

## Quantitative Analysis of Curing Mechanisms of Epoxy Resin by Mid- and Near-Fourier Transform Infra Red Spectroscopy

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### ABSTRACT

This article informs the essence of major work done by a number of researchers on the analysis of two-step curing mechanism of diglycidyl ether of bisphenol A (DGEBA) epoxy resin in presence of amine curing agents using near- and mid-IR technology. Various peaks used as a marker for resin formation are discussed and their implementation is comprehensively studied. In addition to this, a wide range of information about the importance of reference peaks in both near-IR (NIR) and mid-IR (MIR) regions are congregated and their accuracy is audited. Also discrepancies observed by researchers in epoxy conversion ( $\alpha$ ) in NIR and MIR regions are reviewed to highlight the comparative advantages of both regions, one over the other.

**Keywords:** Epoxy resin, amines, FTIR, curing

### NOMENCLATURE

$\alpha$	Epoxy conversion
$A_e, A_r, A$	Rea under epoxy and reference peak respectively
$\beta$	Primary amine group conversion

### 1. INTRODUCTION

Epoxy is a type of ether containing highly active three-member rings in which two carbon atoms connected to one oxygen atom forming an oxirane ring and is widely being studied and used in a large range of applications from engineering<sup>1-3</sup> to medical fields<sup>4</sup>. The final required properties of the epoxy resin is mainly depend on the curing process and therefore monitoring the curing process by various means has become more important than ever before. One of the possible ways of monitoring is the IR spectroscopy which many researchers have already used in many occasions but mostly in a disjointed manner<sup>5-7</sup>.

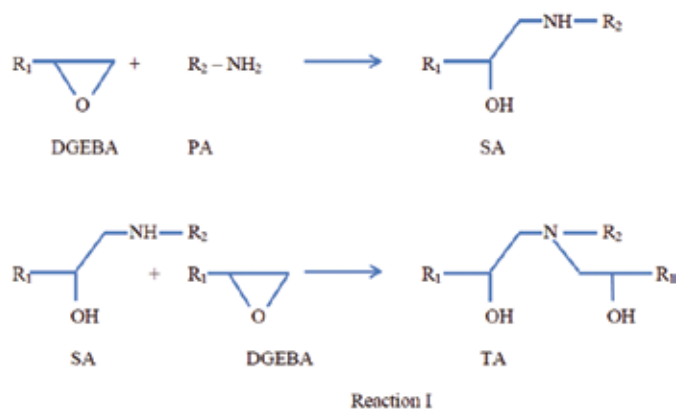
In comparison with the other ethers, epoxy resin shows higher reactivity because of different electronegativities of carbon and oxygen atoms in its oxirane ring and making the carbon atom electrophilic in nature. At the same time linkage between aromatic ring and oxygen shows higher electron withdrawing effect that attracts nucleophilic compounds such as amines towards attacking oxirane group<sup>3,5</sup>. The most commonly used oligomer is diglycidyl ether of bisphenol A (DGEBA) which is generally synthesized by the oxidation of bisphenol A and epichlorohydrin in stoichiometric ratio. DGEBA can be cured with host of chemicals which include

alcohol, phenols, carboxylic acids, amines<sup>8,9</sup> and anhydrides<sup>10</sup>. Among all these hardeners amines are the most commonly used curing agent at room temperature<sup>3,9</sup> as well as at high temperatures<sup>10,11</sup>.

### 2. CURING REACTION AND FTIR CORRELATION

The conversion of liquid DGEBA to a hard, infusible 3D network i.e. the curing reaction generally occurs in two steps: gelation followed by vitrification<sup>8</sup>. In the first stage nucleophile primary amine attracts the electrophilic carbon atom leading to the formation of secondary amine which further transforms into tertiary amine by forming branches as shown in reaction 1 below<sup>5,10,13</sup>. More monomers added to the mixture attach to active ends of chain and increase molecular weight until one molecule is formed. Overall kinetics of the reaction involves varying concentration of four species: Oxirane ring, primary, secondary, and tertiary amine. Therefore, monitoring of crosslinking progress is done by observation of concentration of these four species either by using IR spectroscopy<sup>5,14</sup> as made possible because of polarities of these species<sup>5,14</sup> or by differential scanning calorimetry (DSC)<sup>15-18</sup> which monitors heat flux. In recent years, the former technique is increasingly being used because of its high accuracy and ease of performance.

