

Kinetics Study of(Phenol-Resorcinol-Formaldehyde) Resin

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Abstract

This study concern kinetic reactions of phenol-resorcinol-formaldehyde and compare to kinetic reaction of the polymer phenol- resorcinol-formaldehyde. The rate of reactions were followed through concentration variation as a function of time using hydroxylamine chloride at pH 4.12 . The result shows that the rate of polymer reaction increase with increasing of resorcinol concentration. This is due to presence of two hydroxyl which increase the electron density on the aromatic ring compared to phenol which contains only one active group .

In additions, the product has high glass transition which can be used as a temperature insulator.

1. Introduction

Phenolic resins comprise a large family of oligomers and polymers, which are various product of phenols, react with formaldehyde .They were versatile polymer materials with large range of commercial applications (Fukuda,et.al,1983) . Phenolic resin were prepared by reacting phenol or substituted phenol such as (resorcinol, cresol,....etc.) with

formaldehyde or other aldehydes such as(furfural, acetaldehyde,....etc) depending on the reaction conditions e.g. pH, the ratio of phenol to formaldehyde and temperature. (Ohta,et.al,1988).

Two types of phenolic resin were obtained : Novolac was derived from an excess of phenol with formaldehyde under neutral to acidic medium while reaction under basic condition

using an excess of formaldehyde resulted in resole (Borisov, et.al.1983). Phenolic resins were discovered by Baeyer in 1872 through acid catalyzed reaction of phenol and acetaldehyde. In 1891 Kleeberg found that resinous product could also be formed by reacting phenol with formaldehyde (Patel and Patel,1987). Where in 1906 Baekland granted patents describing base catalyzed resoles (known as Bakelite resins) and acid catalyzed novolac products (Patel and Patel,1987). Phenolic resins were a widely used as industrial materials because it has a good heat resistance, electrical insulation, dimensional stability and chemical resistance (Karo,1994-Megson,1958).

Many researches were carried out to improvement of phenolic resins properties ,especially heat resistance which is required particularly for industrial field . Also it has been found that these resin have many application such as floor and silt coverings, anticorrosion coatings, wood-particle adhesive, concrete-binders and used in graphitization (Megson,1972; Knop and Pilato,1985).

Several papers studied the kinetic reactions of phenol / formaldehyde (Mostawie,et.al.2008-Livant,et.al.1997),so in this study has been planned to kinetic study of (phenol /resorcinol-formaldehyde) reaction and to estimate the rate of reaction

2.Experemental

2.1.Chemicals

The chemical used in this study are:

1. phenol, Resorcinol , Hydrochloric acid, Hydroxylamine hydrochloride, from (BDH) company.
2. formalin solution(37-40)% ,Sodium bicarbonate from (H&W) company.
3. sodium hydroxide from (Fluka) company.

2.2. Instruments

-pH meter model pH M62

-FTIR model (8400) shimadzu company.

-DSC model (6100) shimadzu company.

2.3. Preparation of resins

2.3.1. Methylation of phenol and resorcinol
: (5g) of Phenol or resorcinol were dissolved in (50ml) of (0.1N) sodium hydroxide solution and the solution was kept at (60C⁰) for 75 min with continuous stirring using three neck round bottom flask equipped with thermometer , reflux condenser and mechanical stirrer.

In order to keep the pH-value of the reaction mixture constant during the reaction, a buffur solution was employed by using NaHCO₃ to adjust the pH-value at (4.12).

Then the reaction flask was placed in constant temperature bath,where the reaction was run induplicate at (30C⁰ ,40C⁰ , 50C⁰ and 60C⁰),then (2.1g) formaldehyde solution was

added; the time of the formaldehyde concentration was recorded .

Predetermined quantities from resorcinol and phenol as shows in table

2.3.2.Methylation of Copolymer resorcinol- phenol-

(1) were dissolved in 50ml (0.1N) sodium hydroxide at 60C⁰ .

formaldehyde(50%w/w):

Table (1): The components of the resorcinol phenol(R),phenol(P),and RPF(50%).

