Synthesis and thermal properties of some phenolic resins

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SCIENTIFIC RESEARCH

ABSTRACT

Introduction: Phenolic resins have been in use since the early twentieth century and are considered the first class of synthetic polymers to achieve commercial success, moreover phenolic resins continue to succeed and attract special interest in a large range of industrial applications such as adhesives, paints, and composites; because of their unique physical and chemical properties. **Materials and Methods:** Prepolymers resol resins (RR, RH, RP, and RC) were synthesized by the reaction of phenolic compounds (resorcinol, hydroquinone, phloroglucinol, and catechol) respectively, with formaldehyde at molar ratio phenol/ formaldehyde 1/1.5, using sodium hydroxide as a catalyst. These resins were characterized by FTIR. The curing reaction of these resins was evaluated using differential scanning calorimetry (DSC), while the thermal stability study was evaluated using thermogravimetric analysis (TGA). **Results and Discussion**: From the results showing that these prepolymers have different curing temperatures and curing energy, while the TGA study showed that the cured resins have decomposition temperature more than 300 °C, and char residue at 650 °C more than 60%. **Conclusions:** These resol resins have different gel times (8-55) min, and viscosities (435-350) mpa.s. The curing temperature of these resin obtained from DSC curves was (120, 129, 105 and 127 °C), while the thermal behavior of the cured resins obtained from TGA curves showed that these cured resin have two decomposition temperatures and the rate of decomposition in the order of RC < RR<

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INTRODUCCTION

Phenolic resins are the oldest synthetic polymers used commercially around the beginning of the 20th century. These thermoset resins have typically been cured at high temperatures (130 - 170) °C and usually high pressures. Commonly, phenolic resins are used in a broad range of applications such as paints, adhesives and, composites [1, 2].

There are two types of phenolic resin; the resol type and novolac type depending on the method of synthesis and the catalysts used [3, 4]. Phenolic resin provides intermolecular hydrogen bonding as a domain driving force to interact with hydroxyl, carbonyl, amide, ester and other hydrogen bonding functional groups [5, 6]. Also, the characteristic of the phenolic resin is to be determined by its physical properties, thermal and electrical properties [7]. During the last century phenolic resin played an important role as engineering plastics, at the first commercialized synthesis resin, phenol formaldehyde (PF) resin became indispensable because of it is excellent mechanical properties, thermal stability and chemical resistance [8, 9]. Formaldehyde usually used as an aqueous solution between 35 and 40 wt% , is essential for the preparation of PF resin [10, 11].

DSC and TGA have been used extensively to characterize the curing process and thermal stability of some phenolic resin. This present study was designed to synthesize, characterize and study of some properties of the phenolic resin. In order to achieve this objective, DSC was chosen to follow the thermal behavior and the cure chemistry while TGA used to evaluate the thermal stability of cured phenolic resin prepared in this study.

MATERIALS AND METHOD

Phenolic compounds (Resorcinol, Hydroquinone, Catechol, Phloroglucinol) and formalin solution 35% were purchased from fluka Co. other analytical chemicals such as sodium hydroxide pellets, ethanol, methanol, hydroxylamine hydrochloride, and hydrochloric acid (98%) were obtained from Merck Co.

CHN elemental analysis:
The percent of carbon and hydrogen in the cured phenolic resins were measured using (Vario EL cube elemental analyzer).

Viscosity Measurements:
The viscosity of the phenolic resins (resols) prepared in this study was measured using Brookfield rotary Viscometer Type Alpha series code VI00002 with the spindle at 25±2 °C. An average value of three replicate measurements was reported.

Fourier Transform Infrared (FT-IR) Spectroscopy Test:
The FTIR spectra of cured phenolic resins were performed in Shimadzu, FTIR-8400S. Each spectrum was recorded in a frequency range of 400 – 4000 cm-1 using potassium bromide (KBr) disc. The KBr was previously oven-dried at 300 °C to reduce the interference of water.

Differential Scanning Calorimetry (DSC) Test:
DSC measurement was conducted on Shimadzu DSC-60. Dynamic scans were conducted in a temperature range of 25-350 °C, at a constant heating rate of 10 °C/min, under a nitrogen atmosphere at a flux rate of 20 mL/min. About 10-15 mg of uncured resin was used in an aluminum crucible.

Thermogravimetric Analysis (TGA):
TGA measurement was evaluated on TGAQ50V20.13Build39. The dynamic scan was

measured in a temperature range 25-700 °C, at constant heating rate of 50 °C/min, under a nitrogen atmosphere at a flow rate of 30 ml/min.

Free Formaldehyde Content:

The free formaldehyde content (FFC) of the prepared the resin is determined by the hydroxylamine hydrochloride method. Accurately weighted about 0.003-0.005 g of the resin sample was transferred into 250 mL beaker and dissolved in 50 mL of methyl alcohol. Simultaneously, the pH value of the solution was adjusted to 3.5 by adding 1 N hydrochloric acid solution. 25 mL of 10% Hydroxylamine hydrochloride solution was added and stirred for 10 min. Finally, the mixture solution was titrated with 0.1 N sodium hydroxide solution. Free formaldehyde content was calculated by:

$$\% \text{ FFC} = \frac{3C\,(V_1 - V_0)}{m}$$

Where "V_1, V_0" are volumes of sodium hydroxide solution required in the titration for sample and blank respectively. "C" is the exact normality of sodium hydroxide solution; "m" is the weight of the sample in grams.

Resin Solid Content:

The percent of resin solid content (S), was calculated by the following equation:

$$\% \text{ S} = \frac{S_1}{S_0} \times 100$$

Where S_0 and S_1 are the weight of the resin before and after dried (3 hrs. at 105 °C) respectively.

Synthesis:

Synthesis of resol resins[12] **(general procedure):**

Resol prepolymer resins (RR, RH, RP, and RC) were synthesized with F/P molar ratio 1.5/1 in the presence of sodium hydroxide solution as a catalyst, in 250 ml RB flask fitted with a reflux condenser, mechanical stirrer, and digital thermometer. The resin was prepared by mixing the required amounts of phenolic compounds (used in this study) with formaldehyde solution 35%. In the presence of 10% sodium hydroxide solution, the reaction mixture was stirred and heat at 90 °C for 1-1.5 hrs until the mixture became viscose, then the mixture cooled to ambient temperature and neutralized by 10% phosphoric acid solution. The product was isolated from an aqueous solution, and dried under vacuum oven to get brown viscose material samples from each prepolymer isolated to DSC study.

Curing of resol resin:

The curing of the prepared resol resins was made by heating the resins first at 70 °C for 5 hrs followed at 120 °C for 3 hrs and finally, post cure at 150 °C for 3 hrs in order to complete cure chemistry. A sample from each resin was taken for TGA study [13].
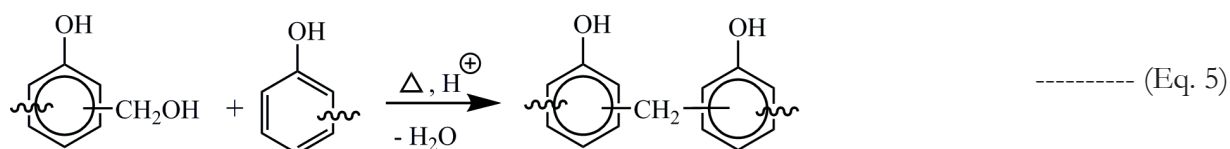
RESULTS

Reaction mechanism:

Typically, the resol is obtained at an F/P molar ratio more than one (excessive formaldehyde) with basic catalyst (eq. 1). Sodium hydroxide is the most often used catalyst, even though other base catalysts. The first step in resols polycondensation is the formation of phenolate ion and then electrophilic attack of carbonyl compound on the para- and ortho-position of a phenolate anion as shown in (eq. 2 and 3) [13].