Both IR technologies i.e. mid-IR (mIR) as well as near-IR (nIR) show characteristic peaks corresponding to oxirane groups and amines in the region 600 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> and 4000 cm<sup>-1</sup> to 7000 cm<sup>-1</sup> respectively. Taking advantage of this special feature, many researchers<sup>14,19,20</sup> have used these



techniques for monitoring curing reactions. Concentrations of above mentioned four species in the curing reaction are linearly related to peak area ratios in the IR region<sup>21</sup> and therefore their intensities can be used (to calculate area) to follow the mechanism of curing<sup>5,20,22-26</sup>. Considering the fact that absorption increases with increasing concentration, Beer-Lamberts law can be simplified as<sup>21</sup>

$$A/A_{max} = adc \quad (1)$$

In the Eqn. (1),  $a$ ,  $d$ , and  $c$  are absorptivity, sample thickness and concentration respectively and the letter  $A$  represents area under the corresponding peak of the species such as epoxy or amine, which can be readily calculated using standard instrument<sup>27</sup>. The validity of Eqn. (1) became questionable because of the uncertainty in producing the sample with absolutely uniform thickness<sup>20</sup>. Also shrinkage during curing or initial sample thermosetting can cause major errors in peak integration. This causes the need for an internal reference band<sup>20</sup> and therefore many researchers<sup>19,24,28-31</sup> have started using a band associated with a component that remains constant during the curing process as an internal reference peak. Most commonly, aromatic ring absorption peaks are taken to normalise the epoxy and amine peaks as aromatic rings do not participate in polymerization or crosslinking process<sup>11,16</sup>. Hence an updated version of Eqn. (1) becomes<sup>13,20,21,24</sup>

$$\alpha = 1 - \frac{(A_{et})(A_{r0})}{(A_{rt})(A_{e0})} \quad (2)$$

where  $\alpha$  is amount of epoxy conversion and  $A$  refers to the area under the peak calculated in the absorption mode.  $A_{r0}$  denotes the area under reference peak at the start of the experiment and  $A_{rt}$  represents the area after certain curing time  $t$ . Similarly,  $A_e$  represents the area under the epoxy peak at different times. Extensive literature<sup>20,24,32</sup> is available suggesting various reference peaks with and without explanations. This study aims at extensively reviewing the all reference peaks available in the literature used by the number of researchers and spotlights their fallouts on the results.

At the same time, this paper audits various possible ways of scrutinizing of epoxy curing with assistance of two groups of peaks – one associated with epoxy groups and the second with amines. Along with this, a vital mechanism which can occur along with the curing reaction i.e. phase separation, can also be studied with the help of FTIR.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

#### 3.1 Characterization of Epoxy by FTIR

Before start implementing the FTIR technique to determine epoxy curing progress and other related mechanisms, it is worthwhile reviewing the spectra of epoxy monomer and understanding the peak positions. Figure 1 shows FTIR spectra of DGEBA in nIR (LY556 from CIBA Geigy) adapted from the work of Poisson<sup>20</sup>, *et al.* and mIR (EL-M from Barnes) region which was collected by the authors. These two spectra are selected in this study to represent the spectra of DGEBA family. Table 1 and 2 elaborate the chemical groups associated with the peaks from Fig. 1 and their role in quantitative study which is further discussed in the later part of this article. It should be noted that, change in peak location is because of different value of  $n$ . Most of the peaks discussed in this report in the mIR section are attributed to the major help of the book written by Socrates<sup>33</sup>.

