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Raman Spectroscopy in Polymer Processing Technologies

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KEY WORDS

Raman Spectroscopy, Polymer, Scattering

ABSTRACT

Presented paper describes the application of Raman spectrometry in polymer process-

ing technologies. Quick and reliable material identification is becoming and serrious issue in polymer processign technologies . Vibrational spectroscopy was long time used in polymer analysis. Preferred technique was the infrared spectroscopy (IR), but actual progress allows easy application of Raman spectroscopy and its main advantages. Raman spectroscopy detects vibrations that generate a change in the molecule's polarizability. The Raman effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. It is a form of electronic (more accurately, vibronic) spectroscopy, although the spectrum contains vibrational frequencies. Modern palmsized Raman spectrometers allows simplified infield application. Quick online material identification on site is possible, or more specifical material characteristic is possible offline, when evaluating measured data with specialized software.

1. Introduction

Vibrational spectroscopy was long time used in polymer analysis. Preferred technique was the infrared spectroscopy (IR), but actual progress allows easy application of Raman spectroscopy and its main advantages. IR and Raman spectroscopy differ fundamentally in their mechanisms for detecting vibrations. IR spec- troscopy detects vibrations that generate a change in the molecule's dipole moment. Raman spectroscopy detects vibrations that generate a change in the molecule's polarizability. Some vibrations can be accompanied by changes in both dipole moment and polarizability; these vibrations are detected by both IR and Raman spectroscopy. In long polymer chains, vibrations of the backbone generally do not induce changes in the dipole moment because adjacent di- poles are cancelled out by repeating units, but the change in polarizability is usually high. This makes Raman spectroscopy particularly useful because it is highly sensitive to the structure and conformation of the polymer backbone. In contrast, IR can be useful for analyzing side chains, so the two techniques can be used complementarily [3].

In the past, Raman spectroscopy was hindered by fluorescence from samples that were highly colored or had fluorescent impurities. Today, however, excitation in the deep red and near-infrared (NIR) regions can be used, which avoids fluorescence in many samples. In addition, manufactur-

ing practices for polymers have vastly improved, so potentially obstructive fluorescent impurities in otherwise non-fluorescent materials are not nearly as prevalent as in the past. Raman spectroscopy is easily incorporated as on-line or in-line process monitoring technique. Figure 1 shows a Raman probe being used to monitor a moving polymer film. Note that the probe does not come in contact with the film.

Fig. 1: *Monitoring a moving polymer film line.*

Raman spectroscopy can be used in several ways to get information from polymers. The simplest is to use the Raman spectrum as a "fingerprint" to quali- tatively identify polymeric materials. Infrared spectroscopy is an analytical technique designed for identification of organic compounds and inorganic substances [6].

2. Raman scattering theory

When light is scattered from a molecule most photons are elastically scattered. The scattered photons have the same energy (frequency) and, therefore, wavelength, as the incident photons. However, a small fraction of light (approximately 1 in 107 photons) is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons. The process leading to this inelastic scatter is the termed the Raman effect. Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. Chemists are concerned primarily with the vibrational Raman effect. We will use the term Raman effect to mean vibrational Raman effect only. The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule. A plot of intensity of scattered light ver-

sus energy difference is a Raman spectrum.

Scattering Process

The Raman effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. It is a form of electronic (more accurately, vibronic) spectroscopy, although the spectrum contains vibrational frequencies. In classical terms, the interaction can be viewed as a perturbation of the molecule's electric field. In quantum mechanics the scattering is described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The scattering event occurs in 10-14 seconds or less.

The energy lost by the photons in the scattering event is called the Raman shift and is defined in energy as $\Delta E_R = E_L - E_S$. It is therefore positive for a Stokes and negative for an anti-Stokes process. Raman shifts are commonly expressed in wave-numbers and will then be denoted $\Delta\nu_R$ (usually in units of[cm^{-1}]). The modulus of the Raman shift corresponds to the wave-number of the vibrational mode ($\nu_v = h_{\omega v}/h_c$) that was involved in the scattering event: $\nu_v = |\Delta\nu_R|$.

The Raman spectrum corresponds to the wavelength- (or energy-) dependence of the Raman scattered intensity at a given incident wavelength. It is commonly shown as Raman intensity as a function of Raman shift (rather than wavelength), as shown in Fig. 2. for an example SERS spectrum. Peaks in the Raman spectrum correspond to vibrational modes of the molecule, in a similar fashion as for an infrared absorption spectrum. The Raman shift of a peak is equal to the vibrational energy of the corresponding mode. There is some broadening (homogeneous and inhomogeneous) of the peaks, but Raman peaks for molecular compounds are typically 'narrow' (5–20 cm^{-1}).

