

Raman spectroscopic methods for polymerization monitoring

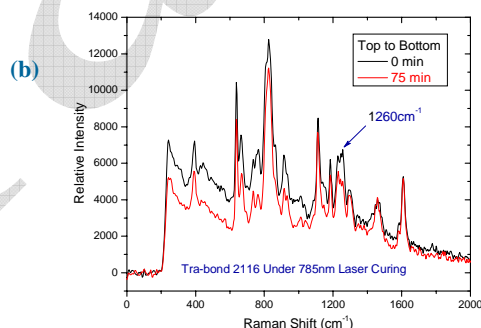
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Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. We show that non-invasive, real-time polymerization monitoring can be successfully performed with our hand-portable, miniature Raman spectroscopic system.

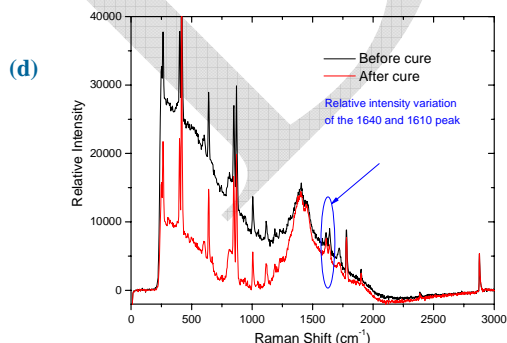
In the first example, a MiniRam™ Raman spectrometer (Fig. 1 (a)) is used to monitor the polymerization status of a Tra-bond 2116 epoxy sample and a TPH3 restorative dental resin sample. The MiniRam™ Raman spectrometer features a rugged turn-key design with a built-in spectral narrowed and stabilized 785nm diode laser and a BTC111/112 CCD array spectrometer. A spectral coverage of $175\text{--}3100\text{cm}^{-1}$ and a spectral resolution of 10 cm^{-1} make it suitable for general Raman spectroscopy applications. The MiniRam™ spectrometer is also equipped with a fiber optic probe that provides OD >6 Rayleigh scattering rejection. Fig. 1 (b) shows the Raman spectra of the Tra-bond 2116 epoxy sample before and after cure. It can be seen that the epoxy band at 1260cm^{-1} decreases as the oxirane ring is opened by the curing reaction, while the phenyl ring stretch at 1610cm^{-1} remains constant which can be used as a reference. The variation of the relative intensity of the epoxy band vs. curing time is plotted in Fig. 1 (c). It can be seen that the intensity decrease of the 1260cm^{-1} epoxy band follows a Gaussian model. This matches well with the previous published results, in which a FT-Raman spectrometer is used to monitor the epoxy curing process. Fig. 1 (d) shows the measured Raman spectra of a TPH3 restorative dental resin before and after the curing process. A variation in the relative intensity of methacrylate C=C stretching mode at 1640 cm^{-1} and the aromatic C=C stretching mode at 1610 cm^{-1} can be used as an indicator of the degree of conversion for the dental resin.



