Macromol. Symp. **2008**, 265, 249–259 DOI: 10.1002/masy.200850528

Ambiguity in Assignment of Near Infrared Vibrational Bands for Polymerisation Monitoring of Epoxy System

Gilbert Lachenal,[*1] Isabelle Stevenson,[1] Alexandra Durand,[1] G. Seytre,[1] D. Bertrand*[2]

The curing process of epoxy affects the chemical structure of the final network so mechanical and physical properties of the polymeric matrix for a composite may be modified according to the polymerisation conditions. This paper describes the ambiguity in assignment of reference bands to follow the cure of poly-epoxy reactive systems using a laboratory-made system which allows the coupling of dielectric analysis and Fourier Transform Near Infrared Spectroscopy (FTNIR). The dielectric measurements were obtained using interdigitated electrode. *In situ* monitoring of extent of reaction was carried out from room temperature up to 160 °C using fibre-optic FTNIR spectroscopy. For the DGEBA/MCDEA system the epoxy band at 6060 cm^{-1} was chosen in preference to the band at 4530 cm^{-1} as representative of the epoxy function evolution during polymerisation because a small unknown peak probably due to the hardener appears in the 4530 cm^{-1} region. The bands at 4620 and 4680 cm^{-1} assigned to aromatic combination bands and widely used as reference bands are not unique for this formulation hence the band at 5980 cm^{-1} is used as reference. The Principal Components Analysis (PCA) shows clearly also that the bands at 4620 and 4680 cm^{-1} vary during the polymerisation. Surprisingly, the band at 4530 cm^{-1} is equivalent to the one at 6060 cm^{-1} to calculate the conversion rate. It is probably due to the fact that the hardener band near 4530 cm^{-1} follows the same behaviour as the epoxy band at 4530 cm^{-1}.

Keywords: dielectric spectroscopy; in-situ monitoring; near infrared spectroscopy; poly-epoxy reactive system; polymer; PCA

Introduction

Epoxy resins are widely used as adhesive, coating, casting and matrix for glass or carbon composites. They represent an important class of high-performance materials characterized by properties such as good mechanical and thermal behaviours, high resistance to solvents and corrosive agents, outstanding adhesion to various substrate, low shrinkage upon curing and easy processing under a wide range of conditions. These advantages make them attractive in high technology applications such as encapsulation of micro circuitry in the electronic industry, the use as matrices for fibre composites in aerospace applications.

The main reactions during epoxy –amine polymerisation are primary amine epoxy addition, secondary amine addition and etherification (hydroxy-epoxy). These reactions may be catalysed by impurities present in the resin or by hydroxyl.[1] For a stoechiometric molar ratio the etherification is generally low. The homopolymerisation of epoxy groups is generally considered as negligible without Lewis acid or base catalysts.

---

[1] Université de Lyon, Université Lyon 1, IMP/LMPB, Laboratoire des Matériaux Polymères et des Biomatériaux, Ingénierie des Matériaux Polymères IMP, UMR CNRS 5223, Bât. ISTIL 15, Bld Latarjet 69622 Villeurbanne Cedex – France
E-mail: gilbert.lachenal@univ-lyon1.fr, isabelle.stevenson@univ-lyon1.fr

[2] ENITIAA-INRA, Unité de Sensométrie et Chimiométrie, BP 82225-44322 Nantes Cedex 03 (France)

It is important to monitor polymerisation reactions since the curing process of thermosetting resins i.e. epoxy affects the chemical structure of the final network so mechanical and physical properties of the polymer[1] or the polymeric matrix for a composite may be modified according to the polymerisation temperature.

The main ad-, and disadvantages of alternative methods for reaction control are given as follows:

- Chemical analysis for reaction are time consuming, needs hazardous reagents and leads to sample destruction.
- Differential scanning calorimetry is an usual method for studying cure but is only able to provide the overall extent of reaction.[1]
- HPLC may be used for individual chemical component only before the gel point
- These methods cannot be used for in situ real time monitoring.
- Due to large absorbance coefficient Mid Infrared can be used only for thin sample which often are not representative of industrial samples.[2] In addition, several authors[3,4] warn against using the 915 cm^{-1} band to calculate extent of epoxy reaction because this also originates from another functional group. Alternative methods for monitoring polymerisation reaction are also widely discussed in Billaud et al. [5–6]

Near infrared (NIR) spectroscopy allows to have access to the degree of conversion by following the epoxy band absorption.[3] In situ real-time monitoring of reactive systems by remote fibre optic NIR spectroscopy have been studied and reaction kinetics by coupling NIR spectroscopy with dielectric spectroscopy on model and multifunctional epoxy/amine systems have been compared previously.[7–8] Nevertheless, nobody up to now, has discussed the vibrational band assignment of the reference bands. The extent of reaction calculated using Beer-Lambert's law when considering the peak at 4530 cm^{-1} as representative of the epoxy function evolution (decrease of epoxy functions with polymerisation time) and the band at 4620 cm^{-1} as reference has been successfully presented by several authors.[5–8] This band was chosen instead of the band at 6060 cm^{-1} since it was less overlapped with other neighbouring bands. Unfortunately, a small unknown peak appears in the 4530 cm^{-1} region for the hardener (see Fig. 1), this band was already seen by Min et al.[6]. On the other hand the

