

Role of F/P Ratio on Curing Behavior for Phenolic Resol and Novolac Resins by FT-IR

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FT-IR 분석에 의한 레졸과 노블락 페놀 수지의 경화거동에 미치는 F/P 몰비

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요 약

포름알데히드/페놀의 몰비에 따른 레졸과 노블락 수지의 경화거동을 FT-IR 분석법으로 연구하였다. 일정한 경화온도(레졸 수지: 130°C, 160°C, 180°C, 노블락 수지: 160°C, 170°C, 180°C)에서 경화시간(3, 5, 7, 10, 20, 60분)에 따른 경화 정도를 비교하였다. 경화정도(conversion, α)는 경화되지 않은 수지의 FT-IR 스펙트라 3300 cm^{-1} 에 나타나는 OH 피크의 면적을 기준으로 각각 주어진 경화시간의 OH 피크 면적 비율로 구하였다. 그 결과 포름알데히드/페놀의 몰비와 경화온도가 증가함에 따라서 레졸과 노블락 수지의 초기 경화는 증가하였다. 특정한 경화 온도에서 integral method 분석에 의한 결과 포름알데히드/페놀의 몰비가 증가함에 따라서 레졸과 노블락 수지의 초기 경화는 증가하였다.

ABSTRACT

The curing behavior of a phenolic resin (F/P: 1.3, 1.9, 2.5 for resol resin, F/P: 0.5, 0.7, 0.9 for novolac resin) has been studied by FT-IR spectroscopy. In this study is to synthesis of resol and novolac type phenolic resin with different F/P molar ratios and to compare the level of cure at different curing temperature conditions (130°C, 160°C, 180°C for resol resin, 160°C, 170°C, 180°C for novolac resin) for 3, 5, 7, 10, 20, and 60 (min.), respectively. The conversion (α) was determined by the ratio of the peak area with time to the peak area of non-baked phenolic OH (3300 cm^{-1}) at spectra. It is concluded that the initial curing rate of resol and novolac resin was increased as the molar ratio of formaldehyde/phenol increased and as the curing temperature of resin increased.

According to the analysis was by the homogenous first-order model, the initial curing rate of resol and novolac resin was increased as the molar ratio of formaldehyde/phenol increased at specific curing temperature.

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- 2001년 7월 12일 접수 (received), 2001년 7월 31일 채택(accepted)
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KEYWORDS: RESOL & NOVOLAC RESIN, CURING BEHAVIOR, KINETIC BEHAVIOR, FT-IR, INTEGRAL METHOD

INTRODUCTION

Phenol-formaldehyde resins are a class of materials having wide applications in temperature resistance and moderate flame many areas, largely due to their high resistance. Today, academic interest is improvement of properties by chemical modifications,^[1] understanding of cure mechanisms^[2,3] and decomposition mechanisms studies.^[4,5] The kinetic investigation is probably the most active research field.

It has already been confirmed that the cure of phenol-formaldehyde resins is accomplished in a two-step process.^[6] The first step involves the addition of formaldehyde to phenol to form hydroxymethyl phenol and the second one involves the condensation of hydroxymethyl phenols to form methylene and methylene-ether-bridged di- or high-molecular compounds. Eventually, the methylene ether bridge may lead to methylene-bridged phenol, water and formaldehyde by disproportionation.

Although phenolic resins have been used for many decades, detailed chemical understanding of their formation and cure has been speculative and not fully elucidated. One of the reasons is that the resin has a complicated mechanism of reaction. One reaction is the addition of formaldehyde to ortho- and para phenol positions. The other reaction is condensation with formation of water and formaldehyde.

Significant progress in performance characteristics will not occur unless intimate knowledge concerning the structure, the mechanism and the kinetics of resin

formation and cure is obtained

In this study, the curing behavior of thermosetting phenolic resol and novolac resins has been studied by FT-IR spectroscopy and the obtained isothermal conversion-time data has been discussed.

