industrially processed polyetherimide, recording the FT Raman spectra with both macro and micro collection geometries under the same experimental conditions (Figures 2 A and B). Such a material is known as a difficult sample since no conventional Raman signal of this industrial material can be detected due to the high level of fluorescence emited in the visible.

Although the spatial resolution has not been experimentally measured, the lateral resolution must be poorer than 20 μm which corresponds to the laser beam diameter in the case of the micro-FT-Raman experiment. Such resolution may be improved by reducing the focused volume of the laser beam at the sample as long as the sample does not show some heating effects. Axial resolution would be lower due to the fact that no limiting pinhole was used in this study. Actually, it was experimentally noted that the spatial resolution, particularly the axial resolution, obtained with the micro-FT-Raman instrument, is much poorer than that obtained with a conventional Raman microprobe using an Ar^{+} ion laser operating at 514.5 nm (24).

The experimental work was carried out on commercial polyethylene terephthalate (PET) films submitted to visible laser radiation (514.5 nm; 5 mw at sample) for 20 seconds. The laser degraded zone is investigated by using the NIR-micro-FT-Raman instrument. The optical micrograph given in Figure 3 illustrates the degraded region of about 150 μm diameter. In a previous work (29,30) the variation of the conformers in PET was obtained as a function of the temperature of treatment. This work was made by using FTIR spectroscopy with Photoacoustic detection (29) and FT Raman spectroscopy (30) and allowed to follow the evolution of the trans crystalline, trans amorphous and gauche amorphous conformers with the different thermal treatments submitted to PET. Although the variation of the bandwidth of the Raman band at 1725 cm^{-1} (C=O stretching) is often associated with crystallinity (31), in fact, it is really due to the conformational changes in the polymer (29,30,32). Similarly, the Raman band at 1094 cm^{-1} (stretching of ring CC, ester C(O)-O and ethylene glycol CC bands) was assigned to trans conformations (29,30,32). As the Raman band at 1117 cm^{-1} does not show any changes with annealing treatment, it has been usually used as a reference band (32).

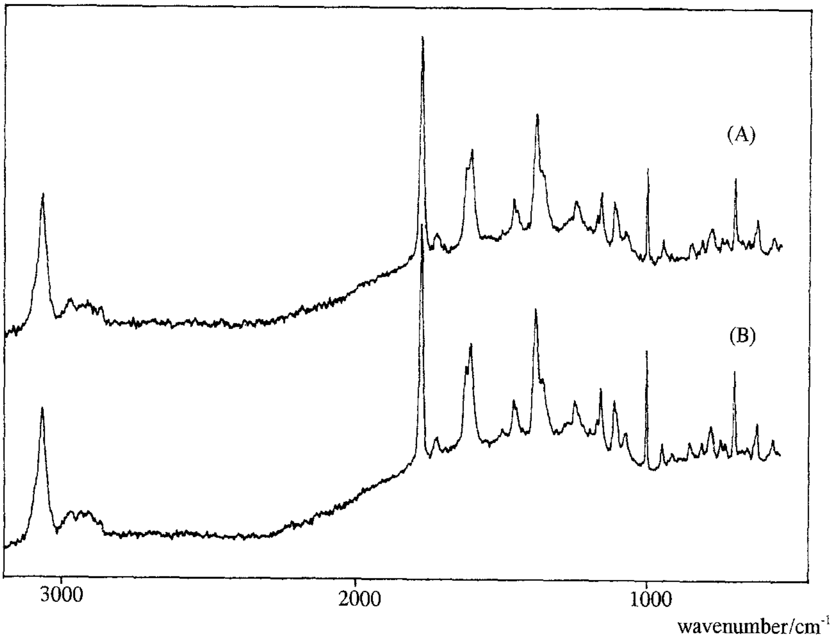

Figure 2. Micro (A) and macro (B) FT-Raman spectra of polyetherimide (resolution: 4 cm^{-1}, 50 scans, laser power:300 mW).

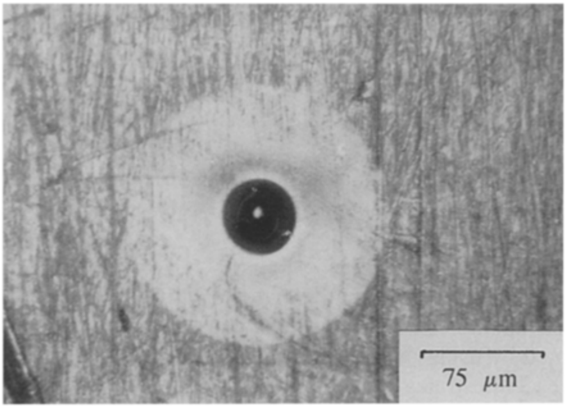

Figure 3. Optical micrograph of a laser degraded region in PET.

