Quasi real-time monitoring of epoxy resin crosslinking via Raman microscopy

Hana Vašková, Vojtěch Křesálek

Abstract**—**Raman spectroscopy has become a powerful analytical tool providing detailed and specific information at a molecular level. This benefit together with rapidity and other features of the method yields an advantage of quasi real time monitoring and measuring the structure changes dynamics. There is no doubt that Raman spectroscopy can be ranked among powerful and useful research and analytical methods 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 what involves identification localisation of the principal chemical bonds localisation of epoxy resin in Raman spectra. A mathematical model for a storage temperature of epoxy resin pre-pregs prediction was also proposed.

Keywords**—**Crosslinking, curing process, epoxy pre-preg, epoxy resin, Raman spectroscopy.

I. INTRODUCTION

EPOXY 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, fibre optics or optoelectronics.

To obtain epoxy resin in a hard and infusible material, it is needful to cure the resin, a low-molecular-weight polymer with epoxy groups usually at each end, with a curing agent (hardener), usually diamine. The epoxy group, shown in Fig. 1, is also known as oxirane or ethoxyline group is a three-membered ring consisting of two carbons and one oxygen atom,. This special molecular structure enables an easy participation in the addition reactions through opening the cycle, and thus it easily polymerizes.

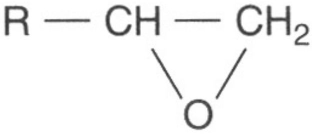

Fig. 1 The epoxy ring structure

During a curing chemical epoxide groups in epoxy resin react with hardener and from a liquid mixture a highly crosslinked, three-dimensional network is formed as illustrated in Fig. 2. A mobility of molecules in the system successively diminishes as the network formation reaction proceeds. Above mentioned properties of epoxy resins depend on the chemical structure and the amount of the curing agent and also on curing conditions [1] [2].

The behaviour of curing process of epoxy resins, the state of matter transformation and resin properties assessments has been already surveyed by various analytical techniques such as differential scanning calorimetry, gel permeation chromatography, nuclear magnetic resonance, electrical and thermal conductivity or Fourier-transform infrared spectroscopy [3, 4]. 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 their stiffness detection.
- Ultrasonic method as a measurement [5] of velocity and acoustic wave attenuation.
- Dielectric spectroscopy.

Another possible tool for studying crosslinking process is Raman spectroscopy, which has become a powerful analytical method with a wide scope in recent years.

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 revival even in the last two decades hand in hand with technical progress in the new extremely sensitive detection devices latest developments, efficient filters and

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H. Vaskova and V Kresalek are with the Tomas Bata University in Zlin, Faculty of Applied Informatics, nam. T.G.Masaryka 5555, 760 01 Zlín, Czech (phone: +420 576 035 228; e-mail: vaskova@fai.utb.cz, phone: +420 576 035 253; e-mail: kresalek@fai.utb.cz).

