

## 실시간 FT-IR 분광분석법을 이용한 우레아-폼알데하이드 수지의 경화반응

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### Curing Reaction of Urea-formaldehyde Resin Using Real Time FT-IR Spectroscopy

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**Abstract:** In this paper, the curing reaction of UF resins was investigated by a real time FT-IR method. The curing temperature range of the UF resin was 25 ~ 200°C. It was found that the reactions of UF resin at different temperatures resulted in resins with different cross-linked structures. A real time FT-IR spectroscopy can be considered as a good routine analytical tool for following the progress of UF resin curing.

**Keywords:** urea-formaldehyde resin, real time FT-IR, cross-linked structure

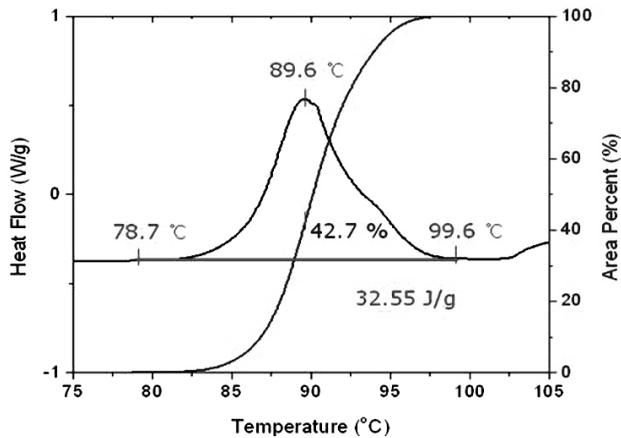
### 1. Introduction

Urea-formaldehyde (UF) resins have been extensively used in wood-based panel industries for more than 100 years, due to their good performances in the production of wood-based panels, as they have high reactivity and low cost. UF resins are water-based thermosetting resins built up by condensation polymerization. The reaction parameters that mostly affect the properties of the final product are the molar ratio of formaldehyde to urea, pH, temperature, concentration, and time. The synthesis of UF resins from urea and formaldehyde often proceeds in two steps[1-3]. (1) The first is the so-called methylation reaction, which is catalyzed by both acids and bases and leads to the formation of hydroxymethyl compounds.

Monomethylol-, dimethylol-, and trimethylolurea have been isolated by controlling the ratio of the reactants and identified by means of NMR spectroscopy, while tetramethylolurea has never been observed. (2) Subsequently, condensation reactions between the various methylol species and urea are taking place. These reactions are mainly acid catalyzed and lead to a complex mixture of low molecular weight UF adducts (oligomers). The condensing moieties link together by methylene or by dimethylene ether links (N-CH<sub>2</sub>-N and N-CH<sub>2</sub>OCH<sub>2</sub>-N, respectively). Dimethylene ether links can be formed under alkaline conditions inter- or intramolecularly. In the latter case cyclic compounds are formed.

Their processing is greatly influenced by curing conditions, especially by the degree of cure, therefore it is very important to study the curing characteristics of the resins. Various methods for evaluating curing character-

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**Figure 1.** DSC curve of UF resins at a heating rate of 10°C/min.

istics of UF resins have been proposed and used in practice. The thermal behavior of the resins during curing has been followed by thermogravimetric analysis, differential thermal analysis, differential scanning calorimetry, supported by data from IR spectroscopy and  $^{13}\text{C}$  NMR spectroscopy.

Spectroscopic monitoring of the degree of cure, or the rate of polymerization, is one of the most utilized methods. Unlike other kinetic techniques, this method allows the cure reaction to be continuously and rapidly monitored, in real time, at the molecular level without significant post-cure errors. The principle for using the real time FT-IR technique for kinetic studies is based on the direct measurements of changes in the chemical structure of formulation components during cross-linking by FT-IR spectroscopy. Thus, the monomer decrease or the polymer increase can be spectroscopically recorded as a function of reaction time[4].

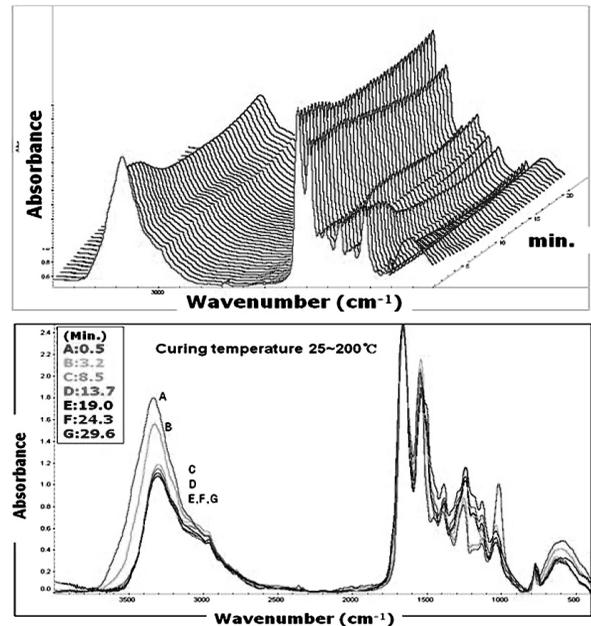
In the present work, the curing reaction of UF resins was investigated by a real time FT-IR method. The curing temperature range of the UF resin was 25~200°C.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Urea-formaldehyde Resin

