Novel Raman microscopic applications in technology of multicomponent materials

Thesis of Ph.D. Dissertation

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1. Introduction, Preliminary Results and Aims

The applicability of Raman examination methods in direct way, without sample preparation, the possibility of exact chemical identification, the micrometer scale 3D resolution of microscopic technique allowed the spread of Raman (micro)spectroscopy in very diverse fields. Looking for novel applications of Raman microscope we planned to study how it can extent the traditional analytical methods and provide additional information supporting the modern (e.g. pharmaceutical and plastic industrial) technologies. This way the dissertation does not apply an analytical basic discipline approach, but a technological approach, wishing to demonstrate that analytical methods coupled to technological developments are useful even in cases when the complexity of the studied systems does not allow an exact analytical approach.

According to this concept the state of art and the preliminary results can be summarized as follows:

1. *Qualitative and quantitative Raman measurements in pharmaceutical technology:* The Raman (micro)spectroscopy is much less widespread in the pharmaceutical industry than NIR and mid IR absorption spectroscopy, there are only a few fields (eg. the examination of polymorphic forms), where it acquired its own place. The comprehensive Raman examination of solid drug forms – including the identification of technological methods – which was one of the aims of the dissertation – is, as far as we know, without precedence.
2. *“Off line” and “on line” Raman measurements supporting and understanding of technological processes of flame retarded polymer systems:* Although the Raman microscopy is a widely used technique in the field of polymer technologies, its advantages are not utilized as far as it could be possible. Our aim was to discover fields where Raman methods are suitable to achieve novel technological and theoretical results. Such field is the investigation of flame retarded polymer systems (e.g. EVA copolymer containing metal hydroxide and polymer systems containing intumescent flame retardant additive). Combination of the additive system with the multi-layer composite technology was planned to develop a method for recycling of the waste polymers as high value materials.
3. *Contribution of Raman methods to the optimization of the technologies of carbon nanotubes:* Results of the recent studies show that the carbon nanotubes are applicable not only to provide a simple and quick Raman-spectrum-based mapping of the tension distribution in polymer systems but take an effect on the conductivity, thermal stability, flame retardancy and other properties of the polymers. Aiming to get Raman information

about the thermal stability of the nanotube containing nanocomposites it was important to investigate the carbon nanotubes on their own. Although a well ordered structure of nanotubes results in a simple Raman spectrum, the structural changes are recognizable in the characteristics of the Raman bands. This phenomenon could be utilized in the technology if exact relations were defined. The existing disputable relations, however, are not suitable to calculate the changes of the Raman spectra of the commonly used miscellaneously structured nanotube systems. We aimed at making these relationships clearer and thus supporting the relevant technology.

4. *Establishing the theory behind a technology by means of Raman examinations of fluid/gas enclosures:* The investigation of the gas bubbles occurring in the reinforcing mineral (e.g. basalt) fibers or other minerals helps to understand technologies and geological processes. Although the Micro-Raman investigation of gas enclosures is known, there exist many unclear methodological aspects. Our aim was to discover the possibilities and limits of the Raman method in the investigation of special enclosed gas composition. Besides, we aimed at developing analytical methods supporting the mineral-based or earthquake-defense technologies.

The general goal of the dissertation was to promote the use of technological support of Raman microscopic methods by presenting a wide range of fields where Raman microscopy could be applied. Due to the results the technologies might become more controllable and safe.

2. Experimental Methods

The Raman examinations were carried out with a Jobin Yvon Labram Raman microscope. Three different exciting light sources (He-Ne (633 nm) frequency-doubled Nd:YAG (532 nm) and diode (785 nm)) were applied. Changeable objectives [10× (NA 0.25); 50× (NA 0.7 / NA 0.5); 100× (N 0.9); macrolense (focal length: 40 mm)] were applied to change the volume of the examined sample unit. (The highest lateral resolution was 0.7 μm (100×), the lowest was ~500 μm). In cases where there was need to avoid the damage of the samples the power of the exciting light was reduced by means of different filters. The Raman photons were detected with a CCD detector.

To monitor chemical and temperature dependent processes the equipment was equipped with an optical cable system and a temperature programmed plate.

The registered spectra were evaluated with the LabSpec 4.14 software. The SpectralID software was used to assign the spectra digitally.