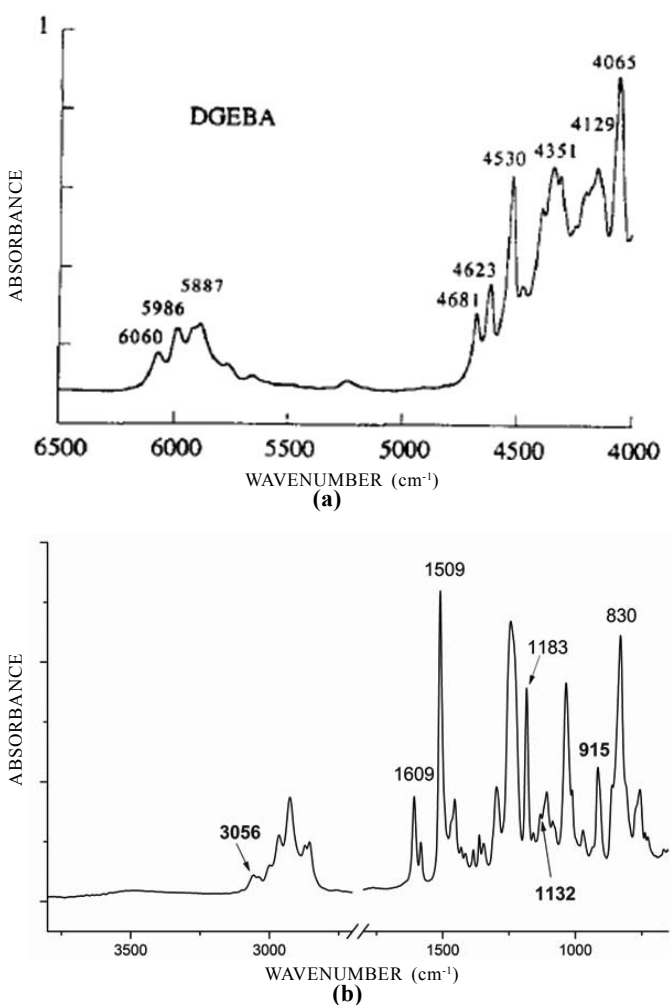


Figure 1. Typical FTIR spectra of DGEBA in (a) nIR<sup>20</sup> (b) mIR.

#### 3.2 Monitoring the Curing Process

Considering the two step epoxy curing reaction, which results in a decrease in concentration of functional group associated with the monomer, progress can be determined by observing intensities of respective peaks and using Eqn.(2). Different researchers use different peaks for this calculation.

**Table 1. Tentative bands assigned for different chemical groups from nIR absorption spectra of DGEBA**

Wave number (cm <sup>-1</sup> )	Tentative band assignment	Role in quantitative study
6067	First overtone of terminal –CH fundamental stretching vibration <sup>5,20</sup>	
5988	Overtone of –CH aromatic stretch <sup>29</sup>	Reference peak <sup>29</sup>
4681/4623	Combination band of aromatic conjugated C=C stretch with aromatic –CH fundamental stretch (phenyl group) <sup>5,19,20,28,29</sup>	Reference peak <sup>19, 28,29</sup>
4530	combination of the second overtone of the epoxy ring with fundamental C – H stretching <sup>5,13,20,29</sup>	Epoxy peak <sup>5,13,20,29</sup>
4065	Aromatic combination band/ phenyl group <sup>6,19,20,22,34</sup>	Reference peak <sup>6,19,20,22,34</sup>

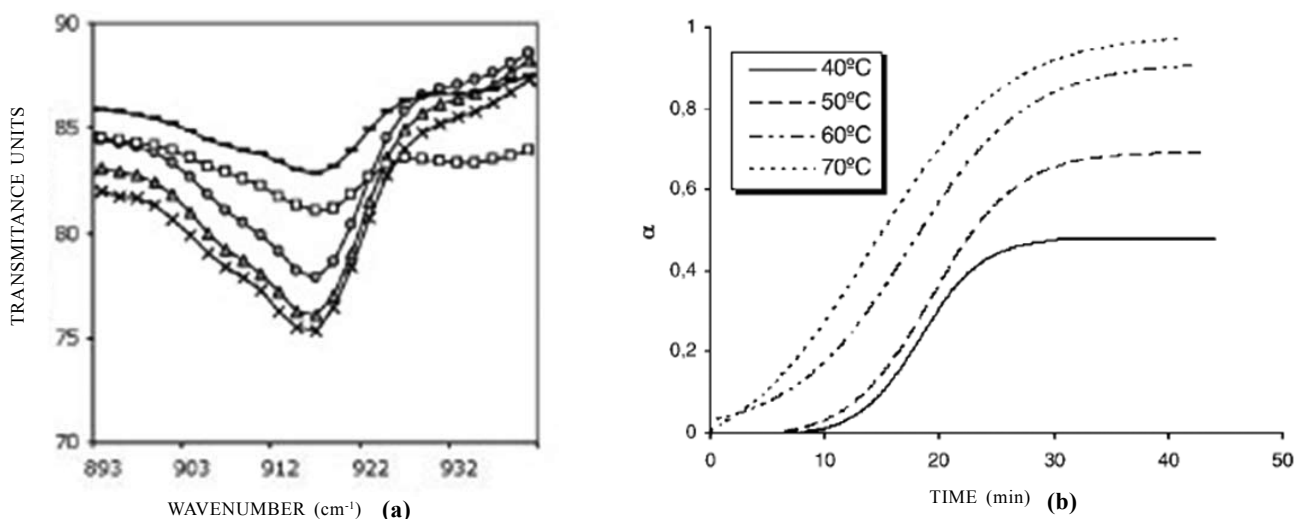
**Table 2. List of peaks used as either indication of epoxy group concentration or reference peak in DGEBA**

