

Epoxy Curing Reaction Studied by Using Two-Dimensional Correlation Infrared and Near-Infrared Spectroscopy

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ABSTRACT: The isothermal curing process of bisphenol A epoxy resin with polyamine reagent (1,6-diaminohexane) was monitored *in situ* by using temperature-controlled Fourier-transform infrared (FTIR) and Fourier-transform near infrared (FTNIR) spectroscopy to elucidate the relative changes in functional groups during the curing reaction. It was shown that generalized two-dimensional correlation spectroscopy can provide new information about the mechanisms and kinetics of the curing process, and the band assignments for complex NIR spectrum asso-

ciated with this system. The sequential order of relative changes in functional groups during the curing process was examined by generalized 2D correlation spectroscopy and NIR-IR hetero-correlation spectroscopy, and the details of the complex epoxy curing reaction involving both primary and secondary amino group were revealed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 871–881, 2011

Key words: FTIR; FTNIR; 2Dcos; epoxy resin; polyamine; kinetics

INTRODUCTION

Epoxy resins are compounds with two or more epoxy groups in the molecule, which harden by curing or crosslinking. This class of resins are widely used for various scientific and industrial purposes, for instance, adhesives and IC packages. It was known that the curing reaction forms a three dimensional reticulation structure, via the addition polymerization of the epoxy groups with a curing reagent, such as polyamine and acid anhydride.^{1–3} The analysis of the curing reaction of epoxy resin is possible by monitoring the absorption band due to epoxy groups by using Fourier-transform infrared (FTIR) spectroscopy.^{2,4–7} However, the specific sequence of the intensity changes of various IR bands related to the mechanisms and kinetics of curing reaction has not yet been fully revealed. For instance, it is rather difficult to pursue the behavior of polyamine in the curing process by using FTIR.^{6,8} The peak due to polyamine is comparatively small in intensity and it is often heavily overlapped with other peaks.^{8,9}

Even if some spectral subtraction treatment is applied, such overlapping peaks are inseparable in many cases.

In addition, the curing process becomes even more complex when using the primary amine as a curing reagent, because the reaction may go through the formation of the secondary and tertiary amine.^{2,7,8} As an existing technique, for example, it is known the amount of the amine is appreciable by the titrimetrical methods for curing process.^{1,7,10,11} However, this method is troublesome work, a discontinuous measurement, and an additionally artificial error margin is large.

The near-infrared (NIR) range of vibrational spectra between 8000 and 4400 cm^{-1} contains absorption bands that result from the overtones and combination modes mainly associated vibrations involving hydrogen atoms. This is why compounds containing C–H, O–H, and N–H bonds are particularly sensitive to and suitable for the analysis by means of FTNIR spectroscopy. Thus, the curing behavior of the polyamine was investigated by using FTNIR.^{5–7,12,13}

In this article, isothermal curing process of bisphenol A epoxy resin/polyamine system was monitored by using temperature-controlled FTIR and FTNIR spectroscopy. The evaluation of detailed curing process was carried out based on generalized two-dimensional (2D) correlation spectroscopy, which is an attractive tool capable of emphasizing the spectral features that are not easily observable in conventional one-dimensional spectra.^{14–16} Moreover, to investigate variations of pertinent functional groups and proper band assignments, and the determination of the order of certain events taking place

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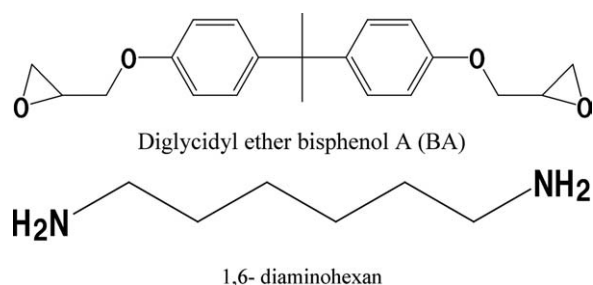


Figure 1 Chemical structures of epoxy resin and polyamine.

during the curing process, 2D IR-NIR hetero-spectral correlation analysis was applied.^{17–20}

EXPERIMENTAL

The epoxy resin studied was a commercial grade diglycidyl ether bisphenol A epoxy (jER828, epoxide eq. 190 ± 5 , $M_n = 380$), and the polyamine used as the curing agent was 1,6-diaminohexane. All the chemicals were used as received purification. The chemical structures are shown in Figure 1.

Fourier-transform near-infrared spectroscopy (FTNIR) and mid-infrared spectroscopy (FTIR) measurements were performed by using Varian FTS3000 and UMA600 Spectrometer with spectral range cover-

ing from 8000 to 700 cm^{-1} . This instrument was equipped with a KBr/Ge or a Quartz beam-splitter and MCT detector. The IR spectra were recorded in the 4000 to 700 cm^{-1} range, while the NIR spectra were obtained in the 7800 to 4300 cm^{-1} range at 8 cm^{-1} resolution with 256 scans. IR and NIR spectrum were collected every 30 second for 60 min. The isothermal curing reaction was carried out on the Linkam Heat-Stage 10036 at 80°C, under N_2 atmosphere. The sample was prepared by mixing epoxy resin and polyamine, by matching the epoxy equivalent weight to hydrogen equivalent weight. The sample used for IR measurement was sandwiched between two-BaF₂ windows, and the thickness of which was 3 μm . For NIR, 0.2 mm thickness sample was prepared between a slide glass board and a cover glass. 2D correlation analysis of spectral data was carried out by using the public free software (2Dshige (c), Shigeaki Morita) available from the webpage of Professor Yukihiro Ozaki of Kwansei Gakuin University. (http://sci-tech.ksc.kwansei.ac.jp/~ozaki/e_2D.htm).

