

Raman spectroscopy of epoxy resin crosslinking

HANA VAŠKOVÁ, VOJTĚCH KŘESÁLEK

Faculty of Applied Informatics

Tomas Bata University in Zlín

Nám. T. G. Masaryka 5555, 760 01 Zlín

CZECH REPUBLIC

vaskova@fai.utb.cz kresalek@fai.utb.cz <http://www.fai.utb.cz>

Abstract: - Raman spectroscopy has become an efficient analytical method providing detailed and specific information on a molecular level. There is no doubt that Raman spectroscopy can be ranked among powerful and useful research and analytical tool applicable across the sciences and also industrial and manufacturing branches. The focus of this paper is in the possibility of using Raman spectroscopy for the process of epoxy resin crosslinking monitoring and particularly a prediction of a model for a storage temperature of epoxy resin pre-pregs.

Key-Words: - Raman spectroscopy, epoxy resin, crosslinking, curing, epoxy prep-preg.

1 Introduction

Epoxy resins belong among the most versatile polymers which find very broad range of assertion and are intensively used in various technical applications.

The first epoxy resin was synthesized at the end of 1930's. A number of epoxy monomers and hardeners with different properties have been developed up to present time.

Epoxy-based materials have very good adhesion and mechanical properties as high strength and stiffness or on the contrary extra ordinary flexibility, excellent electrical properties, also resistance to thermal, moisture and mechanical shock. Epoxy resins are used as adhesives, coatings and potting materials, in electronics industry as electrical insulators, in integrated circuits etc., in aerospace and marine industry, in industrial tooling for laminates, fixtures, molds and also in art. Some epoxies which are responsive to ultraviolet light find applications in dentistry, fiber optics or optoelectronics.

To obtain epoxy resin in a hard and infusible material, it is needful to cure the resin with a curing agent (hardener). During a curing chemical epoxide groups in epoxy resin react with hardener and from this liquid mixture a highly crosslinked, three-dimensional network is formed. A mobility of molecules in the system successively diminishes as the network formation reaction proceeds. Above mentioned properties depend on the chemical structure of the curing agent and also on curing conditions [1].

The behavior and kinetics of curing process of epoxy resins has been already surveyed by various analytical techniques such as differential scanning calorimetry, gel permeation chromatography, nuclear magnetic resonance [2]. Other available methods for the study of hardening of epoxy resins are:

- Mechanical methods as viscosity measurements of resins as a function of time or detection of their stiffness.
- Ultrasonic method as a measurement [3] of velocity and acoustic wave attenuation.
- Dielectric spectroscopy

Another possibility of studying crosslinking process is to use Raman spectroscopy, which has become a powerful analytical method since last few decades.

Raman spectroscopy is based on Raman effect, which was discovered at the beginning of the twentieth century by Indian physicist Sir Chandrasekhara Venkata Raman (1888 - 1970), almost one hundred years ago. However, Raman spectroscopy passes through its renaissance even in the last two decades hand in hand with technical progress in the new extremely sensitive detection devices latest developments, efficient filters and laser technology designs [4].

Raman spectroscopy provides a unique "fingerprint" of every individual substance as a characteristic for its identification. It is a versatile tool because of its applicability to a wide range of substances.

Raman spectroscopy has doubtless advantages against the other listed methods. When using Raman

spectroscopy, a sample or a surface of the sample is not disrupted and influenced because Raman spectroscopy allows non-contact and non-destructive measurements without a necessity of sample preparation. It also enables to measure samples with covering layers and also with packaging. This technique is also rapid - a spectrum can be acquired within a seconds what spares much time with comparison e. g. with chemical analyses.

2 Problem Formulation

An epoxy pre-preg is pre-impregnated composite system shaped as a fiber or a sheet containing even the resin and hardener. Epoxy resin pre-pregs have to be storage in cooled areas to avoid the crosslinking of the material. Low temperature causes increasing viscosity which affects deterioration of molecule reaction and suspension of crosslinking process. For further use of the pre-preg the activation by heat is needed. Then viscosity of storage matter decreases and the crosslinking process is initiated.