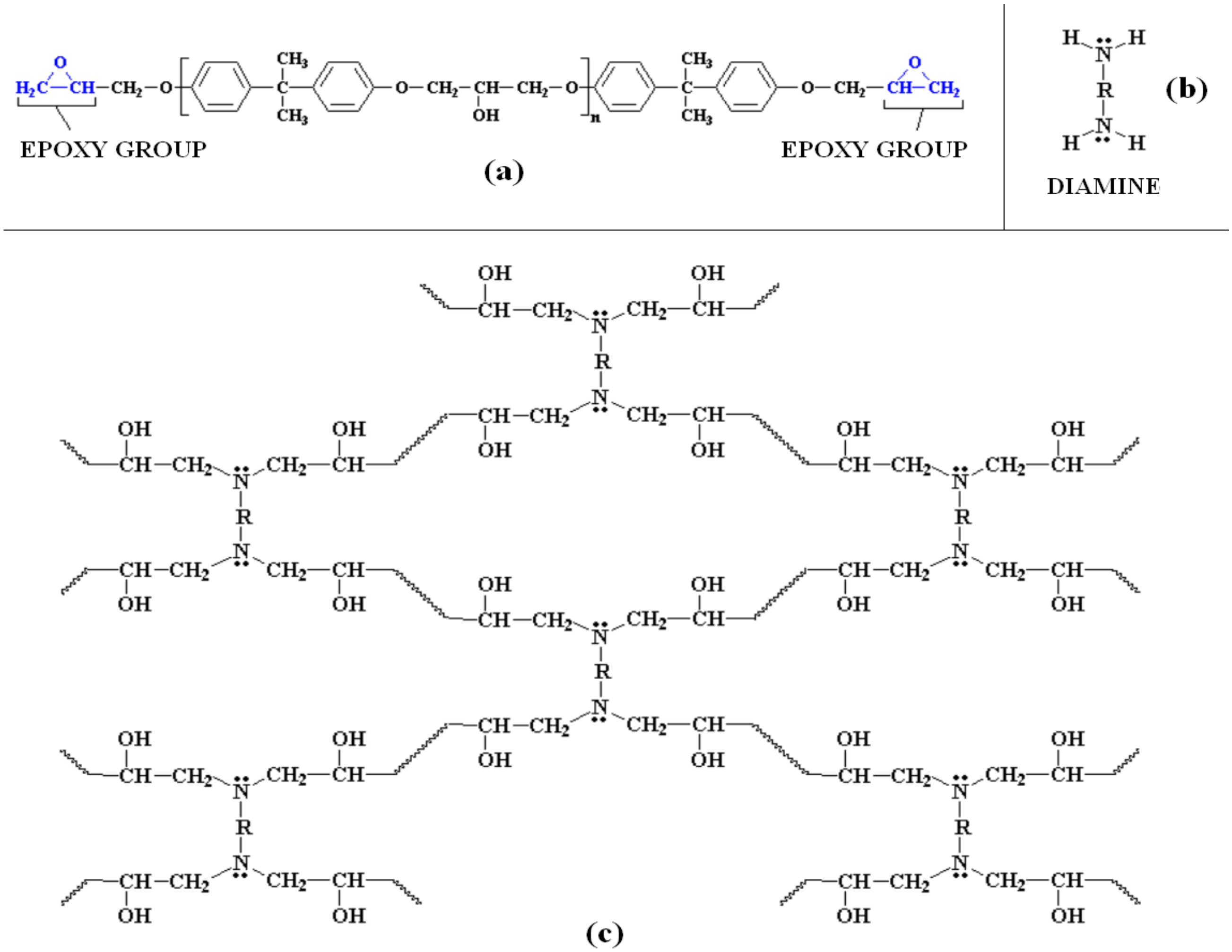

Fig. 2 Chemical structure of (a) DGEBA (b) a diamine. (c) The principle of crosslinking reaction of epoxy resin. [6]

especially laser technology designs [7].

Raman effect is a non-elastic scattering of an incident monochromatic light on molecules of specimen. This interaction causes vibrations of the molecule, its excitation and consequently reemission of a photon with changed wavelength in comparison with the initial one. The wavelengths differences are characteristic for the concrete material. Therefore, Raman spectroscopy provides a unique chemical “fingerprint” of every individual substance as a characteristic for its identification analogously to the fact that every single human being has different, highly specific set of fingerprints. This prospective technique enables *in situ* measurements and ability to control the material at the molecular level, i. e. on the micro/nano scale. It is a versatile tool because of its applicability to a wide range of substances as liquids, solids (except majority of metals and alloys) and gasses in different forms (powders, fibres, thin layers, solutions), organic and inorganic as well.

Raman spectroscopy has doubtless advantages against the other listed methods [8]. 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 in most cases. It also enables to measure samples with covering layers and packaging from other materials as polymers or glass. This technique is also rapid - a spectrum can be acquired within a seconds what spares much time with comparison e. g. with chemical analyses. Benefit of rapidity opens the doorway for quasi real time monitoring and studying the curing reactions.

II. PROBLEM FORMULATION

An epoxy pre-preg is pre-impregnated composite system shaped to the form of a fiber or a sheet containing even the resin and hardener. Pre-pregs are generally one of the most obvious mechanical models with multiphase composite material trait, heterogeneity and anisotropy [9].

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 reactants are disposed to rebound again, so the crosslinking process is initiated.

Therefore, the aim of this paper is to show ability of Raman spectroscopy for quasi real-time monitoring of the crosslinking process of epoxy resin and to find the model for specifying a storage temperature of retained epoxy resin pre-pregs.

III. EXPERIMENTAL PART

A. *Methods*

Several experiments concerning investigation of epoxy resins properties by Raman spectroscopy have been already done as showed a literature search [3, 5, 10].

From above mentioned advantages of method, its nature and also certain kind assay mark of innovatory, Raman spectroscopy was chosen as the major technique for the study of crosslinking reaction and dielectric spectrometry as a complementary method for results completion and discussing. Optical methods differ from the dielectric spectroscopy in the sense of possibility of focusing on the concrete chemical component, whereas dielectric spectrometry conflates contributions of all components of the crosslinking process. This can be in some cases benefiting in other rather a handicap of the method.