RESULT AND DISCUSSION

Fourier-transform infrared spectroscopy analysis

Figure 2 shows the IR spectra collected every 5 min for the BA/polyamine system during the curing

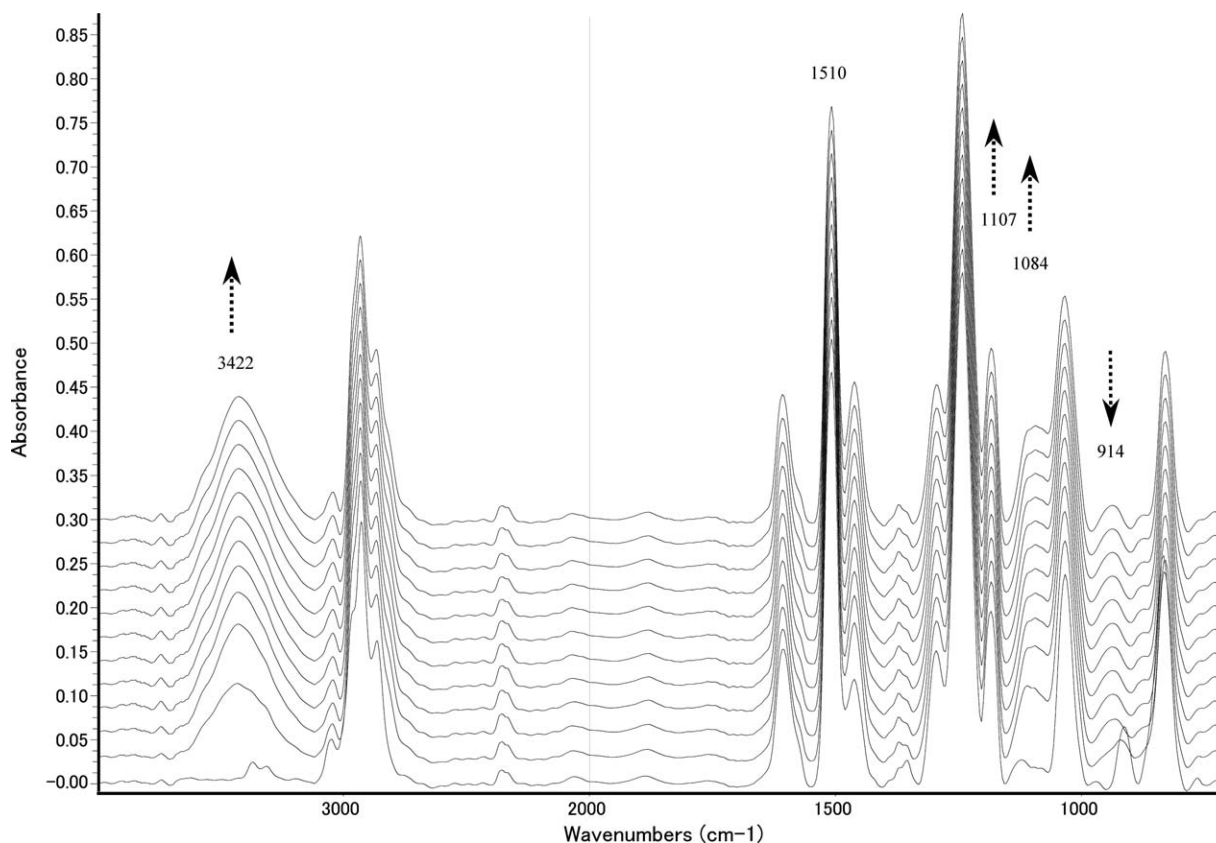


Figure 2 FTIR spectra collected every 5 min (12 spectra) of BA and polyamine system isothermally cured at 80°C.

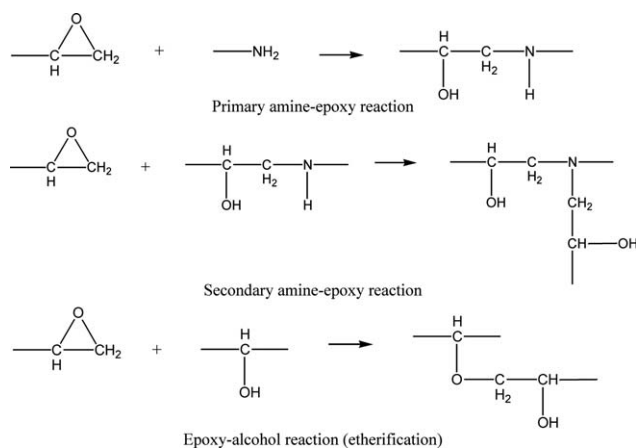


Figure 3 The curing mechanism of an epoxy/polyamine system.

process. The spectra have been baseline-corrected. Intensities of O—H stretching vibration with the peak maximum at 3422 cm^{-1} and aliphatic C—O stretching vibration observed broadly between 1150 and 1000 cm^{-1} were both increased. On the other hand, the intensities of oxirane ring having the peak maximum at 914 cm^{-1} and N—H stretching vibration at 3310 and 3370 cm^{-1} were reduced. The curing mechanism of BA/polyamine system is complex, as depicted in Figure 3. In general, it is known that the primary reaction occurs between the epoxide group and the amine hydrogen. The reaction forms a bond between the amine nitrogen and the terminal

carbon of the oxirane ring, it produced a secondary amino group, and one hydroxyl group. Continuously, the secondary amine reacts an other epoxide group, it generates the tertiary amine and one hydroxyl group. On the other hand, the etherification occurs concurrently between the hydroxyl group formed in the reaction previously described and epoxide group. It is thought that the reactions proceeding to the tertiary amine and the etherification are advanced competitively.^{1-3,7,13,21-26} The existence of significant etherification depends on the curing temperature and the basicity of the amine.²⁶⁻²⁸

The extent of curing was calculated by using the intensity of epoxy band, centered at 914 cm^{-1} to examine the reaction kinetics.^{2,8} Figure 4 shows the relative intensity of the bands taking part in the curing process, attributed respectively to oxirane ring, ether groups, and hydroxyl groups, which are all normalized by the aromatic band centered around 1510 cm^{-1} .

It was confirmed that the relative intensity of oxirane ring disappeared after about 13 min of curing. The band intensities of hydroxyl and ether groups also increased until around the same time and then remained constant afterward. It is difficult to evaluate the band attributed to N—H stretching vibration, because of the heavy overlapping with the O—H stretching band. In this curing system, it is presumed the hydroxyl groups generated at the early stage react with other epoxide group as an acid-