UF resin with the dry resin content of 59.4% was prepared. For the hardener, 20% of  $\text{NH}_4\text{Cl}$  solution was used. According to the degree of formaldehyde emission, the UF resins were classified as belonging to the E<sub>2</sub> class with a viscosity of  $250 \pm 20$  mPa · s.



**Figure 2.** Real time FT-IR spectra of the band variations of the UF resin from the beginning of the reaction to 200°C (400~4000  $\text{cm}^{-1}$ ).

### 2.2. Test Methods

#### 2.2.1. Differential Scanning Calorimetry (DSC)

All DSC measurements were made with DSC Q 1000 (NICEM, Seoul National University) that equipped with a thermal analysis system (TA Instruments) and software. The sample resins were tested by placing about 3 mg of each sample into a hermetic pan. A heating rate of 10°C/min and a scanned temperature range of 25~200°C were selected.

#### 2.2.2. Real Time FT-IR Spectroscopy

FTIR spectroscopy measurements were continuously performed in curing UF resin at different temperatures by a series of real time method (Magma 6700, Nicloet). Spectra in the range of 400~4,000  $\text{cm}^{-1}$  were recorded as the spectrum every 1 min at a scan rate of 32 scans per spectrum at different curing temperatures (25~200°C).

## 3. Results and Discussion

### 3.1. Curing Behavior of UF Resin Determined by DSC

It is generally believed that in the presence of an acid catalyst, the exotherm arises from the polycondensation reaction of primary amino groups of unreacted urea with hydroxymethyl groups of resin. The curing reaction of

**Table 1.** Wavenumbers of the FT-IR bands [7,10]

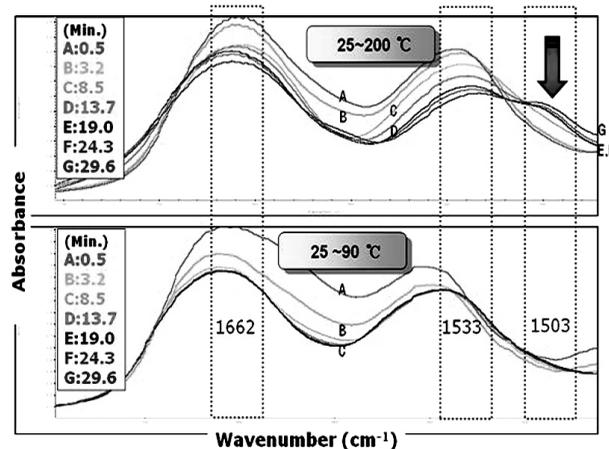
Wavenumber (cm <sup>-1</sup> )	Band
3200~3440	Urea N-H stretch (NH mode in free NH <sub>2</sub> )
3320~3360	Monosubstituted urea N-H stretch (NH mode of bonded NH <sub>2</sub> )
3015~3020	CH mode in of the -CH <sub>2</sub> -O-CH <sub>2</sub>
2960~2970	CH mode in of CH <sub>2</sub> of ether, CH <sub>2</sub> OH and N-CH <sub>2</sub>
2900~2910	CH mode of CH <sub>2</sub> OH
1656~1660	C=O stretch, primary amide -NH <sub>2</sub> (urea)
1533	Secondary amide -NH- (methylol and methylene urea; N-H bending)
1503	N-C-N of a proper methylene bridge (-CH <sub>2</sub> -)
1289	-CH <sub>2</sub> - of -CH <sub>2</sub> -O-CH <sub>2</sub> Aliphatic ether C-O stretch plus
1132	C-N stretch in Amide II N-CH <sub>2</sub> -N

UF resins is typically exothermic, so it was hypothesized that the reaction enthalpy would simply be proportional to the degree of conversion during the curing process. The DSC results in Figure 1 show that the peak temperature was changed according to the type of scavenger. The UF resins present exotherms in the temperature range, with curing peak temperatures observed between 78.7 and 99.6°C in Figure 1. The peak area is the amount of energy required to complete the cure of the resin, which is the area under the exothermic DSC curve. The areas of these peaks should, therefore, be proportional to the amounts of -CH<sub>2</sub>-O-CH<sub>2</sub>- linkages in the UF resins[5,6].