EXPERIMENTAL

SYNTHESIS OF RESOLS & NOVOLACS

The resin syntheses were carried out in a laboratory glass reactor equipped with a stirrer, thermometer and reflux condenser, as shown in Figure 1. The mixture of phenol and 37% aqueous formaldehyde were heated up to temperature of 45°C and then the catalyst, 10% sodium hydroxide solution for resol resin, 2% oxalic acid solution for novolac resin, was added. After heating the components to 90°C for 30 min. and then heating continued at 90°C for 60 min.

The fundamental properties of resol and novolac resin are listed in Table 1.

FT-IR ANALYSIS

A Perkin-Elmer Spectrum BX FTIR spectrometer at resolution of 4 cm⁻¹ was employed in the absorbance mode for both resin characterization and kinetic study.

In order to remove moisture from the resins, the resins were mounted in the vacuum dry oven at 40°C for 48 hours.

The resin was mixed with KBr (resin: KBr=1:70) to plate and it cured in the dry oven.

IR analysis is based on the fact that each chemical group in a sample absorbs

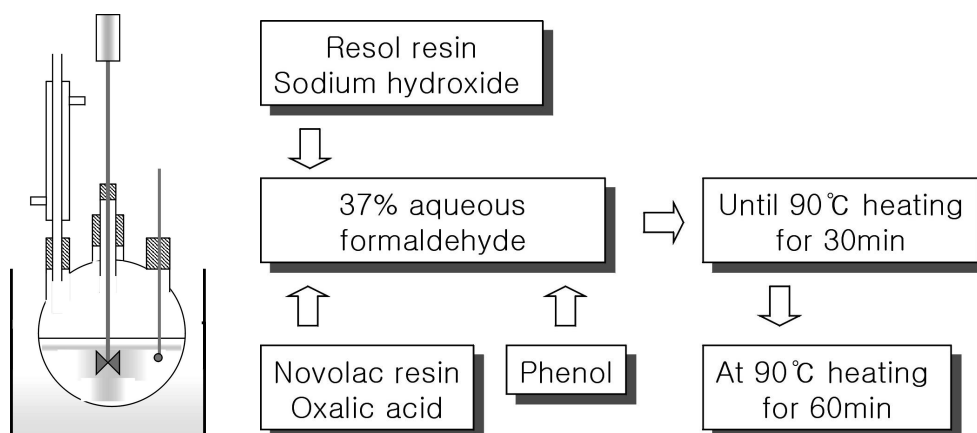


Figure 1. Apparatus used in the preparation of resol & novolac resin.

Table 1. Condensation Conditions of the Phenolic Resins

Code	Resol			Novolac		
	1	2	3	1	2	3
F/P Molar Ratio	1.3	1.9	2.5	0.5	0.7	0.9
M_n	240	380	400	380	390	390
M_w	460	630	670	540	560	580
M_w / M_n	1.92	1.66	1.67	1.44	1.42	1.49
Non-volatile content (%)	59.2	53.5	50.4	46.6	45.4	45.9
Viscosity (mPa · s)	157	445	1390	22.6	25.7	29.8

IR radiation of some characteristic frequencies. IR analysis is based on the fact that each chemical group in a sample absorbs IR radiation of some characteristic frequencies.

And then, the resin, mixed with KBr, was cured at different curing temperature conditions (130°C, 160°C, 180°C for resol resin, 160°C, 170°C, 180°C for novolac resin) for 3, 5, 7, 10, 20, and 60 (min.), respectively.

RESULTS AND DISCUSSION

The principal IR absorption bands of a methylolated phenol molecule are listed

Table 2. Assignments of Methylolated Phenol IR Absorption Bands

Functional Group	Absorption	Wave number (cm ⁻¹)
H-O	Stretching	3330
-CH ₂ -	Stretching	2900
C-C	Stretching	1612
C-C	Stretching	1598
C-C	Stretching	1480
-CH ₂ -	Bending	1450
H-O	Bending	1359
Ar-O	Stretching	1200
CH ₂ -OH	Stretching	1100

in Table 2. According to the correlation described in the literatures,^[7,8] The FTIR spectrum of non-cure resin is shown in Figure 2. The deformation vibrations of C-H bond in benzene rings give absorption bands in the 770~740 cm⁻¹ range. This group disappears during the polymerization therefore, its concentration can be used as an index of the polymerization conversion. The deformation vibration of C-C bonds in phenolic groups absorbs in the regions of 1500~1400 cm⁻¹. This group does not participate in any chemical reaction during the polymerization. However, the peak showed a gradual decrease as the polymerization proceeded, because when