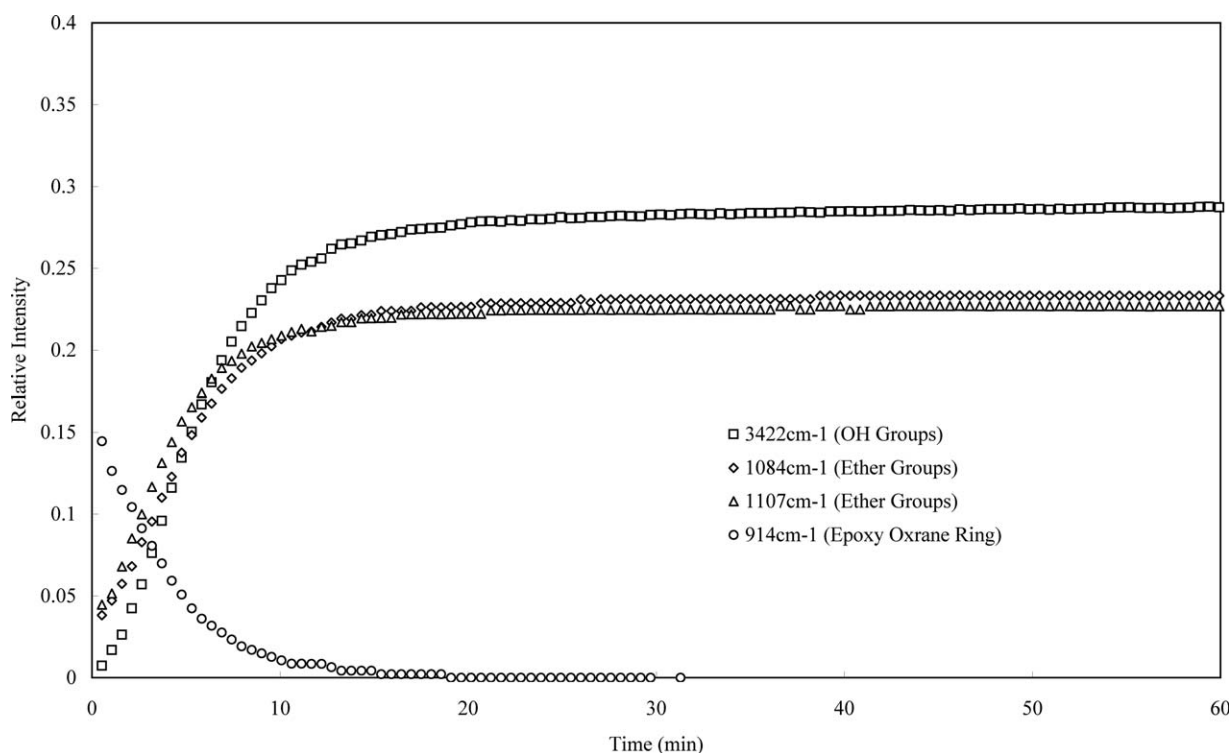


Figure 4 Relative band intensities of functional groups normalized by the aromatic band.

catalyzed epoxy reaction mechanism, and it would advance the etherification.^{7,13,21,22,25,26}

Two-dimensional correlation analysis

The concept of generalized 2D correlation spectroscopy was originally proposed by Noda in 1993,¹⁴ and it has been further modified and improved by many researchers. This method can analyze a set of not only conventional spectroscopic data but also many other types of analytical data, collected for a system under some type of external perturbations.^{14–16,29,30} The intensity of a peak located at the diagonal position, called autopeak, corresponds to the autocorrelation function of observed spectral intensity variations induced by an external perturbation. Thus, an autopeak represents the overall susceptibility of the corresponding spectral region to change in spectral intensity as an external perturbation is applied to the system. Cross peaks located at the off-diagonal position of a synchronous 2D spectrum represent simultaneous or coincidental changes of spectral intensities observed at two different spectral variable ν_1 and ν_2 . The sign of a synchronous cross peak becomes positive if the spectral intensities at the two spectral variables corresponding to the coordinates of the cross peak are either increasing or decreasing together as functions of the external perturbation variable. On the other hand, negative sign of the cross peak intensity indicates one of the spectral intensities is increasing, while the other is decreasing.

The intensity of an asynchronous spectrum represents sequential or successive changes of spectral intensities observed separately at ν_1 and ν_2 . The sign of an asynchronous cross peak provides useful information about the sequential order of the events observed by the spectroscopic technique along the external perturbation variable. The sign of an asynchronous cross peak becomes positive if the intensity change at ν_1 occurs predominantly before that at ν_2 . On the other hand, the peak sign becomes negative if the change at ν_1 occurs predominantly after ν_2 . However, this sign rule is reversed if the synchronous correlation intensity at the same coordinate becomes negative. The construction of a generalized 2D correlation phase map (phase angle $\Theta = \tan^{-1}(\Psi/\Phi)$) is a reasonable approach to evaluating the sequential order of the events.^{31,32}

Two-dimensional correlation analysis of mid-infrared spectra

Figure 5 shows the synchronous and asynchronous 2D correlation spectra and phase maps, calculated from all data set of the epoxy resin/polyamine system in the region of 4000–800 cm^{-1} during the isothermal curing. In the synchronous spectra, three

autocorrelation peaks are observed at 3422, 1084, and 914 cm^{-1} , which indicates respectively the significant change of O—H bands, aliphatic C—O bands, and epoxy band during the curing process. A positive cross peak is observed at (3422, 1084) and four distinct negative cross peaks exist at (1084, 914), (1084, 830), (914, 3422), and (830, 3422), which are respectively related during the curing process.

In the corresponding asynchronous spectra, positive asynchronous peaks are observed at (3500, 3370), (1070, 914), (1070, 840), (1120, 3400), and (1050, 3370), while negative asynchronous peaks exist at (1122, 1084), (1130, 914), (1130, 840), (914, 3380), and (840, 3400). In the asynchronous spectra, the peaks attributed to O—H stretching band and aliphatic C—O band are observed as a pair of positive and negative correlation peaks.³⁰

It is noted that these bands are highly overlapped with each other. When the region 1000–1150 cm^{-1} is considered, in the synchronous 2D spectrum, only one broad peak is observed, while in the asynchronous 2D spectrum, two distinct peaks are clearly observed. It is indicated that different species or variation behaviors exist in the epoxy/polyamine system.

In the phase maps, the variations of respective bands are indicated such that the aliphatic C—O bands and O—H bands change after epoxy bands, and aliphatic C—O bands and O—H bands change simultaneously. Therefore, it is concluded that right after the oxirane ring was opened, etherification reaction immediately takes place.

Fourier-transform near-infrared spectroscopy analysis

Figure 6 shows the FTNIR spectra of the BA epoxy resin/polyamine system collected every 5 min during the curing process.

