

# Evaluation of phenolic resins from one-pot microwave synthesis

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## Abstract

The characteristics of oxalic acid catalyzed phenolic resins, synthesized using the conventional heating method and by a one-pot microwave process, were evaluated and compared. Phenolic resins were produced in an autoclave with reflux times of 3, 5 and 7 hours, and by one-pot microwave synthesis at different power levels (176.364, 315.092, 453.820, 592.548W) for reaction times of 15–90 minutes. UV-vis spectroscopy and FT-IR analyses showed similarities in the characteristics of the resins synthesized by both methods. Concentration of residual phenol in the products decreased with reaction time. For the conventional method the decrease in phenol after an initial 3hrs of reaction were 4.3% (in 5hrs) and 22.3% (7hrs), while in microwave synthesis at a power level of 176.364W and an initial reaction time of 30mins the phenol decreased by 33.05% (in 60mins) and 91.61% (in 90mins). At a power level of 315.092W and an reaction time of 15mins it decreased by 36.3% (in 20mins), 16.5% (in 25mins) and 10.8% (in 30mins).

For resins from the conventional method, melting points increased with increasing reaction time 83°C, 97°C and 109°C for respectively 3hrs, 5hrs and 7hrs, and between 95°C and 103°C for resins from the microwave method at various power levels and reaction times. The FT-IR spectra analyses for the products showed strong similarity in characteristics, while the melting point data supported the GC-MS results that for the conventional method mostly the degree of polymerization depends on reaction time.

The substitution of phenol with cresol results in resins with improved hardness and melting points, but these differences were not obvious in the spectral characteristics. It was also observed that for the conventional heating method the melting points of the CF pre-polymers produced were higher than those of the PF prepolymers (119°C and 127°C for 3hr and 5hr CF). One-pot microwave synthesis was found to reduce the polymerization time significantly and produced resins with shorter gel times. Closest similarities in characteristics were found between resins heated in an autoclave for 7hrs and the resins made by one-pot microwave synthesis at reduced reaction times.

*Keywords: phenolic resins, microwave synthesis, GC-MS, FT-IR spectroscopy, prepolymers, condensation polymerization.*



## 1 Introduction

Phenolic resins, like other thermosetting resins, are very important because their use as engineering materials is increasing rapidly due to their good mechanical properties, high hardness, and excellent stability at high temperatures [1]. Traditionally, phenolic resins are synthesized by step-growth polymerization in an autoclave from phenol or substituted phenols with formaldehyde. The type of resin synthesized depends on the catalyst and the mole ratio of phenol to formaldehyde. The catalyst can be acid, base or neutral divalent metal such as Co, Mg, Zn, Cu or Ni. Figure 1 displays the reaction for the acid catalyzed formation of phenol formaldehyde (PF) which involves the hydrolysis of formaldehyde to methyl glycol. Phenolic resins prepared under acidic conditions are known as novolak, while resins prepared under basic conditions are called resoles [2–4].

Microwave chemistry applies microwave irradiation to chemical synthesis. Recent developments in microwave chemistry have provided scientists with a method of organic synthesis that is more efficient than traditional heating. Microwaves are a form of electromagnetic energy with wavelengths between 300-300,000 megahertz (MHz). Molecular rotation is a property that is affected within this region of electromagnetic spectrum however, molecular structure is not. Samples can be heated using microwave irradiation due to the wave-material interactions. These interactions transform electromagnetic energy from the microwave into heat through dipole rotation or ionic conduction. An important advantage that microwave-assisted organic synthesis has over conventional heating methods is that samples are heated rapidly in a homogeneous manner. Homogeneous heating creates higher yields and faster reaction times. This type of heating occurs in microwave synthesis because heat is generated within the reaction medium rather than being transferred from an external source [5–7].