3. Summary of Results

The new results on the fields of pharmaceutical-, polymer-, nanotube- and geotechnologies are summarized in the following thesis points:

Theses:

3.1 The ability of the Raman microscope to qualify and quantify solid pharmaceuticals and supporting the formulation technology is certified as it follows:

- Local Raman microscopic examination of the ingredients (including chemical identification, morphology and particle size determination without fracturing the samples) could be attained and thus even the producer of the product can be identified in many cases.
- The relative arrangement of the ingredients (secondary structure) could be determined by mapping and thus the formulation technology could be identified.
- The primary composition data determined by Raman examination were found a good base for a trial and error iteration cycle, to recompose and thus determine the correct ratio of the ingredients.
- Applicability of Raman methods for on-line quality assurance was demonstrated on a model mixture examined through packaging.

In addition:

  - The effect of particle size and space filling on the quantification, examined by macro and micro lenses, has been shown.
  - The suitability of the TiO_2 as inner standard in quantification has been demonstrated.
  - A rotating sample holder has been developed for handling inhomogeneity of tablets.

3.2. Raman micro-spectroscopy have been successfully applied in the field of polymer-technology for complementing the traditionally used techniques (SEM, XRD etc.), and for solving special analytical problems where it is the only applicable method:

- The gradient character of heat radiation-induced thermal degradation has been foremost shown by depth profile measurements without sample fracturing. Based on these results economic core shell structure flame retarded systems has been developed.
- Sensibility of Raman microscope makes it possible to monitor changes occurring in fabrication technology (degradation) by super head (optical cable).

- It was certified that for determination some special technical/material prosperity such as clay distribution and nucleation the only applicable method is Raman microscopy, while other analytical techniques fail because of disturbing components being present.
- Raman microscopic methods have been used for detecting changes caused by fire in a solid phase active intumescent flame retarding system in PP (such as reaction of boroxo-siloxanes and induced clay migration).
- Technology related differences have been shown in the interfaces of layered structure composites by Raman methods.
- It has been shown that monitoring of laboratory or industrial reactions by Raman microscopy is more efficient in alumina micro reactors than in traditional glass reactors.

3.3. Relationship between the properties of single- and multi-wall nanotubes, the examination parameters (laser power and energy) and theirs spectral consequences is as follows:

- The uncertainty of diameter determination is influenced by the interactions between tubes, the resonance effect, and the measurement range.
- The spectral changes, caused by temperature variation, have been determined, thus the reversible and irreversible changes in the spectra (and the sample) caused by laser irradiation have been identified. Similarities between heat treatment and the heat effect of laser irradiation have been observed and the correlation has been quantified. The temperature dependence of RBM frequencies has been found altering from the literature.
- We observed that the laser irradiation of the residual catalyst contamination (originating from the preparation technology of nanotubes) causes the nanotubes in the environment of the catalyst to alter in the direction of more regulated state e.g. tube synthesis;
- We determined that the MWNT-s are more sensitive to the measuring parameters than the SWNT-s, furthermore their way of transformation is more differentiate than in case of the SWNT-s.

3.4. The composition of the gas inclusions (in fluid state) locked into natural minerals was determined. As this composition reflects the circumstances of the formation of these inclusions. These data are important starting parameters for geological and geophysical calculations in the modelling of underground processes:

- Examining the fluid state gas inclusions by micro-Raman system we came to the novel statement, that the inclusions from lower crust contain in most cases, besides carbon dioxide, carbon monoxide as well.
- In contrast to the expectations we have not encountered methane or other hydrocarbons in any of the examined inclusions, which queries the preliminary assumptions in the literature about the occurrence of methane.
- Nevertheless the characteristic Raman peaks of hydrogen sulphide, nitrogen and carbon could be identified from the spectra of the inclusions in most cases.
- As the in situ formation of carbon can be excluded, it could be determined that carbon was present in some of the inclusions, in form of floating particles, before the examinations.
- We have detected inclusion reactions, due to permanent laser irradiation, which caused the floating carbon content to regraphitize and form a new, more ordered thin graphite layer on the wall of the inclusion.

4. Practical Utilization of the Results

The results were utilized in specific industrial technologies, in industrial laboratory methodologies and in the elaboration of predictive mathematical methods as follows:

- Richter Gedeon Pharmaceutical Company utilizes the results in their pharmaceutical technology developments;
- PEMÜ PLC utilizes the results in the elaboration of technology for production of flame retarded polymer systems;
- in the frame of Nanofire EU-6 project in the Belgian company Nanocyl utilizes the results in the development of technology and quality control for the production of nanotubes and
- in the frame of BACOMP Széchenyi project Toplan company in Tapolca utilizes the results in the development of basalt fibre production; and the Department of Petrology and Geochemistry of ELTE uses the provided data in their geological model calculations.

4. Publications from the subject of the dissertation

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