In the NIR spectrum, a characteristic band attributed to the oxirane ring can be identified at 4530 cm^{-1} . It is known that the peak is due to the combination bands of CH_2 vibrations of glycidyl groups.³³ The peak due to primary amine is observed at 4935 cm^{-1} , which is known to be attributed to the combination band of NH_2 group vibrations. The intensities of both absorptions disappeared completely during the curing process. On the other hand, the broad bands between 6600 and 6380 cm^{-1} attributed to the first overtone of NH stretching of the primary and secondary amine are observed at almost the same frequency. In addition, the broad peak between 7200 and 6700 cm^{-1} having the peak maximum at 7000 cm^{-1} is due to the first overtone of OH stretching. The intensity of the OH band absorption increased during the curing process.¹²

Figure 7 shows the relative intensities of bands observed during the curing process, which are all normalized by the aromatic band centered at

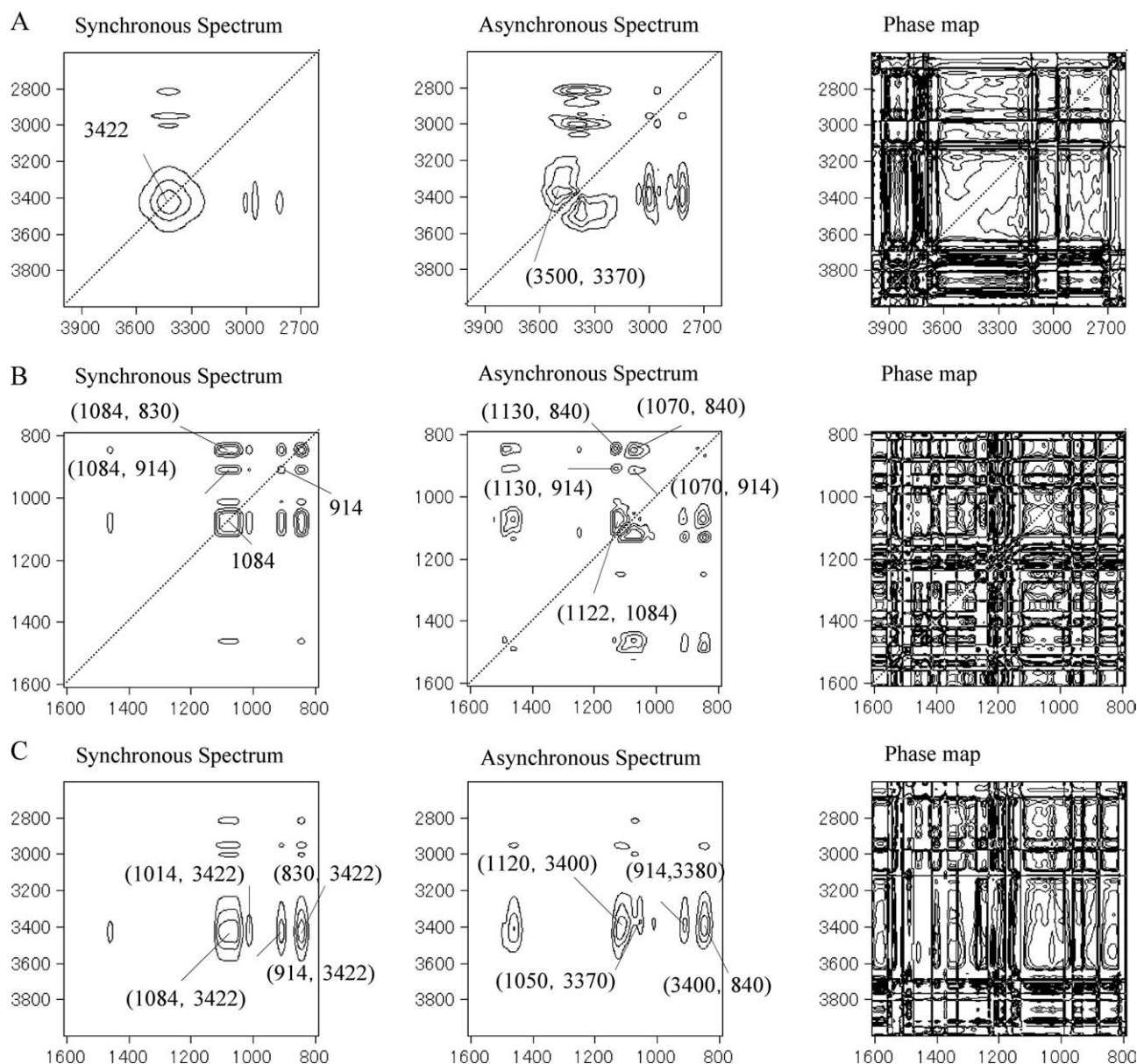


Figure 5 2D correlation spectra calculated from the IR spectra of the isothermal curing process at 80°C. Negative peaks are indicated by shading.

4620 cm^{-1} . They are attributed, respectively, to oxirane ring, primary amine (NH_2 vibration), sum of primary and secondary amine (NH vibration), and hydroxyl group. It was confirmed that the relative NIR intensity of epoxy group disappeared, and NH group decreased after about 13 min of curing, while hydroxyl group increased until around the same time and then remained constant afterward. On the other hand, the relative intensity of NH_2 attributed to the primary amine disappeared after about 9 min.

Two-dimensional correlation analysis of near-infrared spectra

Figure 8 shows the synchronous and asynchronous 2D correlation spectra, and the phase maps calculated

from the data of epoxy resin/polyamine system in the region 7300–4400 cm^{-1} during the isothermal curing. In the synchronous spectra, autocorrelation peaks are observed at 7000, 6507, 6065, 4935, 4830, and 4530 cm^{-1} , which indicates the significant change of OH bands, NH bands, NH_2 band and epoxy band during the curing process. The positive cross peaks are observed at (4935, 4530), (4530, 6065), and (4530, 6507), while the negative cross peaks exist at (7000, 6507), (7000, 6065), (4935, 4830), (4830, 4530), and (4530, 7000).

In the corresponding asynchronous spectra, positive asynchronous peaks are observed at (7000, 6540), (6530, 6460), (4935, 4530), (4935, 6507), and (4530, 6460), while negative asynchronous peaks exist at (7000, 6450), (6460, 6530), (4830, 6460), (4830,

