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RAMAN SENSORS: INTEREST AND APPLICATIONS

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Abstract – We demonstrate the interest of the Raman sensors in various aspects of studies in chemistry and physics. We illustrate the advantages of this technique in two applications that we have recently investigated. For the first industrial application, we related the stress of a polymer during its deformation with the Raman intensity and for the second, we managed to determine the NaCl concentration in a liquid solution. For these two applications, we develop our own signal processing to extract information from the Raman intensity.

Keywords: Raman sensor, optical probe

1. INTRODUCTION

Raman spectroscopy (RS) is a well established technique to study the vibrational properties of a solid, liquid or gas, in relation with the structure and properties of the substance. It is less frequent to use RS as a probe of physical characteristics of a substance. Raman sensors are enabled to employ recent technical improvements in the development of smart apparatus, with higher spatial resolution and possibilities of long-distance or on-line measurements.

One of the main advantages of the Raman sensor is the combination of the determination of a physical parameter, as in usual sensors, with the physical microscopic mechanism associated with the change of this parameter. An additional advantage of the Raman probe is its non-destructive character as any optical technique, and furthermore in contrast with many other ones, it does not need any preparation of the specimen, allowing an on-site measurement, and only a small volume of the substance (diameter of one micrometer or even less) is necessary for the analysis.

Two examples recently investigated in our lab are presented, showing the abilities of a Raman sensor in two completely different applications. The first application consists into the determination of a mechanical deformation in a polymer. The second demonstration concerns the measurement of the concentration of a salt in a diluted solution.

It is reminded that the RS results in an inelastic collision between the exciting light beam with the substance under study and the energy shift of the photons provides the energy (frequency) of the optical phonons characterizing the substance. The efficiency of the Raman effect and thus the scattered light intensity depends on the deformability and polarizability of chemical bonds. A Raman line is often specific for a chemical bond. Therefore RS can be used to identify the vibrational mode and thus the associated chemical bond responsible by example for a phase transition.

Three informations can be usually derived from the treatment of a Raman line. The first one is the position of the maximum of the peak, which provides approximately the frequency of a particular optical phonon. This phonon frequency is sensitive to any external parameter such as the temperature, the pressure, … influencing the substance. The FWHM (Full Width at Half Maximum) of the Raman peak is related to the phonon damping and reflects the ordered or disordered character of the structure. At last, the third parameter is the intensity at the peak maximum, or still the integrated intensity of the Raman line. The absolute value of the scattered intensity obviously depends on the experimental conditions, such as the laser beam power, the optics of the setup, the spectrometer resolution… However, it is possible to relate the relative change of intensity to concentration of the species active in a particular vibrational mode and associated peak.

The peak position (mode frequency), the linewidth (damping) and intensity extracted from a Raman line can be therefore used for the determination of physical parameters in a Raman sensor. The choice of the relevant parameter among these three possibilities mainly depends on the efficiency, the resolution and the accuracy which can be achieved using frequency, damping or intensity. In addition, it is generally possible to identify which chemical bond is responsible to a peculiar property of the substance and/or is affected by a change of an external parameter. As a consequence, a Raman line can be considered as a real fingerprint of a chemical bond. It is easier to assign the Raman lines to the different vibrational modes in crystals than in disordered substances such as liquids and amorphous solids. The Raman spectrum obeys to selection rules related to the symmetry of the matter. Furthermore, in ordered materials, the various phonons can be distinguished by using polarized Raman spectroscopy.

2. SENSOR APPLICATIONS

2.1. Determination of the strain in a polymer

The first application concerns the characterization of a semi-crystalline polymer during its uniaxial deformation. In particular we have studied the effects of the mechanical stress on the microstructure of an isotactic polypropylene (iPP). The initial degree of crystallinity, determined by differential scanning calorimetry, is equal to 56 % ± 3 % in weight. Crystalline phase is mainly composed of radial spherulites into α-monoclinic form. Dumbbell-shape test specimens were machined out of injection-moulding plates as seen in Fig. 1. Tensile experiments were performed on a video-controlled testing machine at 30 °C and 5.10^{-3} s^{-1} as the strain rate [1]. Specimens are deformed along the **z**-longitudinal axis and submitted to different growing states of deformation ε_{zz}= 0, 0.06, 0.15, 0.3, 0.5, 0.8, 1 and 1.2.