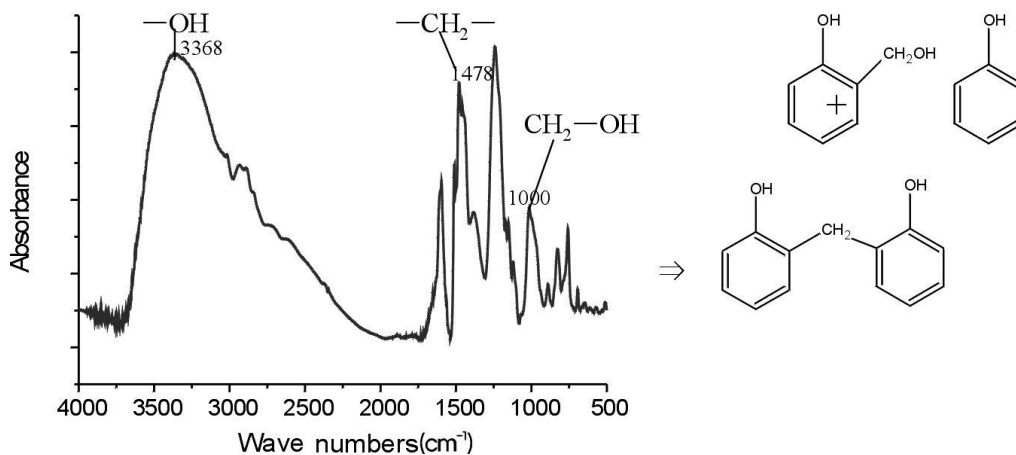


Figure 2. FTIR spectrum of non-cure resol resin.

the reaction takes place, the volume of the system contracts. In particular, the absorbances at maximum of the absorption, i.e., at 740 and 1480 cm^{-1} , have been followed and scanned in the study of the reaction kinetic. The absorption peaks at 740 and 1480 cm^{-1} are named sample peak and reference peak, respectively.^[7]

Consequently, the most important reaction involved in the alkaline polymerization of a resin is the condensation of hydroxymethyl groups with unreacted active position of other phenolic rings.

A chemical spectra conversion profiles for resol resin at 130°C , 160°C and 180°C and for novolac resin at 160°C , 170°C and 180°C were shown in Figure 3. Curing time of resol and novolac resins was 3, 5, 7, 10, 20 and 60 (min.), respectively.

The phenolic resin OH, which caused the phenolic resin to link together to form polymerization each other. As shown in Figures 2 and 3 at uncured temperature, there is a high band in regions from 3600 to 3000 cm^{-1} , where the hydroxyl stretching vibration can be observed. This is attributed to the wide distribution of the hydrogen-bonded hydroxyl group, whereas a low band is observed at low curing temperature, which is the free hydroxyl

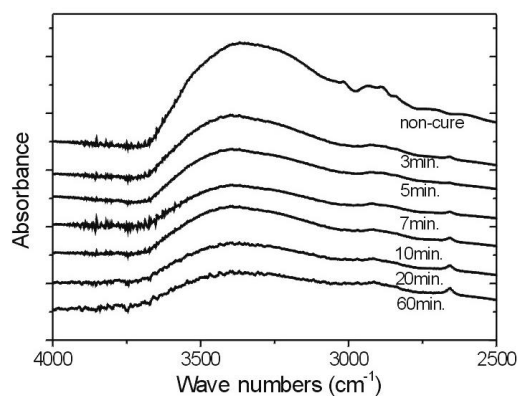


Figure 3. FT-IR spectra a of resol resin (F/P=2.5) at 160°C .

group. As the temperature increased, the relative absorption of the free hydroxyl group increased while that of the hydrogen-bonded hydroxyl group decreased. This result is similar to other previous studies.^[7,9]

The conversion (α) was determined by the ratio of the peak area with time to the peak area of non-baked phenolic OH (3300 cm^{-1}) at spectra.^[10]

The conversion (α) was calculated from following procedures:

$$A_t/A_{\text{int}(0)} = 1 - \alpha \quad (1)$$

Where A_t is the peak area of phenolic

OH (around 3300 cm^{-1}) for various curing times and $A_{\text{int}(0)}$ is the peak area of a phenolic OH non-cure sample.