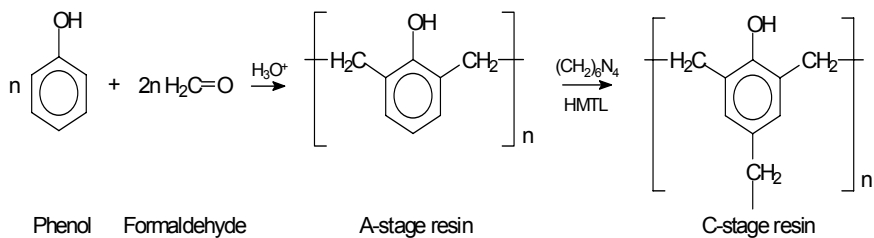


Figure 1: Typical reactions for formation of phenol-formaldehyde [2].

## 2 Experimental

### 2.1 Materials

The reagents used for the synthesis were formaldehyde solution (36.5 – 38% v/v) from VWR International, loose phenol crystals, oxalic acid from Fisher Scientific Company and liquid m-cresol (99% purity) from Alfa Aesar.

## 2.2 Resin synthesis

Acid catalyzed phenol-formaldehyde (PF) and cresol formaldehyde (CF) prepolymers were synthesized using molar ratios of phenol or cresol to formaldehyde of 1: 0.8. The PF prepolymers were produced in autoclave with constant stirring and reaction times of 3, 5 and 7 hours. They were also produced by one-pot microwave synthesis at different power levels (PL): 176.364W (PL1), 315.092W (PL3), 453.82W (PL5), and 592.548W (PL7), for reaction times ranging from 15-90 minutes. The CF prepolymers were synthesized in autoclave with constant stirring for reflux times of 3 and 5 hours.

## 2.3 Resins analysis

The Fourier transformed infrared spectroscopy (FT-IR) of the resins was obtained with a Nicolet spectroscopy, model 6700. The analysis conditions were 500 – 4000  $\text{cm}^{-1}$  spectral range, 10 scans, and a resolution of 4 $\text{cm}^{-1}$ . The samples were ground and vacuum pressed on KBr pellets of approximately 1mm thick.

The determination of residual phenol in the resins were made with uv-vis spectroscopy by phenol absorbance method. Figure 2 shows a plot of uv absorbance determined for the molar concentration of phenol in aqueous solution. The plot used as reference source for the evaluation of residual phenol in the resins.

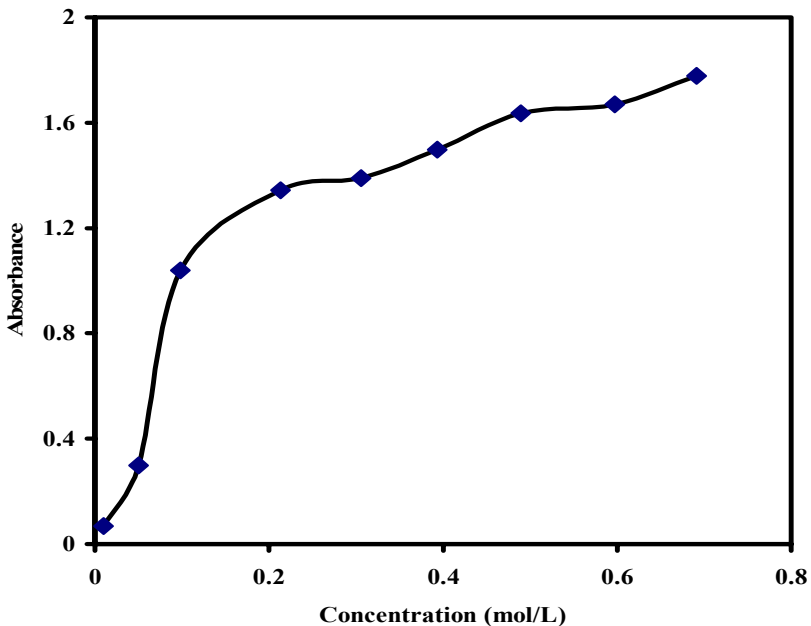


Figure 2: UV Absorbance versus concentration of phenol in aqueous solution.