Raman backscattering measurements were performed on the deformed area of the samples using an exciting line in the near-infrared (λ = 785 nm, diode laser) through a confocal microscope (100x objective, 1000x magnification and 0.9 numerical aperture). The system is equipped with a set of two polarizers which offers the possibility to polarize the electric fields **E** of the incident and scattered lights independently. The polarization analysis gives insight into the symmetry of vibrational modes. Raman bands are influenced by the relative spatial orientation of the associated chemical bonds towards the polarization direction. Experiments were carried out by remaining **E** parallel to the tensile direction. The useful spectrum under consideration is ranging from 950 – 1010 cm^{-1}.

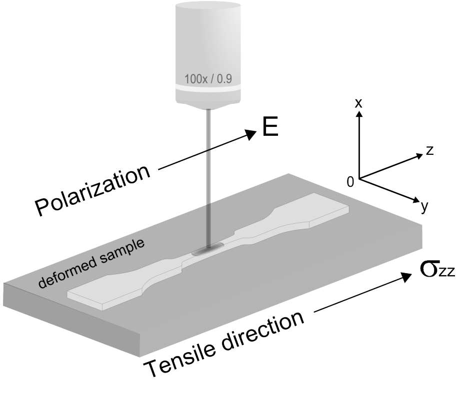

Fig. 1. Schematic setup for the backscattering Raman measurements of a stressed polymer as function of light polarization.

Fig. 2 shows two Raman bands located at 973 and 998 cm^{-1}. Both are related to macromolecules in the 3_1 helical conformation of the α-monoclinic form [2]. The first one is principally assigned to the asymmetric stretching mode of the C-C skeletal backbones while the second is referred to the rocking mode of the CH_3 lateral alkyl groups. A large difference in bands intensities is observed between a non deformed (ε_{zz}= 0) and a deformed sample (ε_{zz}= 1.2). For ε_{zz}= 0, band at 973 cm^{-1} is dominant while band at 998 cm^{-1} is weak. This is amplified for ε_{zz}= 1.2. By remaining light polarization direction parallel to the tensile direction, Raman scattering is principally excited from the C-C skeletal backbones mainly oriented towards the deformation direction. It explains the increase of the 973 cm^{-1} band intensity. Simultaneously, Raman scattering produced from the CH_3 lateral alkyl groups is less activated with the deformation which explains the decrease of the 998 cm^{-1} band intensity. The ratio $R_{orient} = I_{(C-C)} / I_{(CH3)}$ of the integrated intensity of these two particular bands can be therefore used to evaluate the preferential orientation of the carbon chains in the crystalline phase. We have recently validated the use of this spectral criterion by comparing Raman and X-ray scattering results [3]. A good correlation is observed between R_{orient} and the well-established Hermans's orientation factor.

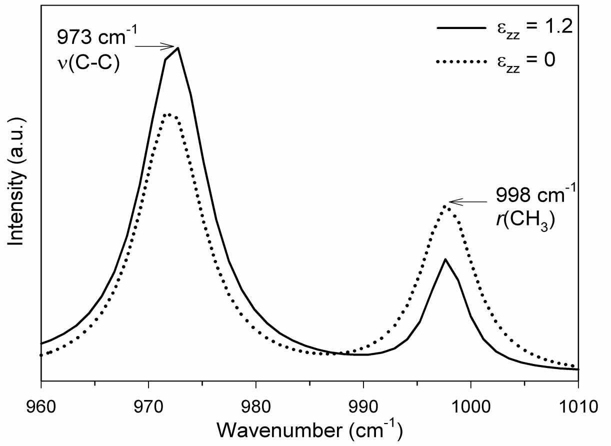

Fig. 2. Part of the Raman spectrum measured in polarized configuration on isotactic polypropylene samples. The dependence of the intensity on the magnitude of the strain is shown.

For each state of deformation, the ratio R_{orient} is calculated and plotted versus the corresponding strain on the Fig. 3. The constitutive mechanical σ_{zz}– ε_{zz} curve of the iPP is also reported. As expected, R_{orient} increases with the deformation and reflects a progressive orientation of the crystalline phase chains along the tensile direction. This behaviour is not linear and exhibits a slope change at ε_{zz}= 0.35. Below this point, the orientation mechanism is inhibited while beyond the crystalline orientation development is growing. At the first stage of the deformation $\varepsilon_{zz} < 0.35$ (viscoelastic deformation stage), only the amorphous inter-lamellae phase undergoes deformation by extension of chains towards the tensile direction. Contribution to crystalline orientation is negligible. On further stretching up to $\varepsilon_{zz} > 0.35$ (plastic deformation stage), initial disoriented lamellae of the radial spherulite are submitted to a shear stress which promotes their rotation towards the tensile direction. Thus, this tilt leads to an important increase of the whole crystalline orientation degree in the material. This interpretation based on Raman results is in good agreement with the general descriptive Peterlin's model [4].

