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Raman system for monitoring dye doping to hybrid polymer network

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Being a relatively low-temperature technique, the sol-gel technology enables the synthesis of hybrid polymers doped by organic dyes. In order to ensure the required properties of the final product, however, the mixing of sol and dye must be strictly controlled to avoid unwanted chemical reactions between them. Raman spectroscopic *in-situ* monitoring of the process was used to address this problem. Problems encountered in spectroscopic studies of non-transparent dye-doped sols, arising from intensive scattering, attenuation of the Raman signal inside the investigated material, and fluorescence induced by the laser beam, are discussed. The Raman measuring system constructed for the research presented in this paper uses a diode laser and a compact spectrometer connected to a reaction glass vessel by a fibre optic probe. Proper selection of the excitation beam wavelength and suitable design of the opto-mechanical setup results in an increase of the Raman signal and improved rejection of interfering signals. The system presented does not require access inside the vessel. *In-situ* monitoring was carried out for the process conducted at room temperature and up to 87 °C. As the intensity of the Raman bands assigned to the dye did not change during the process, it can be concluded that dye does not decompose.

Key words: *Raman monitoring; dye doped materials; sol-gel*

1. Introduction

Due to its relatively low temperature, the sol-gel process enables the inclusion of large organic particles, i.e. dyes or antigens, into a hybrid organic-inorganic polymer network. The doping procedure of sol by the functional particles, however, must be strictly controlled to avoid unwanted chemical reactions and, consequently, their decomposition. This requirement stimulates the search for effective diagnostic tools for *in-situ* monitoring of the synthesis process of doped materials.

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The main aim of the research presented in this paper was to apply Raman spectroscopy to studies of doping hybrid polymers with dye particles. The procedure of mixing the dye, dissolved in acetone, with the sol was the subject of real-time Raman monitoring. The main objective of this investigation was to make sure that no chemical reaction takes place between the sol and dye and that the latter is not being decomposed during the mixing. The investigation of dye-doped sols, usually non-transparent, is a difficult metrological task due to scattering and attenuation of the Raman signal inside the material investigated. Moreover, a strong fluorescence signal induced in the organic part of the material by the laser beam must be taken into account [1].

2. Experimental

2.1. Investigated sol-gel process

The sol was prepared using the following precursors: glycidyloxypropyltrimethoxysilane (GPTS), methacryloxypropyltrimethoxysilane (MPTS), 2-hydroxyethylmethacrylate (HEMA), tetramethoxysilane (TMOS), and aluminium-tri-sec-butoxide ($AlOBu_3$). The dye – commercially available NIR-absorbing IR165 – was dissolved in acetone and subsequently mixed with the sol. A two-neck 50 ml glass vessel and a smaller, one-neck 10 ml vessel were used in the experiments. The sol-gel reaction vessels were equipped with a magnetic stirrer as well as an oil bath system for reactions requiring heating.

2.2. Raman monitoring system

In order to perform real-time monitoring of sol and dye mixing, a dedicated Raman scattering measurement system was built and coupled with a glass reaction vessel by a fibre optic probe. The measurement set-up is presented in Fig. 1a. The Raman system consists of an excitation diode laser, emitting an 830 nm beam and providing power on sample that can be varied from 0 to 200 mW. The application of a NIR laser reduces the interfering fluorescence signal [2]. An axial transmissive spectrograph with a transmission holographic grating (wavelength from 850 to 1000 nm), developed at VTT Electronics, and an Oriel InstaSpec IV Spectroscopy CCD camera, TE-cooled to –30 °C, were used in the detection part. Comparative measurements were made using CCD-Raman system Ramstas, developed at VTT Electronics [2]. The Raman ranges of both systems extend from 200 cm^{-1} to 2000 cm^{-1}, with a resolution of 8 cm^{-1}.

The fibre optic probe used in the investigation of dye-doped sol-gel materials works in a backscattering configuration of Raman optics, which is especially useful in the study of highly absorbing samples [3]. The setup of the probe as well as its connection with the reaction vessel is presented in Fig. 1b. In comparison to typical, commercially available Raman spectrometers equipped with fibre optic probes, e.g. systems made by Ocean Optics [4] and standard configurations of Ramstas developed by VTT [2], the system presented in this paper is equipped with a more sophisticated, dedicated focusing lens system. Moreover, this system uses a dedicated opto-mechanical setup based on a micrometric-grade 3-D positioning system of the Raman probe, which enables a precise adjustment of the measurement optics and effective optical coupling between the reaction vessel and the probe.