Gas Chromatography Mass Spectrometry (GC-MS) using an ICB-WAX 30m x 0.25mm ID x 0.25 $\mu$ m film column (J & K Scientific, Milton, Ont., Canada) was used to monitor phenol residues. GC conditions were: initial oven temperature 80°C, hold 1min, and then 20°C/min to 250°C; injector temperature 225°C; MS interface temperature 280°C. Phenol eluted at 6.6min. Chromatographic Total Ion Current (TIC) peak height and peak area were used for quantification.

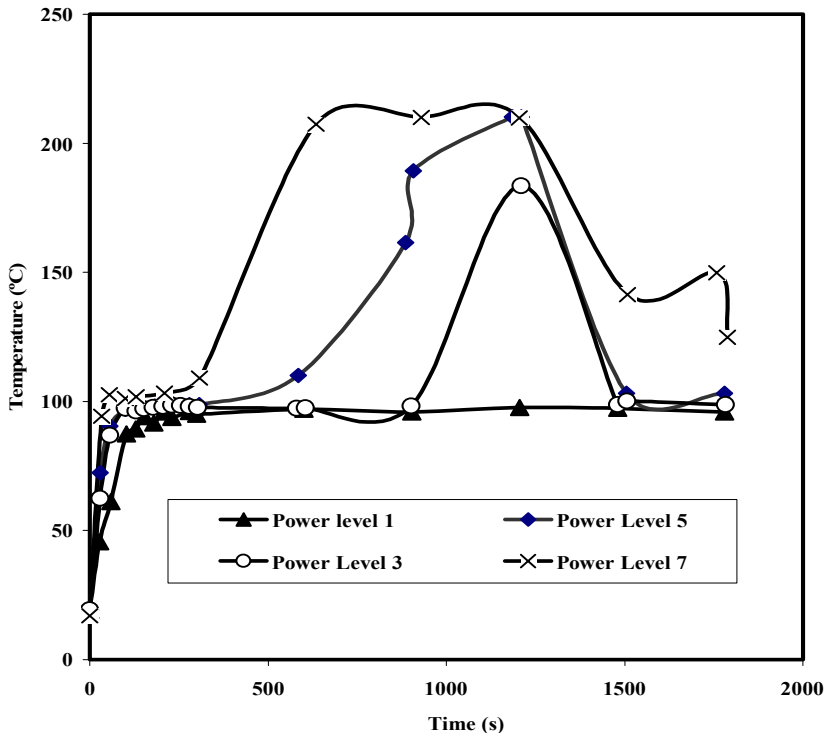


Figure 3: Relationship between time and temperature for 30min. microwave reactions of PF at different power levels.

### 3 Discussion of results

The temperature was recorded at regular time intervals throughout the microwave synthesis processes. Figure 3 shows the relationship between temperature and time for PF synthesized in 30 minutes at different power levels. For each power level the temperature rapidly increased within the first 60 seconds to about 100°C. After this period of time the temperature of the reaction mixture increased steadily at different rates depending on the power level in use, except for PL 1 which remained at 100°C throughout the duration of the reaction. The pattern of increase in temperature of the reaction was similar for the other

three power levels, peaking in 20 minutes at different temperatures. The temperature difference observed for different power levels has also been reported by Liao et al [8], who showed that the higher the power, the higher the temperature and different equilibrium temperature is reached for each power level.

Analyses from UV-Vis and GC-MS showed that the concentration of unreacted phenol in the products of PF prepolymers synthesized from one-pot microwave synthesis and conventional heating decreased with reaction time. Typical GC-MS chromatograms and spectra for phenolic resins using the conventional heating method for 7 hours and with microwave method for 30 minutes are compared in Figure 4. The decrease in phenol for the conventional method with an initial reaction time of 3hrs was by 4.3% (5hrs) and 22.3% (7hrs) as shown in Figure 5, while the decrease in phenol for the microwave synthesis of PF prepolymers at 176.364W after an initial reaction time of 30mins was by 33.05% (in 60mins) and 91.61% (in 90mins). At 315.092W after an initial reaction time of 15mins it decreased by 36.3% (in 20mins), 16.5% (in 25mins) and 10.8% (in 30mins). These trends are shown in Figure 6, and could account for the temperature profiles observed in Figure 3. The UV-Vis results are shown in Table 1.