Wave number (cm <sup>-1</sup> )	Tentative band assignment	Role in quantitative study
3056	Symmetric stretching of C–H of the oxirane ring <sup>24,27</sup>	Epoxy peak <sup>24,35</sup>
1609	C = C stretching aromatic ring <sup>33</sup>	Reference peak <sup>21</sup>
1509	C – C stretching of aromatic ring <sup>11,21,26</sup>	Reference peak <sup>11,21,26</sup>
1183	C – O aromatic ring stretching <sup>28,29</sup>	Reference peak <sup>11,21,29</sup>
1132	C – O – C stretching of ether group <sup>24,32</sup>	Epoxy peak <sup>32</sup>
1113	Aromatic stretching <sup>28</sup>	Reference peak <sup>28</sup>
915	C – O oxirane stretching <sup>5,11,20,21,24,28</sup>	Epoxy peak <sup>5,11,20,24,25</sup>
830	Aromatic absorbance <sup>11,20,24</sup>	Reference peak <sup>11,20</sup>

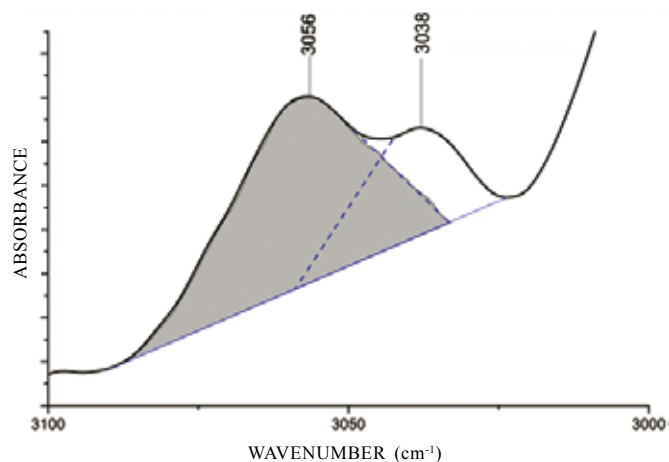
In mIR, 915 cm<sup>-1</sup> is most commonly used peak<sup>5,11,20,21,24,28</sup> which is assigned to C – O stretching vibration in the oxirane ring<sup>5,11,17,20,21,24</sup>. One example from this category of study is Fraga<sup>26</sup>, *et al.* whose results are shown in Fig. 2(a)<sup>26</sup> where 915 cm<sup>-1</sup> peak response on curing of DGEBA/isophorenediamine (IPD) at 70 °C can be seen clearly. Figure 2(b)<sup>26</sup> shows the epoxy conversion calculated using peak 915 cm<sup>-1</sup> normalised with the peak 1510 cm<sup>-1</sup> which is assigned to phenyl group and also effectively used by other researchers<sup>11,21,26</sup>. Peak 915 cm<sup>-1</sup> is sharp and well separated from others in fingerprint region and therefore it is also broadly used with the other reference peaks such as 830 cm<sup>-1</sup><sup>11,20</sup>, 1183 cm<sup>-1</sup><sup>24,28,29</sup> and 1509 cm<sup>-1</sup><sup>11,21,26</sup> representing stable aromatic ring. Another peak representing the oxirane group i.e. 1132 cm<sup>-1</sup> normalised with 2970 cm<sup>-1</sup> is also used by Fouchal<sup>32</sup> but weak intensity and crowded

neighbouring peaks make it hard to get reliable data hence rarely used by any other researchers.

One more reacting peak in epoxy curing is observed near 3050 cm<sup>-1</sup>. This is also being used by number of researchers<sup>20,24,30,34</sup>, however its position and small size force others to neglect it. This peak is sandwiched between a strong broad –OH peak at 3500 cm<sup>-1</sup> and the 3038 cm<sup>-1</sup> peak attributed to the –CH groups in the aromatic rings (see Fig. 1(b) and Fig. 3). The main challenge to use 3050 cm<sup>-1</sup> peak is to determine the accurate area under the peak as it is intermixed with 3038 cm<sup>-1</sup>. Care should be taken to cut out 3038 cm<sup>-1</sup> area from 3050 cm<sup>-1</sup> peak. The practise has been done by Zlatkovic<sup>34</sup> by calculating share of epoxy peak by mathematical method of square covering as postulated in encyclopaedia of elementary mathematics<sup>35</sup>.