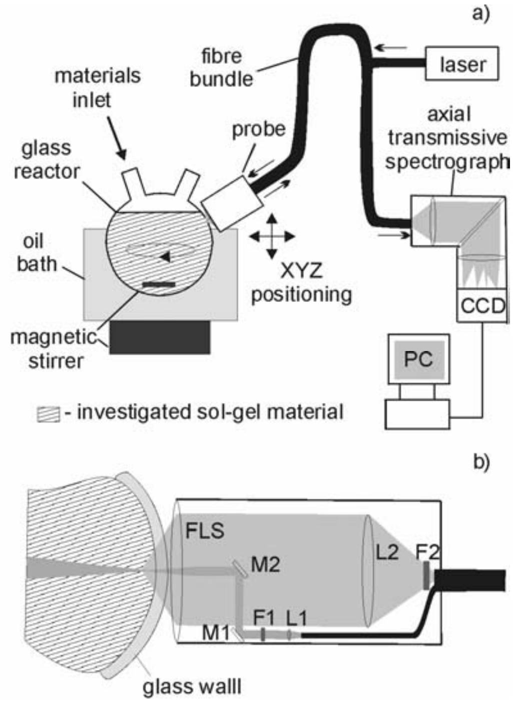

Fig. 1. Schematic diagram of: a) Raman system for in-situ monitoring of dye and sol mixing, b) optical rays inside the probe coupled with the reaction vessel

Laser radiation is transmitted through a single fibre and collimated by the lens (L1). A band pass filter (F1) cuts off fluorescence while two mirrors (M1 and M2) and a dedicated focusing lens system (FLS) enable transmission and focusing the laser beam inside the glass vessel. Having a focal length variable in the range of 12.5–25 mm, the FLS is used for focusing the laser beam inside the vessel and collecting the scattering signal. Part of the scattering signal collected by the FLS is transmitted by an edge filter (F2) that cuts off the Rayleigh scattering signal, while the Raman signal in the Stokes band is transmitted. The lens L2 focuses the scattering radiation into a fibre bundle that transmits it to the spectrometer [2].

As a result of careful optimisation of the FLS design, it is possible to avoid the excitation of interfering Raman scattering in the glass wall of the reaction vessel for a broad range of wall thicknesses and vessel diameters. The location of the focal point can be adjusted, using the micrometric 3-D positioning system and FLS, in order to reduce the intensity of the Raman band at 450 cm^{-1} originating from the glass wall and to obtain intensive Raman peaks originating from the investigated materials. The peak at 1144 cm^{-1}, observed in the spectrum of IR165, can be used for adjusting the measurement system when Raman monitoring is started after inserting the dye inside the vessel. For experiments in which Raman monitoring is to be started before adding the dye, a peak at 1448 cm^{-1}, assigned to $\delta(CH_3)$ bending in the sol, can be used for preliminary Raman system adjustment. As the liquid inside the flask is stirred with high velocity (from 100 to 700 rev./min.), it can be assumed that measurements carried out for one point are representative of the whole volume.

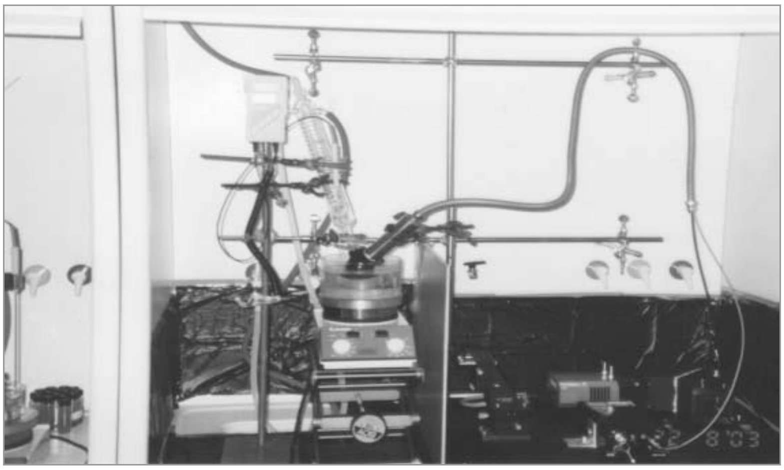

Fig. 2. Raman system coupled with a reaction glass vessel
equipped with a magnetic stirrer and oil bath heating system

Measurements were carried out in a remote way. The Raman system was used for monitoring the doping process *in-situ*, carried out at room temperature and up to 87 °C in an oil bath during mixing (Fig. 2). Contrary to Raman systems presented elsewhere [5, 6], a reaction vessel dedicated to Raman monitoring is not required. Moreover, any part of the spectroscopic fibre optic system presented in this paper does not need to be placed inside the vessel and consequently does not interfere with the investigated process. Furthermore, continuous stirring of the solution reduces the risk of thermal damage to the sol-gel material by the focused laser beam [3].