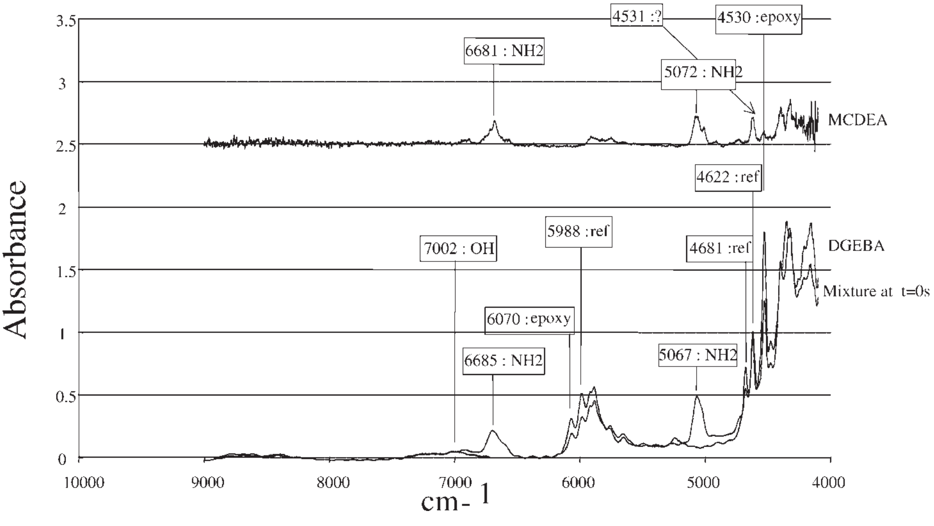


Figure 1.
NIR spectra for the DGEBA/MCDEA system hardener blending before and after polymerisation.

vibrational band at 4620 cm^{-1} has been widely used in the literature for numerous types of epoxy systems but in our case it varies independently of curing which has led us to choose preferably the overlapped vibrational band at 5980 cm^{-1}. The main drawback of the NIR spectroscopy is the difficulty to make classical quantitative analysis for strongly overlapped spectra. Multivariate techniques enable the exploitation of a complex and large set of spectra by improving at the same time selectivity and reliability. These techniques have gained acceptance as routine methods for process analysis. One goal of multivariate techniques is a data reduction without loss of information. The multivariate strategy can lead to new synthetic variables data with higher information content. Chemometric methods are numerous. The Partial Least Squares (PLS) techniques[9,2] are widely used, but need calibrations using primary quantitative analysis techniques. Nevertheless, without reference methods this multivariate analysis fails. On the other hand, Dittmar and Siesler[10] have studied the synthesis of diphenylurethane from phenol and phenyl-isocyanate in chloroform solution, by NIR and multivariate techniques (PLS) and suggested that the familiar Principal Component Analysis[11,12] (PCA) can be appropriate for monitoring the extent of reaction under certain conditions.

PCA can be used to reveal small variations of spectra for samples with differences in chemical (or physical) composition. The main advantage of identification using PCA is that only a limited number of the scores of a spectrum are used. The vectors are usually sorted in order of decreasing eigenvalues, hence, the amount of variance described by the first principal component is greater than the second and so on. The first few principal components (also called factors, latent variables or eigenvectors) depict the largest amount of variance and the noise is contained in the remaining ones. PCA estimates the correlation structure of the variables. Multivariate analysis may provide a base for interpretation of chemical species, identification, classification, or prediction models. Nevertheless, the conversion extent at the final stage must be known for quantification with PCA method.

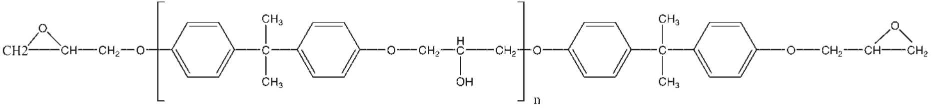
In this paper, the use of FT-NIR spectroscopy in transmission mode to monitor in situ the curing of epoxy formulation is presented. The band selection is discussed. The extent of reaction versus time obtained from Beer-Lambert analysis and using the PCA will be compared.

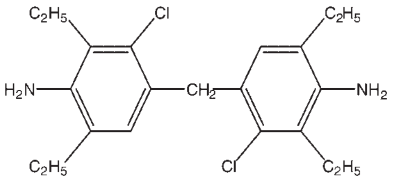
Experimental Part

Materials

The thermoset systems used for this study consists of: the polyepoxy resin of DGEBA (Diglycidyl Ether of Bisphenol A) type from CIBA Switzerland-Basel (LY556) with n = 0.15 and a hardener such as MCDEA (4,4′-methylenebis[3-chloro-2,6-diethylaniline] (from LONZA-Levallois-Perret-France) which formulae are given below:

DGEBA





MCDEA

MCDEA hardener is less studied than DDS or DDM hardeners but is less toxic to use which explains mainly why it was chosen for this study.

