MULTI-WAVELENGTH RAMAN SPECTROSCOPY OF POLY(FURFURYL ALCOHOL)

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Keywords: *Poly(furfuryl alcohol), Raman Spectroscopy*

ABSTRACT

Poly(furfuryl alcohol) (PFA) [1-2, 4-10], produced through polymerization of furfuryl alcohol, is a thermosetting polymer [3] and basis of thermoset resin systems, and it has been investigated in several studies (IR, 13C-NMR, Raman, DSC), new aspects being considered each time [4-10]. Nevertheless, PFA still remains an intriguing polymer, since curing [3, 8-10], apart from being promoted by the presence of an acid catalyst, can be also induced by heat or suitable radiation, the resulting molecular structure of PFA consequently not being that obvious. Despite the scientific literature already available concerning the Raman spectra of PFA [4-7], at present an unambiguous assignation of the Raman bands recorded in cured, cross-linked, and consequently irreversibly hardened PFA is still missing [4-10]. The purpose of the present study was to investigate the presence and the grade of cross-linking and of conjugation in cured, hardened (thermosetted) PFA [8] in comparison to the pristine, viscous PFA [2] by means of multi-wavelength Raman spectroscopy in the visible and in the ultraviolet spectral range, using excitation wavelengths from several laser sources and from a synchrotron light source. Additionally, by taking advantage from previous findings and foreseen possible molecular structures of PFA [8], Raman spectra were simulated by first-principles and semi-empiric methods for exploiting them to evaluate their matching with experimental ones. Comparison of published PFA Raman spectra [5-7] with those obtained in our study evidences important differences for the pristine, viscous PFA and the cured, irreversibly hardened and cross-linked PFA, due to a different molecular structure of the polymer as consequence of the curing process. Furthermore, with excitation wavelengths in the UV range, resonance Raman enhancements can be observed, being also the case in the simulated spectra. Furthermore, Raman measurements of a cured, irreversibly hardened PFA sample in a temperature range between -160°C and 300°C showed some remarkable changes of the spectral profile across this temperature range, being associable with the glass transition described in [9-10]. This Raman spectroscopic study of viscous and cured PFA enables us to get a deeper understanding of the spectral features observable in the Raman spectra, possibly improving knowledge for the various applications of PFA, e.g. described in [1, 8-10].

Acknowledgements

The authors acknowledge financial support provided by the European Regional Development Fund and Interreg V-A Italy Austria 2014–2020 through the Interreg Italy Austria project ITAT1023 InCIMa "Smart Characterization of Intelligent Materials" and ITAT1059 InCIMa4 "InCIMa for Science and SMEs".

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