FTIR spectra between 3600 cm^{-1} and 3000 cm^{-1} for resol and novolac resin at curing temperature are shown in Figure 3. The spectra show phenolic OH around 3300 cm^{-1} . The diminishing in the OH peak of the phenolic resin may result in progressing of crosslinking between phenolic resins.

The comparative conversion behaviors obtained from isothermal analysis at different curing temperatures are shown in Figures 4, 5 and 6 for resol resins. The symbols represent the value of the conversion at different curing times and the solid line is the regression curve. The peak area decreased as increasing curing time. The higher conversion was more curing than lower conversion.

The conversions of Figure 4 were sharply increased for initial curing time, especially high curing temperature of 180°C . However, there was no difference in conversion between 130°C and 160°C at various curing times, it is concluded that optimum curing temperature of resol resin (F/P:1.3) had to more higher temperature than 160°C .

As shown in Figure 5, the tendency of conversion for initial curing time was different from molar ratios of F/P=1.9. The conversion of curing time for 20 min. was 64%, 86% and 96% at 130°C , 160°C and 180°C , respectively. The higher conversion temperature was more faster curing procedure than lower curing temperature. From the result, we can suppose that suitable curing temperature resin was 160°C for molar ratio of 1.9 (F/P).

The tendency of conversion for curing time in molar ratio of F/P=2.5 had a slight tilt to one side, as shown in Figure 6. The initial curing rate of resol resin was increased as the molar ratio of

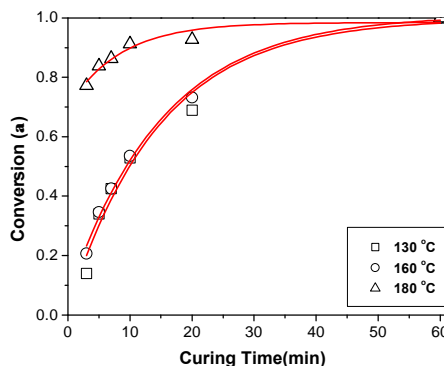


Figure 4. Conversions of phenolic OH in resol resin (F/P=1.3).

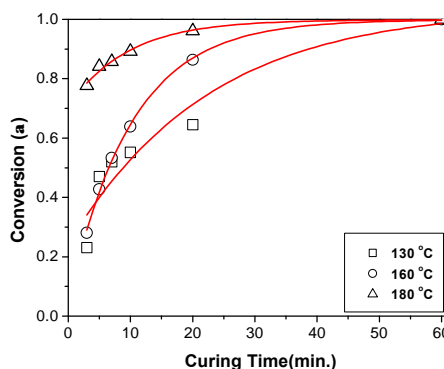


Figure 5. Conversions of phenolic OH in resol resin (F/P=1.9).

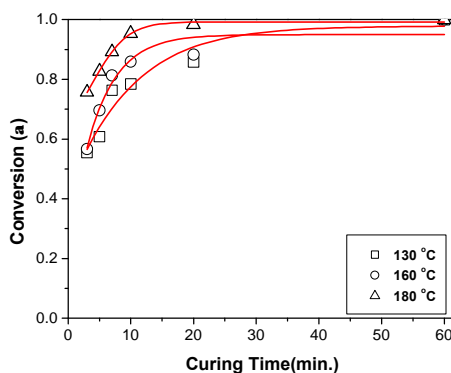


Figure 6. Conversions of phenolic OH in resol resin (F/P=2.5).

formaldehyde/phenol increased and as the curing temperature of resins increased. These results tended toward reports.^[11,12]

As shown in Figures 7, 8 and 9, the

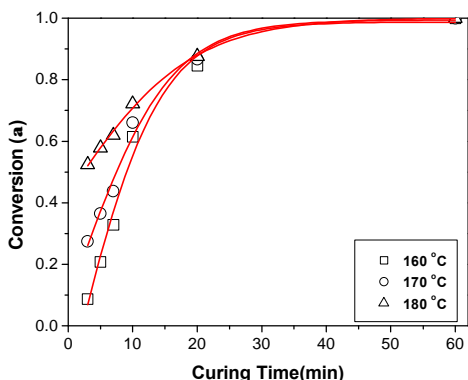


Figure 7. Conversions of phenolic OH in novolac resin (F/P=0.5).