**Figure 2. (a) gradual decrease of intensity of peak 915 cm<sup>-1</sup> on curing of DGEBA/IPD system at 70 °C and corresponding epoxy conversion is shown in (b) along with different temperatures of curing<sup>26</sup>.**

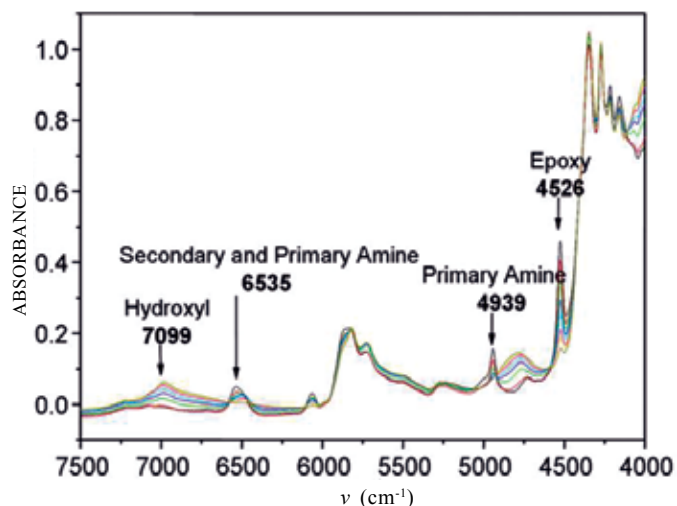


**Figure 3.** Intermixed network of 3057 and 3038  $\text{cm}^{-1}$  wavenumber.

Although some researchers<sup>5,20</sup> have expressed uncertainty using the  $915 \text{ cm}^{-1}$  peak at the final stage of curing, where the concentration of epoxy group becomes small and apparently area determination becomes more challenging,  $915 \text{ cm}^{-1}$  peak is most reliable and gives most accurate results in mIR region and can be normalised with number of reference peaks.

Number of analyst prefer nIR over mIR because of its higher accuracy due to various reasons explained in detail in the next section of this study. Same principle can be used in nIR region taking  $4530 \text{ cm}^{-1}$  peak as proof of epoxy group remaining<sup>5,13,20,29,36</sup>. This peak speaks for combination of the second overtone of the epoxy ring with fundamental C–H stretching<sup>5,11,20,29</sup>. Peaks representing non-reacting aromatic group,  $5988$ <sup>29</sup>,  $4681$ ,  $4623$ <sup>5,19,20,28,29,31,36</sup> and  $4065 \text{ cm}^{-1}$  peaks<sup>6,20,22,37</sup> are used to normalise the epoxy peak. Figure 4 shows variation of epoxy concentration of hydrated DGEBA/amino system cured at  $70^\circ\text{C}$  and the related epoxy conversion is shown in Fig. 5(a).

Unlike mIR, peaks revealing transformation of amine concentrations are readily visible in nIR (see Fig. 4) and hence quantitative estimation of conversion of amine ( $\beta$ ) groups



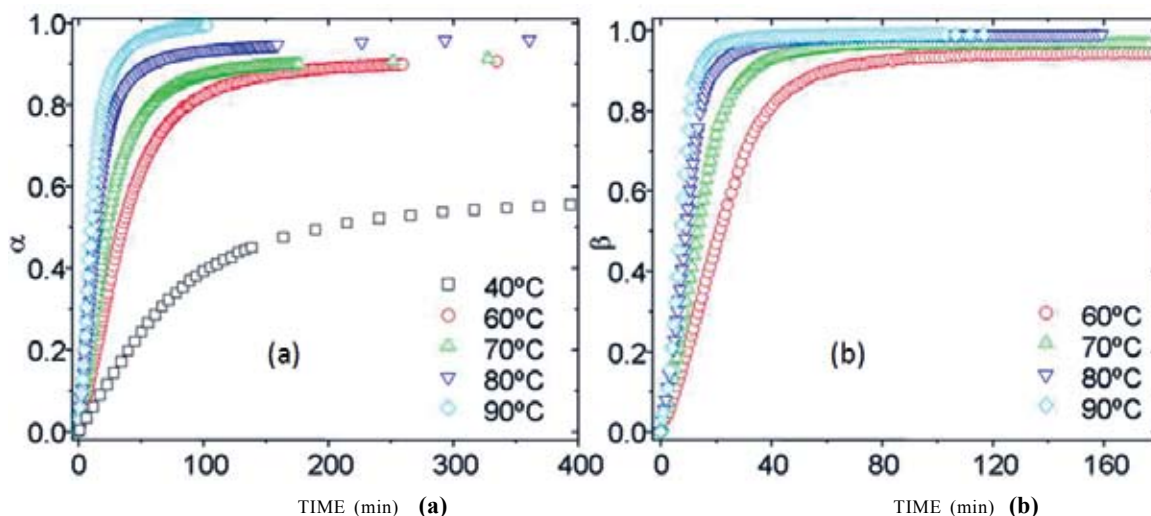
**Figure 4.** nIR spectra during isothermal curing at  $70^\circ\text{C}$  of hydrated DGEBA/poly(3-aminopropylmethyl)siloxane system<sup>5</sup>.