Every single substance has its own unique Raman spectrum and the arrangement of peaks what is essential for identification and assessment of materials. Raman spectrum represents the dependence of Raman intensity / counts, usually given in arbitrary units, on Raman shift / wavenumbers, given in cm^{-1}. Wavenumbers of peaks in Raman spectra are characteristic for present Raman active chemical groups of measured matters. They can be slightly shifted when using different excitation wavelength of laser.

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 2μm was coupled to the Raman spectrometer. All measurements ware 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. Parameters as exposure time, number of acquisitions and the laser power remained the same all along the experiments. Samples were scanned from 300 to 2200 cm^{-1} at a spectral resolution of 2 cm^{-1}.

The fundamental principle lies in inserting the examined specimen between conductive electrodes with time variable voltage which evokes dielectric polarization of the surveyed material. 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.

B. *Materials*

Commercially available two-part firm and quick-drying Alteco F-05 3-Ton Clear Epoxy Adhesive was used as experimental material for the measurement. Examined samples were obtained by mixing two reactants, the resin on diglicidyl ethers of bisphenol-A (DGEBA) base and the hardener (N'-(3-aminopropyl)-N, N-dimethylpropan-1,3-diamin). DGEBA is formed as a product of the reaction of bisphenol A with the epichlorohydrin (1-chloro-2, 3-epoxy propane; d-chloropropylene oxide), as is showed in Fig. 3. DGEBA is the fundamental component of about 90% of various epoxy resins used on the present. Bisphenol-A based resins are noted for their uncommon ability to resist a sudden impact of energy. Macroscopic failure caused by chemical bonds breaking as an effect of mentioned impact often occurs for weaker polymers.

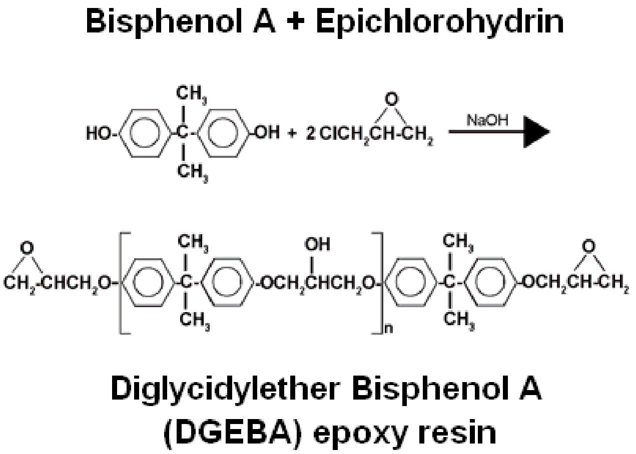

Fig. 3 DGEBA as a product of chemical reaction

The stoichiometric ratio of two reactants was 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 to curing studies the most optimal degree is achieved when equivalent numbers of the functional groups take part in the crosslinking process [1]. On the other hand the effectivity and of crosslinking reaction could be enhanced by addition of slightly more hardener's chemical groups.

C. *Mathematical model*

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 described by the function

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

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

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

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

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 first three dimensional network in the whole volume of the sample.

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

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

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

IV. RESULTS

For 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. Spectra were manipulated using the Wire 3.0.TM software. Fig. 4 and Fig. 5 show the spectra of the resin and the hardener. Spectra were scanned in the spectral range from 300 to 2200 cm^{-1} and from 2200 to 3200 cm^{-1}. Determination of the chemical groups participating in the curing reaction followed. Assignments for used epoxy resin from Raman spectra are displayed in table I. Raman bands corresponding to epoxy vibration are located in the range of 1230 cm^{-1} and 1280 cm^{-1} according to [11, 12], with closer