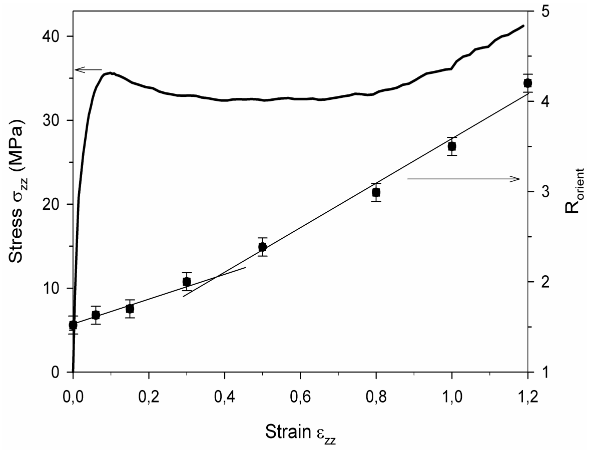

Fig. 3. Dependence on the strain of the Raman criterion R_{orient} as signature of the crystalline phase orientation in isotactic polypropylene under uniaxial deformation. Stress – strain curve is as well reported for comparison.

The ratio $R_{orient} = I_{(C-C)} / I_{(CH3)}$ between two integrated Raman intensities can be therefore considered as a pertinent parameter to measure the strain and the partial orientation in this kinds of polymers. A Raman sensor of the mechanical deformations based on this method is under progress.

2.2. Determination of the salt concentration in a solution

In the second application, we prove that Raman sensor is an efficient tool to determine the salt concentration in a liquid aqueous solution. Furthermore, each type of salt presenting a specific signature, the nature of the salt can be identified as well. As an example, Fig. 4a exhibits the *O-H* stretching mode region in the Raman spectrum of an aqueous solution of NaCl recorded at room temperature for different concentrations. These spectra were collected in a backscattering configuration, using a 514 nm excitation line through a long-working-distance objective 50x. It is to note that data were nearly unaffected by the light polarization. As a consequence, in order to achieve the maximum of the signal, no polarizer of the incident or scattered beams was used in final measurements.

The comparison of these NaCl aqueous solution spectra (Fig. 4a) with the one of pure liquid water (see Fig. 4b) allows identifying the specific effect of salt on water. Thus, we can note that the highest frequency part of the *O-H* stretching Raman spectrum is enhanced by the introduction of salt in the liquid. In fact, we can demonstrate that this part of the spectrum is associated with the asymmetric *O-H* stretching modes [5], [6]. These modes are related to the *O-H* pairs of water molecules whose hydrogen bonds are disrupted due to some external factor, for instance the temperature or the addition of a certain substance in water.

Thus, the incorporation of NaCl in the water weakens the hydrogen bonds between water molecules [7] and thus favours the asymmetric vibrations of the *O-H* bond. This gives rise to a continuous change in the line shape since the asymmetric *O-H* part becomes preponderant.