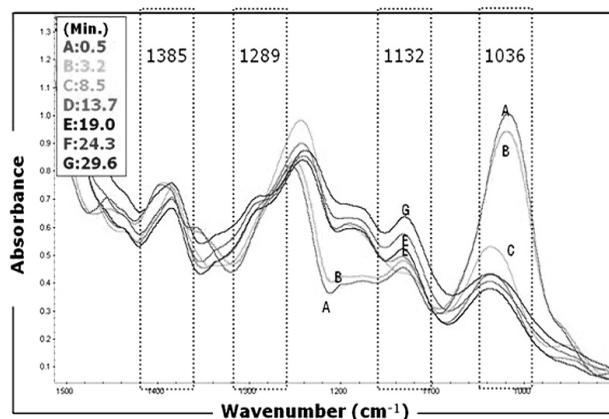
### 3.2. Investigation of UF Resin Cure by Real Time FT-IR

The FT-IR spectrum in Figure 2 shows the total phase of the reaction of urea-formaldehyde from the beginning form 20°C to 200°C for 30 min. In Figure 2, one can observe OH of water (3,400~3,300 cm<sup>-1</sup>) in urea and formaldehyde, and this is followed by a decrease in the water content due to curing process. The -OH of water is eliminated in the condensation of urea and formaldehyde, and this is followed by a decrease in the water content due to evaporation and the reaching of the reflux phase of the resin preparation[7].

A medium or weak absorption band appeared at around



**Figure 3.** Real time FT-IR spectra of the band variations of the UF resin from the beginning of the reaction to 200°C (1,400~1,700 cm<sup>-1</sup>).



**Figure 4.** Real time FT-IR spectra of the band variations of the UF resin from the beginning of the reaction to 200°C (900~1,500 cm<sup>-1</sup>).

3,200~3,100 cm<sup>-1</sup>, which is characteristic of the C-H stretching mode of the -CH<sub>2</sub>-O-CH<sub>2</sub>- group. On the basis of model compounds, this band at 3,015 cm<sup>-1</sup> was assigned to the asymmetric CH<sub>2</sub> stretching of the -CH<sub>2</sub>-O-CH<sub>2</sub>-group. A sharp strong band appeared at 2,960 cm<sup>-1</sup>, which is a combination of the asymmetric CH stretching modes of ether, alcohol, and N-CH<sub>2</sub>-N group, as indicated in Table 1. As expected, the symmetric stretching mode was more intense than the asymmetric mode. A weak yet distinct absorption band appeared at around 2,900 cm<sup>-1</sup>[8].

In Figure 3, the -CONH<sub>2</sub> unreacted amide group of urea (1,662 cm<sup>-1</sup>) decreases as it begins reacting with formaldehyde. And the 1,533 cm<sup>-1</sup> band, representative of

the C-N stretch and NH deformation decreases. This indicates that the UF reaction starts already in the very initial phase of the preparation, even at relatively low temperatures. Whereas simultaneously, the  $1,503\text{ cm}^{-1}$  band, representative of the methylene bridge ( $\text{CH}_2\text{-O-CH}_2$ ) increases, the shoulders at  $1,660$  and  $1,550\text{ cm}^{-1}$  are indications of differently substituted urea reacting further and thus decreasing[7]. However, the series of bands in the  $1,503\text{ cm}^{-1}$  are no change at  $25\sim 90^\circ\text{C}$ . The curing reaction did not appear at lower temperature.

In Figure 4, the series of bands in the  $1,000\sim 1,500\text{ cm}^{-1}$  range indicate the increase in the proportion of methylene ( $\text{CH}_2$ ) bridges. This band appears as a shoulder on the  $1,289\text{ cm}^{-1}$  peak in our spectra for cured UF resin. During UF resin cure the spectra indicate that they become much more distinct. Primary alcohols exhibit the OH deformation absorption at about  $1,300\text{ cm}^{-1}$ . It is very likely that this accounts for the absorptions noted for methylol containing model compounds and for uncured UF resin. However, the  $\text{CH}_2\text{OH}$  content in UF resin must decrease during cure so that the observed was divided into two peaks  $1,290$  and  $1,260\text{ cm}^{-1}$ . Those regions during cure reflect the growth of structures other than  $\text{CH}_2\text{OH}$ .

And the bands at  $1,036\text{ cm}^{-1}$  decrease, indicating the decrease in the C-O-C bonds and thus either (1) the progressive decrease of two types of the  $-\text{CH}_2\text{OCH}_2-$  urea to urea bridges as these reorganize into  $-\text{CH}_2-$  bridges and methylol groups or (2) the progressive decrease of the  $-\text{CH}_2\text{OCH}_2-$  urea to urea bridges for one peak and for the other peak of the hemiacetals formed by a reaction of the methanol obtained by Cannizzaro side reaction[1,7,9].

## 4. Conclusion

The FT-IR result has been shown to clearly detect the same trends of molecular species at different stages in the curing process of UF resin. The analysis by real time FT-IR is simpler technique for deducing what the main trends are in the changes of the distribution of just the main groups of molecular species during UF resin curing. In this context, it can be considered as a good routine analysis tool for following the progress of UF resin curing.

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