Compound	wt (g)	NaOH(g)	NaHCO ₃ (g)	Formaldehyde(g)
Resorcinol	5	0.6	0.5	2.1
phenol	5	0.83	0.6	6.5
R/P	5.5	1.6	1.5	8.6

2.3.3. The concentration of formaldehyde in the solution was measured periodically during the reaction time adopting the literature (8) procedure as following:

.The solution was titrated (using (0.5 N)to PH of (4.12) by using (0.5 N) NaOH) .The formaldehyde concentration was calculated as:

(5 ml) of reaction solutions were removed at predetermined time intervals during the reaction and add to (2.5 ml) beaker followed by dilution with (50 ml) of cold distilled water

$$\text{meq. of NaOH} = \text{meq. of HCl} = \text{meq. of formaldehyde}$$

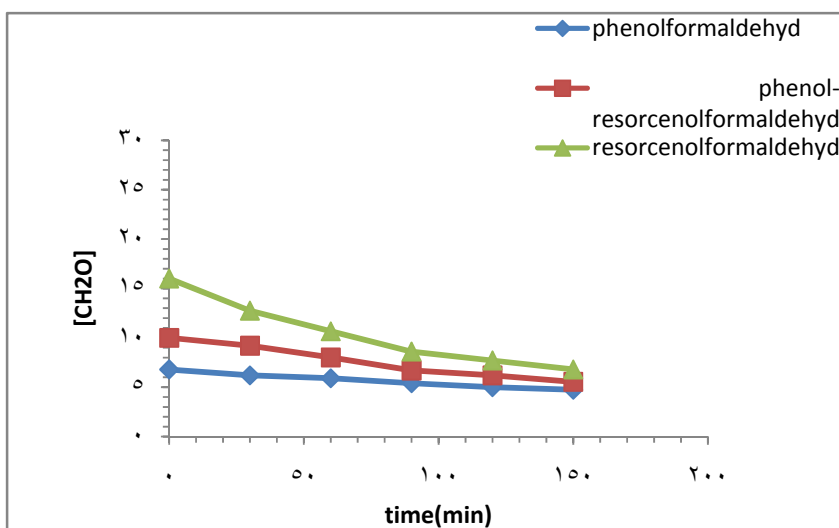


Fig. (1): The variation of formaldehyde concentration with methylation time of phenol formaldehyde , resorcinol formaldehyde and copolymer phenol-resorcenol formaldehyde resin at 30 C⁰.

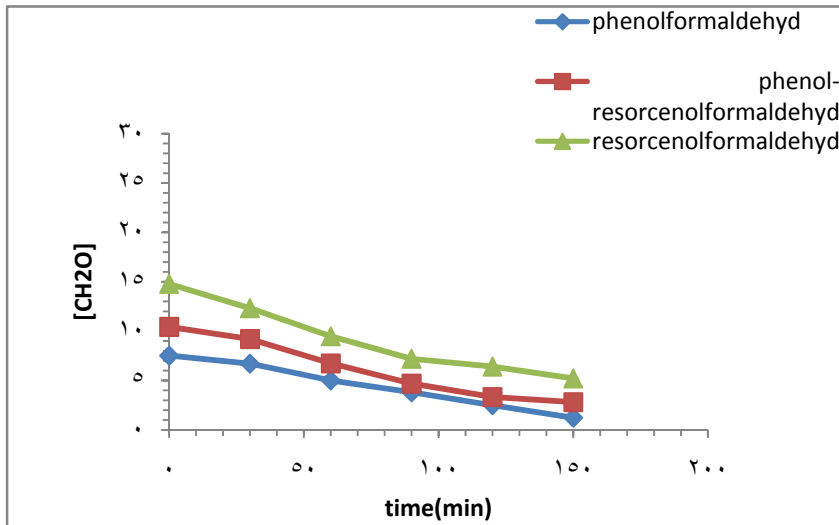


Fig. (2): The variation of formaldehyde concentration with methylolation time of phenol formaldehyde , resorcinol formaldehyde and copolymer phenol-resorcinol formaldehyde resin at 40 C °.