3. Results and discussion

Raman spectra of the following materials were recorded: GPTS, MPTS, HEMA, TMOS, $AlOBu_3$, and sols based on them, as well as the dye, acetone, and the dye dissolved in acetone. Moreover, the mixing of the dye with the sol was monitored in real time. The spectra of the dye dissolved in acetone, pure acetone, and the sol are presented in Figures 3–5, respectively. The spectra of the solid dye (not shown) and the dye dissolved in acetone are identical. In the spectrum of the dye dissolved in acetone, peaks originating from acetone were not recorded, although visual observation suggested that acetone did not evaporate from the closed flask. An absence of a signal originating from acetone in the spectrum of dye/acetone solution was probably caused

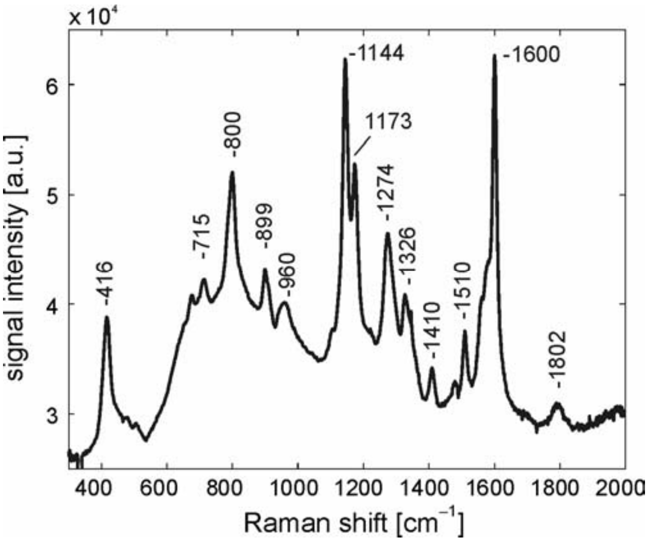

Fig. 3. Raman spectrum of the dye dissolved in acetone

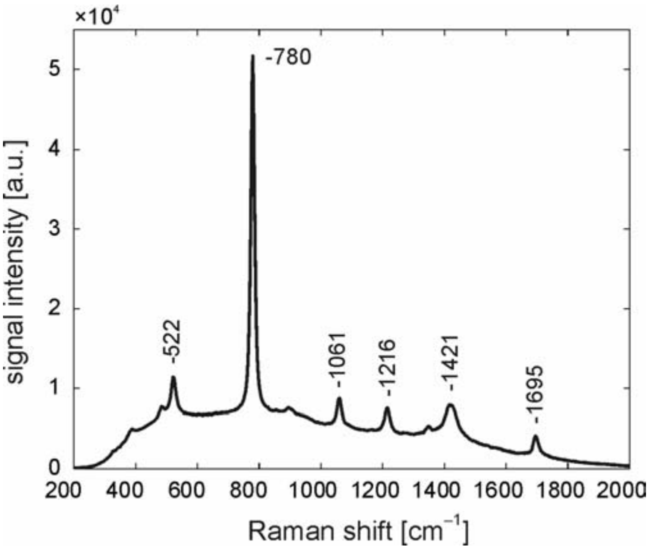

Fig. 4. Raman spectrum of pure acetone

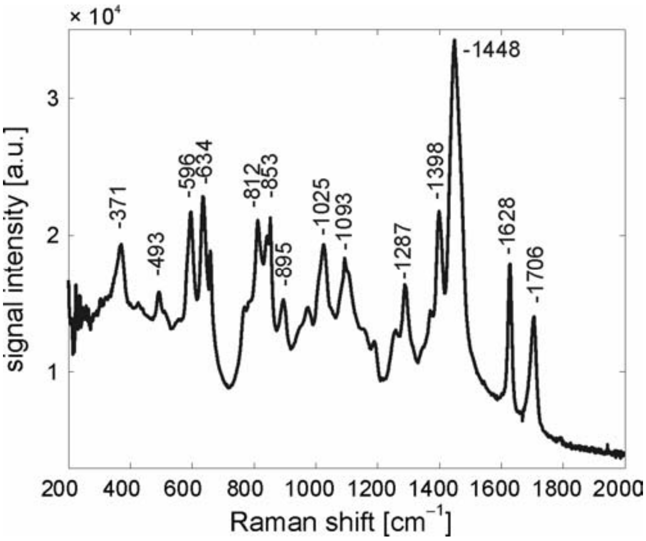

Fig. 5. Raman spectrum of the sol

by the reduced penetration length of the excitation beam in the mixture and by a modification of the acquisition cone, which results from significant differences in the refractive index and optical density of the solution containing particles of the dye as compared to pure transparent materials (e.g. acetone).

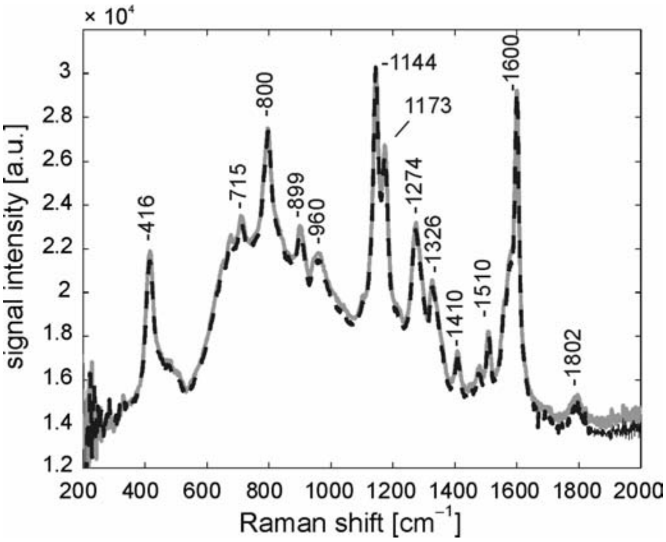

Fig. 6. Raman spectra recorded after adding the dye to the sol (solid grey line) and after subsequent 16 hour-and-20 minute of mixing (black dashed curve)

Changes in the Raman spectrum of sol and dye during mixing, conducted at room temperature, are shown in Fig. 6. Based on a comparison between the Raman spectra of the components (Figs. 3–5) and the spectrum of the full system, the origin of peaks can be determined. Similarly to the spectrum of the dye dissolved in acetone, it can be noted that peaks assigned to the dye also dominate in the spectrum of the dye–sol mixture. It can be therefore concluded that also in the case of the investigated dye–sol systems, the dye determines optical properties of the material. As a result, peaks originating from the sol cannot be recorded. However, an investigation dye decomposition can be carried out if the Raman spectrum is monitored in a sufficiently wide range of the Raman wave numbers.

