

CARBON NANOTUBE-POLYMER COMPOSITES FOR USE AS REMOTE STRAIN-SENSOR COATINGS

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ABSTRACT

Nanocomposites and nanostructured polymers with unique opto-mechanical properties have been developed as smart coatings for use in a novel, high resolution, and non-contact strain-measuring application. Remote polarized Raman spectroscopy has been used to monitor optical strain sensitivity of deformed coatings (deformation micromechanics), and determine local strains on the micron scale directly from stress/strain induced Raman band shifts. The research is aimed at providing a novel high-resolution non-contact technique for the determination of surface stresses and strains in a wide variety of engineering components used in both laboratory and in-the-field (external) applications.

1. INTRODUCTION

Smart materials can be defined as materials that incorporate the functions of sensing, actuation and control. In this study, we aimed to develop a novel high-resolution, non-contact Raman technique to measure surface stresses and strains of a wide range of Raman-inactive engineering components.

It is widely recognised that some crystalline materials are capable of undergoing stress/strain induced Raman band shifts [1, 2]. As a material is strained, the interatomic distance changes, giving rise to a change in the interatomic force constant, and therefore a change in the vibrational frequency. Following the peak position enables the stress or strain applied to that material to be measured. A recent study in Japan [3], has reported the development of PbO coatings for strain measurement applications. Such coatings, however, are brittle (breaking strain ~ 0.5 %) and have relatively small strain-induced Raman band shifts (~ -2 cm^{-1} / % strain) with substantial errors arising from the weak Raman scattering.

The present study is concerned with the development of stress-sensitive coatings by combining materials that undergo resonant Raman scattering within high performance polymer matrices. Polyurethanes were therefore used because of their excellent and wide-ranging physical properties and ease of processing. Two types of coatings were developed: (i) microphase-separated copolyurethanes (DA-coPU) where the Raman active species are nanoscale-dispersed diacetylene-containing hard segments (DA) that are produced *in situ* [4] and (ii) polyurethane nanocomposites (SWNT-PU) filled with dispersed HiPco single-wall carbon nanotubes.

Polydiacetylenes [5, 6] and DA-coPU systems have been extensively studied in the past fifteen years [7-10], whereas most research based on embedded nanotubes is usually centred on epoxy resins or PMMA as matrices [11-16].

2. PRINCIPLES

In the case of a perfectly bonded coating of negligible thickness, it can be considered that the strains developed at the surface of a specimen are transmitted without any significant change to a coating of negligible thickness. Thus, in plane-stress problems, the response to stress of a

perfectly bonded coating produced by stresses on the surface of a specimen (Figure 1) can be described by the following equations:

$$\sigma_{xx}^c = \frac{E^c}{E^s(1-\nu^{c2})} \left[(1-\nu^c\nu^s)\sigma_{xx}^s + (\nu^c - \nu^s)\sigma_{yy}^s \right] \text{ and}$$

$$\sigma_{yy}^c = \frac{E^c}{E^s(1-\nu^{c2})} \left[(1-\nu^c\nu^s)\sigma_{yy}^s + (\nu^c - \nu^s)\sigma_{xx}^s \right]$$

where σ_{xx} and σ_{yy} are the normal stress components in Cartesian coordinates, E is the elastic modulus and ν is the Poisson's ratio: the superscripts s and c refer to the substrate and coating, respectively.

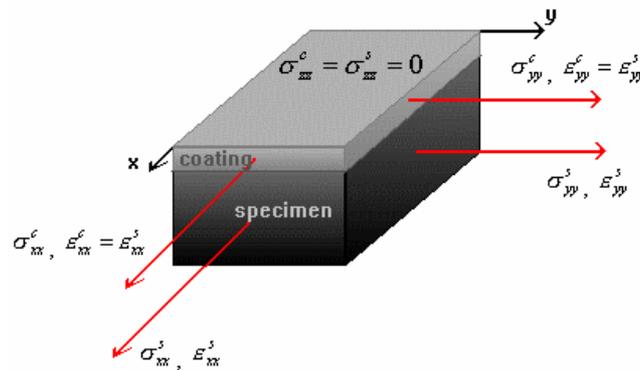


Figure 1. Elemental section of coating and specimen showing stresses and strains

The simple mathematical models described above do not only demonstrate that such coatings can be used as strain sensors but also indicate specific problems that may arise. Raman microscopy is a surface-analysis technique as its penetration depth can be limited to only a few tens of nanometres for coloured materials. This limitation must be considered even though the calculation of the penetration depth is difficult.