The aim of this paper is to find the model for finding a storage temperature of retained epoxy resin pre-pregs.

3 Experimental Methods

Several experiments concerning investigation of epoxy resins properties by Raman spectroscopy have been already done as showed a literature search. [2][3].

Raman spectroscopy was chosen as the major technique for the study of crosslinking and Dielectric spectrometry as a complementary method for results discussing.

Wavenumbers of peaks in Raman spectra are characteristic for present Raman active chemical groups of measured matters. Every single substance has its own unique Raman spectrum and the arrangement of peaks.

For recording Raman spectra was used Renishaw InVia Basis Raman microscope equipped with 514 nm excitation argon ion laser with laser maximum output power of 20mW. A Leica DM 2500 confocal microscope with the resolution up to 2 μ m is coupled to the Raman spectrometer. All measurements were collected at 50x magnification. Even if the aimed area is very small, the measurements from other spots of the same sample gave corresponding results. From 80 to 120 spectra was recorded during each measurement with exposure time 5 seconds and the delay between the acquisition was 10

seconds. The samples were scanned from 300 to 2200 cm^{-1} at a spectral resolution of 2 cm^{-1} .

Precision LCR meter HP4284A with a frequency range 20 Hz – 1 MHz was used for acquiring dielectric spectrometry data. Measuring of dissipation factor was performed on the frequency 1 kHz and the voltage of 1 V.

Commercially available two component firm and quick-drying Alteco F-05 3-Ton Clear Epoxy Adhesive was used for the measurement. Measured samples were obtained by mixing two reactants, the resin (diglicidyl ethers of bisphenol-A) and the hardener (N'-3-aminopropyl)-N,N-dimethylpropan-1,3-diamin) in stoichiometric ratio 1:1 according to advised information from the producer. The degree of crosslinking is fundamentally influenced by the ratio of the chemical active groups. According curing studies the most optimal degree is achieved when equivalent numbers of the functional groups take part in the crosslinking process [1]

Initial mathematical models bring following equations (1) and (4). These models are expected as the first approximation for the description of the crosslinking process. Two independent concurrently processes are presumed. The description of the progress of particular peaks $f(t)$ in Raman spectra in time is

$$f(t) = A \cdot e^{-Bt} + C \cdot t \cdot e^{-D(t-\delta)^2} + E. \quad (1)$$

The first equation term describes a decay of a number of free epoxide groups during networking and the second term represents the Raman activity of epoxy groups related to a change of viscosity. In the equation (1) $f(t)$ is proportional to the amount of the epoxide groups expressed in an arbitrary units as constants A and E, C is in the arbitrary unit per second. B and D are defined as

$$B = \frac{1}{\tau_1}, \quad (2)$$

$$D = \frac{1}{\tau_2^2}, \quad (3)$$

where τ_1 and τ_2 are time constants of the processes.

Gelation time is the time interval between the addition of the catalyst, the hardener, into a liquid adhesive system and the formation of a gel.

The dependence of gelation time corresponding to given temperature T of crosslinking on time t is

$$T = T_\infty + \frac{T_0 - T_\infty}{1 + \frac{t}{\tau}}. \quad (4)$$

Then the storage temperature must be lower than obtained T_∞ .

4 Results

For the monitoring of the epoxy resin crosslinking reaction time series measurements on Raman microscope were made. All spectra were acquired in the absence of room lights to avoid any interference. Firstly Raman spectra of plain epoxy resin and the hardener were recorded at the room temperature. The spectra were manipulated using the Wire 3.0.TM software. Fig. 1 shows the spectra of the resin and the hardener.