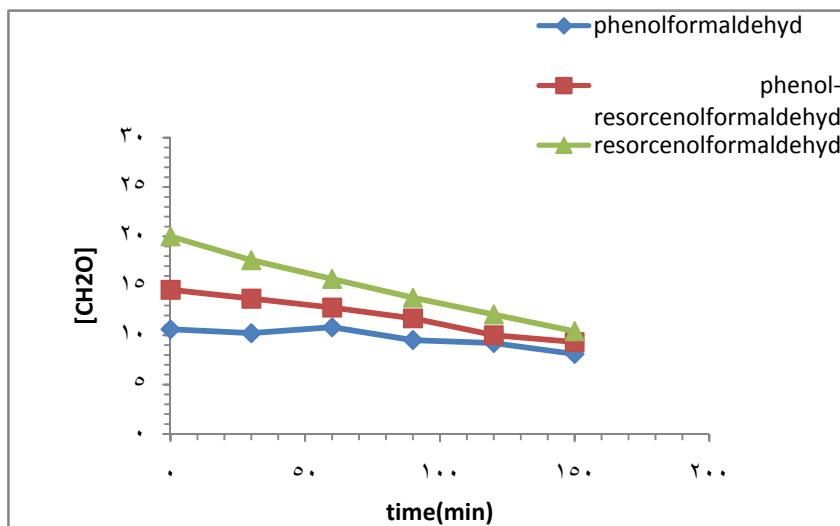


Fig. (3): The variation of formaldehyde concentration with methylolation time of phenol formaldehyde , resorcinol formaldehyde and copolymer phenol-resorcinol formaldehyde resin at 50 C °.

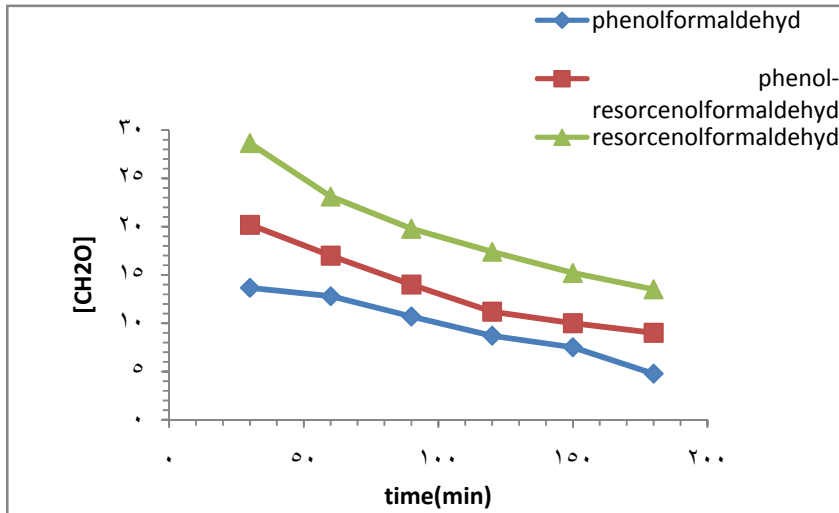


Fig. (4): The variation of formaldehyde concentration with methylation time of phenol formaldehyde , resorcinol formaldehyde and copolymer phenol-resorcenol formaldehyde resin at 60 C °.