OH → phenolate ion

---------- (Eq. 1)

---------- (Eq. 2)

O- methylol

---------- (Eq. 3)
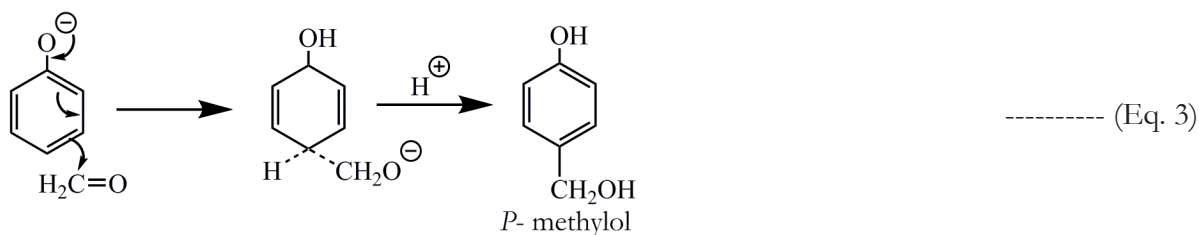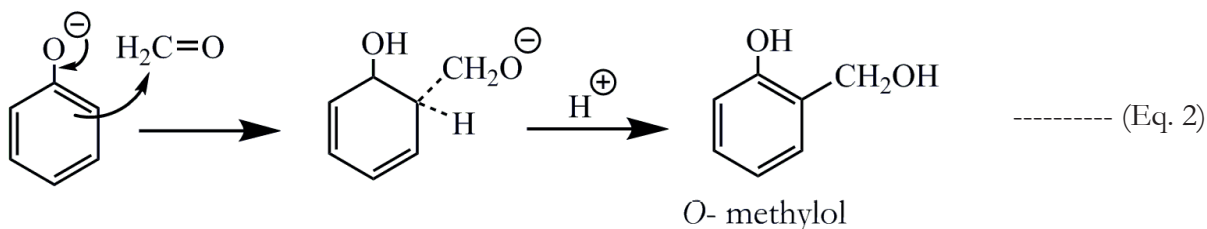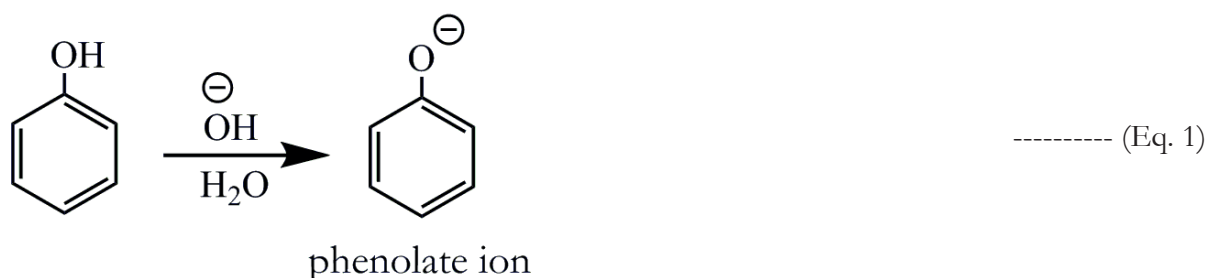
P- methylol

Sometime methylol groups can react to form dimethylene ether bridges under reactions with the generation of water according to (eq. 4) or methylol group reacts with the benzene ring to form methylene linkage (eq.5) [14]

$$2 \text{ —CH}_2\text{OH} \xrightarrow[- H_2O]{\Delta} \text{—CH}_2\text{OCH}_2\text{—}$$

---------- (Eq. 4)

$$\text{—CH}_2\text{OH} + \xrightarrow[- H_2O]{\Delta, H^{+}} \text{—CH}_2\text{—}$$

---------- (Eq. 5)
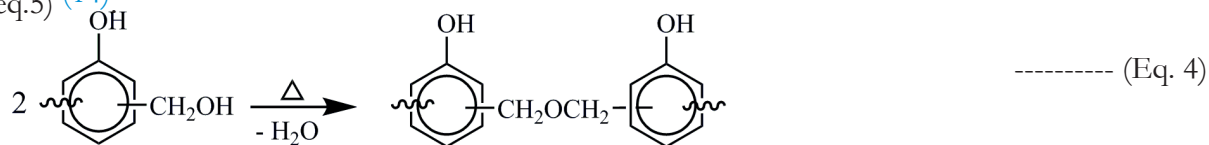
Then, the ether linkage (Eq. 4) converts after more heat under curing to methylene bridge with the generation of formaldehyde, as shown in (eq. 6).

$$\text{—CH}_2\text{OCH}_2\text{—} \xrightarrow[- CH_2O]{\Delta} \text{—CH}_2\text{—}$$

---------- (Eq. 6)
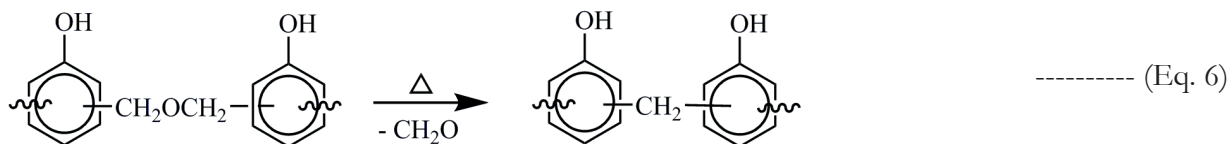
Here the reactivity of phenolic resin differs slightly due to the position of the hydroxyl group so the result of gel time and dry solid content is shown in Table 1. From the results, the gel time of resol resins prepared from resorcinol was less than other phenolic compounds. Also, the dry solid content of the resol resin of resorcinol was 69% which, is more than other phenolic resins due to more reactivity and more methylol groups present in their structures. The expected structure of the methylol resin prepared in this study are shown in Table 2, which indicated by CHN elemental analysis (Table 3).

Table 1. Some physical properties of resol resins.