(primary to secondary to tertiary) is also possible using Eqn. (3)<sup>13,38</sup>.

$$\beta = 1 - \frac{(A_{4940 \text{ t}})(A_{4623 \text{ o}})}{(A_{4623 \text{ t}})(A_{4940 \text{ o}})} \quad (3)$$

Like Eqn. (2), similar terms are used in Eqn. (3). The primary amine peak at  $4940 \text{ cm}^{-1}$  is normalised by aromatic peak at  $4623 \text{ cm}^{-1}$ , and conversion is shown in Fig. 5(b). As curing progresses the primary amine combination band decreases. In Fig. 4 it is clearly visible that at the stage when primary amine is completely disappeared, epoxy group is still available which reacts with secondary amine (transformed from primary amine) to start vitrification process<sup>5</sup> and forms tertiary amine. Concentration of secondary and tertiary amines can be calculated using the different mathematical models based on initial concentrations of species as described by a number of investigators<sup>5,13,32</sup>.

Figure 5 shows that after initial curing stage,  $\beta$  always reaches a plateau value near to 1 hence it can be concluded that at



**Figure 5.** (a) epoxy conversion and (b) amine conversion of hydrated DGEBA/poly(3-aminopropylmethyl)siloxane system at different temperatures<sup>3</sup>.

all temperatures primary amine is fully consumed and converted to secondary and/or tertiary amines<sup>5</sup>. Figure 4 and 5 where system reaches a plateau value (i.e. maximum epoxy conversion) indicate optimum times required to achieve maximum curing of the hydrated DGEBA/poly (3-aminopropylmethyl) siloxane system at given temperatures.

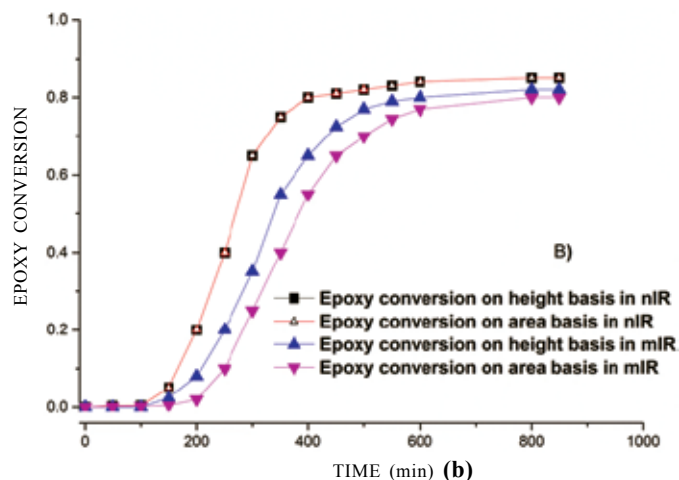
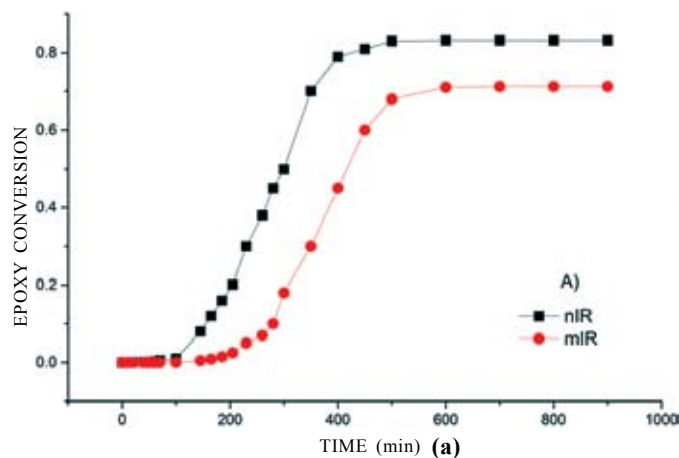
### 3.3 nIR over mIR

nIR contains overtones and combination bands of the fundamental vibrations seen in mIR and hence nIR gives characteristics isolated bands especially for primary and secondary amines<sup>5</sup> which are overlapped with broad -OH in mIR that makes it hard to distinguish. Apart from this, many researchers<sup>20,37</sup> found epoxy conversion obtained from nIR and mIR are not the same and show perceptible differences.

