Progress in Organic Coatings 88 (2015) 32–38

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Non-destructive 3-dimensional mapping of microcapsules in polymeric coatings by confocal Raman spectroscopy

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ARTICLE INFO

Article history:
Received 14 March 2015
Received in revised form 5 June 2015
Accepted 9 June 2015
Available online 8 July 2015

Keywords:
Confocal Raman spectroscopy
Three-dimensional imaging
Coating
Polymer
Microcapsules

ABSTRACT

Nowadays, the properties of polymeric coatings are enhanced by various additives mixed into the resin. Recently, embedding of polymeric microcapsules into the coating matrix has been investigated to provide special on-demand features to the coating. The detection and characterization of such microcapsules in a polymeric coating are of major importance but difficult, because both are built up by similar molecules with similar densities. Current analysis methods require complex sample preparation to allow reliable measurements.

In contrast, confocal Raman spectroscopy allows fast and non-destructive differentiation between characteristic molecular bonds at a spatial resolution below one micrometer. Hence, the objective of this research was to apply this technique on microcapsules embedded in a coating and provide answers to the following questions: Can one detect microcapsules embedded in a coating and clearly identify them? Can one differentiate between full and empty microcapsules and the coating matrix? Can one determine the exact location of the capsules and their distribution in the coating?

Therefore, several two-dimensional confocal Raman spectroscopy mappings recorded at different depths allowed a three-dimensional reconstruction of the polymeric coating with the polymeric microcapsules in it. Thereby, the distribution of the capsules within the coating could be determined with micrometer resolution. As a result Raman tomography provides a more detailed insight into the distribution of microcapsules through the possibility of three-dimensional reconstruction.

1. Introduction

Pharmaceutical industry uses micro- and nanoencapsulation technology extensively to control the release of drugs [1]. In the last 15 years, microcapsules were also embedded in polymers to provide additional properties to coatings [2–4]. The existence, the distribution [5], the shape [6], the size [7] and the loading of such capsules [8,9] as well as the release of their content [10–12] are crucial factors. In general, either the capsules are analyzed alone (not embedded in the coating) or the effect of the leached content is measured [13]. In the first – the ex situ – case, electron microscopy (SEM or TEM) provides high-resolution images for determination of the shape and size. The loading is usually determined by chromatographic measurements as for example high-pressure liquid chromatography (HPLC) [12]. In the second – the indirect – case, the leaching out of the encapsulated agent from the capsules embedded in the coating is generally proven by either colored dyes [14] or by mechanical adhesion tests of broken and "self-glued" bulk polymer samples [15]. However, the addition of a dye during the encapsulation procedure might alter the results of the microcapsule synthesis (e.g. reaction of the dye with the encapsulated agent or with the capsule matrix) and mechanical adhesion tests of coated samples do not show the strength of the coating itself. Therefore, the possibility to analyze capsules and their contents without a marker or dye within the coating would give more certainty and allow evaluating effects such as the leaking of encapsulated core content into the coating.

Many organic molecules can be distinguished from similar molecules based on their specific fingerprint-like spectrum collected by Raman spectroscopy (RS) [16,17]. The position of a peak can even depend on the underlying substrate as in the case of surface enhanced Raman spectroscopy (SERS) [17]. Zhu et al. differentiated between the different layers of a 100 μm big capsule based on the respective Raman spectra: depending on the depth of

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http://dx.doi.org/10.1016/j.porgcoat.2015.06.009
0300-9440/

focus they measured the glycidyl methacrylate core or parts of its multiple-layer-shell consisting of poly-melamine-formaldehyde, poly-methyl methacrylate and paraffin wax [18]. Alternatively, also two dimensional maps across cross-sections of multi-layered microcapsules can be recorded [19]. Yuan et al. on the other hand embedded microcapsules containing an epoxy and a thiol based hardener in a polymeric coating matrix for self-healing applications [20]. The authors followed the reaction of the two reactive agents at the polymer fracture interface by monitoring the disappearance of the thiol peak over time. But also the penetration depth of one graft polymer into another can be followed with RS [21]. In the same publication also the density of graft and depth of functionalization was monitored with RS. Schrof et al. described the potential of confocal Raman spectroscopy with a confined measuring volume of only about 1 μm^3 [22]. However, the three layered UV-coating made a 3D representation redundant and they limited their results to a depth profile with a step size of about 5 μm similar to Zhu et al. [18]. Froud et al. presented the use of an oil immersion objective on a sample with 11 polymer layers to increase scan depth to 100 μm and a better depth resolution compared to measuring in air [23].