To interpret the micro-FT Raman spectra recorded in the degraded zone and the region non affected by the laser irradiation were used those former results. Thus, in Figure 4 it can be observed that the bandwidth of the C=O stretching mode increases in the damaged zone. Furthermore, the intensity ratio between that of the bands at 1094 cm^{-1} and 1117 cm^{-1} is found to decrease in the laser treated region. We can conclude that the irradiated region presents a lower degree of order (higher amorphous conformers) (29,30) than in the non treated region. This result can be explained by the fact that the zone submitted to laser irradiation has locally melted followed by a poorer degree of reorganization.

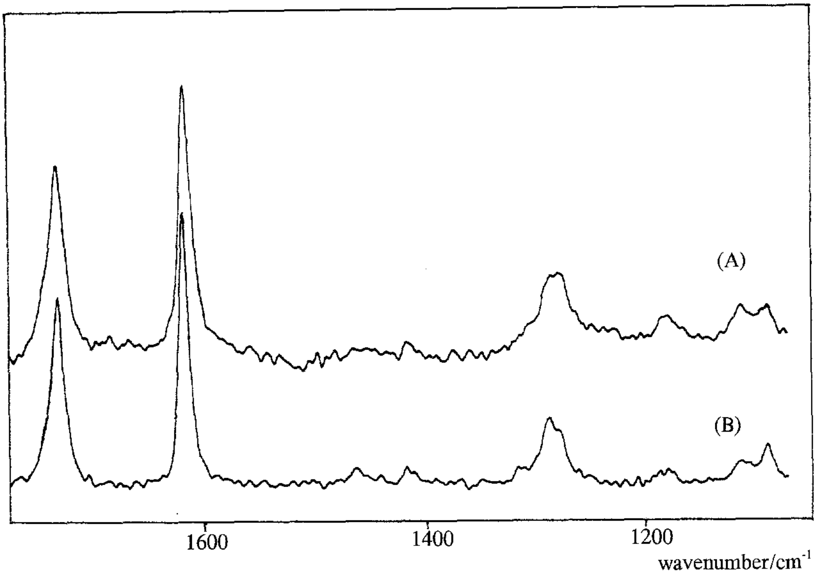

Figure 4. Micro-FT-Raman spectra of PET recorded in the degraded region (A) and in the non-damaged zone (B). (resolution:4 cm^{-1}, 1000 scans, laser power: 300 mW).

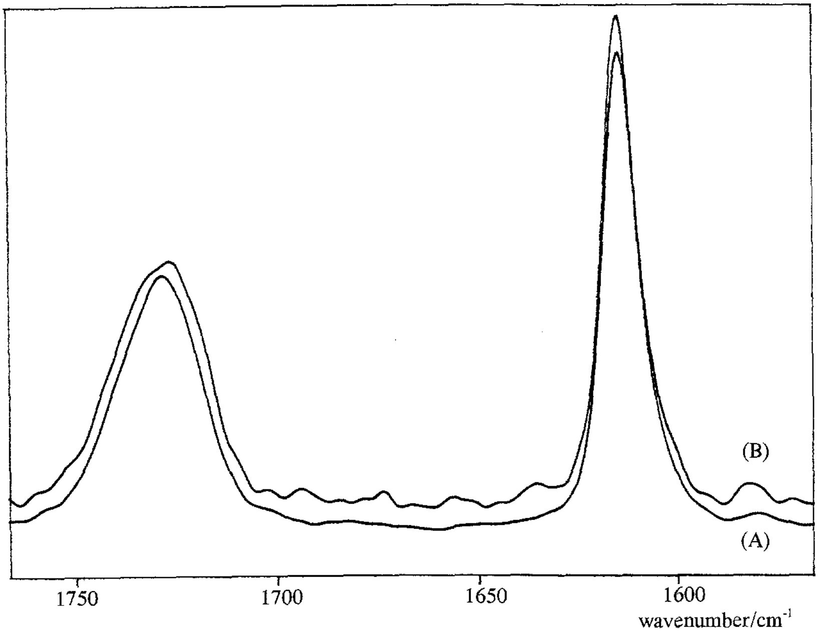

Figure 5. Micro-FT-Raman spectra of PET recorded in the laser annealed (A) and non laser annealed (B) regions. (resolution:4 cm^{-1}, 200 scans, laser power: 400 mw).

Conversely, a prolonged NIR (1.06 μm; 1.3 w at sample) laser irradiation during 1 hour of an amorphous PET was found to slightly augment the degree of order (higher crystalline trans conformers) (29,30) in the irradiated zone. This is observed as a decrease in the bandwidth of the C=O stretching mode at 1725 cm^{-1} for the FT-spectrum recorded in the laser irradiated region (Figure 5). It can be precised here that the information obtained from Figures 4 and 5 cannot be achieved using the conventional micro-Raman spectrometer as a result of the high fluorescence emitted in the laser treated zone.

CONCLUSIONS

This study indicates that it is possible to get structural information in some small localized regions in polymeric materials by using a NIR-FT-Raman instrument with a microscopical accessory. The use of this technique on Polyethylene Terephthalate irradiated with a laser beam, enables the analysis of the conformational order inside and outside the damaged area. The visible radiation produces a lost of crystalline trans conformers (less order), while the NIR radiation provokes an increase in the crystalline trans conformers (more order).

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