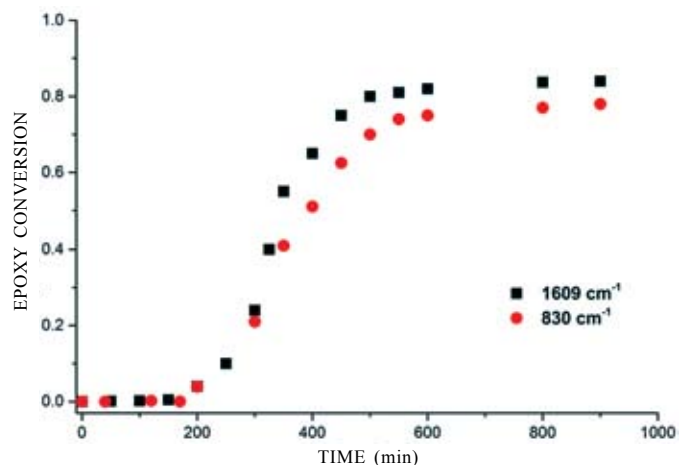
A significant study by Poisson<sup>20</sup>, *et al.*, to compare mIR and nIR result of Diuron accelerated DGEBA is shown in Figure 6, which shows -A) comparison of epoxy conversion of Diuron accelerated LY556/DDA system estimated using areas of absorption peaks in the nIR and mIR range<sup>20</sup>. The epoxy absorption peaks at  $4530\text{ cm}^{-1}$  in nIR and  $915\text{ cm}^{-1}$  in mIR were observed and  $4065\text{ cm}^{-1}$  and  $830\text{ cm}^{-1}$  peaks were taken as internal reference peaks correspond to non-reacting species. Figure 6 (a) clearly shows that at an early stage conversion curve start showing deviation and nIR calculations show higher extent of reaction. At one point nIR shows 35% higher epoxy conversion to that of mIR. The validation of nIR was done after performing chemical titration and size exclusion chromatography (SEC) on the same system which showed results similar to nIR<sup>20</sup>. Many supporting reasons have been presented as to the difference observed by the researchers over the period of time. Dannenberg and Harp<sup>9</sup> stated that a strong band at  $915\text{ cm}^{-1}$  is also present as a result of an unknown group and this lowers the mIR epoxy conversion. Another possible reason can be the overlapping of a non reactive peak with  $915\text{ cm}^{-1}$  (see Fig. 4) which could affect observed absorption of remaining epoxy measured at  $915\text{ cm}^{-1}$ . Also other peaks from hardener present in the vicinity of  $915\text{ cm}^{-1}$  peak could cause some serious deviation. These mentioned reasons alter the area of the peak at  $915\text{ cm}^{-1}$  so Poisson<sup>20</sup>, *et al.* calculated epoxy conversion using a peak height formula (rather the peak area) and found that converse is higher than that calculated using area values, as can be seen in Fig. 6 (b).

The hurdles arising at peak  $915\text{ cm}^{-1}$  can be avoided by selecting other epoxy peaks, for instant,  $3056\text{ cm}^{-1}$ <sup>5,24,34</sup>,  $1132\text{ cm}^{-1}$ <sup>32</sup> and  $1345$  and  $1430\text{ cm}^{-1}$ <sup>20</sup>. These peak scan be selected as indications of reaction progress but their low intensity and overlapping with other peaks gives less accuracy in quantification<sup>5,20</sup>

Different reference peaks were also adopted by Poisson<sup>20</sup>, *et al.* as this can be another possible reason behind the error in mIR. Change observed in results are shown in Fig. 7 and it was observed that results can be improved by selecting a peak which is well isolated from other peaks but achieving accuracy as high as nIR is not possible in mIR. Lower observed values in case of the  $830\text{ cm}^{-1}$  reference peak can be associated with the presence of a shoulder peak at  $863\text{ cm}^{-1}$  as found by many researchers.



**Figure 6.** Comparison of epoxy conversion versus time on (a) area basis in nIR and mIR range and (b) area and height basis<sup>20</sup>. Note: In Fig. 6 (b) both curves (i.e. area basis and height basis calculation lines) for nIR follow same trend hence overlapped each other.



**Figure 7.** Comparison of epoxy conversion calculation based on two reference peaks ( $830$  and  $1607\text{ cm}^{-1}$ ) and primary peak at  $915\text{ cm}^{-1}$  wave number<sup>20</sup>.