Prepolymer No.	Free Formaldehyde Content %	Gel time (min) Loss of fluidity at 100 °C	Viscosity (mpa.s) at 25 °C ±2	Dry solid content (%) at 105 °C 3hrs.
RR	0.12	8	435	66.51
RH	0.15	22	333	41.28
RP	0.11	55	412	59.81
RC	0.17	21	387	49.32

Table 2. The expected structure of Resol Resins prepared in this study.
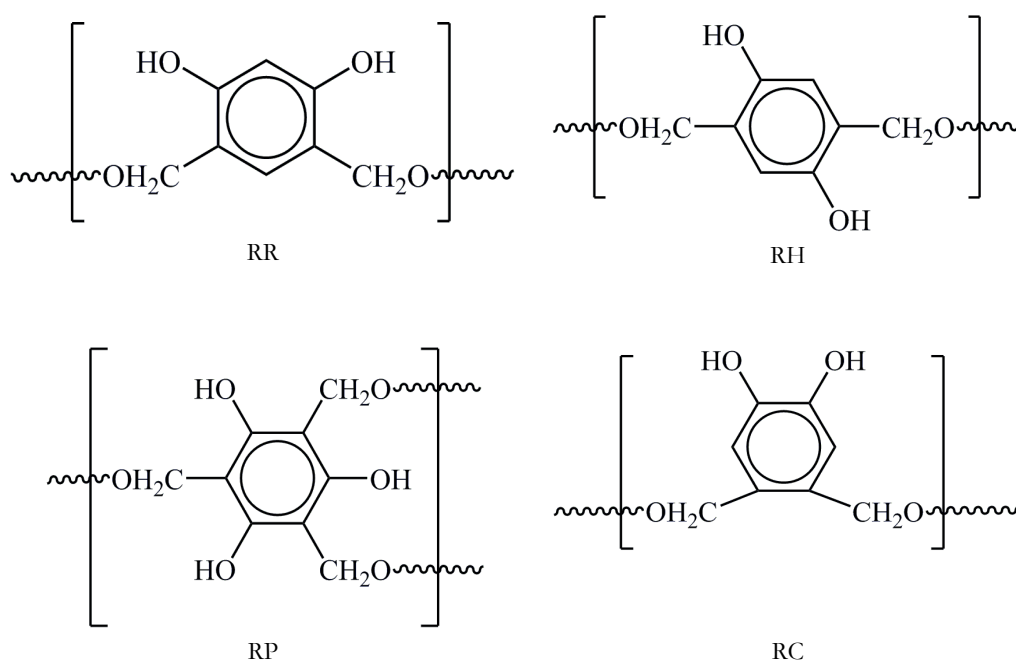
Table 3. CHN analysis.

Resin		Percent %	
		C	H
RR	theoretical	56.467	5.923
	experimental	58.600	4.900
RH	theoretical	56.467	5.923
	experimental	55.200	5.300
RC	theoretical	56.467	5.923
	experimental	58.800	5.500
RP	theoretical	50.001	5.594
	experimental	50.300	4.800

FTIR-analysis:

The FTIR spectra of prepared phenolic resin are shown in Table 4, while the spectra are shown in figures (1-4).

Table 4. Some characteristic band in cm⁻¹ of the prepared phenolic resin.

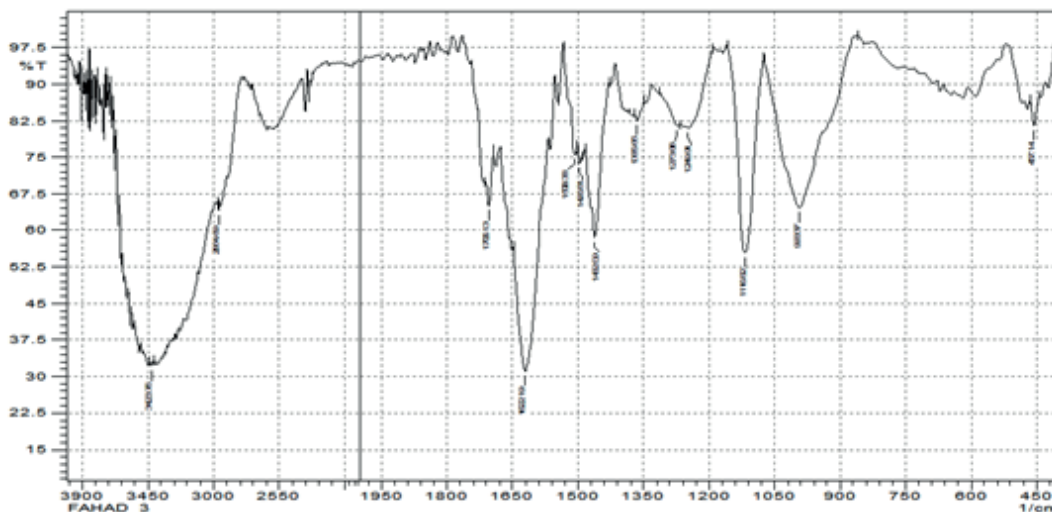| Resol resin No.	-OH group	-CH2- Aliphatic	-C=C- Aromatic	-CH2- bending	C-O bond	C-O-C bond
RR	3448 .84	2854.74 2926.11	1608 .76	147752	129235	1093 .57
RH	3417.98	2955.04 2889.46	1647.26	1435.09	1249.91	1116.82
RP	3423.76	2964.69	1622.19	1462.09	1249.91	1116.82
RC	3462.70	2951.19	1608.69	1442.80	1180.47	993.73

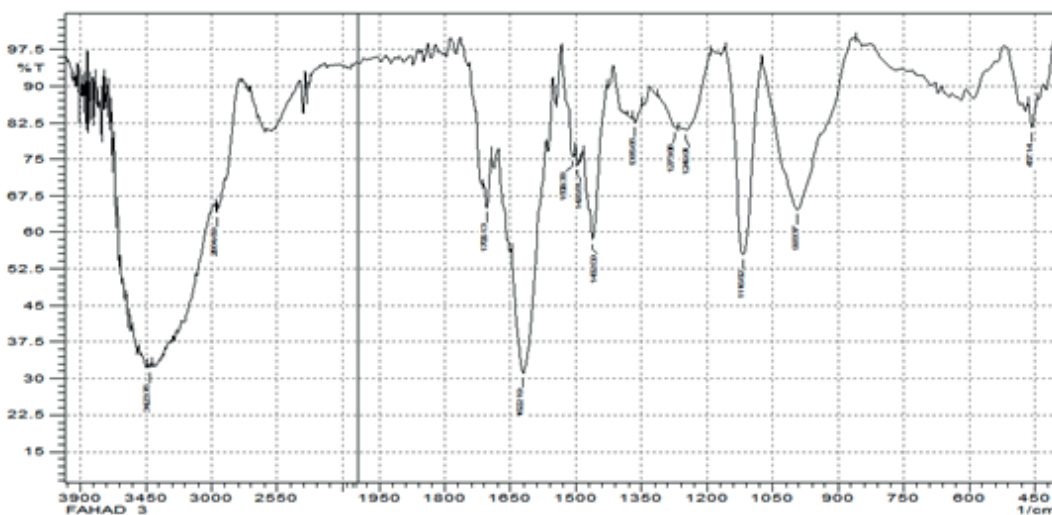**Figure 1.** The FTIR spectrum of the RR phenolic resin