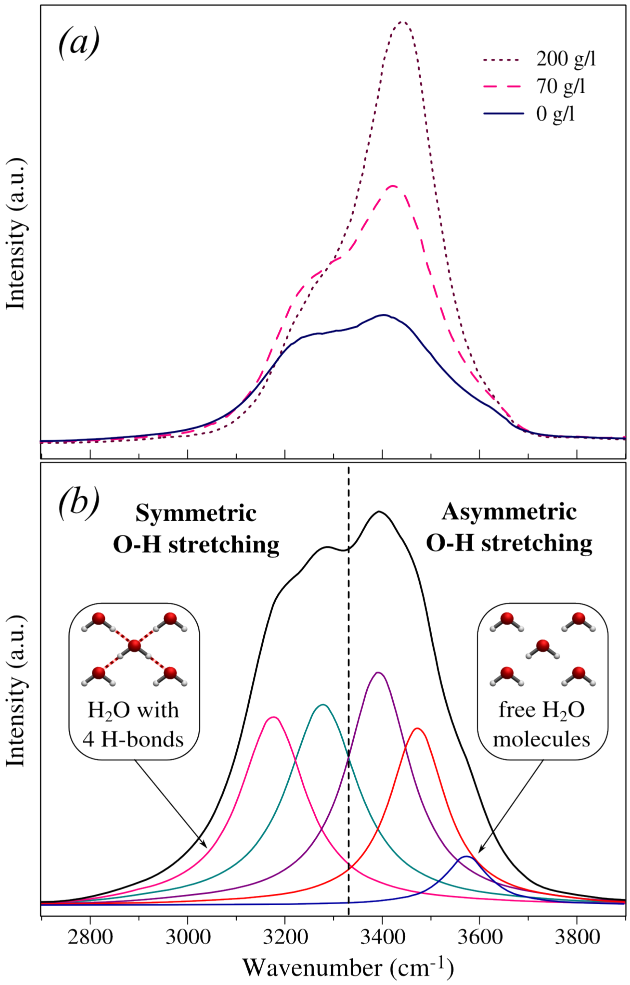

Fig. 4. *O-H* stretching mode of the Raman spectrum of the NaCl aqueous solutions, recorded at room temperature (20°C) and standard pressure. Influence of salt concentration (a). Deconvolution of the spectrum of pure liquid water (b).

The frequency and damping of these various modes are affected by the salt introduction as well. Nevertheless, to determine the salt concentration, the exploitation of the scattered intensity was chosen rather than the frequency or damping, since these last quantities need the deconvolution of the spectra and the derived fitted parameters can be subject to controversies owing to large uncertainty in the values deduced from a fit of a very broad spectrum.

As a consequence, we use the ratio R_{conc} between the integrated intensities of the high-frequency and low-frequency parts of the *O-H* stretching Raman spectrum in order to determine the concentration in salt of the solution. The spectral bands used for the calculation of this ratio are:

$$R_{conc} = \frac{I_{int}\,(3325 - 3700\ \text{cm}^{-1})}{I_{int}\,(3000 - 3325\ \text{cm}^{-1})}$$

Fig. 5 used for the calibration of our Raman sensor shows the excellent correlation which is achieved between this ratio and the salt concentration.

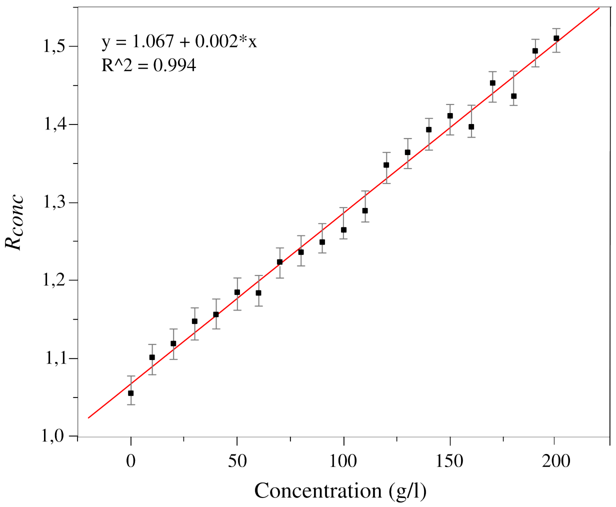

Fig. 5. Sensor calibration at room temperature (20°C): correlation between the Ratio R_{conc} of integrated Raman intensities and the salt concentration.

3. CONCLUSIONS

Raman sensors based on spectroscopy apparatus can be efficiently used to determine various quantities which can affect the vibrational modes specific to a substance. Three parameters can be deduced from the change of the Raman spectrum of the substance submitted to the influence of the quantity to be determined. The peak position or mode frequency, the width or mode damping and the integrated intensity can thus be used in these sensors. In addition, Raman spectrum can generally provide the microscopic mechanism associated with the change of the quantity under study. Another important advantage of the Raman probe is to allow the on-line measurements of the sample. The spatial resolution of the apparatus is about one micrometer squared, so that the homogeneity and anisotropy in the properties can be investigated. The Raman probes exhibit good accuracy and resolution in the determination of a physical quantity.

Two examples were reported to illustrate the interest of Raman sensors. We successively considered the measurement of stress in partly crystalline polymer, and the determination of a concentration of a salt in a solution. The integrated intensity of specific Raman lines is used in each case to deduce the physical quantity. In fact, the ratio between intensities of lines associated with vibrational modes linked to particular chemical bonds is exploited. This method is easy and quick to be employed, the deconvolution of obtained Raman spectra not being necessary.

Since the scattered intensity is proportional to the concentration of species, a very small quantity is not able to be derived from intensity measurements. It is the main drawback of this method. Frequency or damping of the phonon associated with a Raman line is more easily exploited in the case of ordered structure, but it requires the adjustment of the Raman spectrum. The interest of Raman sensors is reinforced by the fact that such sensors can be successfully employed in the cases described above, of partly amorphous solid and a liquid. Raman probes can be efficiently used as sensors in different industrial context.

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