The FT-IR spectra analyses of the m-cresol modified PF resins showed strong similarity in characteristics between the resins. Figure 7 demonstrates the spectra of three different resins synthesized by microwave method at reaction times of 30 minutes. The modified resins were rusty brown colour and highly viscous, which formed very brittle solids.

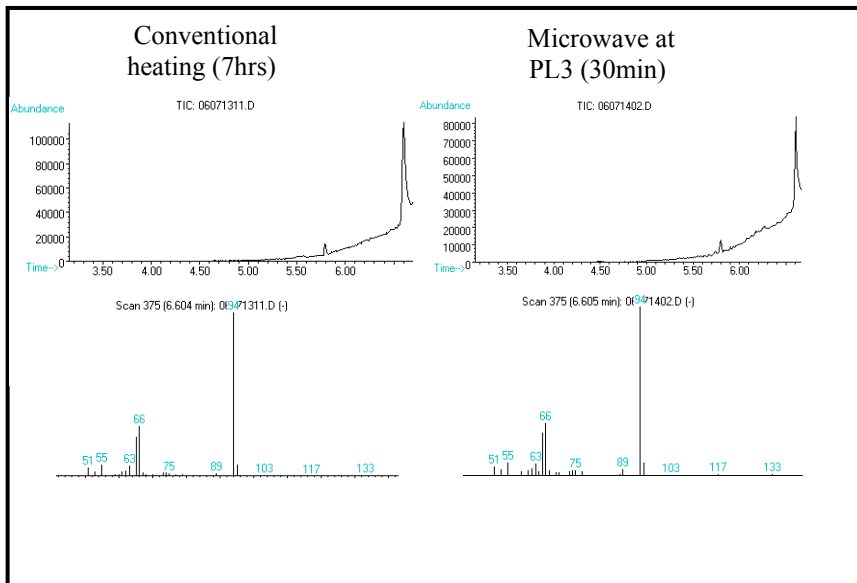


Figure 4: GC-MS chromatograms and spectra of residual phenol with two different synthesis techniques.

Table 1: Method, reaction time, and absorbance at 297nm of residual phenol obtained from UV-Vis analyses.

Microwave Energy	Reaction Time	Uv-vis absorbance	Residual Phenol (molar)
173.364W	30mins	1.139	0.122
	60mins	1.117	0.115
315.092W	15mins	1.222	0.147
	20mins	1.205	0.140
Conventional	3hrs	1.131	0.118
	5hrs	1.118	0.115
	7hrs	0.974	0.089

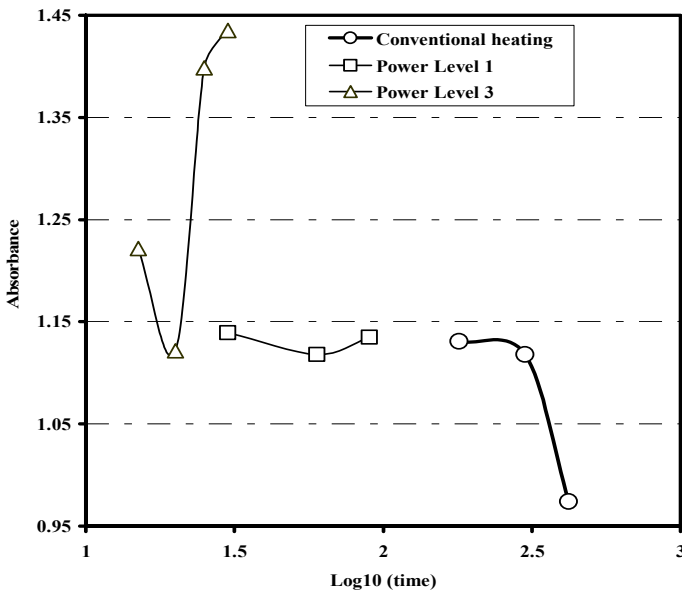


Figure 5: Comparison of absorbance of residual phenol with time at different process conditions.