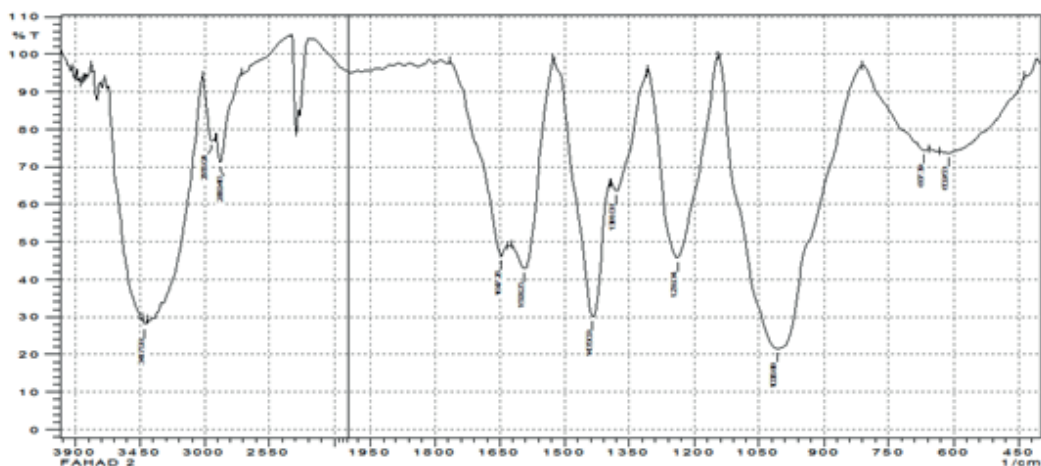**Figure 2.** The FTIR spectrum of the RH phenolic resin
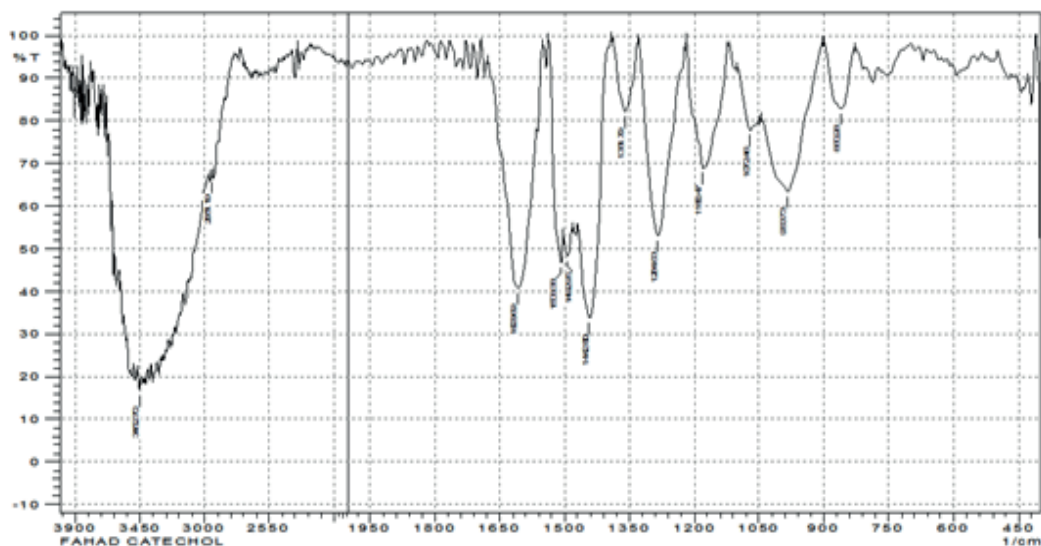
Figure 3. The FTIR spectrum of the RP phenolic resin

Figure 4. The FTIR spectrum of the RC phenolic resin

Thermal study:

TGA study:

The thermal stability of polymers is defined as the resistance of polymers towards thermal or thermo-chemical degradation [15, 16]. The thermal stability of any material can be expressed either as a function of temperature or as temperature, time limit. The thermal behavior of polymers can be investigated by several techniques such as thermal gravimetric analysis (TGA), differential thermal analysis (DTA), dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The thermal degradation of phenolic resin has been widely reported [17, 18]. Mainly, it focused on the chemistry of the main vola-

tile products. Different mechanisms for the degradation process and for a different range of temperature were proposed for some type of phenolic resin [19]. So the thermal degradation of the prepared phenolic resin occurs by scission of polymer chains forming some volatile compounds and residue products, and the percentage of char residue depends on the presence of aromatic structure in their polymer chains. Figures (5-8) show the TGA/DTG thermograms of four cured resol resins prepared in this study, while the thermal parameters obtained from these thermograms are listed in the Table (5 and 6) respectively.

Table 5. Some thermal parameter of cured resol resin obtained from TGA thermograms.

Polymer no.	Decomposition temp. °C	Temp. of 50% weight loss	Char residue at 650 °C	Rate of de composition %/min
RR	408, 549, 578	>700	72	0.023
RH	155, 313, 517, 574	>700	63	0.028
RP	374, 530	>700	68	0.024
RC	186, 346, 384	>700	81	0.015

Table 6. Weight loss percentage of the cured resol resins at different temperatures obtained from TGA thermograms.

Polymer no.	Weight loss % at 100 °C	Weight loss % at 200 °C	Weight loss % at 300 °C	Weight loss % at 400 °C	Weight loss % at 500 °C
RR	1.58	3.16	3.95	7.36	14.74
RH	1.32	2.37	4.47	12.50	20.00
RP	2.11	4.21	6.32	14.74	21.58
RC	0.33	1.70	3.50	8.00	16.30
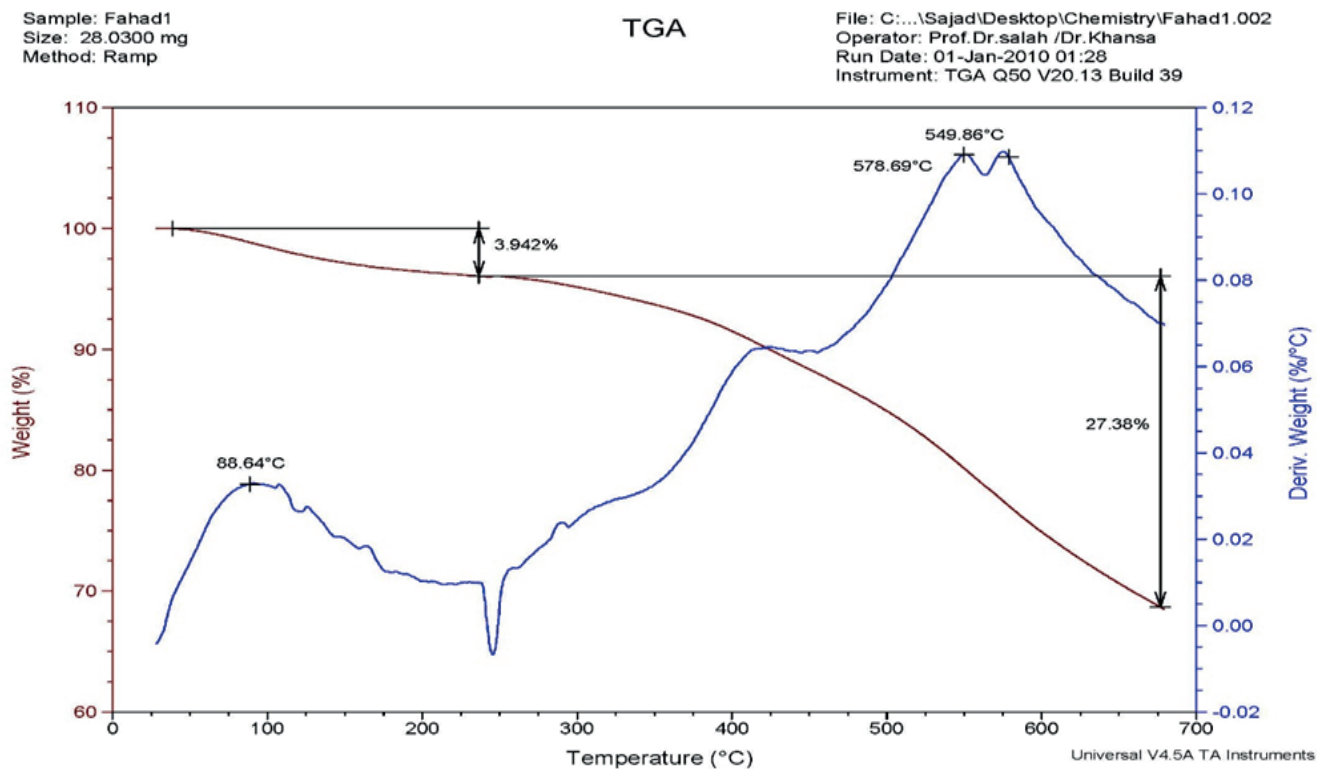
Figure 5. TGA/DTG thermogram of cured (RR) resin.
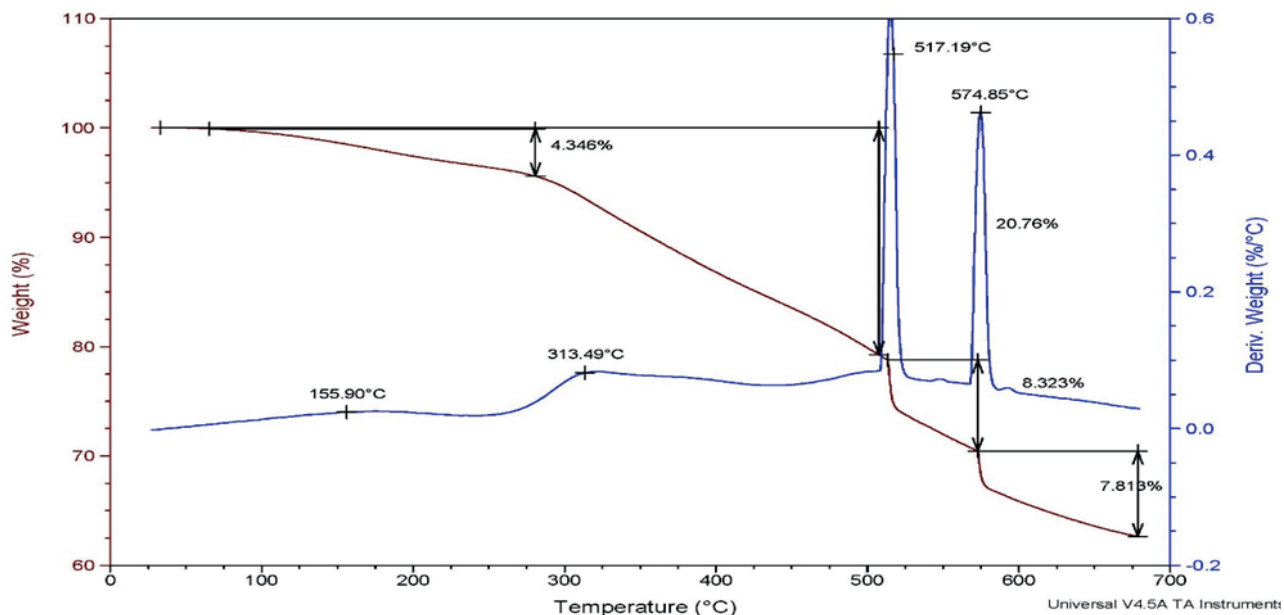
Figure 6. TGA/DTG thermogram of cured (RH) resin.