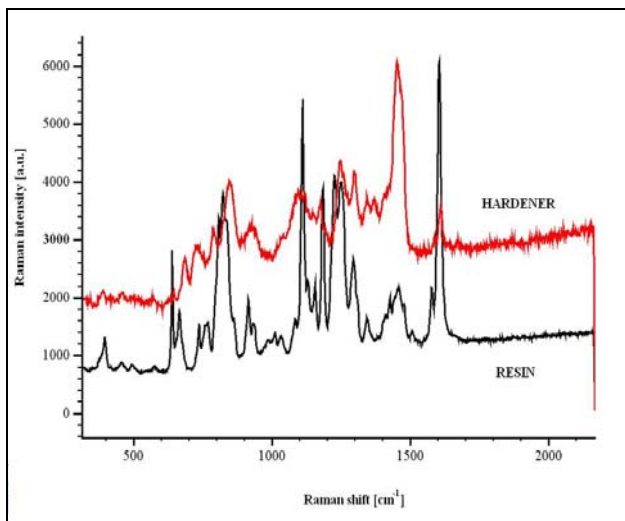


Fig. 1. Raman spectra of epoxy resin and the hardener

Determination of the chemical groups participating in the curing reaction followed. Raman bands corresponding to epoxide vibration are in the range of 1230 cm^{-1} and 1280 cm^{-1} according to [5] here the epoxide vibration band is at 1252 cm^{-1} (breathing of the epoxide ring). The intensity of this peak is linearly dependent on the concentration of epoxide groups in the resin mixture [6]. The peak at 916 cm^{-1} assigned to the epoxide ring deformation is much weaker. Other Raman peaks at 1112 cm^{-1} , 1186 cm^{-1} and 1608 cm^{-1} assigning to resin backbone vibrations did not change the intensity during the curing reaction.

When observing the epoxy bands at about 1252 cm^{-1} and also 1230 cm^{-1} , they are decreasing with time (Fig. 2). The Raman intensity is proportional to the concentration of the substance (or the bonds) in the sample, what can be interpreted as the consuming of the free epoxide groups during the vitrification of epoxy resin curing process. On the other hand an apparent reducing of the Raman peak at 2575 cm^{-1} pertaining to the used hardener was observed (Fig. 3). This reduction is much more notable at the beginning of the networking reaction, when the resin and the hardener come in the contact.

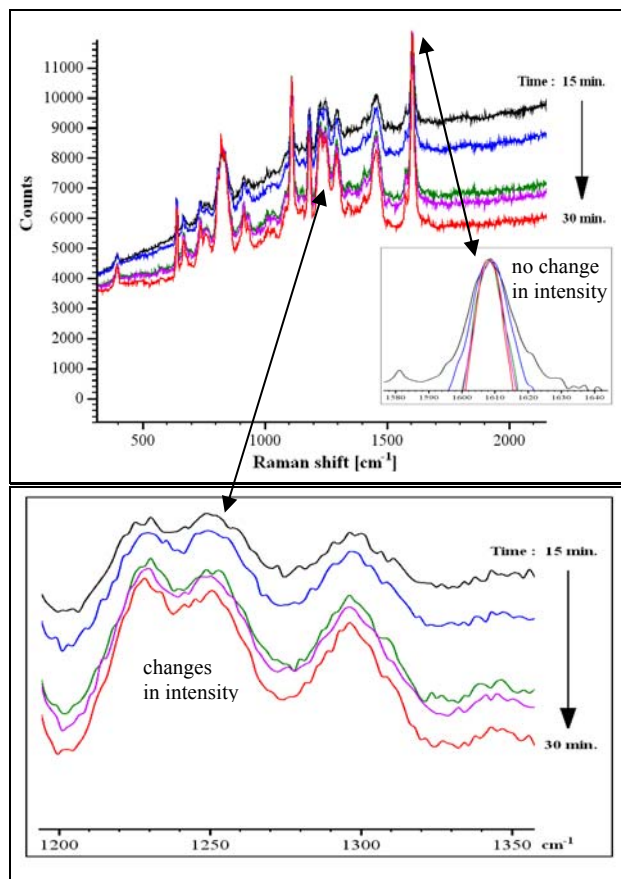


Fig. 2. Time progress of Raman spectra in time and (no) changes in intensity of particular peaks.