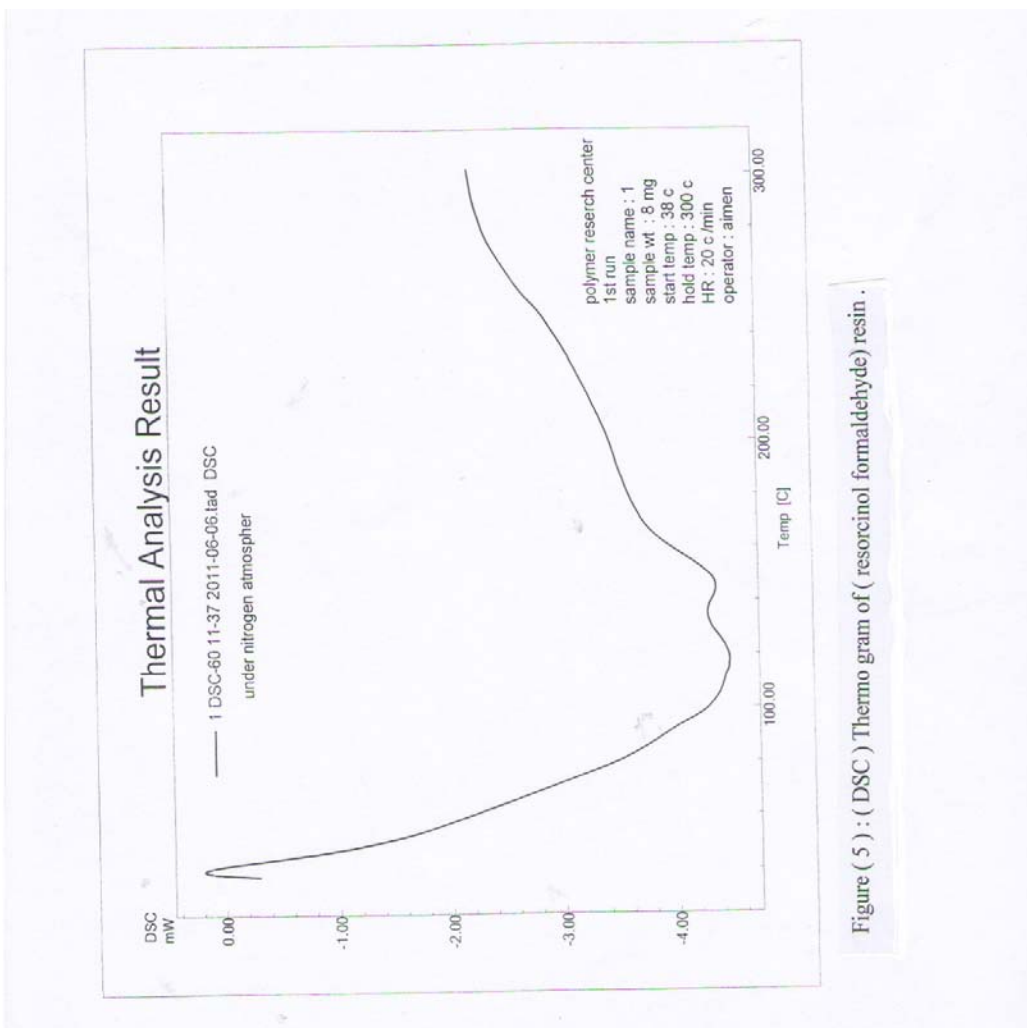


Figure (5) : (DSC) Thermo gram of (resorcinol formaldehyde) resin .