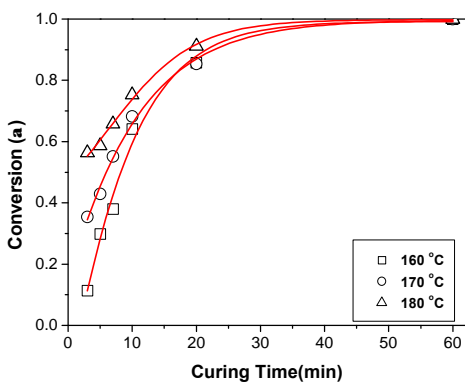


Figure 8. Conversions of phenolic OH in novolac resin (F/P=0.7).

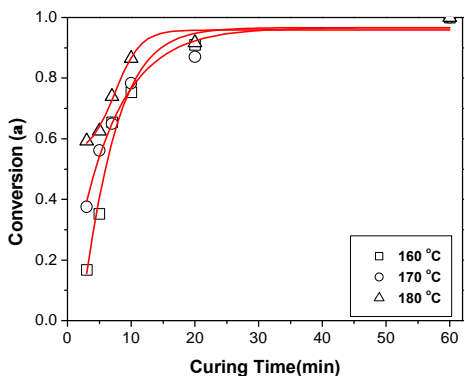


Figure 9. Conversions of phenolic OH in novolac resin (F/P=0.9).

tendency of conversion for different curing time was similar. As same resol resin, conversion of novolac resin was increased

as the molar ratio of formaldehyde/phenol increased.

The comparative conversion behaviors obtained from isothermal analysis at different temperatures are shown in Figures 10, 11, 12 and 13 for resol resin and Figures 14, 15, 16 and 17 for novolac resin. A good linear correlation, characterized by a high regression coefficient and a low intercept value, was observed at high temperatures and increased molar ratio.

Figures 10, 11 and 12 show a plot of isothermal hold time vs $-\ln(1-\alpha)$ for the homogeneous first-order model. The plots obtained from isothermal experiments performed for curing temperature were analysed by the integral method. This graphic representation is very useful because it allows an easy visual analysis of the model fitting capacity.

The curing rate tendency for F/P=1.3 and F/P=1.9 resol resin was nearly similar at curing temperature of 130°C and 160°C. While F/P=2.5 resol resin was increased as curing temperature in Figures 10 and 11.

As shown in Figure 12, however, the curing rate of resol resin was rapidly increased, regardless of F/P molar ratio, at curing temperature of 180°C

The results obtained are shown in Figure 13. Relatively, high molar ratio resin (F/P=2.5) was curing at lower curing temperature.

On the basis of previous results^(13,14), the amount of free ortho and para positions decrease and ortho methylol group, p-p' methylene bridges and hemi-formal structures increase as a function of the increasing F/P molar ratio.

Roczniak et al.⁽¹⁵⁾ identified the band at approximately 1450 cm^{-1} was assigned to methylene bridges in p-p', the band at 1460 cm^{-1} was assigned to the methylene bridge in o-o' and the band at 1480 cm^{-1} was assigned to the o-p' position. These

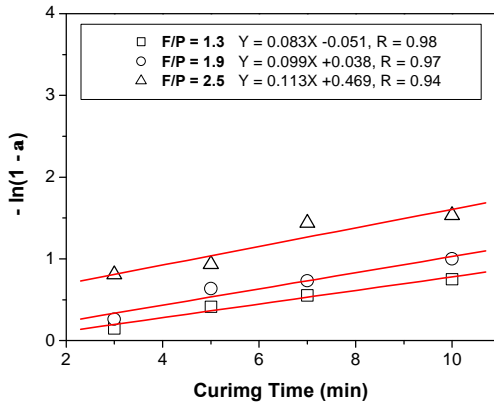


Figure 10. Isothermal vs $-\ln(1-\alpha)$ hold time for the homogeneous first-order model at 130°C for resol type.