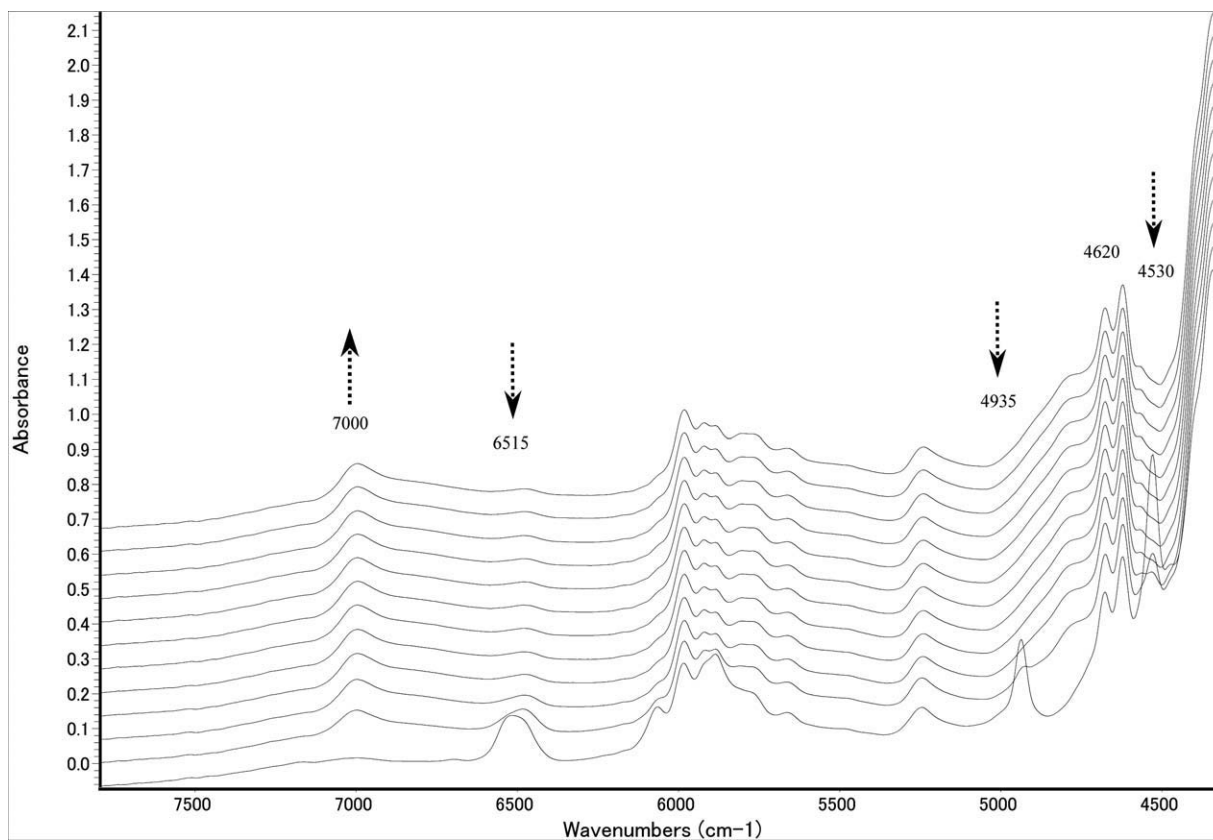


Figure 6 FTNIR spectra of BA and polyamine system collected every 5 min (12 spectra) while isothermally cured at 80°C.

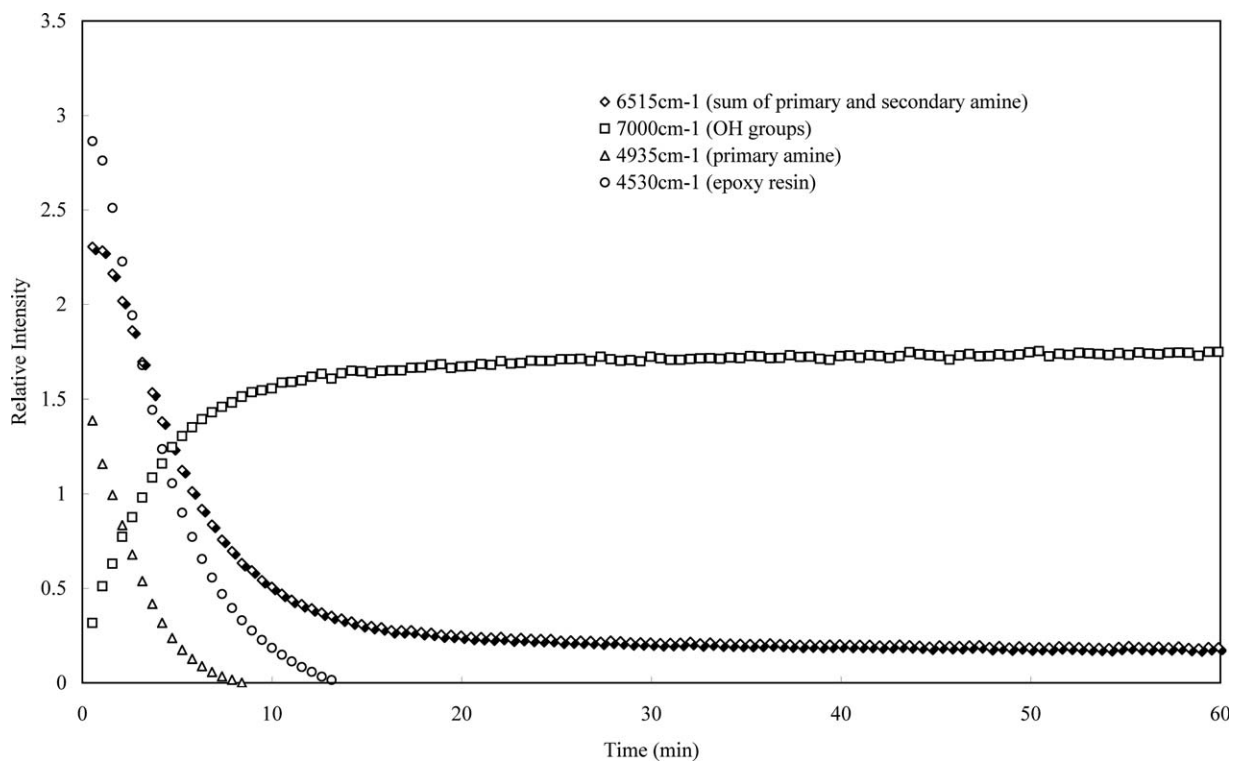


Figure 7 Relative intensities of the bands normalized by the aromatic band.