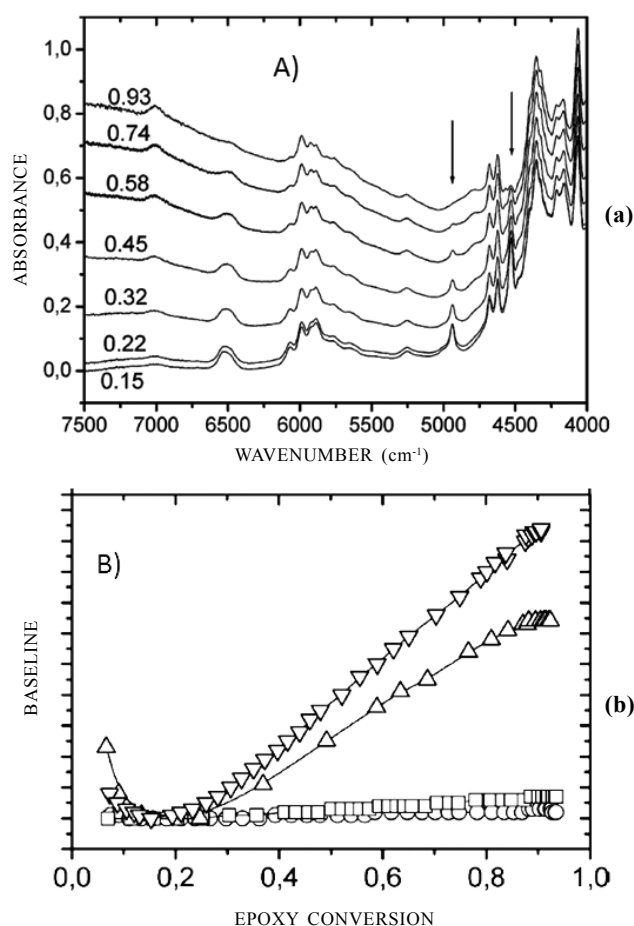
### 3.4 FTIR to Observe Phase Separation

To improve the toughness, epoxy is being modified with reinforcement by various thermoplastic materials which form a separate phase in the resin matrix<sup>39-41</sup>. As a consequence of



phase separation, particles or domain of very small size having different refractive indices are formed. When they are big enough they become light scatterers and the mixture becomes cloudy in the visible range. At these larger scales, IR radiation can also be used to determine the onset of phase separation and characterize the growth of the nascent structures<sup>5,39,40</sup>. Both mid- and near-IR range can be used to study phase separation<sup>35</sup> whilst near-IR is more popular because of its shorter wavelength whereas longer wavelength mid-IR is more useful for the systems containing bigger particles or to avoid interferences due to colours of the systems<sup>5</sup>.

A pioneer study was done in this aspect in 1999 by Bhargava and team<sup>39</sup>. In this study to observe phase separation in the system, they showed that the baseline change in FTIR is associated with change in the blend transparency to the near-IR radiation<sup>39</sup>. Using same principle Cabanelas<sup>14</sup>, *et al.* studied progress of a continuous network of PMMA in DGEBA. Figure 8 (a) shows FTIR spectra of DGEBA/PMMA/PAMS (poly(am inopropylmethylsiloxane)) system with corresponding increase in baseline as a function of epoxy conversion in Fig. 8 (b).



**Figure 8.** (a) FTIR spectra of DGEBA/PMMA/PAMS system obtained at different curing times. Digits on left side of spectra show epoxy conversion. (b) Shows corresponding baseline changes observed in DGEBA/PMMA/PAMS system (with varying wt. % of PMMA) at 6300  $\text{cm}^{-1}$  as a function of epoxy conversion of same system at various PMMA weight %<sup>14</sup>. ( $\nabla$ ) shows baseline corresponding to spectra shown in Fig. 8 (a).

Baseline is taken in the region where no peak is observed<sup>14</sup>, for example in Fig. 8 change in baseline is observed at 6300  $\text{cm}^{-1}$ . In Fig. 8 (b), baseline reduces to zero and stays unchanged which indicates a homogenous mixture with respect to near-IR. And after attending some conversion values, baseline starts increasing as a result of formation of various phases with different refractive indices

#### 4. CONCLUSION

FTIR can effectively be used to analyse the curing reaction of DGEBA quantitatively. After reviewing various ways of analysing the data can be concluded that because of well isolated peaks, the near-IR range gives more reliable results in determining both oxirane and amine group concentrations at any stage of the reaction. However, among the all epoxy peaks in mIR range the 915  $\text{cm}^{-1}$  peak gives most reliable data with various aromatic peaks. Near-IR also FTIR technique proves a valuable tool to study kinetics of phase separation in thermoplastic toughening processes.

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