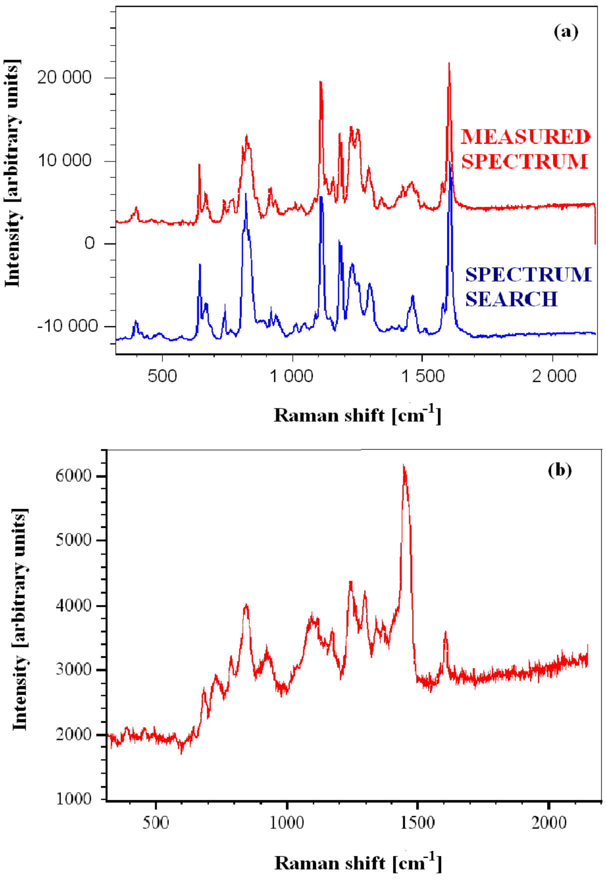

Fig. 4 (a) Comparison of acquired Raman spectrum of Epoxy resin with the Raman database spectrum, (b) the region (300 – 2200 cm^{-1}) of the Raman spectra of used hardener.

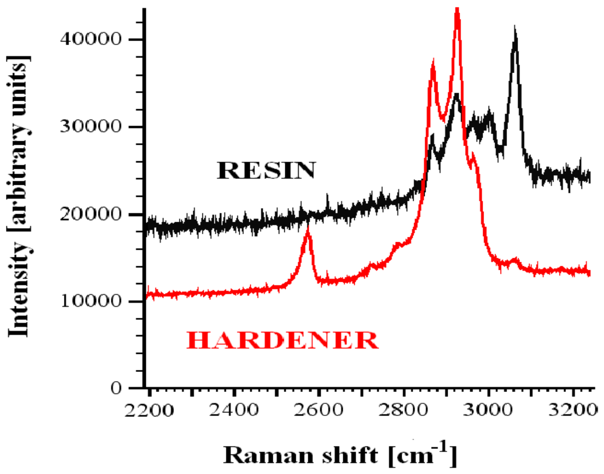

Fig. 5 The region 2200 – 3200 cm^{-1} of the Raman spectra of used epoxy resin and hardener.

Table I Raman peaks assignments for epoxy resin

Raman band [cm^{-1}]	Intensity* [a. u.]	Assignment**
3213(3210), 3157(3165)	w	C-H aromatic
3070	vs	C-H aromatic
3007	m	=C-H
2930	s	C-H aliphatic
2972(2968),2870	m	C-H aliphatic
1610	s	aromatic ring stretch
1584 (1580)	sh	aromatic ring stretch
1460 (1458)	m	CH$_2$ def
1366 (1345)	w	CH$_3$ bend
1258 (1252)	**s, broad**	**epoxy ring breathing**
1188 (1186)	s	CH wag
1112	s	epoxy ring
1026 (1031)	vw	C-O stretch
1012	vw	aromatic ring stretch
936	w	CH wag
918 (916)	m	epoxy ring def
821	m	CH wag
718 (736)	w	epoxy ring def
642 (639)	w	epoxy ring def

*s-strong, m-medium, w-weak, sh-shoulder, v-very; (number) measured slightly different

**stretch - stretching, def - derformation, bend - bending , wag - wagging specification [13] the epoxy vibration band is at 1252 cm^{-1} (breathing of the epoxy ring). The intensity of this peak is linearly dependent on concentration of epoxy groups in the resin mixture [10]. The peak at 916 cm^{-1}, 736 cm^{-1}, and 639 cm^{-1},assigned to the epoxy ring deformation is much weaker. Other Raman peaks located at 1112 cm^{-1}, 1186 cm^{-1} and 1610 cm^{-1} assigning to resin backbone vibrations. Particularly peak at 1610 is invariant during the course of curing reaction and did not change the intensity. This peak can be use to normalise data.