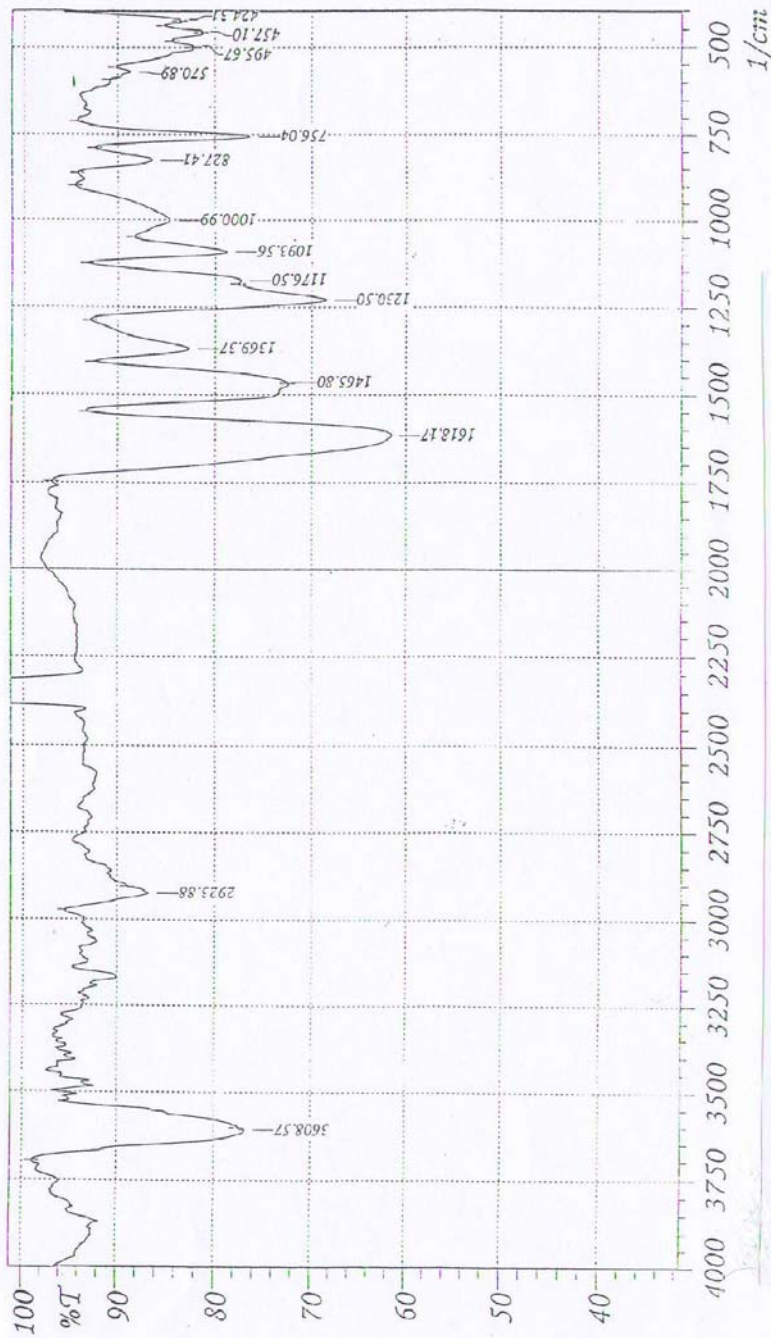
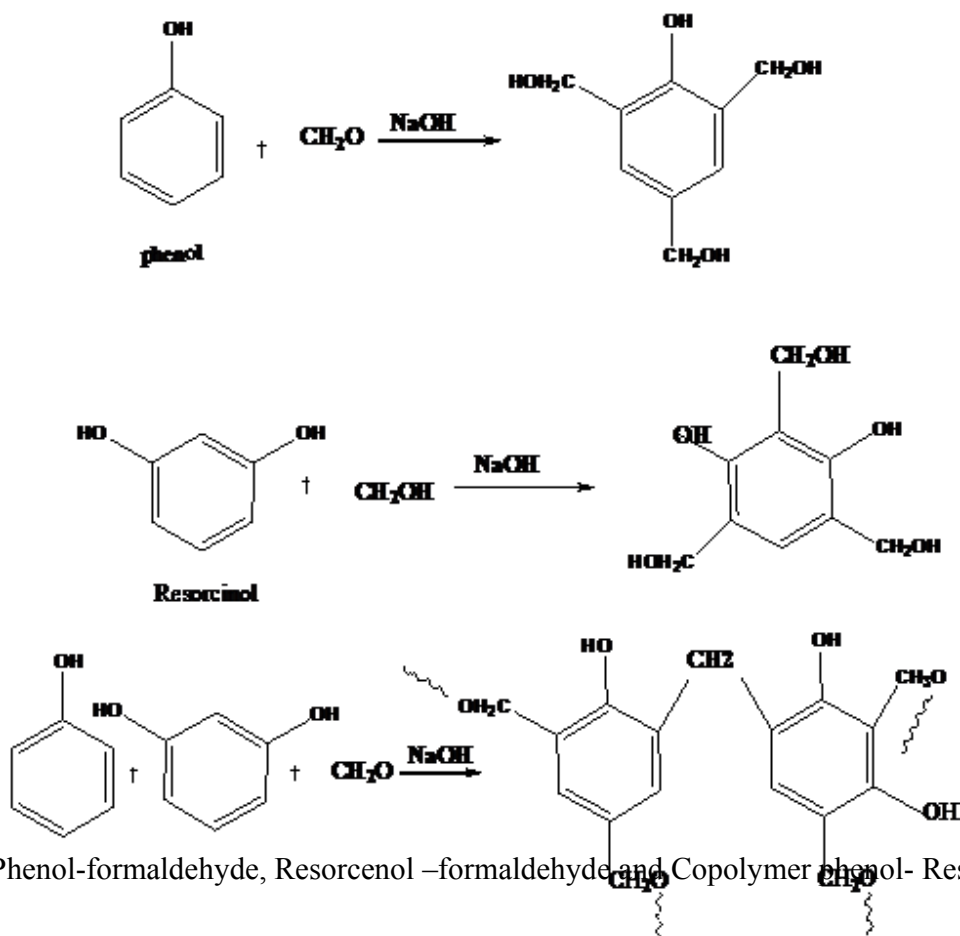