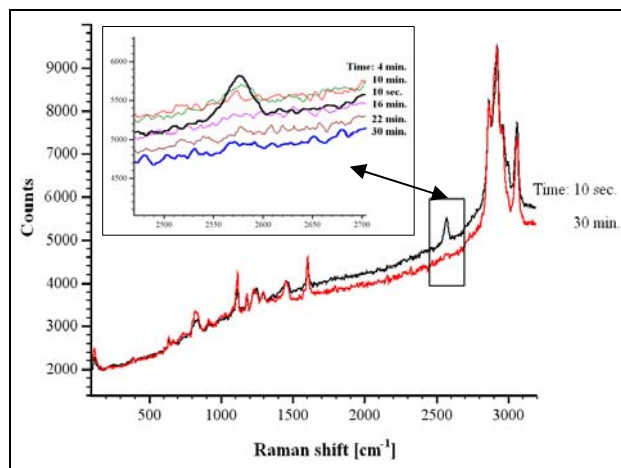


Fig. 3. Reducing of the Raman peak at 2575 cm^{-1} due to networking reaction.

Three-dimensional maps of the kinetics of the curing process in three different temperatures 20°C and 25°C monitored in 30 minutes after putting two reactants into contact are displayed in Fig. 4, Fig. 5 and Fig. 6. The different positions of the maximal increase of the curves (tracked along Data set ~ time) correspond with the gelation time. The lower temperature exerts influence upon the later achievement of gelation time.

The temperature influence on the crosslinking process is significant. Crosslinking is significantly slowed down at the temperature slightly below 15°C [1]. That was also verified by measurements and using obtained data and proposed mathematical model. At the temperature below 5°C the process practically stops.

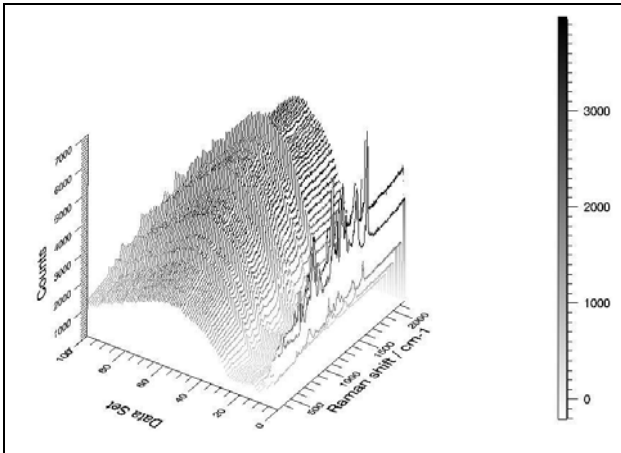


Fig. 4. 3D map of crosslinking process at the temperature 20°C.

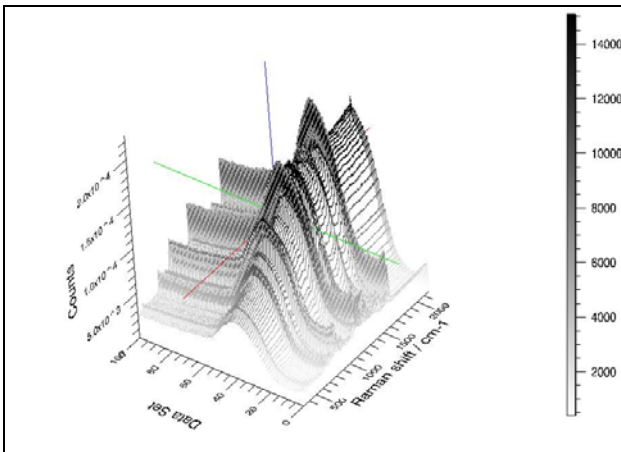


Fig. 5. 3D map of crosslinking process at the temperature 25°C.

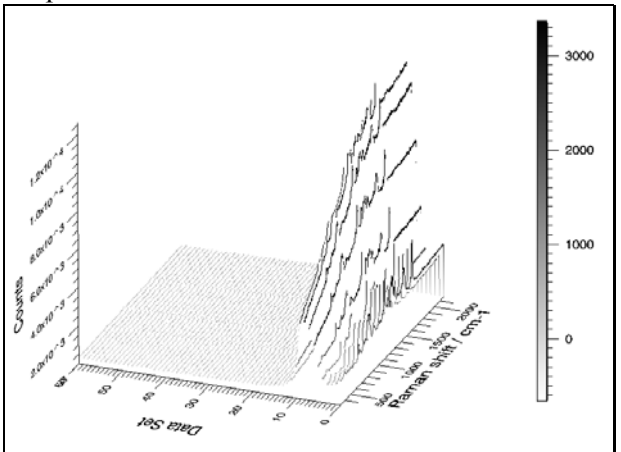


Fig. 6. 3D map of crosslinking process at the temperature 45°C.