When observing the epoxy bands at about 1252 cm^{-1} and also 1230 cm^{-1}, they are decreasing with time. The Fig. 6 illustrates these changes in intensity. 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

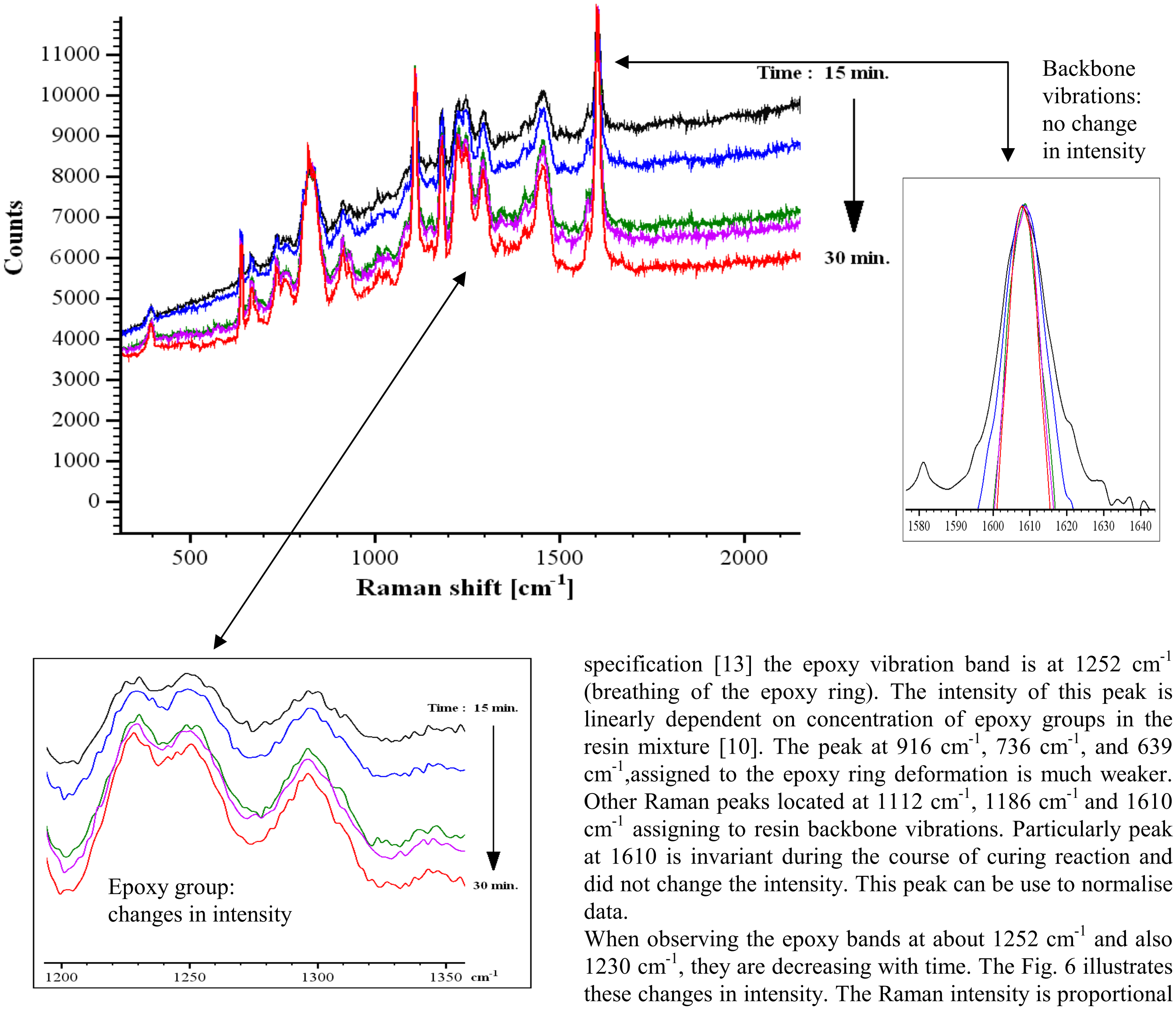

Fig. 6 Time progress of Raman spectra in time and (no) changes in intensity of particular peaks.