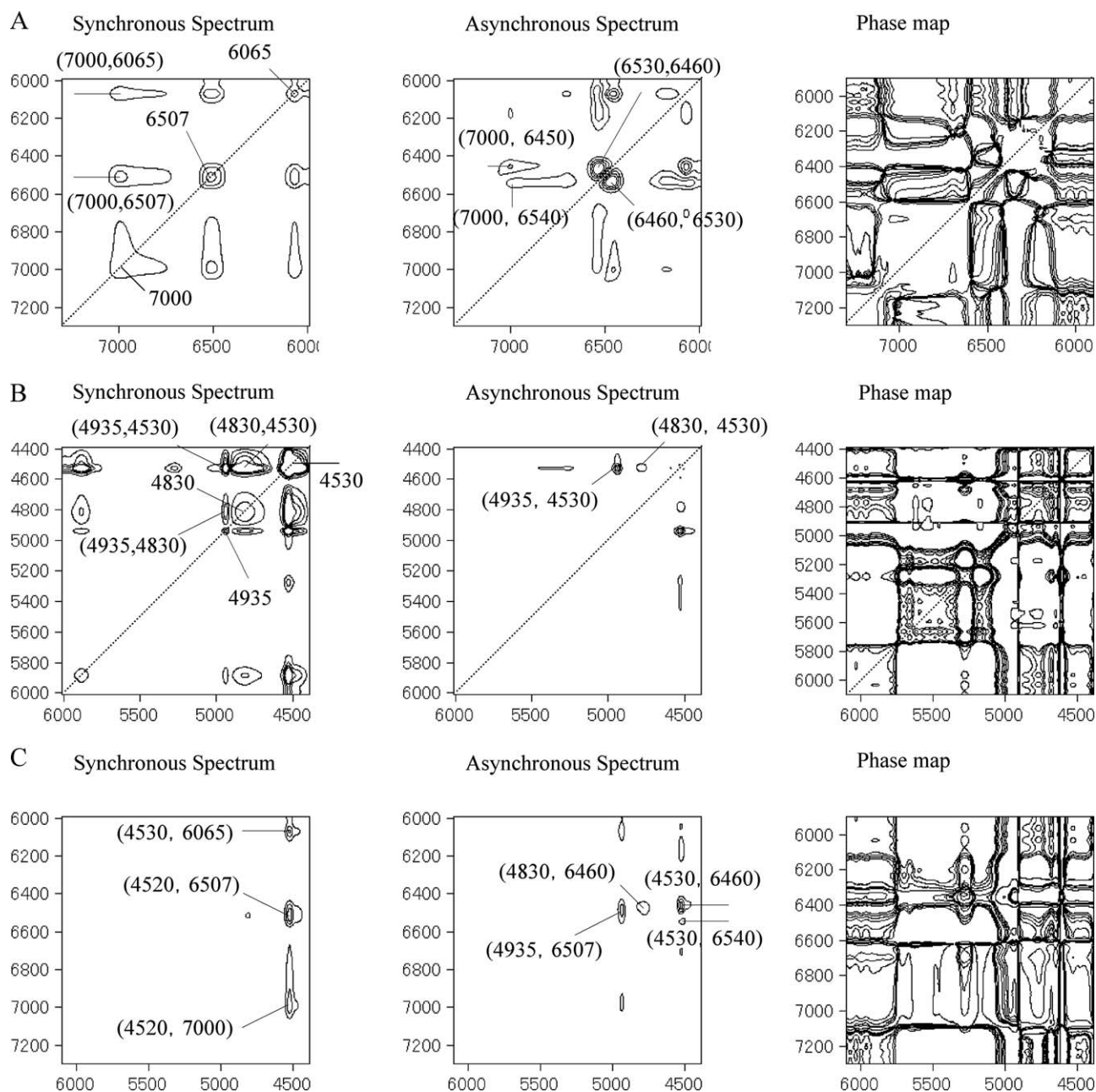


Figure 8 2D correlation spectra calculated from the NIR spectra of the isothermal curing process at 80°C. Negative peaks are indicated by shading.

4530), and (4530, 6540). Therefore, it is confirmed that for this epoxy resin system, hydroxyl, primary, and secondary amine groups, all have different characteristic reaction times during the curing process.

Furthermore, a pair of asynchronous peaks attributed to NH stretching bands are observed,³⁰ indicating the intensity variations of highly overlapped bands. They arise from different species or variation behaviors existing within this epoxy/polyamine system. It is suggested that the higher and lower frequency band signify, respectively, the primary and secondary amine. Such a result is difficult to be revealed by using only IR spectroscopy.

By using the phase maps, the sequential variations of respective bands are readily examined, such that NH₂ band and NH bands corresponding to the primary amine change before OH bands, while NH bands attributed to the secondary amine change after OH bands. The variations of epoxy band are occurring before OH bands. The apparent delay in the intensity changes of the secondary amine compared to other groups may be interpreted as the result of two competing reactions involving this group, i.e., initial production by the reaction of primary amine and subsequent consumption by the reaction with epoxy group.

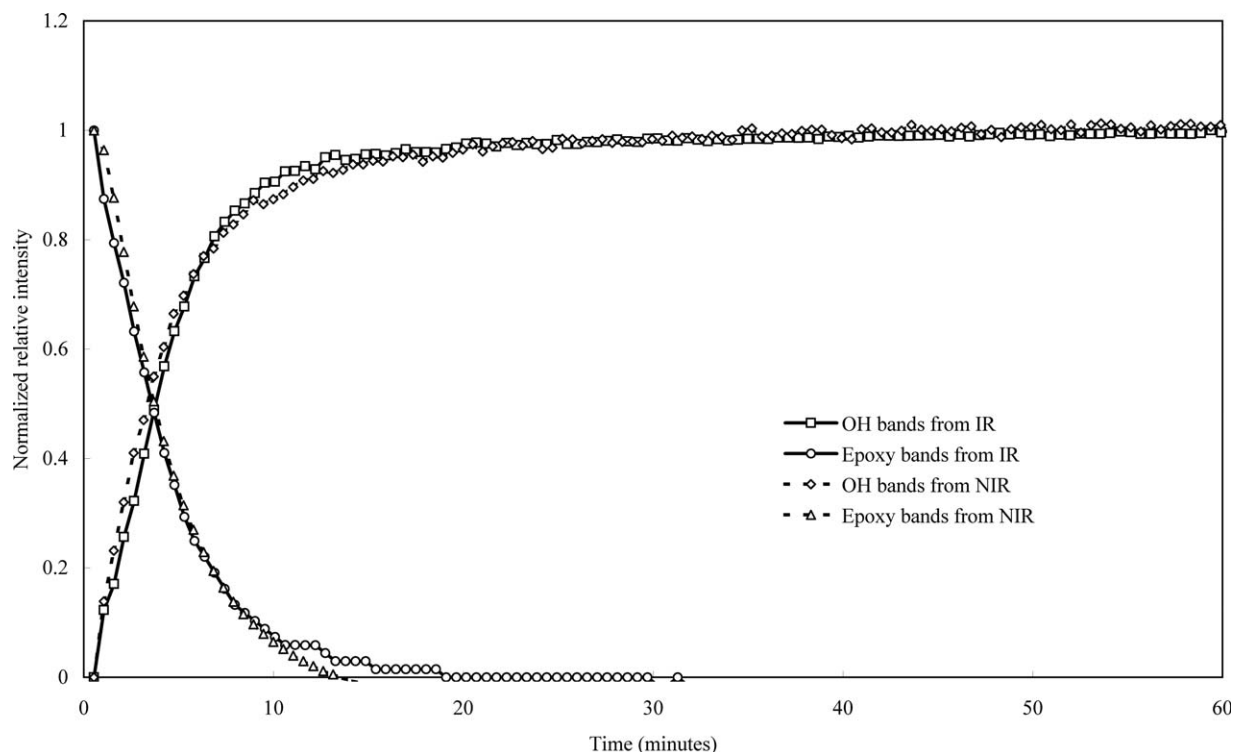


Figure 9 Normalized relative intensities of OH and epoxy bands by IR and NIR.