Figure (6) : FTIR spectrum of (resorcinol formaldehyde) resin .



Scheme(1): Phenol-formaldehyde, Resorcinol –formaldehyde and Copolymer phenol- Resorcinol Resin.

4. Results and Discussion

Phenol and its derivatives react with formaldehyde in the presence of acid or base catalyst to form phenolic resin or phenol formaldehyde resin, and their reactivity with formaldehyde depend on the chemical structure of the phenol compounds and the number of hydroxyl group on the benzene ring . This study concern reactive of phenol , Resorcinol , and mixture of (phenol-resorcinol)was reacted with formalin solution 35% in the presence of sodium hydroxide as catalyst, The reactions

followed by two points ,first evaluation of the formaline concentration and the second is the time of the reactions.

The results as shown in Fig's(1-4),the concentration of formaline decrease in the case of resorcinol more than those of phenol and (phenol –resorcinol), which is attributed to more reactivity of resorcinol due to the presence of two active hydroxyl group on the benzene ring as shown in scheme(1) .

Also the results show that the trend of decreasing of formalin in all cases decrease

with increasing the time of reactions nearly complete due to the Methylation reaction, which increasing with time.

On the other hand the Differential Scanning Calorimetry (Fig.5) study of the product obtained from the reaction of resorcinol with formaline at around 148 C° which due to the glass transition temperature (T_g), this higher of (T_g) indicates that the polymer is highly cross linked and the product is infusible and non soluble in most organic solvent .

Finally the consume of formalin concentration increase with increasing temperature.

Fig (6) shows that the FTIR spectrum of (resorcinol-formaldehyde)resin , which indicates that methylation occurs during the reaction , i.e. presence of absorption band at 3608 cm^{-1} attributed to hydroxyl group of (CH_2OH),

and absorption band at 1618 cm^{-1} due to aromating benzene ring and finally absorption band at 1093 cm^{-1} due to (C- O- C) ether link .

5.Conclusion

From this study we conclude that :

Firstly , the reaction of resocinol with formaldehyde .

Secondly, the concentration of formaldehyde decrease with increasing the reaction times ,also the product has

higher glass transition temperature which is a good indication of high thermal stable polymer .

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دراسة حركية التفاعل للبوليمرات المشتركة فينول- ريسورسينول- فورمالديهايد

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المستخلص:

تم في هذا البحث دراسة حركية التفاعل بين الفينول- والريسورسينول – والفورمالديهايد، وقورنت بحركية التفاعل للبوليمر المشترك فينول- ريسورسينول – فورمالديهايد، حيث تمت دراسة سرعة التفاعل من خلال متابعة التغير في تركيز الفورمالديهايد كدالة الى الزمن وذلك بأستخدام مادة هيدروكسيل امين كلورايد بدالة حامضية 4.12 ، ومن النتائج تبين ان سرعة التفاعل للبوليمر المشترك تزداد مع زيادة تركيز الريسورسينول بسبب وجود مجموعتين هيدروكسيل تزيد من الكثافة الالكترونية على الحلقة الاروماتية مقارنة مع الفينول التي تحتوي على مجموعة فعالة واحدة.

ولوحظ إضافة الى ذلك ، أن الناتج له قيمة عالية لدرجة الانتقال الزجاجي مما يعزز تحمله للدرجات الحرارية العالية واستخدامه كبوليمرات عازلة للحرارة .