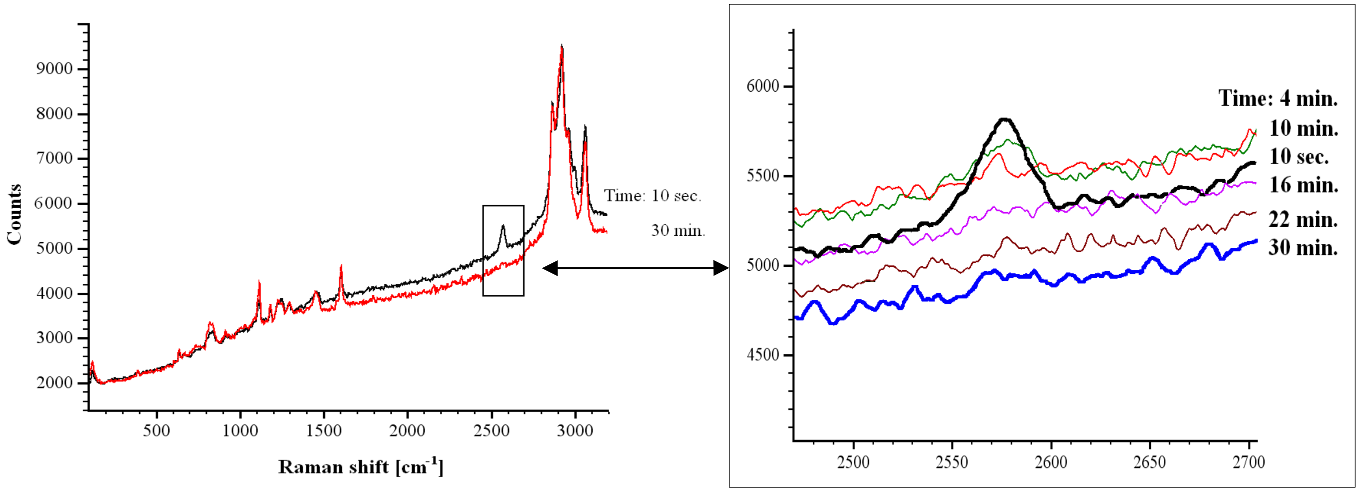

Fig. 7 Raman peak at 2575 cm^{-1} reducing due to a networking reaction

epoxy 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. Highlighted intensity decrease is shown in Fig. 7. This reduction is much more notable at the beginning of the networking reaction, when the resin and the hardener come in the contact.

Three-dimensional maps of the kinetics of the curing process in four different temperatures 20°C, 25°C, 35°C and 45°C monitored in 30 minutes after putting two reactants into contact are displayed in Fig. 8. The different positions of the maximal increase of the curves when 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. The selected epoxy resin is designed for vitrification during the process of polymerization, i.e., the curing reaction is getting slower and slower as there is an insufficient molecular mobility, despite the fact that there are still reactive groups left. In principle, these functional groups could continue in three-dimensional network formation and completing of the curing process. The only necessary