The time dependence of dissipation factor obtained by Dielectric spectrometry is displayed in Fig. 7. Dissipation factor corresponds to viscosity and the peak – the maximum of dissipation factor of the system determine the relaxation time τ ms of epoxide group rotation at the temperature of curing, the ambient temperature, in given time.

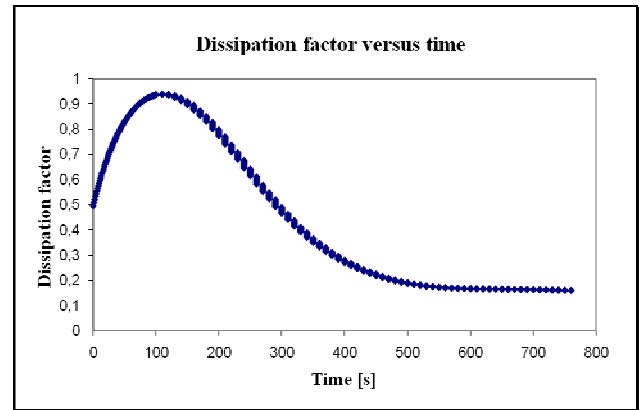


Fig. 7. Dissipation factor versus time

4 Conclusion

The novel method Raman spectroscopy was proposed as an investigative method for epoxy resin crosslinking. This technique can be assessed as an efficient because it has the capability of access to the control of quasi real time in-situ studies of crosslinking reaction and gives information on its kinetics.

Fluorescence the often occurred competing effect that can mask the Raman spectra doesn't cause problems in the spectra and fairly satisfactory signal to noise was obtained.

Raman spectrometers are usually designed as laboratory equipment often combined with microscopes, then only small volume of a sample can be measured. Connecting an optical fiber probe for remote analysis can this method shift to more extensive area of applications, particularly those applications, which has disallowed to bring the sample to the instrument. Probes can be used easily even on the distance of tens of metres and high optical efficiency of measurement is kept. This extension brings benefits for Raman spectrometers, which can be then directly used in processing for processes monitoring during the manufacturing or as a quality control method, e.g. for pre-pregs properties control in stores.

Acknowledgement

This work is supported by the Ministry of Education, Youth and Sports of the Czech Republic under the Research Plan No. MSM 7088352102 and by the European Regional Development Fund under the project CEBIA-Tech No. CZ.1.05/2.1.00/03.0089.

References:

- [1] Lacnjevac, C., M., New Organic Solvent Free Three-Component Waterproof Epoxy-Polyamine Systems. *Sensors&Transducers*, Vol. 08, 2010.
- [2] Rocks, J., Rintoul, L., Vohwinkel, F., The kinetics and mechanism of cure of an aminoglycidyl epoxy resin by a co-anhydride as studied by FT-Raman spectroscopy. *Polymer international*, Vol. 20, 2004.
- [3] Younes, M., Wartewig, S., Lellinger, D., The curing of epoxy-resins as studied by various methods, *Polymer*, Vol. 35, 1994.
- [4] Pitt, G. D., et al. (2005). Engineering aspects and applications of the new Raman instrumentation. *IEE Proc.-Sci. Meas. Technol*, Vol.152, No. 6, 2006.
- [5] Sorates, G., Infrared and Raman Characteristic Group Frequencies. England, 2001.
- [6] Lyon, R. E., Chike, K. E., Angel, S., M. In-situ cure monitoring of epoxy resins using fibre-optic Raman spectroscopy. *Journal of Applied Polymer Science*, Vol. 53, 1994.
- [7] Dusek, K., Ilavsky, M., Lunak, S., Crosslinked epoxies, Berlin, 1987.