On PIR spectra, during the polymerisation reaction epoxy/amine can be seen mainly:

- The opening, thus the disappearance of oxirane (epoxy) rings corresponding to the decrease of the bands around 4530, 6060, 8600 cm^{-1}
- Disappearance of primary amine at 5050 et 6670 cm^{-1}
- Appearance of hydroxyl functions at 4700–4800 cm^{-1} and 7 000 cm^{-1}

These components were mixed in a stoechiometric ratio $r = 1$, r being the ratio amine/epoxy functions. The $T_{g\infty}$ of these systems are greater than 150 °C. $T_{g\infty}$ is the glass transition temperature of the totally crosslinked network.

FT-NIR Spectrometer

An ABB NetworkIR spectrometer (ABB Bomem, Canada, Quebec) equipped with GRAMS 5 NIR software (Version 5.2, Galactic, Galactic Industries Corporation, 395 Main Street, Salem, NH 03079, USA) was used for near infrared measurements. All transmission spectra were measured at 8 cm^{-1} resolution using 50 scans between 10000 and 4000 cm^{-1}. The reactive mixture was placed in a sampling quartz cell (from Hellma-France-Paris) which is 1 mm thick, 1 cm wide and 4 cm high. Two optical fibres plugged with SMA connectors and/or an Axiom probe (Irvine-USA) were used. The ''in'' optical fibre had a diameter of 300 microns and the ''out'' optical fibre a diameter of 1000 microns, both optical fibres have a length of 2 m. The baseline for area calculations was defined manually from one side to the other side of the vibrational bands chosen.

Dielectric Analysis

Dielectric measurement were obtained using Eumetric Microdielectrometer system III (Micromet-Burlington-USA) equipped with a CHIP interdigitated type electrode which is mounted on a flexible polyimide support and which can be introduced in the NIR quartz cell. This sensor is made of interdigitated electrodes to prevent problems of variation of thickness. This interdigitated electrode consists of several interleaved comb shaped metal strips deposited on a non-conducting substrate and the electric field is generated between the metal strips. The available frequency range extends from 5.10^{-3} Hz to 10^5 Hz. The conductivity measurements range was between $\sigma = 10^{-13}$ to 10^{-3} S/cm. More details on dielectric analysis can be found in.[13–15]

Simultaneous Experiments (Coupling between NIR and Dielectric Spectroscopy)

An experimental system using NIR spectroscopy was carried out simultaneously with dielectric analysis using a quartz cell which could be heated from room temperature to curing temperature (±2 °C) in order to polymerise the thermoset systems. Experimental details can be found in.[2] The isothermal curing temperatures were chosen between 80 to 160 °C for the DGEBA/IPD system and between 105 to 160 °C for the DGEBA/MCDEA system.

Results and Discussion

The quantitative analysis may be performed using either univariate or multivariate approaches. The classic assignment of these bands can be found in Table 1.[16,4] Nevertheless caution had to be taken because many band assignments are not unique (for example there are bands which have not been assigned yet in the 5500–6000 cm^{-1} region), in addition OH and NH bands shift according to the strength of hydrogen bonds.[17]Firstly, the extent of reaction (α) for the DGEBA/MCDEA system at any time t is calculated from the initial areas of the epoxy (4530 cm^{-1}) and reference (4623 cm^{-1}) peaks[5–8] $A_{e,0}$ and $A_{r,0}$ respectively, and their corresponding values at time t $A_{e,t}$ and $A_{r,t}$

Table 1.
Tentative band assignments in the NIR region for epoxy/amine resins.[16,4]

Wavenumber (cm^{-1})	Classic Assignments	Kind of vibration
4060	Aromatic combination bands	
4170	Combination bands of the terminal methylene group	
4350	Combination bands of aliphatic methyl group	
4525	Combination band of the oxyrane (ring C–H)	Conjugated epoxy CH_2 deformation band (1460 cm^{-1}) with the aromatic CH fundamental stretch (3050 cm^{-1})
4550	NH combination band	
4620	Aromatic combination band	Combination band of the aromatic conjugated C=C stretch (1626 cm^{-1}) with the aromatic CH fundamental stretch (3050 cm^{-1})
4680	Aromatic combination band	Combination band of the aromatic conjugated C=C stretch (1626 cm^{-1}) with the aromatic CH fundamental stretch (3050 cm^{-1})
4800–5000	Combination of bands of OH	
5000–5070	NH2 stretching and bending combination bands (aliphatic amine)	
5200	NH2 stretching and bending combination bands (aromatic amine) + water humidity	
5700–5850	Overtones of CH, CH2	First overtones of $-CH_2$ and $-CH$ stretching vibrations
5980	Aromatic C–H stretching first overtone	
6060	First overtone of the terminal C–H in the epoxy ring	First overtone of terminal $-CH_2$, $-CH$ fundamental stretching vibration
6500	NH2 overtone stretching	
6650	NH2 + NH overtone	
7000–7100	OH overtone (hydroxyl + H2O)	
8200	OH combination	
8630	Second overtone of the terminal C–H in the epoxy ring	

according to the Beer-Lambert law.

$$\alpha = 1 - [(A_{e,t})(A_{r,0})]/[(A_{e,0})(A_{r,t})] \qquad (1)$$

As usual to check this result of extent of reaction, the reference band at 4680 cm^{-1} was used[15] since the reference band at 4060 cm^{-1} cannot be used due to the too high absorbance. The same kinetic is not obtained when these two bands (4623, 4680 cm^{-1}) are used separately, thus another functional group must be participating to these bands at 4623 and/or 4680 cm^{-1}. After careful examination of spectra it was observed that the intensity of these classical reference bands change during the polymerisation.