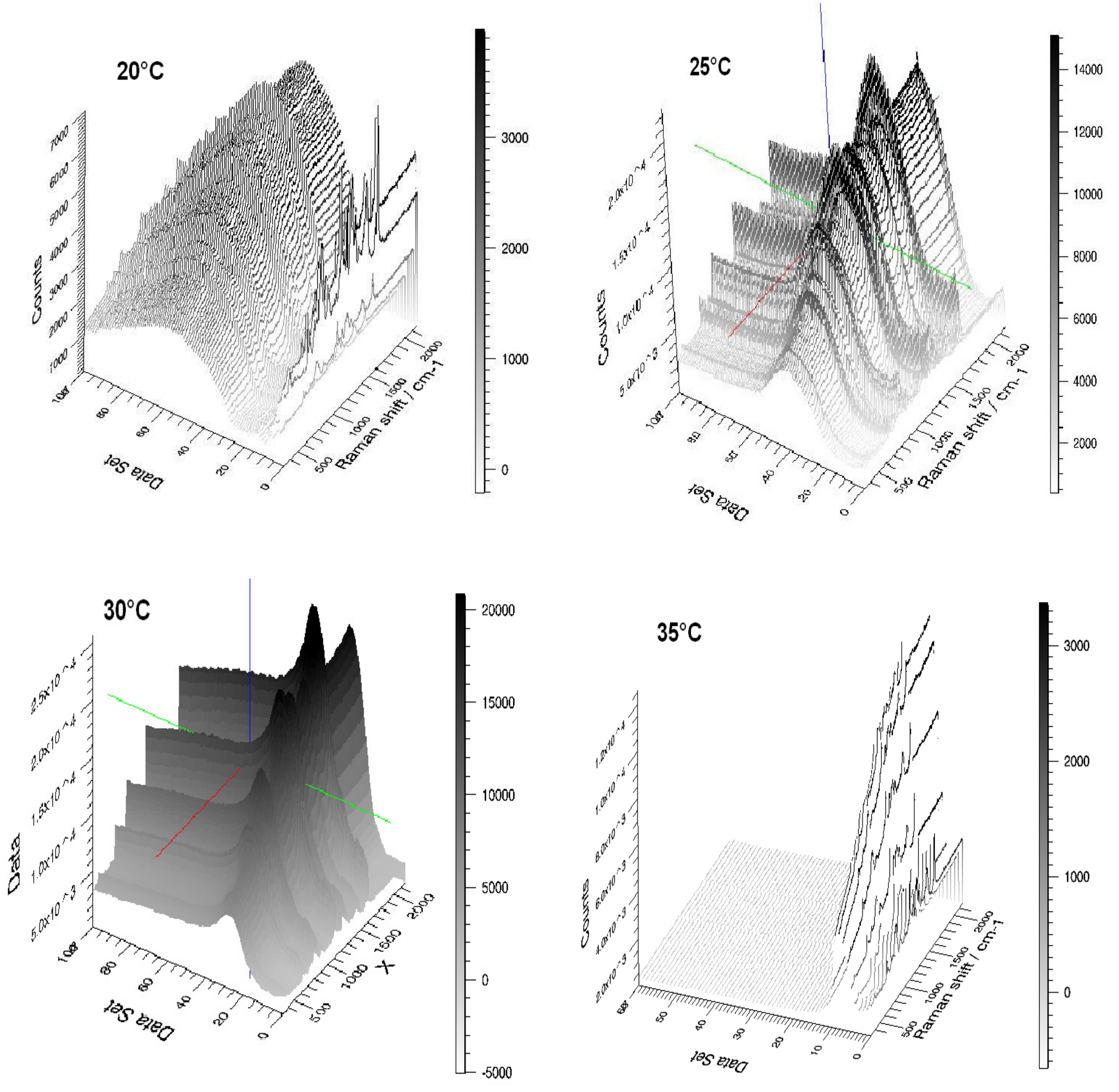

Fig. 8 3D maps of crosslinking process at the temperature 20°C, 25°C, 35°C and 45°C.

condition is the temperature growth. 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.

Behaviour of the epoxy vibrational band located at 1252cm^{-1} in time is displayed in Fig. 9. A combination of the following factors most likely participates on the progress of the dependence:

- Crosslinking reaction is an exothermic reaction hence, the increase of heat occurs [14]. This growth affects the drop of viscosity together with the rising up the molecule vibrations ability what causes the steep increase of Raman signal. After reaching the moment when the network is getting formed and the number of reactive groups is reduced the whole process consecutively evanesces.
- Every set of data (acquired at different temperatures) embodied raised intensity when comparing the beginning and the end of the curing reaction. Raman spectroscopy has only a weak response on polar molecules [15]. That is a reason for lower Raman intensity in the graph at the beginning of the reaction compared with the higher Raman signal obtained after the crosslinking process. During curing reaction the C-O bond is violated and serve for linking to reactive groups of hardener what alters the originally polar molecules into non-polar molecules with the grater Raman response.

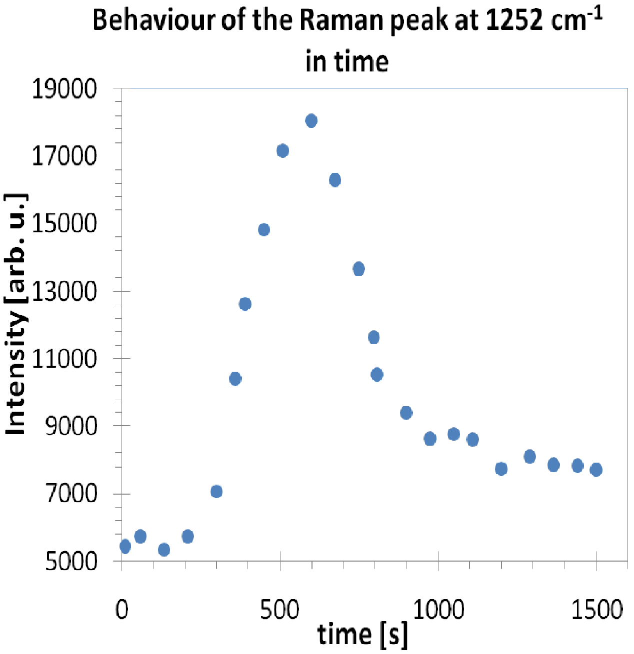

Fig. 9 Time behaviour of the Raman epoxy vibrational band at 1252cm^{-1} at 25°C.