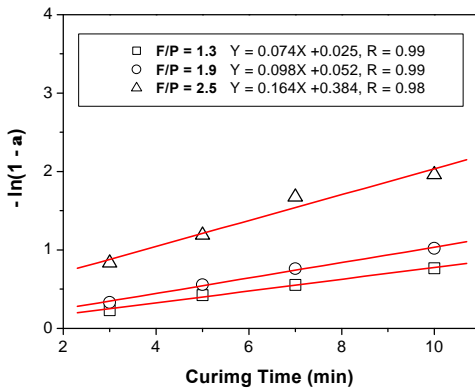


Figure 11. Isothermal vs $-\ln(1-\alpha)$ hold time for the homogeneous first-order model at 160°C for resol type.

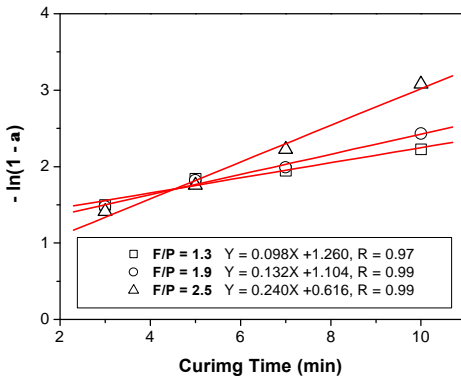


Figure 12. Isothermal vs $-\ln(1-\alpha)$ hold time for the homogeneous first-order model at 180°C for resol type.

bands are higher for the completely cured resin than for the prepolymer of uncured resin. It is an indication that more crosslinking reaction occurs in the curing step than during the synthesis of the resin. The application of this analysis to the resin allow us to determine that the quantity of p-p' bridge is higher than that of the o-p' bridge.

As shown in Figures 14, 15 and 16, the plots of isothermal hold time vs $-\ln(1-\alpha)$ for novolac resins were lower effect for the curing temperature than resol resins.

Especially, as shown in Figures 14 and 15, the curing rate tendency of novolac resins

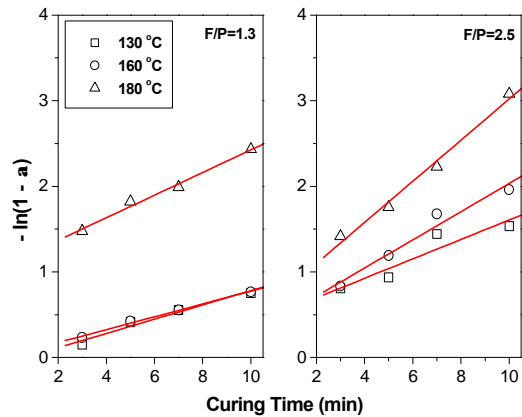


Figure 13. Comparisons of curing rate between $F/P=1.3$ and $F/P=2.5$.

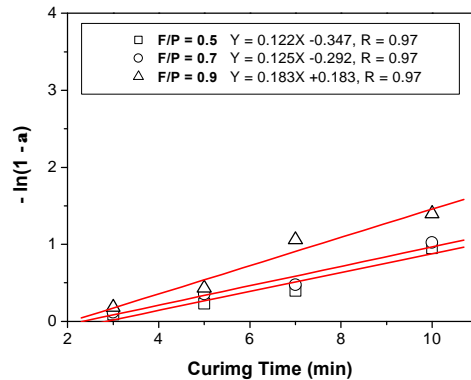


Figure 14. Isothermal vs $-\ln(1-\alpha)$ hold time for the homogeneous first-order model at 160°C for novolac type.

was much the same at curing temperature of 160°C and 170°C. Also, tendency of F/P=0.5, and F/P=0.7 resin was alike, without regard to curing temperature. As shown in Figure 16, curing rate of novolac resin was increased as the molar ratio of formaldehyde/phenol increased, too.