Secondly, as mentioned by Min et al.[6] for the DGEBA/DDS system, a band at 4530 cm^{-1} is present for the amine hardener, this band is also present in MCDEA (see Fig. 1) and can interact with the combination band of the oxirane ring (C–H) which is widely used to follow the kinetics.

Finally, for the DGEBA/MCDEA system the epoxy band at 6060 cm^{-1} was chosen because a small unknown peak appears in the 4530 cm^{-1} region. The band at 5980 cm^{-1} is used as reference. The choice of the baseline can affect the measured areas so that the errors on calculated conversions may be significant and is operator-dependent. The Figure 2 shows the NIR spectra of DGEBA/MCDEA during kinetics of curing at 160 °C.

Band adjustment on the broad 5800–6200 cm^{-1} peak was done using GRAMS software and is shown in Fig. 3 (50/50 Lorentzian/Gaussian contribution, moreover another data treatment such as Voigt

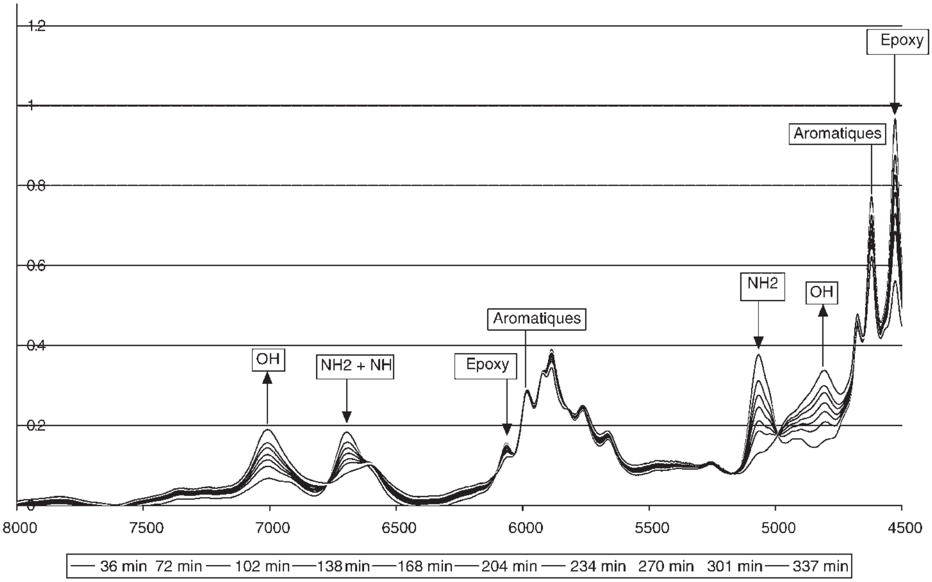


Figure 2.
NIR spectra for the DGEBA/MCDEA system during polymerisation at 140 °C.

functions gave nearly the same peak fitting result). The Fig. 3 also shows that the epoxy peak at 6060 cm^{-1} is not unique, hence a residual area is observed after complete curing reaction. For the calculation of the extent of reaction, this residual spectral area has been removed with the hypothesis that this peak does not change during the polymerisation. It can be noticed that the band at 4530 cm^{-1} has totally disappeared (see Fig. 4) since the curing reaction is completed but the one at 6060 cm^{-1} is still there.

The results given in Figure 4 for DGEBA/MCDEA system show that each functional group can be followed with reaction time.

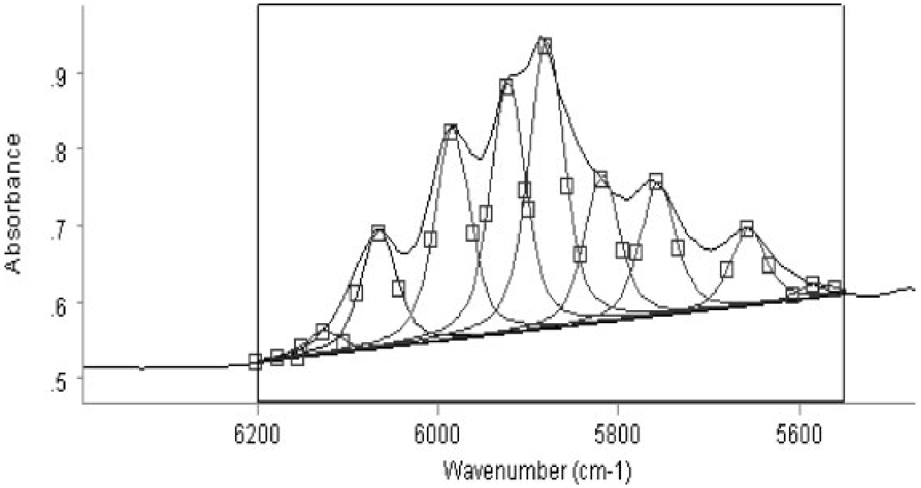


Figure 3.
Band adjustment areas at 6200 and 5550 cm^{-1}.