Figure 7. TGA/DTG thermogram of cured (RP) resin

Figure 8. TGA/DTG thermogram of cured (RC) resin.

DSC study:

DSC has been used extensively in the study of physical transformations and chemical reactions and chemical reactions of materials [20, 21]. The basi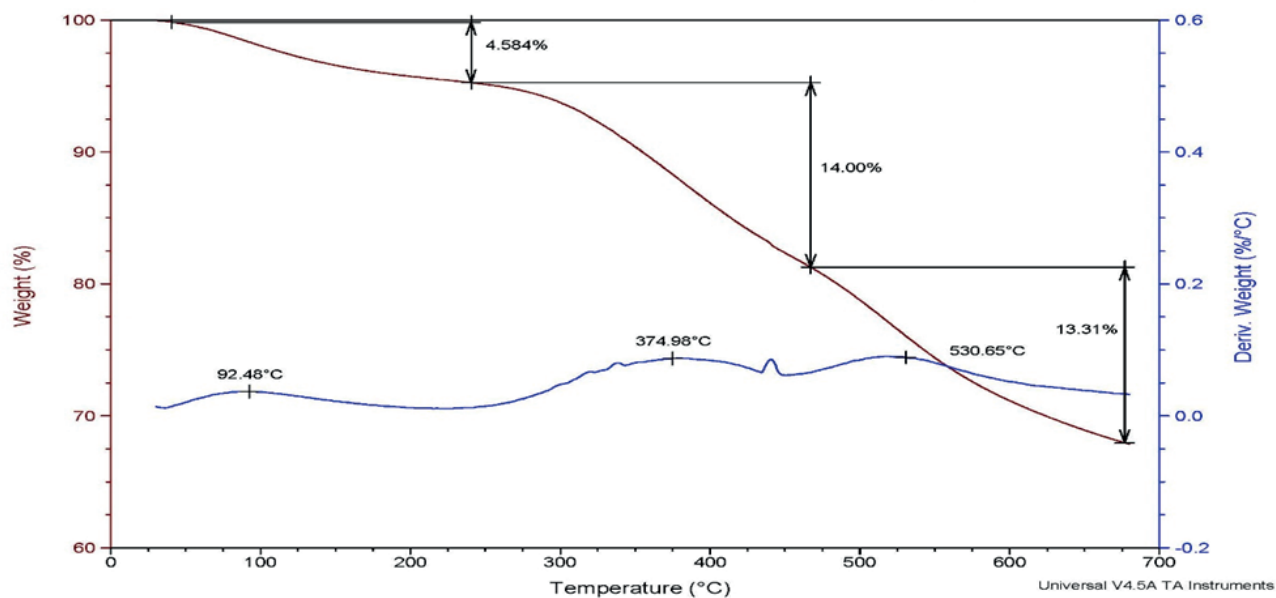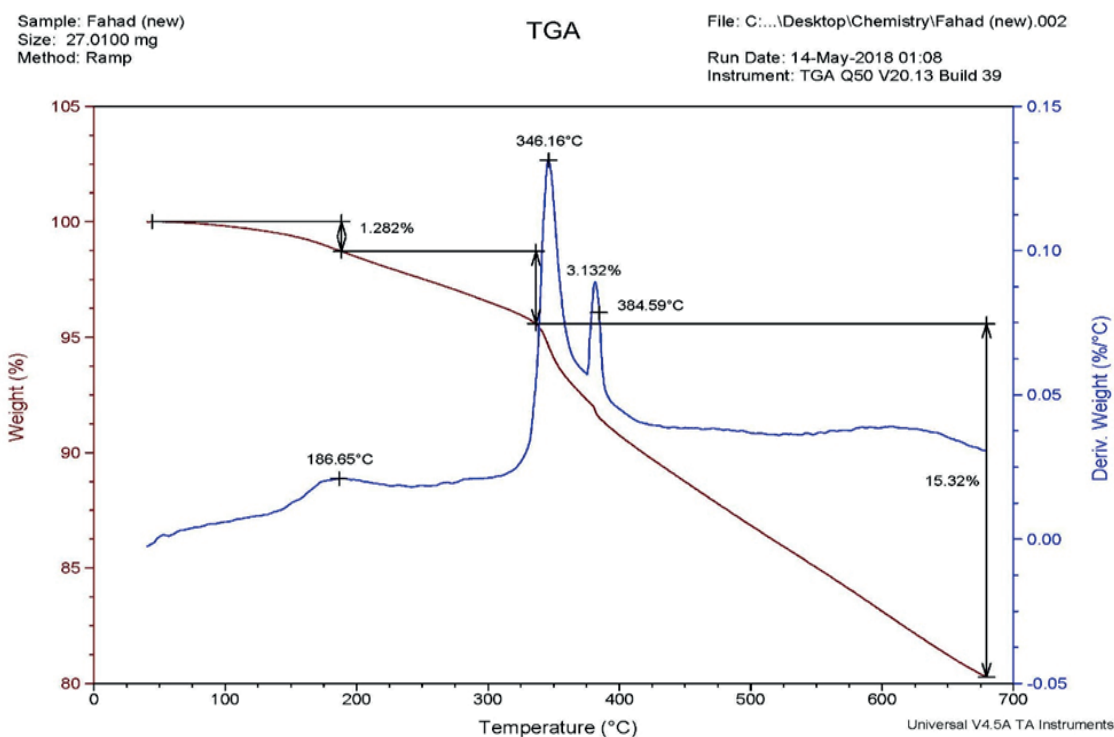c assumption for application of DSC to the cure of thermoset polymers is that the measured heat flow of the reaction as a function of the temperature. Several parameters can be detected from DSC measurements like curing energy of polymerization, the temperature of cure, enthalpy relaxation and glass transition temperature of cured polymers [22].