Currently, industrial coatings often only have thicknesses of a few tens of micrometers and microcapsules therein would be even smaller. Accordingly, much smaller step sizes are needed for their investigation. In this publication the authors will demonstrate the extended potential of confocal Raman spectroscopy by investigation of microcapsules down to 1 μm in diameter within a coating of 15 μm thickness and step sizes of only 1 μm in *x*, *y* and *z* direction. Because of the (partial) transparency of the coating for the excitation laser, Raman spectra can be obtained at different depths in the coating. [22] With high confocality and focus of the laser the intensity of peaks of material around (to the sides and above and below) the measuring volume is negligibly small. By comparing the spectra at different measurement points and choosing characteristic peaks of each molecule of interest, Raman maps can be produced [19,24]. Thereby, the location of the capsules with an organic core within the polymeric coating can be exactly defined with three coordinates (*x*, *y* and *z*).

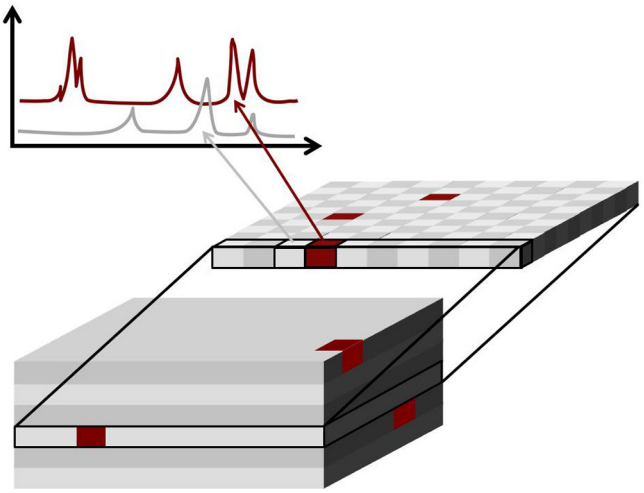
2. Experimental

2.1. Sample preparation

The microcapsules with a diameter between 1 and 5 μm were fabricated by Devan Chemicals. They consist of a melamine formaldehyde based shell and a hydrophobic core. These capsules were analyzed in the first experiment. Afterwards, 8 wt% of these microcapsules were mixed into a water based aliphatic urethane acrylate resin from Allnex NV. Subsequently the resin was applied on a glass plate with a bar coater and UV cured in air resulting in a coating with ~15 μm dry thickness named C15. Another sample named C40 of a ~40 μm thick coating containing ~15 μm big microcapsules was prepared to show the transparency of as well the coating as well the capsules and that the technique is also applicable for thicker samples. Although not shown, the measurements were repeated several times at different locations and also with different samples (different coatings, different microcapsules and different microcapsule content). Similar results were obtained in all cases.

2.2. Confocal Raman spectroscopy

The samples were analyzed with a LabRAM HR Evolution confocal Raman spectrometer from Horiba Scientific. A 532 nm wavelength green laser was used with 50% or approximately 7.5 mW/cm^2 intensity together with an air cooled CCD detector with a 1800 grating resulting in a spectral resolution of 1 cm^{-1}. Either a 50× long distance objective or a 100× objective was used for optical images and recording of the Raman spectra. The data was processed with the standard LabSpec 6.2 software for this instrument including spike removal and background correction on each single spectrum.



Scheme 1. A 3D Raman map is constructed by measuring the whole volume of interest point by point, line by line and layer by layer and comparing the spectra or parts thereof of each point with each other.

2.3. Raman mapping

The above described confocal Raman spectrometer has an automated sample stage. Thus several spectra in a row, on a plane and even in three dimensions can be recorded and compared with each other (see Scheme 1). This way the operator can perform point measurements, one-dimensional cross-sections, two-dimensional (2D) and three-dimensional (3D) mappings. Different peaks (sections of the spectra) were indicated in the spectra and their intensity was compared after integration. Thereby, a representation of the scanned volume (3D map) can be produced based on the intensities of the peaks in all spectra recorded. For the cross-sections and 3D maps, the measured depth of analysis was taken as true value. In fact, because the refractive index of the polymer is higher than the one of air, the true depth of analysis might be off by a factor of about 1.5 [23,25]. However, the exact determination of the depth is not crucial to the outcome of this paper. The comparison of the optical image with a map (2D or 3D) allows a very straight forward determination of the distribution of chemical species (more precisely molecular bonds) within the sample.

3. Results and discussion

3.1. Mapping of core content of single capsules

In a first experiment single dry capsules and a drop of the pure capsule core solution were compared under the Raman microscope. The spectra of the capsules show the same peaks as the spectrum of the reference core solution (Fig. 1, C–H vibrations and alkane chain vibrations (768 cm^{-1}, 827 cm^{-1}, 875 cm^{-1}, 893 cm^{-1}), alkane chain stretching (1040–1150 cm^{-1}), CH_2 skeletal twisting vibrations (1303 cm^{-1}), CH_2 asymmetric stretching at 1420 cm^{-1} and CH_3 asymmetric deformation at 1446 cm^{-1}). This confirms that the capsules contain the initially encapsulated organic liquid.

To investigate the distribution of the core material in a capsule a 2D map of three capsules was recorded. An optical image of the