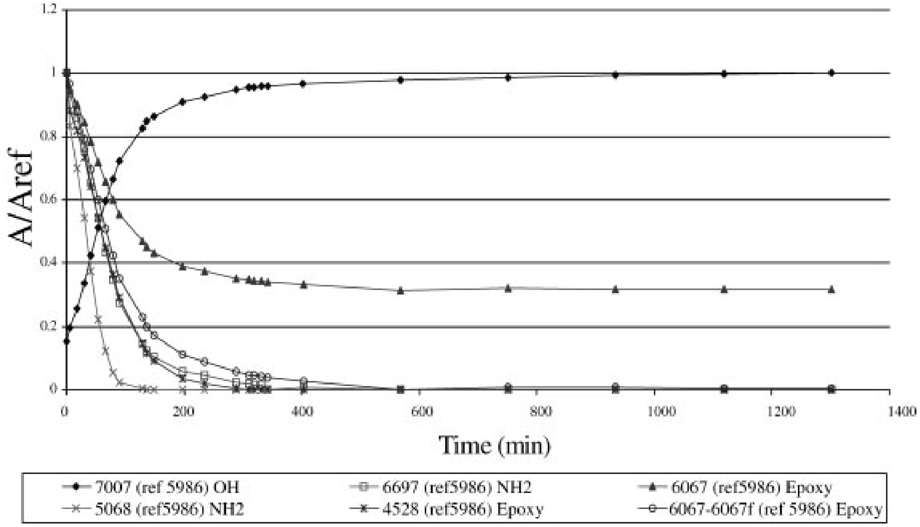


Figure 4.
Normalized absorbance as a function of time for DGEBA/MCDEA during isothermal curing at 160 °C.

OH functions appear and NH_2 as well as epoxy functions disappear.

Another type of quantitative analysis, PCA, can be performed to compare with the previous results. This PCA is first performed on the 4250–9000 cm^{-1} and 4500–6500 cm^{-1} spectral ranges for kinetics above 140 °C where the conversion is full (or seems full). Standard Normal Deviate (SNV) pre-treatment is performed on the unsmoothed spectra. The Standard Normal Deviate transformation normalises each spectrum by dividing the difference between transmittance and the average transmittance by the standard deviation of transmittance.

The first principal component contains about 98–99% of the spectral variance. It was observed that the loading plot of the first factor is linearly correlated to the absorbance changes of the functional groups during the reaction,[9,18–19] hence that it can be used to calculate the conversion by normalising its values between 0 and 1 or the extent final conversion, the conversion extent at the final stage must be known for quantification with PCA method. This kind of result had been already discussed by Maeda and al.[20] They observed that if the spectral variations are very regular, the signal to noise ratio is high and the changes in baseline are small, the loading plot of factor 1 should become very similar to the difference spectrum. This suggests that the plot of this first component as a function of time may be representative of the evolution of the conversion. Such PCA method was successfully applied to evaluate the EVA content,[11] the epoxy extend of cure[21] and more recently for a PU formulation with a reaction induced phase separation.[22] These authors observed a linear correlation between PC1 scores and the extend of reaction measured with a reference method. On the contrary, the second and third components do not seem directly correlated to the conversion. It has to be pointed out that this analysis was carried out on spectra before and after SNV pre-treatment, with no noticeable change.[22]

Figure 5 shows that, at low temperatures (105 °C, 127 °C), the full conversion rate is not achieved. This is in agreement with what is shown in Figure 6 where the vitrification phenomenon can be evidenced by dielectric spectroscopy and not by NIR. When the glass transition temperature of the reactive system reaches the curing temperature, the reaction is limited by the diffusion and the epoxy conversion did not

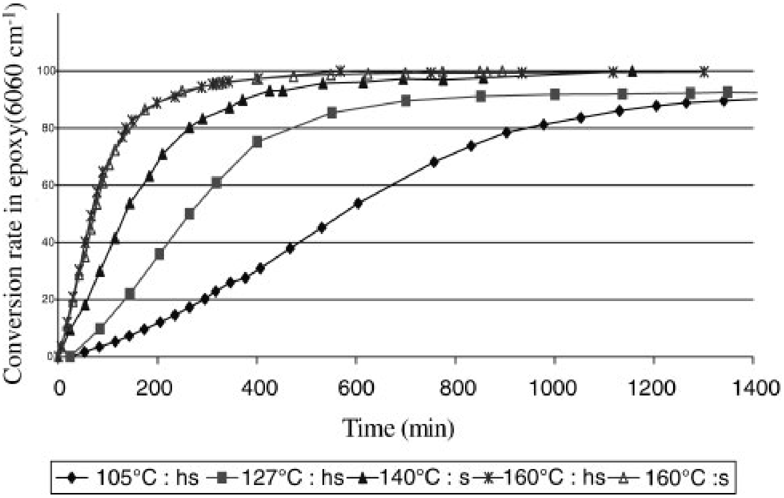


Figure 5.
Conversion rate comparison for different temperatures from 105 °C to 160 °C calculated for the band at 6060 cm^{-1} for DGEBA/MCDEA system. hs = materials stored at −18 °C for 3 months, s = freshly prepared samples.

reach 100% even at long curing times. For 160 °C the two set of points ‘hs’ and ‘s’ are in good agreement meaning that there is no difference during storage of these samples at low temperature.