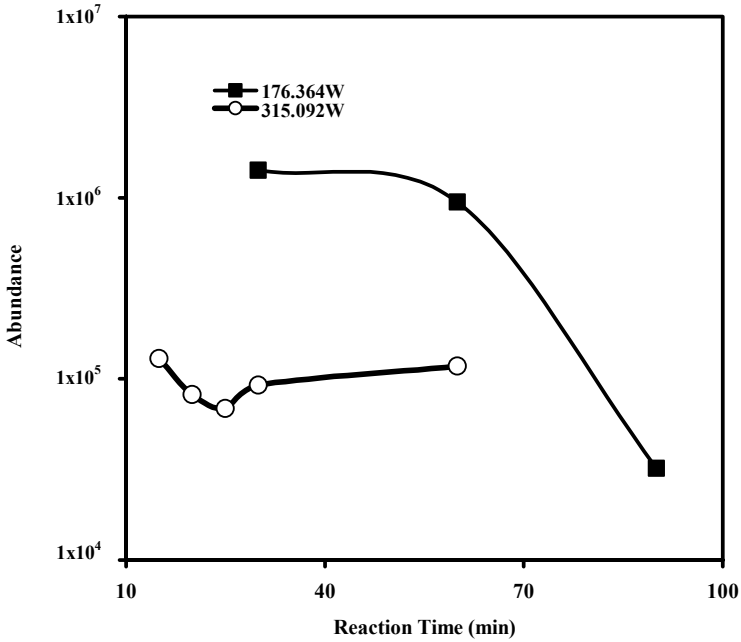


Figure 6: Relative abundance of phenol with reaction time for two power levels.

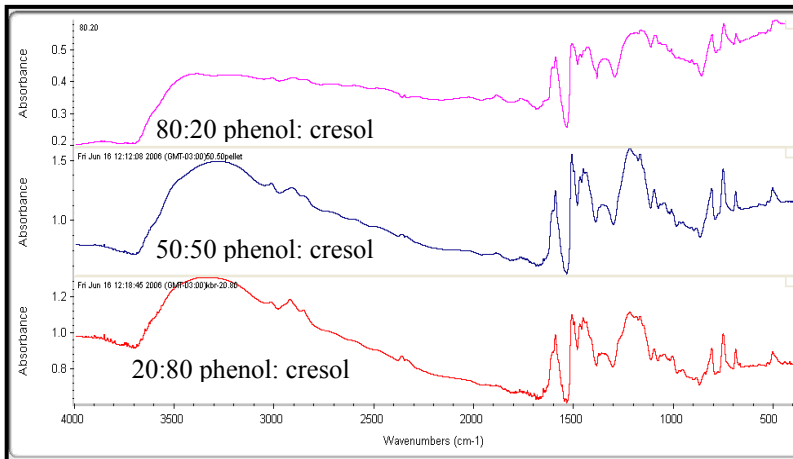


Figure 7: FT-IR spectra for cresol modified PF resins synthesized by Microwave irradiation method at 30 minutes reaction time.

The melting points of the PF prepolymers produced by the conventional heating method increased with increasing reaction time (83°C, 97°C and 109°C respectively for 3hrs, 5hrs and 7hrs). Melting points varied between 95°C and 103°C for the PF resins formed by microwave synthesis at various power levels and reaction time. It was also noted that the melting points for the CF prepolymers produced by the conventional heating method were higher than those for the PF prepolymers produced by the conventional method (119°C and 127°C for 3hr and 5hr CF).

The melting point data supported the GC-MS results that for conventional method mostly, the degree of polymerization depends on reaction time. Finally, close similarity in characteristics were found between resins heated in autoclave for 7hrs and the resins made by one-pot microwave synthesis at reduced reaction time.

## 4 Conclusions

Prepolymers of CF and PF, produced by the conventional heating method, have similar characteristics although PF prepolymers seem to be more malleable and have lower melting points. The degree of polymerization of phenolic resins produced by the conventional method depend on the reaction time and the strongest similarities between prepolymers produced in autoclave and by microwave synthesis is found between those produced by long autoclave reaction times and those produced by short one-pot microwave reaction times.

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