A coating must be considered as a three-dimensional extension of its substrate. It is therefore unrealistic to consider that the strains, transmitted to the coatings by means of shear and normal tractions at the interface, do not become modified or distorted. In the case of perfect bonding, these tractions vary so that the displacements experienced by the coating and the specimen at the interface are identical. However, the following points must also be considered.

The strain at the surface of the coating does not equal the strain at the interface, and a strain gradient exists through the thickness of the coating. This is particularly important for flexural problems.

The coating has a reinforcing effect on the substrate, that is, the coating carries a portion of the load thus reducing the strain on the surface of the substrate.

Simple mechanical models have been used in this study to determine theoretically the magnitude of these effects and to develop optimised coatings. Moreover, a mismatch in Poisson's ratio occurs in almost all cases as ν^c usually exceeds ν^s . This mismatch induces a distortion of the displacement and strain fields through the thickness of the coating especially at boundaries.

3. EXPERIMENTAL

3.1 Materials and preparation

Polyurethane / SWNTs nanocomposites (SWNT-PU) were synthesized using a modified MDI (M143; Dow chemicals), a diol (bisphenol A etoxylate, 2EO/phenol; Aldrich) and HiPco nanotubes (SWNTs). The most common way to disperse nanotubes in a polymer-forming matrix is by the use of sonication. However, dispersion in the modified MDI was not possible as it polymerises under intense sonication, and dispersion in the polyol was only possible by heating it to reduce its viscosity. Efficient dispersion of 0.1 wt % of SWNTs was achieved by using the induced shear forces developed while stirring the heated polyol (50 °C for 1 hour). The liquid MDI was then added, and polyurethane-forming system was stirred for another 15 minutes at room temperature. As before, the system was then cast using a thin-film cube applicator (thickness range from 100 to 400 nm) onto various substrates (steel, aluminum, epoxy resin) or cast in moulds to produce bulk samples. The initial Raman spectrum for the SWNT-PU before deformation is presented in Figure 2. The resonant G'-band at approximately 2600 cm^{-1} is well known to shift with deformation [11-16].

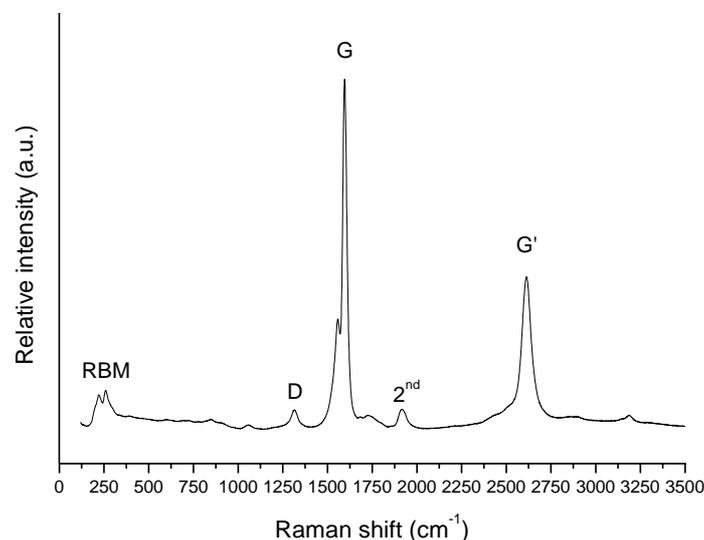


Figure 2. Raman spectrum of a SWNT-PU coated on steel

3.2 Deformation micromechanics

Deformation micromechanics studies were carried out using simultaneous Raman spectroscopy and either tensile or 4-point bending tests. For tensile deformation, an Instron 1122 testing machine was used simultaneously with the remote Raman Renishaw system 100. The 4-point bending tests were carried out according to the ASTM standard using a rig attached to the stage of the optical microscope of a Renishaw system 1000. The 632.8 nm red line of He-Ne laser was used in both the Renishaw 100 and 1000 systems. In all cases, the strains in coatings were measured independently using Series EA strain gauges with 6 mm gauge length (Measurements Group Inc.).