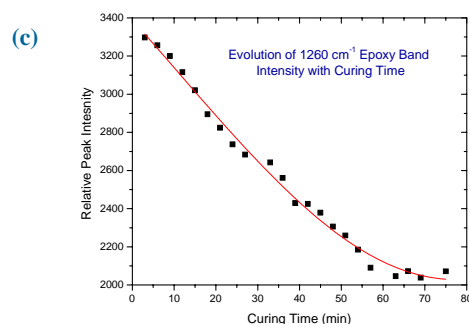
MiniRam™
Raman
spectrometer



Raman spectra of Tra-bond 2116 epoxy
before and after cure



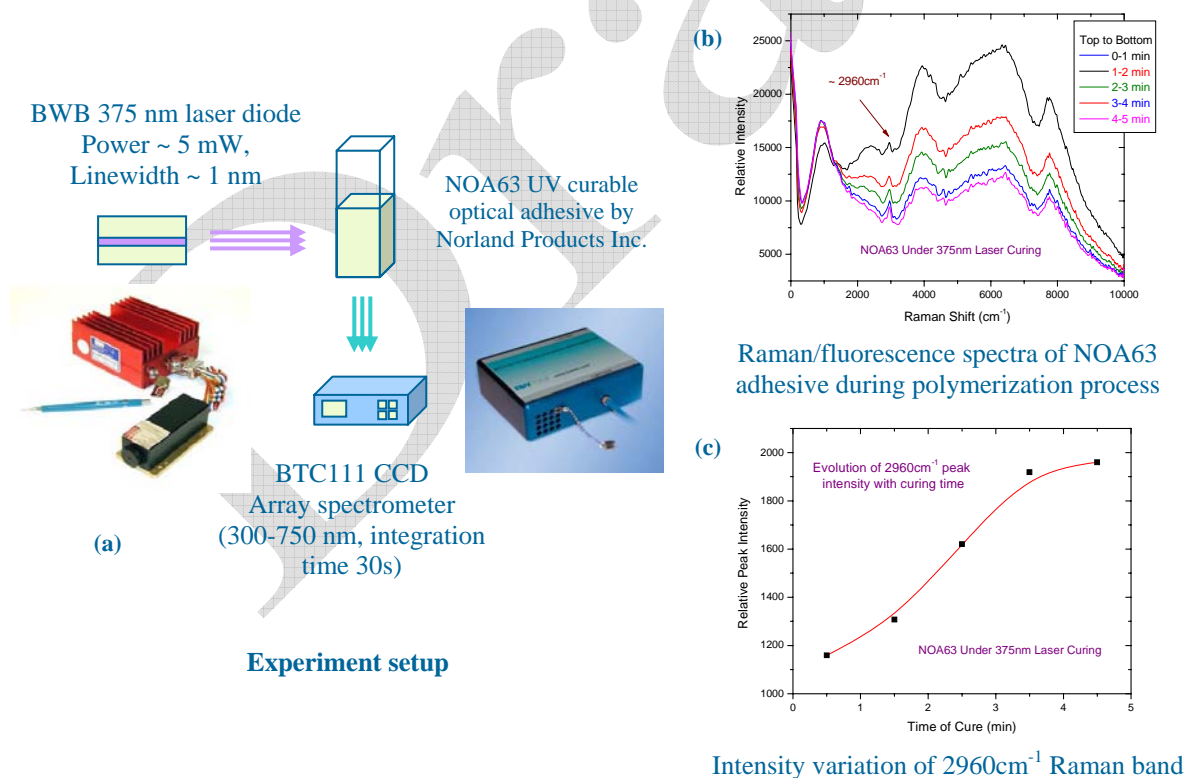
Raman spectra of TPH3 dental resin before
and after cure



Intensity variation of 1260cm^{-1} epoxy band

Laser based curing light sources have been used for industrial applications, such as high precision assembly and stereolithography. For these applications, it is highly desirable to monitor the curing status

of the material in real time as to achieve the optimum performance and maximum productivity. We show that the curing laser itself can be used as the Raman excitation light source for polymerization monitoring. Since the wavelength of the curing laser is generally selected to match with the absorption band of the material, the Raman scattering signal produced by the curing laser may be enhanced by several orders of magnitude through resonance Raman effect. As a result, the Raman signal can be easily detected using low-cost spectrometers. In one example as shown in Fig. 2 (a), a 375nm UV laser diode with 5mW output power is used as the curing and Raman excitation light source. The material to be cured is a NOA63 UV curable optical adhesive manufactured by Norland Products Inc. Full cure of the adhesive requires a curing time of 5 minutes according to its specification. The laser beam is first collimated into a beam size of 1.5mm and then directed to the adhesive sample. The laser light is absorbed by the adhesive and activates its photo-initiators, which trigger the polymerization process. The Raman/fluorescence emission of the adhesive sample during the polymerization process is measured in real time by a BTC111 general-purpose CCD spectrometer. The obtained Raman/fluorescence spectra are shown in Fig. 2 (b). A strong Raman band at around 2960cm^{-1} is observed even without using any Rayleigh scattering rejection filter. This Raman band may be attributed to $-\text{CH}_3$, $-\text{CH}_2$, $-\text{CH}$ stretching modes or their combinations. The Raman band is well separated from the fluorescence emission due to short wavelength of the curing laser. During the polymerization process, the intensity of the fluorescence background drops while the relative intensity of the Raman signal increases. It can be seen that the intensity variation of the Raman signal as shown in Fig. 2 (c) is a good indicator of the polymerization process. The degree of polymerization measured with the spectroscopic sensor is verified by other methods such as hardness test and FTIR analysis. The spectroscopic sensor can be used to provide feed-back control for the curing laser to achieve the optimum curing result.



In conclusion, our portable Raman spectroscopic system has been demonstrated as a viable solution for real-time, none-invasive polymerization monitoring. Its rugged design makes it capable of providing reliable results even under harsh industrial environments.