At room temperature the thermal population of vibrational excited states is low, although not zero. Therefore, the initial state is the ground state, and the scattered photon will have lower energy (longer wavelength) than the exciting photon. This Stokes shifted scatter is what is usually observed in Raman spectroscopy. A small fraction of the molecules are in vibrationally excited states. Raman scattering from vibrationally excited molecules leaves the molecule in the ground state.

The scattered photon appears at higher energy.

This anti-Stokes-shifted Raman spectrum is always weaker than the Stokes-shifted spectrum, but at room temperature it is strong enough to be useful for vibrational frequencies less than about 1500 cm^{-1}. The Stokes and anti-Stokes spectra contain the same frequency information. The ratio of anti-Stokes to Stokes intensity at any vibrational frequency is a measure of temperature. Anti-Stokes Raman scattering is used for contactless thermometry. The anti-Stokes spectrum is also used when the Stokes spectrum is not directly observable, for example because of poor detector response or spectrograph efficiency.
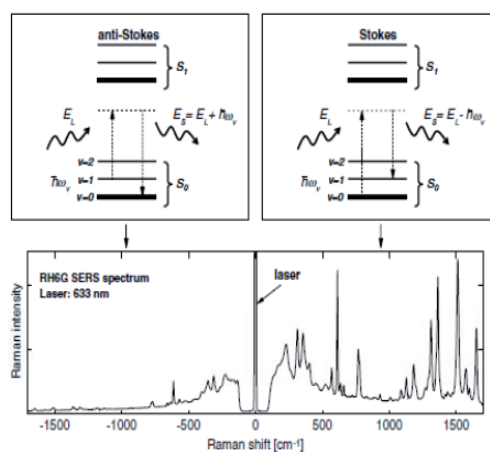

Fig. 2: *Simplified Jablonski diagrams of the anti-Stokes (top left) and Stokes (top right).*

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Vibrational Energies

The energy of a vibrational mode depends on molecular structure and environment. Atomic mass, bond order, molecular substituents, molecular geometry and hydrogen bonding all effect the vibrational force constant which, in turn dictates the vibrational energy. For example, the stretching frequency of a phosphorus-phosphorus bond ranges from 460 to 610 to 775 cm^{-1} for the single, double and triple bonded moieties, respectively.[1] Much effort has been devoted to estimation or measurement of force constants. For small molecules, and even for some extended structures such as peptides, reasonably accurate calculations of vibrational frequencies are possible with commercially available software.

Vibrational Raman spectroscopy is not limited to intramolecular vibrations. Crystal lattice vibrations and other motions of extended solids are Raman-active. Their spectra are important in such fields as polymers and semiconductors. In the gas phase, rotational structure is resolvable on vibrational transitions. The resulting vibration/rotation spectra are widely used to study combustion and gas phase reactions generally. Vibrational Raman spectroscopy in this broad sense is an extraordinarily versatile probe into a wide range of phenomena ranging across disciplines from physical biochemistry to materials science.

Resonance-Enhanced Raman Scattering

Raman spectroscopy is conventionally performed with green, red or near-infrared lasers. The wavelengths are below the first electronic transitions of most molecules, as assumed by scattering theory. The situation changes if the wavelength of the exciting laser within the electronic spectrum of a molecule. In that case the intensity of some Raman-active vibrations increases by a factor of 102-104. This resonance enhancement or resonance Raman effect can be quite useful.

The vibrations whose Raman bands are resonance enhanced fall into two or three general classes. The most common case is Franck-Condon enhancement, in which a component of the normal coordinate of the vibration is in a direction in which the molecule expands during an electronic excitation. The more the molecule expands along this axis when it absorbs light, the larger the enhancement factor. The easily visualized ring breathing (in-plane expansion) modes of porphyrins fall into this class. Vibrations which couple two electronic excited states are also resonance enhanced. This mechanism is called vibronic enhancement. In both cases enhancement factors roughly follow the intensities of the absorption spectrum. [2]

Resonance enhancement does not begin at a sharply defined wavelength. In fact, enhancement of 5X-10X is commonly observed if the exciting laser is even within a few hundred wave numbers below the electronic transition of a molecule. This pre-resonance enhancement can be experimentally useful.

3. Raman spectroscopy in polymer processing technologies

Advances in Raman spectroscopy equipment, allow more sophisticated application in polymer processing technologies. There are already available palm-sized devices like DeltaNU RapidID (Fig. 3). Compact size and no need of sample preparation allows direct application in filed or post analysis of measured data with specialized software (NuSpec). All measured datas are stored in internal memory.