All DSC measurements were made on a Shimadzu DSC-60 with a single heating rate of 5 °C/min and a scanning temperature range from 25 to 350 °C. Analysis of the results of these dynamic scans is listed in the Table (7), while the thermograms curves of DSC for the prepared resol resins are shown in Figures (9-12).

Table 7. Thermal parameter of resol resins obtained from DSC thermograms

Resins no.	Onset temperatures oC	Cure temperature °C	Curing energy J/g
RR	101	120	340.71
RH	124	129	23.39
	157	182	158.31
			16.31
RP	114	105	3.77
	137	141	1.83
RC	121	127	17.02
	140	155	35.64
			128.01

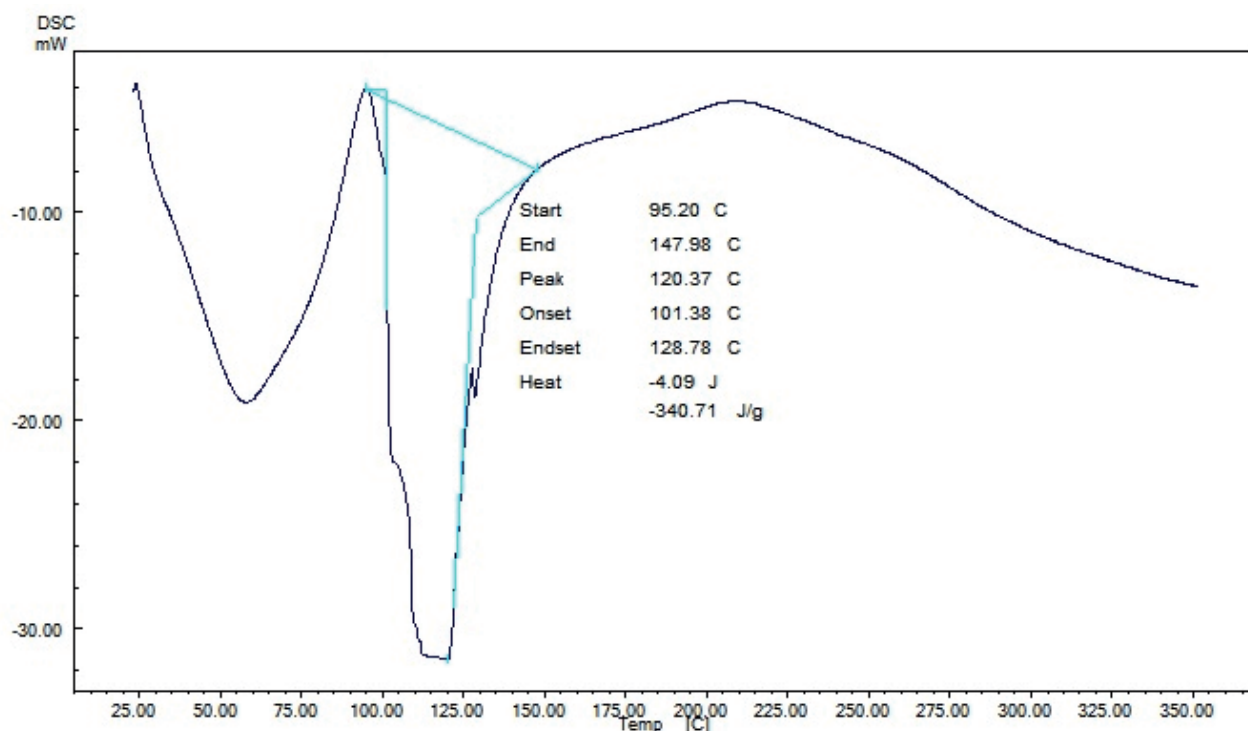**Figure 9.** DSC thermogram of uncured phenolic resin (RR)
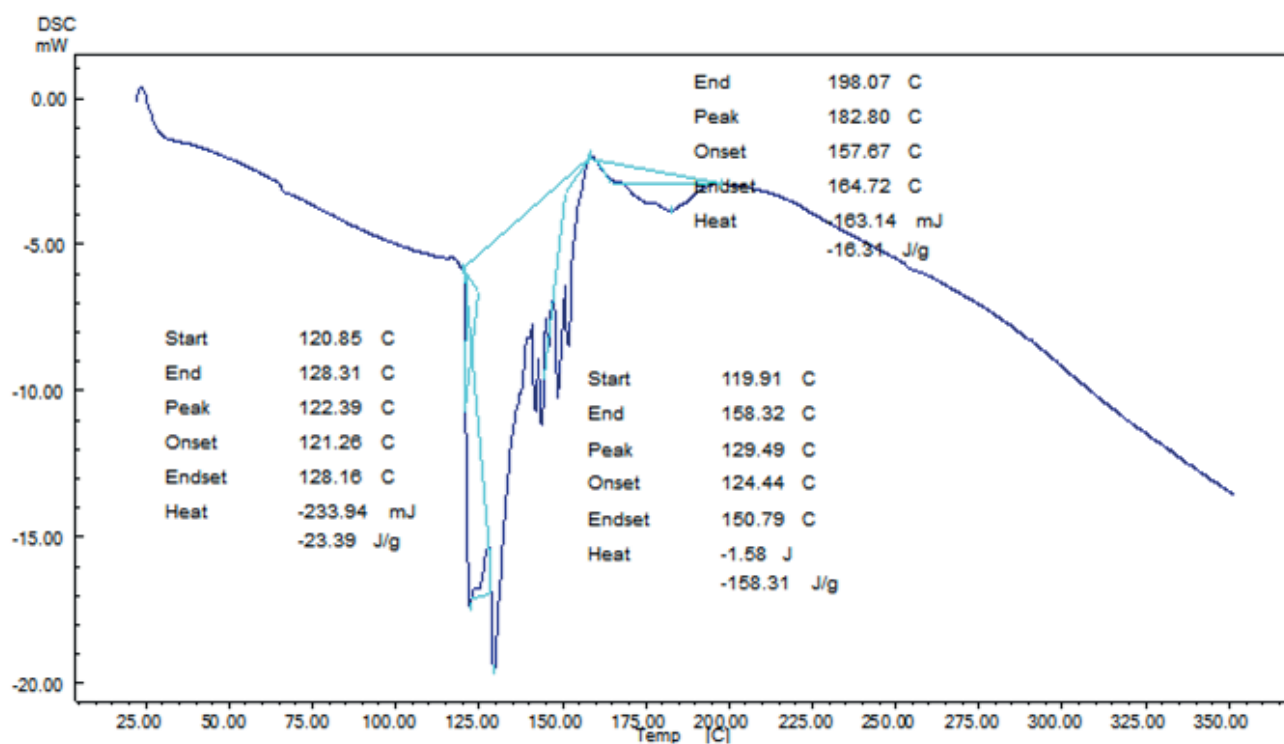
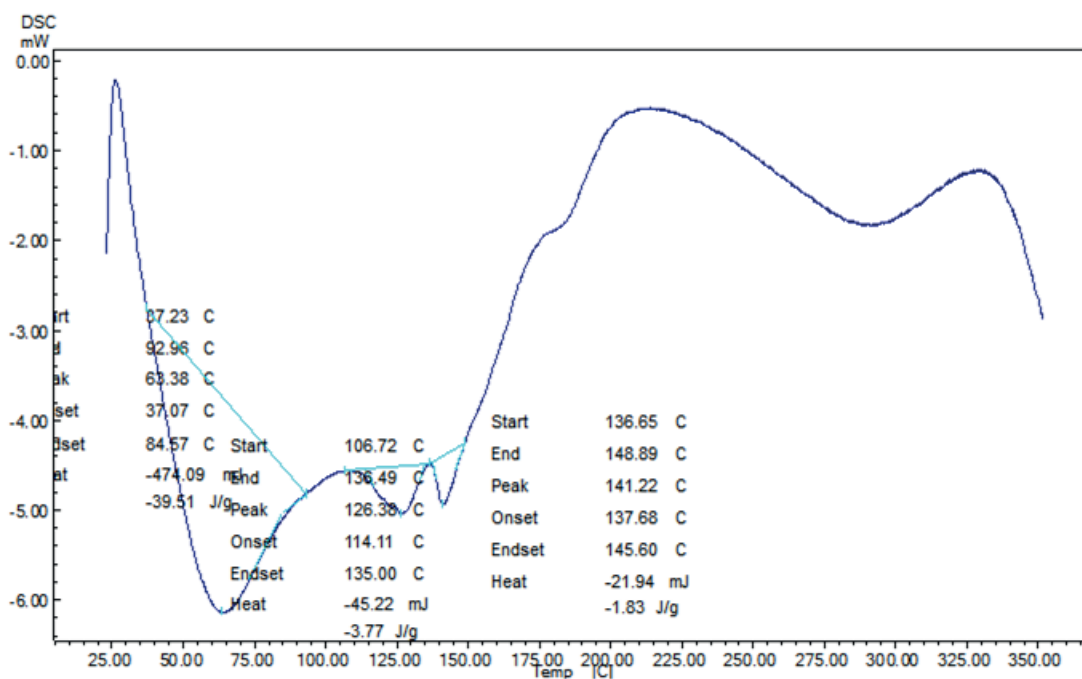**Figure 10.** DSC thermogram of uncured phenolic resin (RH).