Two-dimensional IR-NIR hetero-correlation spectra

It is difficult to investigate the direct relationship between changes in aliphatic C—O bands and N—H bands from the separate 2D correlation analysis of IR and NIR spectra. To investigate the sequential order of variations between aliphatic C—O bands and N—H bands, it will be helpful to carry out the 2D hetero-spectral correlation analysis between IR and NIR spectra. However, to generate 2D hetero-correlation spectra, it is necessary to match the measurement conditions and reactive process for both IR and NIR analysis. In general, it is necessary to prepare the sample for NIR to be much thicker than that for IR.

To assure the comparable consumption time of the epoxy groups and the increase time of the hydroxyl groups, the thickness and the capacity of the sample for NIR must be carefully controlled. Figure 9 shows normalized relative intensities of hydroxyl and epoxy groups along the curing process, the variations of these bands exhibit good correspondence. Therefore, the IR and NIR data sets can be used to calculate 2D hetero-correlation spectra.

2D hetero-correlation analysis is a very attractive tool that combines two separate measurements via some common perturbation-induced phenomenon.^{16–20} Different techniques often provide different information about the system and process, and results from different techniques may often validate each other.

Figure 10 shows the result of 2D hetero-correlation spectra and phase maps from the NIR and IR spectra. In Figure 10(A,B) the region 3700–3000 cm^{-1} and 7400–4400 cm^{-1} , in Figure 10(C,D) the region 1300–1000 cm^{-1} and 7400–4400 cm^{-1} , and in Figure 10(E,F) the region 1000–800 cm^{-1} and 7400–4400 cm^{-1} are correlated. In the synchronous spectra, positive cross peaks are observed at (3425, 7000), (3425, 4800), (914, 6500), (914, 6060), (914, 4935), and (914, 4530), while negative cross peaks exist at (3425, 6500), (3425, 6060), (3425, 4530), and (914, 7000).

Broad ether bands between 1150 and 1000 cm^{-1} in the IR region are related to epoxy bands, and NH band attributed to the primary amine in the NIR region.

In the corresponding asynchronous spectra, positive asynchronous peaks are observed at (3390, 6540), (3370, 6060), (3410, 4935), (3390, 4530), (1072, 6545), (1072, 4935), (1072, 4530), (914, 6460), (845, 6460), (914, 4530), and (850, 4530), while negative asynchronous peaks exist at (3460, 6450), (1122, 6450), (1122, 4530), and (914, 4930). An asynchronous peak is not observed at (3425, 7000), it indicates that there is no influence in the signal variation by the difference of the film thickness of IR and NIR. Cross peaks are observed around 1100 cm^{-1} attributed to aliphatic CO bands correlated to around 6500 cm^{-1} attributed to NH stretching. The higher frequency peak is assigned to the primary amine, and the lower frequency one to the secondary amine.