4. RESULTS & DISCUSSION

4.1 Mechanical and Raman characterization

The Raman band position shifts linearly with strain at low strain values (Figure 3). It is important to notice that these results were perfectly reproducible, independent of the substrate used. SWNT-PU nanocomposites appear to be able to offer a much higher accuracy as strain sensor as the band shift rate is over 2.5 times higher than the one for the DA-coPU systems previously developed [4]. However, the initial peak position scattering of the G' band seems

to totally counteract this advantage. Preliminary spectra at random positions and on various samples were obtained in order to determine the scatter of the peaks position. The scatter of the $-C\equiv C-$ at $\sim 2100\text{ cm}^{-1}$ had been found of approximately $\pm 0.5\text{ cm}^{-1}$ whereas the one of the G' band can be over $\pm 2\text{ cm}^{-1}$.

The initial scatter of the G' band is the result of a combination of factors. First of all, its frequency is known to be dependent on the chiral angle and the diameter of the nanotubes [17]. Then, experiments have proven that the frequency is also affected by the dispersion; isolated nanotubes and bundles of different size have different frequencies due to the heating effect of the laser beam. Following the improvements made on the synthesis of SWNTs, improvements would be expected by only dispersing a single nanotube type (given diameter and chirality). Currently, further work is being carried out in order to try to improve the dispersion at different concentration levels in order to limit the scattering of the initial peak position.

Moreover, non-linear behaviour has also been observed at higher strain for PU/SWNT nanocomposites. As observed on Figure 3 the Raman band shift curve can then be fitted perfectly with an exponential decay function which indicates a change in stress transfer efficiency. This particular behaviour is believed to be the result of the debonding of the SWNTs from the matrix and their slipping within the bundles.

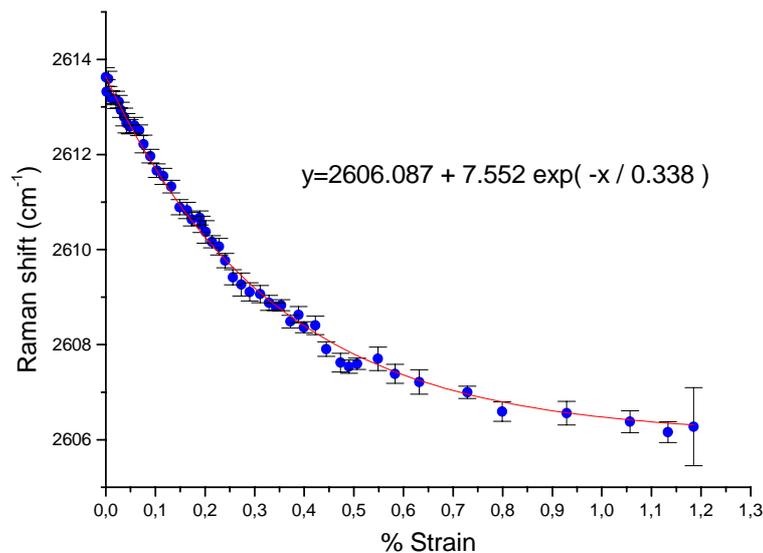


Figure 3. Raman shift versus % Strain from 4-point bending test results on specimens coated with SWNT-PU nanocomposite coating (G'band)

4.2 Use of polarized Raman spectroscopy

Polarized Raman spectroscopy is believed to enable the determination of the stress and strain applied to the coatings in different directions. Frogley, Zhao and Wagner showed how polarized Raman spectroscopy can be used in order to perform direction-sensitive strain mapping [16, 18] using the antenna effect of SWNTs.