DSC mW

rt 07.23 C
d 92.96 C
ak 63.38 C
set 37.07 C
dset 84.57 C
at −474.09 mJ
−39.51 J/g

Start 106.72 C
End 136.49 C
Peak 126.38 C
Onset 114.11 C
Endset 135.00 C
Heat −45.22 mJ
−3.77 J/g

Start 136.65 C
End 148.89 C
Peak 141.22 C
Onset 137.68 C
Endset 145.60 C
Heat −21.94 mJ
−1.83 J/g

Figure 11. DSC thermogram of uncured phenolic resin (RP).

DSC mW

Start 121.45 C
End 125.58 C
Peak 122.30 C
Onset 121.33 C
Endset 130.01 C
Heat −204.22 mJ
−17.02 J/g

Start 126.04 C
End 140.79 C
Peak 127.28 C
Onset 126.15 C
Endset 137.30 C
Heat −427.68 mJ
−35.64 J/g

Start 139.73 C
End 191.68 C
Peak 155.06 C
Onset 140.38 C
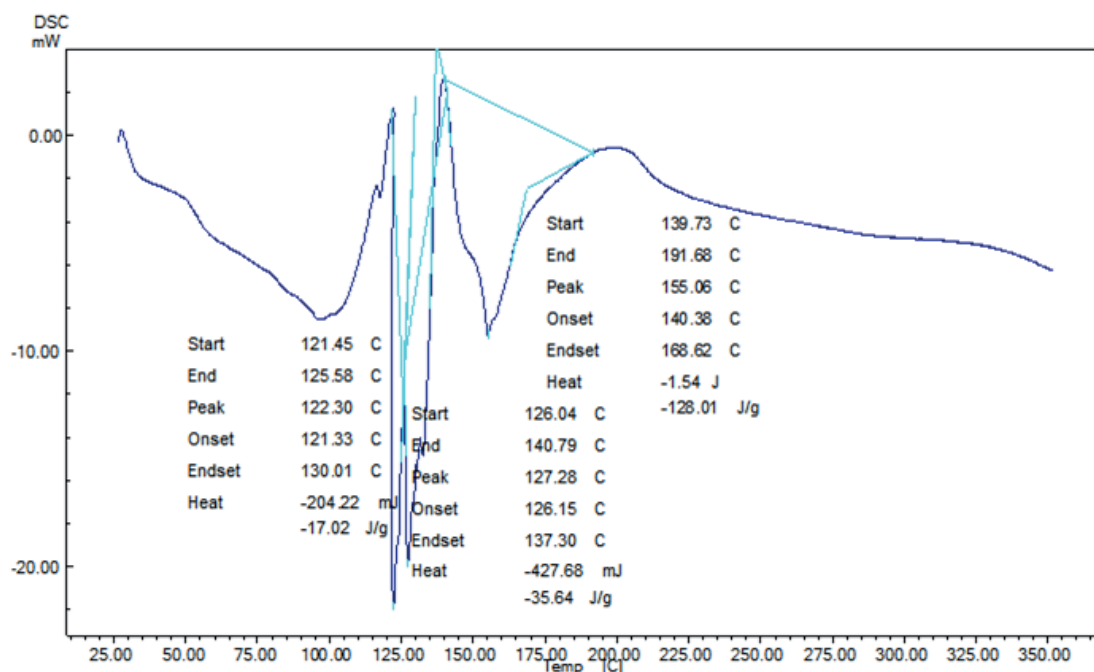Endset 168.62 C
Heat −1.54 J
−128.01 J/g

Figure 12. DSC thermogram of uncured phenolic resin (RC).