Fig. 3: *DeltaNu RapidID, palm sized Raman spectrometer.*

Extrusion

Because Raman spectroscopy uses excitation in the visible or NIR regions, the base unit containing the optical components and the computer used to control the instrument can be located remotely from the probe used to interface with the

sample. Figure 4 shows Raman data acquired of polymer blends during extrusion. A 532-nm probe was coupled to the base unit using a 100-m optical fiber. For quantitation, the ratio of the components is easily determined from the area ratios of their spectral bands.
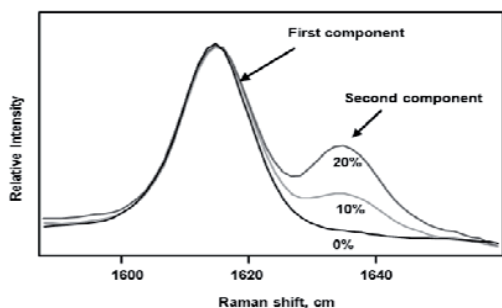

Fig. 4: *On-line Raman spectroscopy of extruded polymer blends.*

Polyethylene Density

One of the most important polymers used to-day is polyethylene (PE), with applications as di-verse as milk jugs, insulation for wires, and gaso-line tanks in automobiles. PE comes in two general forms: high- density polyethylene (HDPE) and low-density poly-ethylene (LDPE). HDPE is generally defined as polyethylene having a density in the range 0.955–0.970 g/cm³, while LDPE has a density of 0.920–0.935 g/cm³. HDPE has greater strength, less creep, and less gas permeability, while LDPE is more flexible and translucent.

Figure 5 contains spectra of polyethylene sam-ples with densities of 0.96, 0.910, and 0.882 g/cm³. Curve- fitting techniques can be used to create a calibration model to correlate the Raman spec-trum of a PE sample to its density.
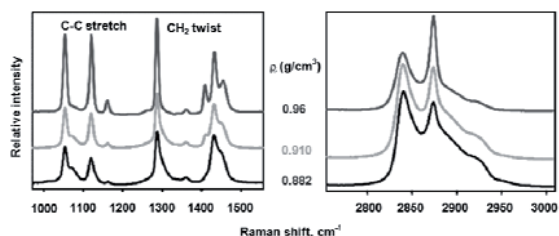

Fig. 5: *Raman spectra comparing polyethylene sam- ples of vari-ous densities.*

Polybutadiene Microstructure

Raman spectroscopy is especially useful for the characterization of polybutadienes because it can distinguish all of the fundamental structural units directly using the $v(C=C)$ bond stretching of 1,2-vi-nyl, 1,4-cis, and 1,4-trans units, which give rise to Raman bands at 1639, 1650, and 1664 cm⁻¹, respec-tively. Figure 6 presents the application of Raman spectra by polymer micro-structure.
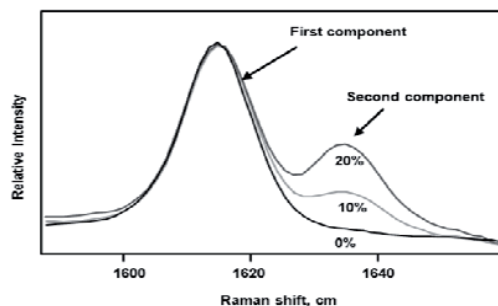

Fig. 6: *Raman spectral region used to identify micro- structure of polybutadienes.*

On site monitoring of raw material

Monitoring the composition of copolymers is very important because many grades are com-mercially available, with the properties-and price-dependent upon the distribution of the different monomers[4]. Figure 7 shows how copolymers of ethylene vinyl acetate can be distinguished ac-cording to the vinyl acetate fraction.Since 1970 we see increasing importance of modern metrology as means to control and improve industrial manu-facturing and the quality ao all kinds of products and processes.[5]
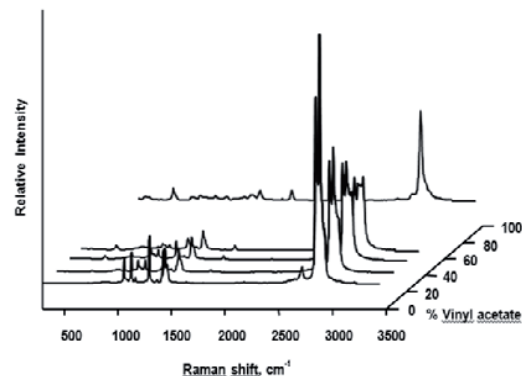

Fig. 7: *Dependence of ethylene vinyl acetate co- polymers Raman spectra on vinyl acetate fraction.*

4. Conclusion

Raman spectroscopy is such a general technique that even reviewing briefly what can be done with it, even in the area of polymer processing technologies. The progress in development of Raman spectrometers equipment leads to simplified on-site application of Raman spectrometers. Measured diagrams present practical application of Raman spectra evaluation in polymer processing technologies. Although the results strongly depends on operator´s knowledge of Raman scattering process to evaluate properly the gathered Raman spectra. Online applications like presented in figure 1, solve simplified problems because they are mostly operated with one type of polymer. Measured results shows also big potential of Raman spectrometry in polymer sorting in recycling industry.

5. Acknowledge

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