During 16 hours and 20 minutes of mixing, the Raman spectrum monitored in the range of 200–2000 cm^{-1} did not change and all the peaks assigned to the dye maintained their intensities and relative ratios, which confirms that the sol did not react with the dye and that the dye did not decompose.

Confirming experiments were conducted and similar Raman monitoring was carried out for the dye–sol system mixed at a 87 °C (the temperature was maintained by an oil bath system). During some of the experiments, the level of optical background increased, but the ratios of the Raman peaks remained constant, which confirms that the dye did not decompose during any of the experiments.

4. Conclusions

An optical system for the Raman investigation of highly scattering and attenuating materials was built and successfully applied. On-line monitoring was performed for the mixing process of the dye and sol as a diagnostic tool, which can be the basis for controlling the dye-sol system.

The Raman system, which can be precisely adjusted for background and fluorescence reduction, does not require any components to be placed inside the reaction vessel. Therefore, it can be attached to standard glass reaction vessels and reactors with glass windows in such a way that eliminates the risk of material pollution by airborne contaminants and prevents the uncontrolled evaporation of some reagents.

The developed Raman system is fully compatible with clean-room conditions. The small sizes of the components (see Fig. 2) and fibre optic probe enable the system to be attached to even complex chemical reactors and *in-situ* process monitoring to be conducted in an industrial environment.

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