The vitrification phenomenon corresponds to the broad peak observed at longer times and the vitrification time is taken to correspond to the peak maximum. The higher the frequency is the earlier appears

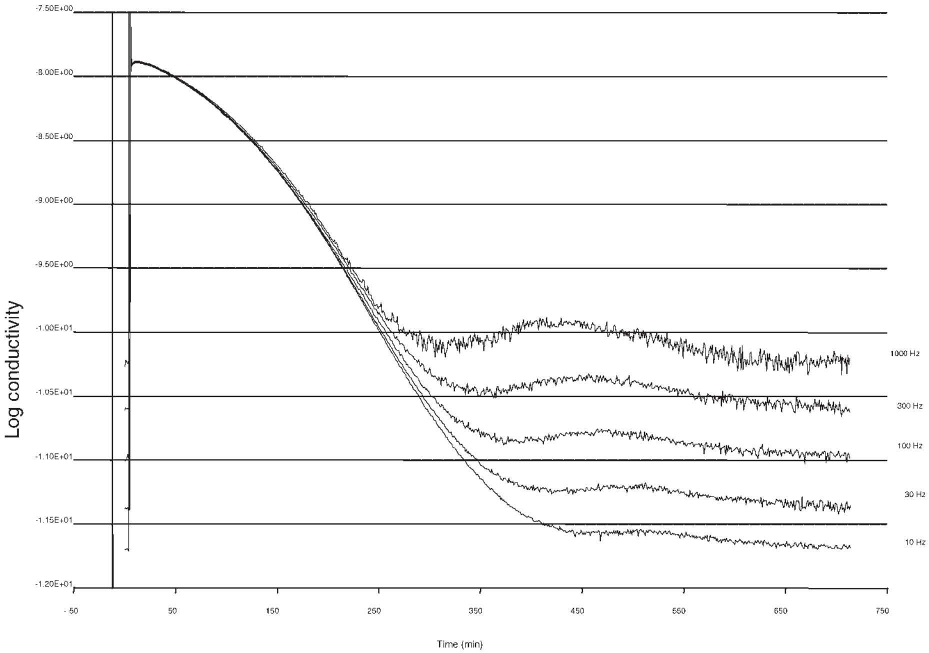


Figure 6.
Dielectric study of the polymerisation kinetics at 127 °C. The same phenomenon occurs at 105 °C.

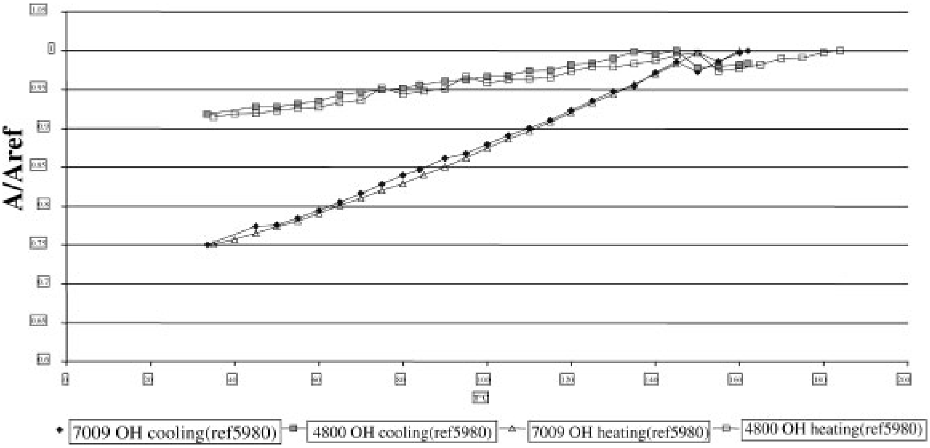


Figure 7.
Band area due to OH vibration at 4800 cm^{-1} and 7009 cm^{-1} which show reversible evolution of hydroxyl bands versus temperature. These measurements were made on a fully cured sample.

the vitrification phenomenon. Vitrification times are respectively: 10 Hz: 530 min, 100Hz: 480 min, 1000 Hz: 425 min.

A strong dependence of OH harmonic band area versus temperature is observed in Fig. 7.