The time dependence of dissipation factor obtained by dielectric spectrometry is displayed in Fig. 10. Dissipation factor corresponds to viscosity and the peak – the maximum of dissipation factor of the system determine the relaxation time 1ms of epoxide group rotation at the temperature of curing, the ambient temperature, in given time.

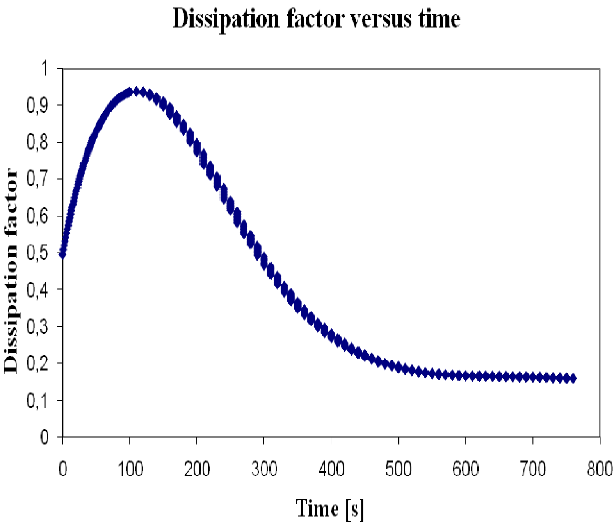

Fig. 10 Dissipation factor versus time

V. CONCLUSION

Raman spectroscopy was proposed as a novel investigative method for epoxy resin crosslinking. This technique appears to be valid and 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 spectroscopes are usually designed as laboratory equipment often combined with microscopes, then only small volume of a sample can be measured. Connecting an optical fibre 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 apparatus. Probes can be used easily even on the distance of tens of metes and high optical efficiency of measurement is kept.

This extension brings benefits for Raman spectroscopes, 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.

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REFERENCES

[1] *Lacnjevac* , C., M., New Organic Solvent Free Three-Component Waterproof Epoxy-Polyamine Systems. *Sensors&Transducers*, Vol. 08, 2010.

[2] Holik, Z., Danek, M., Manas, M., Cerny, J., "The Influence of Cross-linking Agent on Mechanical Properties of Polyamide Modified by Irradiation Cross-linking," in *Proc. 13th WSEAS Int. Conf. on AUTOMATIC CONTROL, MODELLING&SIMULATION (ACMOS'11),* Spain, 2011, pp.222-225.

[3] Rocks, J., Rintoul, L., Vohwinkel, F., The kinetics and mechanism of cure of an amino-glycidyl epoxy resin by a co-anhydride as studied by FT-Raman spectroscopy. *Polymer international*, Vol. 20, 2004.

[4] Arief, Y.Z., Kawano, K., Ohtsuka, S., "Effect of Fillers and Crosslinking Type on Degradation Phenomena of Ethylene Propylene Rubber Due to Electrical Ageing," in *Proc. 5th WSEAS/IASME Int. Conf. on Electric Power Systems, High Voltages, Electric Machines*, Spain, 2005, pp. 187-193.

[5] Younes, M., Wartewig, S., Lellinger, D., The curing of epoxy-resins as studied by various methods, *Polymer*, Vol. 35, 1994.

[6] Available: http://pslc.ws/tour/macrog/epoxy.htm

[7] 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.

[8] Vaskova, H., "Raman spectroscopy: a modern technique for material properties identification", in *Proc. 21st Int. DAAAM Symposium,* Croatia, 2010, pp. 1321-1322.

[9] Teodorescu, H., Vlase, S., Candea, I., "Some Averaging Methods in the Micromechanics of Composite Materials with Periodic Structure," in *Proc. 10th WSEAS Int. Conf. on AUTOMATIC CONTROL, MODELLING & SIMULATION (ACMOS'08)*, Turkey, 2008, pp. 210-214.

[10] 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.

[11] Sorates, G., Infrared and Raman Characteristic Group Frequencies. England, 2001.

[12] Colthup, N. B., Daly, L.H., Wiberley, S. E., Introduction to Infrared and Raman Spectroscopy. Lightning Source UK, Ltd., 2010.

[13] D. Lin-Vien, N.B. Colthup, W.G. Fateley and J.G. Grasselli. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, Boston, MA (1991).

[14] Dusek, K., Ilavsky, M., Lunak, S., Crosslinked epoxies, Berlin, 1987.

[15] Hollas, J., M., "Modern spectroscopy", 4th ed. England: J.Wiley & Sons Ltd. 2004.