This effect is characterized by the fact that the intensities of the resonant bands are strongly dependent on the nanotube orientation and are highest when the incident light polarization is parallel to the nanotube axis. For example, Duesberg et al. showed that the resonant Raman

spectra (G band) from metallic SWNTs are strongly suppressed when the light is polarized perpendicular to the nanotube axis [19].

The use of polarized Raman spectroscopy on isotropic SWNT-PU coatings which contain isotropic dispersions of SWNTs, allows the selection of species lying along the polarization direction just like for and DA-coPU systems [4].

Figure 4 presents a 4-point bending experiment on an epoxy beam coated with a SWNT-PU system. It shows that the use of polarised Raman spectroscopy enables strains to be measured in different directions: negative and positive slopes have been observed depending on whether the polarisation direction is parallel or perpendicular respectively to the applied strain. Even if there is an isotropic dispersion of the nanotubes, these slopes may be dependent on local orientation. Local orientation can therefore induce certain limitations in the development of an accurate strain sensor system and its influence will be investigated.

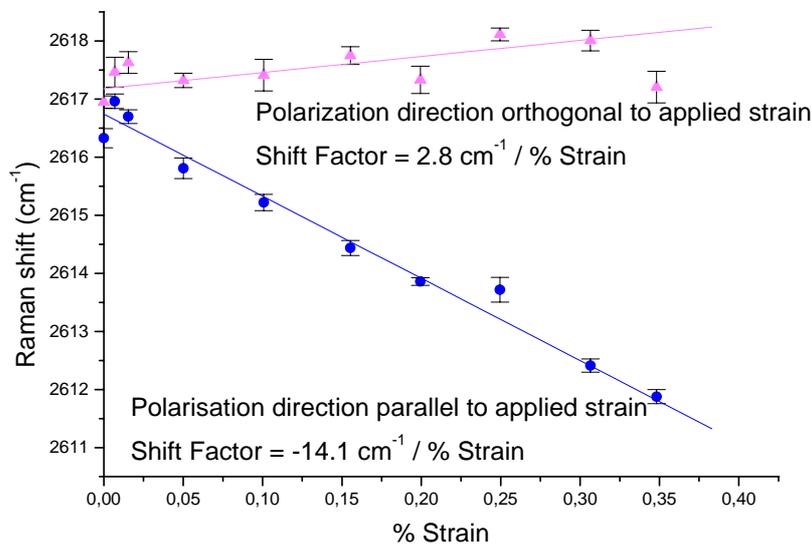


Figure 4. G' Raman shift versus % Strain from a 4-point bending test on an epoxy beam coated with a SWNT-PU nanocomposite using polarized Raman spectroscopy

Theoretical analysis is being carried out in order to understand and optimize the use of polarized Raman spectroscopy as a tool to determine principal strains and stresses. Even if we expect an isotropic dispersion of the nanotubes, the information obtained from polarized Raman spectroscopy will be dependent on local orientation of the nanotubes. This can be easily understood using conventional stress analysis as the strain along the nanotube (isolated or small bundle) axis e_x can be described by the relation

$$e_x = e_\theta (\cos^2 \theta - \nu \sin^2 \theta)$$

where ν is the Poisson's ratio of the PU matrix, e_θ is the strain parallel to the tensile axis, θ is the angle between the nanotube axis and the tensile axis.

5. CONCLUSIONS

Nanostructured polyurethane coatings have been developed with opto-mechanical properties which make them suitable for undertaking stress-strain measurements via Raman spectroscopy. The use of SWNTs as strain sensitive Raman-active material has shown great potential compared to PbO coatings or even diacetylene crystals of DA-coPU. With the rapid progresses in fields such as the synthesis of SWNTs and their dispersion techniques, the limitations highlighted within this work should soon be overcome.

The use of polarised Raman spectroscopy as a tool to determine principal strains and stresses has been described and will be used in order to determine Poisson's ratio of a wide variety of engineering components.

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