The information contained in the first principal component of the PCA in the OH overtone region may be perturbed by the non-validity of the Beer-Lambert law due to hydrogen bonding. It is well known that hydrogen bonding has a strong influence on

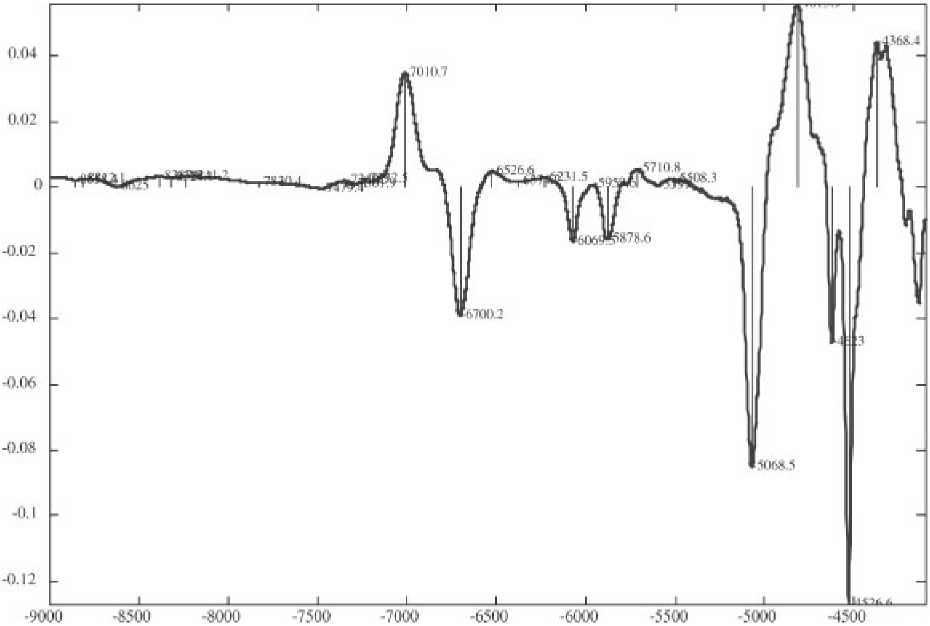


Figure 8.
Principal Component Analysis loading versus wavelength (PC1 98% variability).

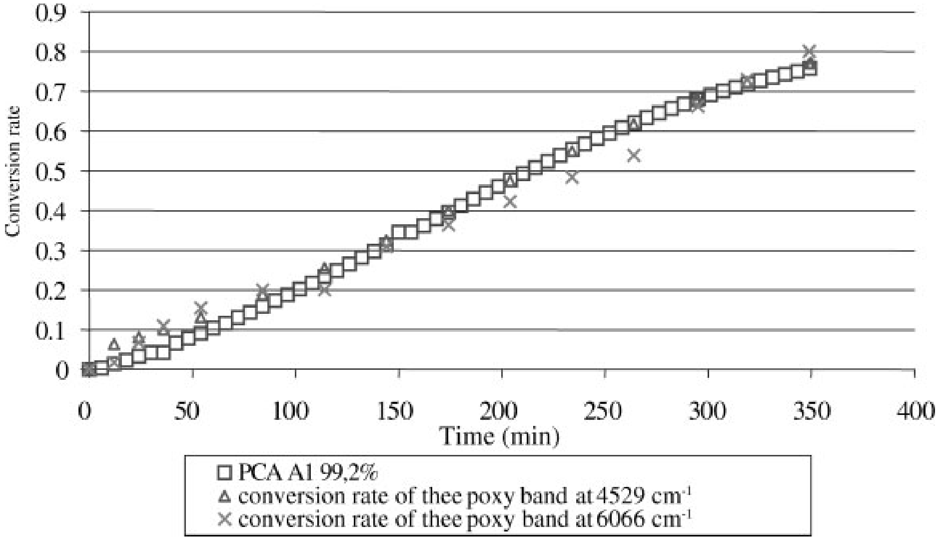


Figure 9.

Comparison between the different data treatments for approximately 6 hours at 140°. It can be noticed that the conversion rates obtained are in relatively good agreement. The epoxy bands at 4530 cm^{-1} and 6060 cm^{-1} give nearly the same extent of reaction using reference band at 5980 cm^{-1}.

NIR spectra.[23] Theoretical and practical studies of the influence of hydrogen bonding on the near infrared spectra, and information concerning the intensity and the position of overtone and combination bands have been presented by Sandorfy.[24] On the other hand the combination band may be shifted according to the strength of hydrogen bonding. However, the stretching bands shift to lower wavenumber while the bending bands shift to higher wavenumber,[24,25] so that this band is not very suitable for quantitative studies of the strength of hydrogen bond formation but on the contrary may be useful for the quantitative analysis.[22] Nevertheless using the 4250–9000 cm^{-1} (including OH and NH harmonic band) and 4500–6500 cm^{-1} spectral ranges for PCA it had been observed very little difference on the first loading of the principal component. The loading of the first PC is similar to difference spectra before and after curing. The choice of bands for the curing monitoring using Beer-Lambert law may be improved by PCA analysis Fig. 8.

Finally, as can be seen in Figure 9, whatever the method (Beer-Lambert law or PCA), whatever the band chosen: nearly equivalent results are obtained.

Conclusion

Everyone has to be very cautious about how to choose the reference band since it can be different for each various system of the same polymer family. Hence, for the DGEBA/MCDEA system the epoxy band at 6060 cm^{-1} was chosen and the band at 5980 cm^{-1} is used as reference. The epoxy band at 6060 cm^{-1} is not unique for this epoxy system. The Principal Components Analysis shows that the band at 4620 cm^{-1} and 4680 cm^{-1} vary. Moreover the band at 4530 cm^{-1} which is at the same place as an hardener band, does not seem to cause any problems, or changes in the same way, however the assignment of this band is not completely elucidated yet and the band at 6060 cm^{-1} can be used also to calculate the conversion rate.