In the result of Figures 14, 15 and 16, low molar ratio novolac resin uncured without hardener. As the shown in Figure 17, F/P=0.9 resin, which molar ratio was similar to resol resin, had sensibility for curing temperature.

According to previous study, at F/P ratio of the resol, ring substitution is

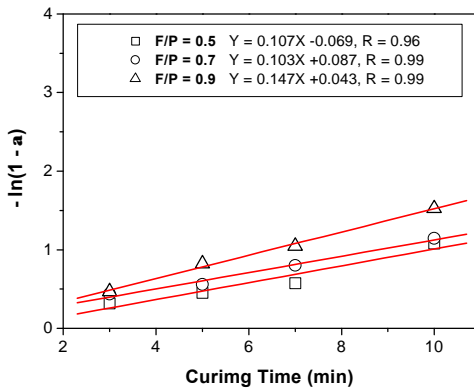


Figure 15. Isothermal vs $-\ln(1 - \alpha)$ hold time for the homogeneous first-order model at 170°C for novolac type.

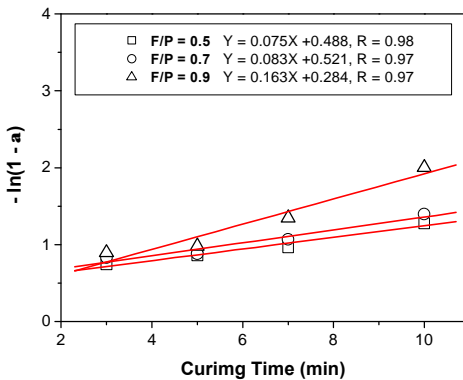


Figure 16. Isothermal vs $-\ln(1 - \alpha)$ hold time for the homogeneous first-order model at 180°C for novolac type.

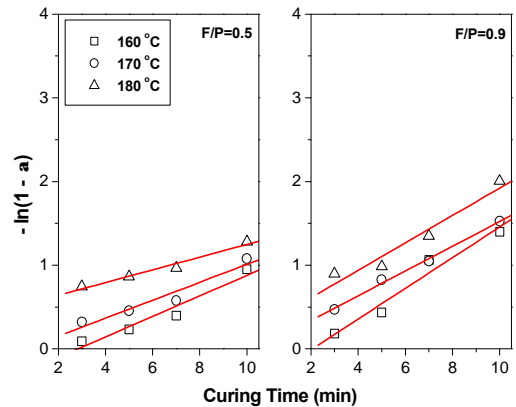


Figure 17. Comparisons of curing rate between F/P=0.5 and F/P=0.9.

favoured during resol synthesis at high F/P ratios, thereby causing the formation of methylene bridges during cross-linking.^[8]

This results show that an increase in temperature will cause the progression of the reaction to increase from the reaction rate.

The initial curing rate of resol and novolac resin was increased as the molar ratio of formaldehyde/phenol increased at specific curing temperature, as shown in other previous studies.^[6,12]

CONCLUSION

The curing behaviors of thermosetting phenolic adhesives, have been studied by FT-IR spectroscopy and also the obtained isothermal conversion-time data have been investigated.

The spectra show phenolic OH around 3300 cm^{-1} , and the diminishing in the OH peak of the phenolic resin may result in progressing of crosslinking between the phenolic oligomers.

The plots obtained from a plot of isothermal hold time vs $-\ln(1-\alpha)$ for the homogeneous first-order model experiments

performed for curing temperature were analysed by the integral method. The linear correlation, characterized by a high regression coefficient and a low intercept value, was observed at high temperatures and increased molar ratio.

Finally, the initial curing rate of resol and novolac resin was increased as the molar ratio of formaldehyde/phenol increased and as the curing temperature of resins increased.

Future works is that the mechanisms of accelerated hardening and networking induced by different molar ratio of hardener, different F/P molar ratio, and different curing conditions are needed.

ACKNOWLEDGE

"This work was conducted in part by Korea Research Foundation Grant. (KRF - 2000 - G00078)"

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