DISCUSSION

FTIR analysis:

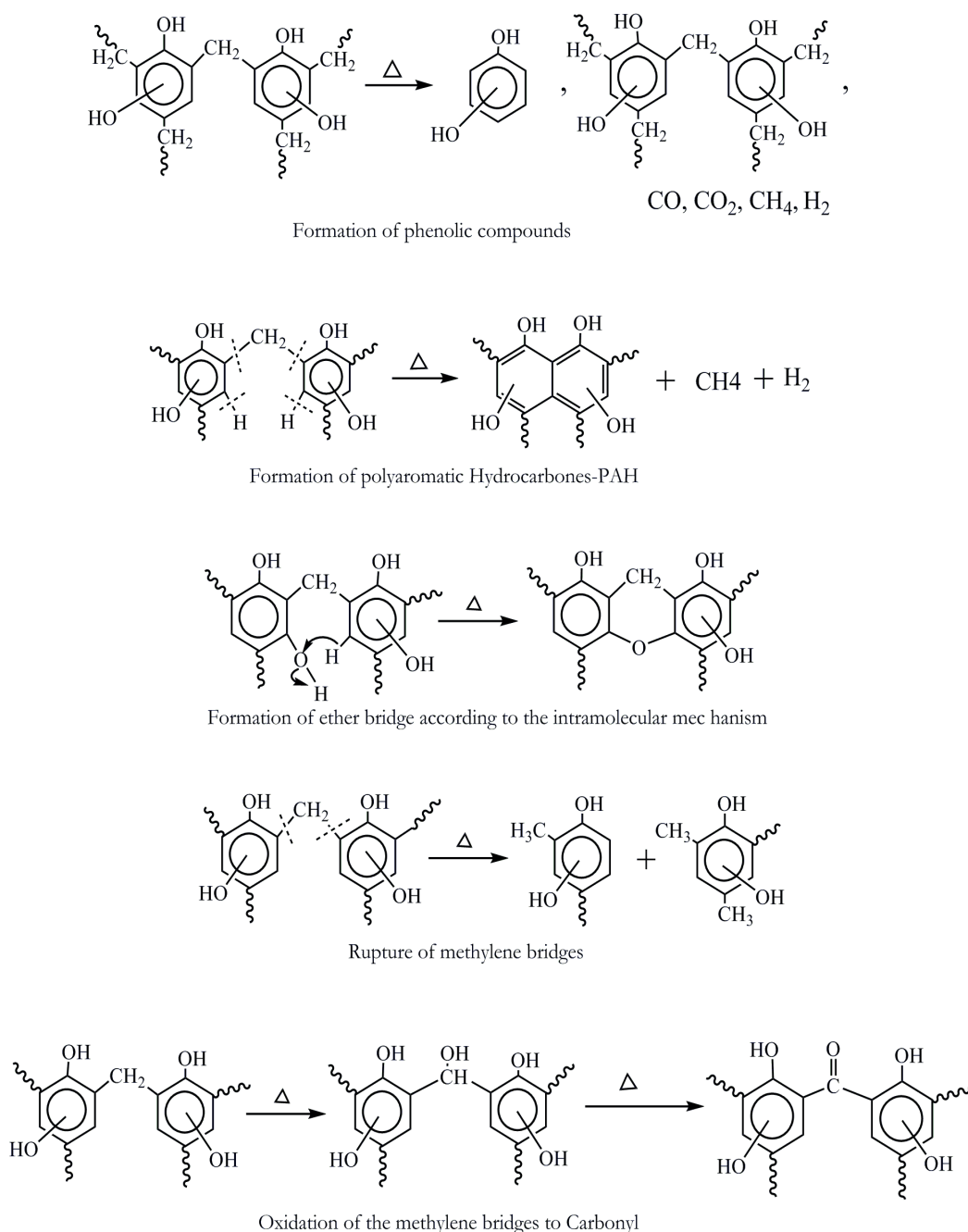From the result , the significant peaks was due to some stretch and bending vibration of functional groups present in their structure like hydroxyl group, aliphatic CH_2-group, C=C aromatic double bond and C-O and C-O-C stretching vibrations [23, 24]. The position of the peaks of those groups somewhat different for the prepared resol resins in this study due to the differences in their chemical environments.

TGA analysis:

From the result in Tables (5 and 6), it is possible to conclude that these resins have several decomposition temperatures more than 155 °C, while the char residue was more than 60% due to the formation polyaromatic hydrocarbons in the network structures and the trends of these resins are (RC > RR > RT > RH). On the other hand, the rate of decomposition of these resins is in the order (RC < RR < RP < RH). The general structures formed through the thermal degradation of the prepared phenolic resin in this study are as indicated in some literature [25, 26]. Most phenolic resins start by the rupture of methylene bridges (present through the polymerization of phenolic compounds with formaldehyde), followed by breaks in phenolic functions and finally the formation of the polyaromatic networks (which indicate the formation of char residue after thermal treatments). The expected mechanism of decomposition is shown in Scheme 1.

CO, CO_2, CH_4, H_2

Formation of phenolic compounds

Formation of polyaromatic Hydrocarbones-PAH

Formation of ether bridge according to the intramolecular mec hanism

Rupture of methylene bridges

Oxidation of the methylene bridges to Carbonyl

Scheme 1. The expected mechanism for the thermal degradation of

The general structures of degradation of the prepared phenolic resins start by the rupture of methylene bridges (present through the polymerization of phenolic compounds), followed by breaks in phenolic functions and finally the formation of polyaromatic networks (which indicate the formation of char residue after thermal treatments).

DSC analysis:

All the resol resins exhibit an endothermic peak during the curing under heat condition without using any catalyst.

From the result, the curing reaction of resol resins of the four phenolic compounds involved mainly two steps, first condensation reaction occurs between methylol groups of the adjusted polymer chains leading to the formation of the ether linkage as showing in eq. 7.

---------- (Eq. 7)
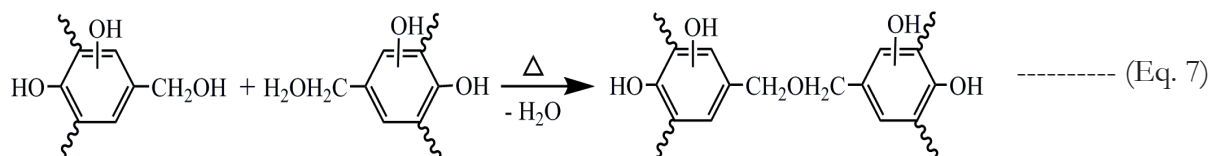
Another reaction takes place for the most phenolic resins (resols) [27]. During the evolution of formaldehyde under heating to the formation of methylene bridges as showing in eq. 8.

---------- (Eq. 8)
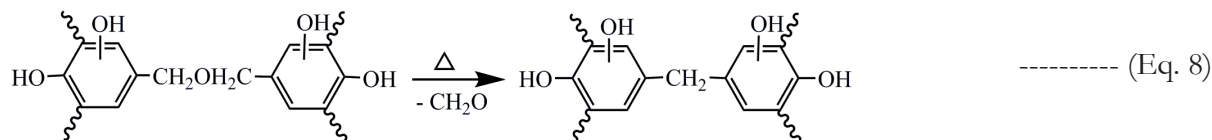
This reaction mainly occurs at a temperature of more than 120 °C. In this study, different curing energy will be obtained this lead to differences in the reactivity of phenolic compounds and also due to how much methylol groups present in their structures.

CONCLUSIONS

Phenolic resins (resol) were prepared through polycondensation of phenolic compounds with formaldehyde using sodium hydroxide as catalyst. These resol resins have different gel times (8-55) min, and viscosities (350-435) mpa.s. The curing temperature of these resin obtained from DSC curves was (120, 129, 105 and 127 °C), while the thermal behavior of the cured resins obtained from TGA curves showed that these cured resin have several decomposition temperatures, higher char content and the rate of decomposition in the order of RC < RR< RP<RH.

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