The Principal Component Analysis can give a precious help to choose the right reference band since it allows us to spot clearly the differences in the spectra when reaction kinetics are studied.

The dielectric analysis can evidence the vitrification phenomenon and when coupled simultaneously to near infrared spectroscopy on the same sample and at the same temperature has allowed us to measure simultaneously the spectroscopic extent of reaction and the variation of the electric degree of transformation via the conductivity.

[1] K. Dusek, in: Rubber-Modified Thermoset Resins, C. K. Riew, J. K. Gilham, Eds, AMC, Washington DC, **1989**. or C. J. De Bakker, G. A. George, N. A. St John, P. M. Frederiks, *Spectrochim. Acta* **1993**, **49A/5/6/739**.

[2] D. Bertrand, E. Dufour, La spectroscopie infrarouge et ses applications analytiques, Tec&Doc, Paris, France **2000**.

[3] H. Dannenberg, *SPE Transactions January*, **1963**, *78*.

[4] G. Lachenal, N. Poisson, H. Sautereau, *Macromol. Symp.* **1997**, *119*, 129–136.

[5] C. Billaud, M. Vandeuren, R. Legras, V. Carlier, *Appl. Spectrosc.* **2002**, *56/11*, 1413–1421.

[6] B. G. Min, Z. H. Stachurski, J. H. Hodgkin, G. R. Heath, *Polymer* **1993**, *34*, 3620.

[7] L. Hassi, A. Durand, G. Lachenal, I. Stevenson, G. Seytre, G. Boiteux, *Journal of NIR Spectroscopy* **2006**, *14*, 161–166.

[8] N. Poisson, G. Lachenal, H. Sautereau, *Vibrational Spectros.* **1996**, *12*, 237–247.

[9] H. Martens, T. Naes, Multivariation Calibration, John Wiley & sons. Chichester, UK **1989**.

[10] K. Dittmar, H. W. Siesler, J. Fresenius, Near-infrared light-fiber spectroscopic reaction monitoring of the synthesis of diphenylurethane, *Anal. Chem.* **1998**, *362*, 109.

[11] I. T. Joliffe, Principal Component Analysis, Springer Verlab, N.Y, USA **1996**.

[12] R. E. Aries, J. Sellors, R. A. Spragg, Analytical Applications of spectroscopy II, A. M. C. Davies, C. S. , Eds., RCS, Cambridge, UK **1998**.

[13] K. Friedrich, J. Ulanski, G. Boiteux, G. Seytre, *IEEE Transactions on Dielectrics. and Electrical Insulation.* **2000**, *8/3*, 572–576.

[14] G. P. Johari, D. A. Wasylyshyn, *J. Polym. Sci, Polym. Phys.* **2000**, *38/1*, 122–126.

[15] D. E. Kranbuehl, J. Rogozinski, J. Warner, P. Best, A. Bonnet, J. P. Pascault, H. Sautereau, G. Boiteux, G. Seytre, *Macromol. Symp.* **2003**, *198*(1), 377–388.

[16] N. A. St John, G. A. George, *Polymer* **1992**, *33*, 2679.

[17] G. Lachenal, I. Stevenson, *NIR news* **1996**, *7/6*, 10.

[18] J. F. Aust, K. S. Booksh, C. M. Stellman, R. S. Parnas, M. L. Myrick, Precise Determination of Percent Cure of Epoxide Polymers and Composites via Fibers-Optics Raman Spectroscopy and Multivariate Analysis, *Applied Spectrosc.* **1997**, *51*, 247.

[19] J. Dupuy, S. Benali, A. Maazouz, G. Lachenal, D. Bertrand, *Macromol. Symp.* **2002**, *184*, 249–260.

[20] H. Maeda, Y. Osaki, M. Tanaka, N. Hayashi, T. Kojima, Near infrared spectroscopy and chemometrics studies of temperature-dependent spectral variations of water: relationship between spectral changes and hydrogen bonds, *J. of Near Infrared Spectrosc.* **1995**, *3*, 191–201.

[21] M. G. Hansen, S. Vedula, In-line fiber-optic near-infrared spectroscopy: Monitoring of rheological properties in an extrusion process. Part I., J.A.P.S., **1998**, *68*, 859.

[22] S. Benali, D. Bertrand, J. Dupuy, G. Lachenal, A. Maazouz, *Trans. Inst. Measurement Control* **2007**, In press.

[23] G. Lachenal, I. Stevenson, *NIR news.* **1996**, *7/6*, 10.

[24] C. Sandorfy, Overtones and combination tones: application to the study of molecular associations, in: *Infrared and Raman spectroscopy of biological molecules*, Th. M. Theophanides, D. Reidel, Eds., Dordrecht, Holland **1979**, 305–318

[25] B. Chabert, G. Lachenal, C. Vinh Tung, *Macromol. Symp.* **1995**, *94*, 145–158.