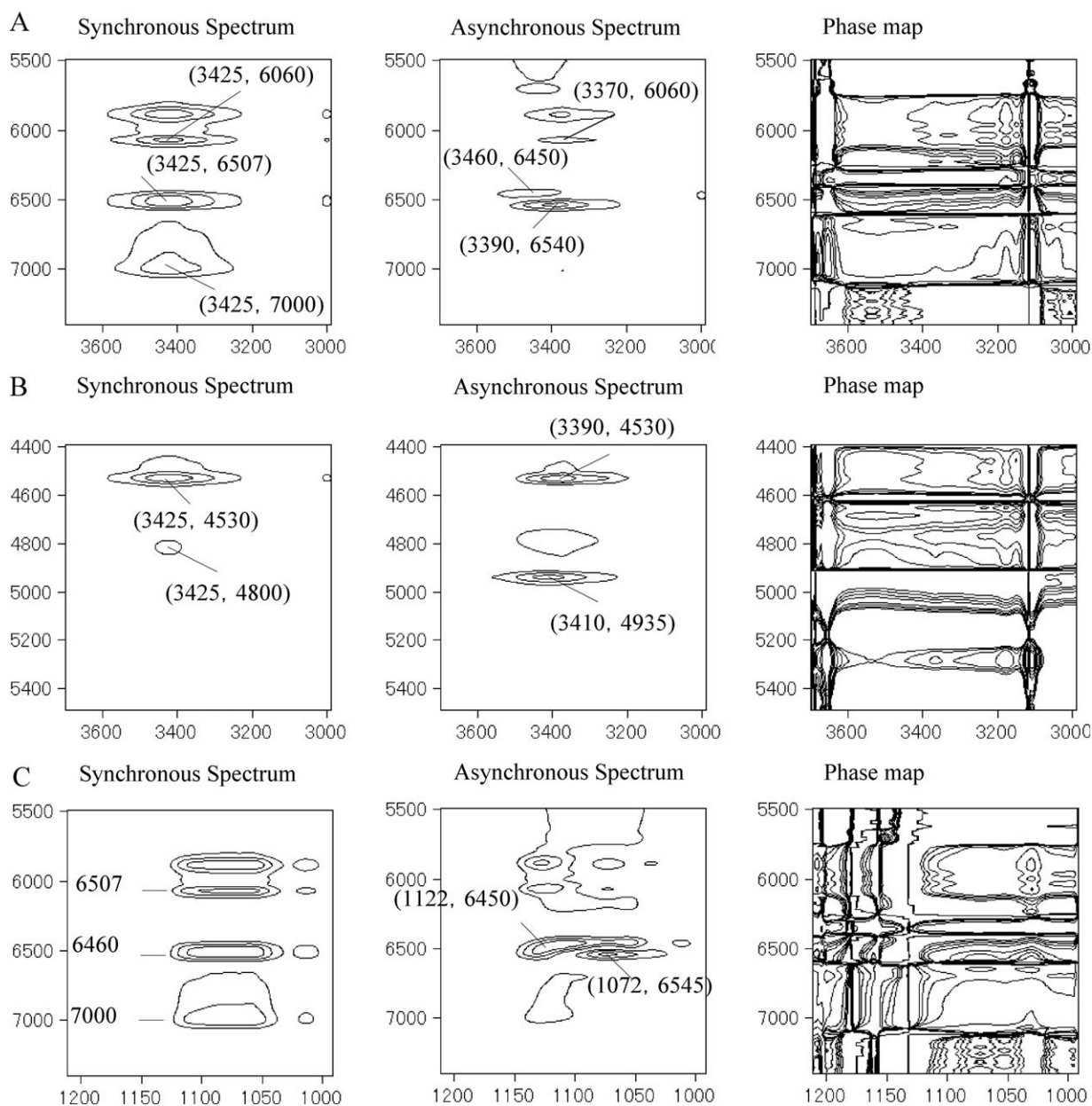


Figure 10 2D IR-NIR hetero-correlation spectra of isothermal curing process at 80°C. Negative peaks are indicated by shading.

In the phase maps, the sequential variations of respective bands are examined, such that the aliphatic CO bands change after NH band of the primary amine and epoxy band, before NH band of the secondary amine and almost simultaneous with OH bands. Meanwhile, NH band of primary amine change before epoxy band. These findings are consistent with the previous result of 2D IR and NIR correlation analysis, revealing the details of the complex epoxy curing reaction involving both primary and secondary amine groups. It is presumed that the reaction of primary amine occurs first with epoxy group, and hydroxyl group and secondary amine are generated by oxirane ring opened after that

etherification proceeds immediately as the generated hydroxyl group reacts with other epoxy group, and then, secondary amine reacts with other epoxy group in this curing process.

CONCLUSION

The isothermal curing reaction of bisphenol A type epoxy resin with polyamine was studied with FTIR and FTNIR spectroscopy. Generalized 2D correlation analysis of IR and NIR spectra made it possible to distinguish the reaction dynamics of primary and secondary amine. When IR and NIR spectra were

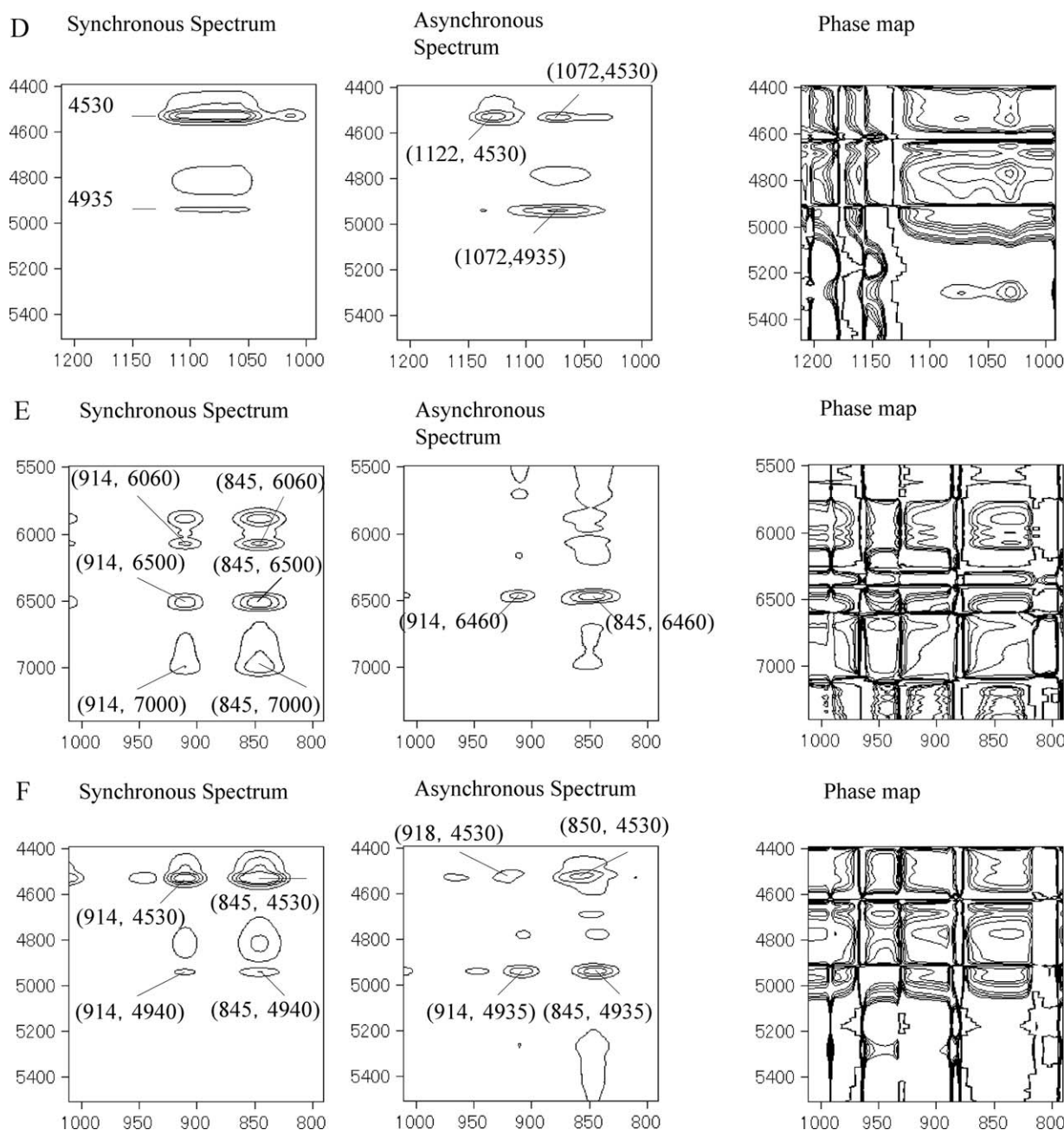


Figure 10 (Continued from the previous page)

evaluated together by using the 2D hetero-spectral correlation, the sequential order of the changes in the ether group and the polyamine was elucidated to successively reveal the details of the complex epoxy curing reaction involving both primary and secondary amine groups. Changes in NH_2 and NH bands for primary amine occurs first followed by aliphatic CO bands before those for OH and epoxy bands. Changes in NH bands for the secondary amine is delayed due to the competing reactions of the secondary amine, i.e., initial production by reaction of primary amine and subsequent consumption by the epoxy reaction with epoxy groups.

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