



SYNTHESIS, CHARACTERIZATION, CURING, AND BIOCIDAL ACTIVITY OF PHENOL-ALDEHYDE RESIN

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ABSTRACT

A series of Phenol-Aldehyde novolac resins were synthesized by the reaction of phenols and aromatic aldehydes (2:1 ratio) in acidic medium. The afforded resins were further cured with hexamethyltetraamine (HMTA). They all were characterized by spectroscopic and thermal analysis. Biocidal properties of the products were also investigated.

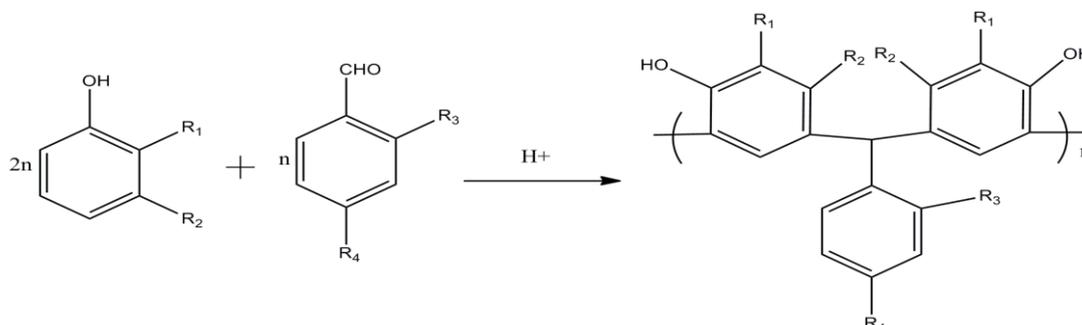
KEYWORDS – Biocidal, Curing, Hmta, Novolac, Phenol-Aldehyde, Resin

1. INTRODUCTION

Despite the discovery of novolac resins more than a century ago by Baekeland,[1] there has been continued interest in this field among researchers till date.[2][3] Much of the earlier work was devoted in the domain of resins derived from phenol and formaldehyde as starting materials for their potential applications[4] and properties. For example, Manasse et al. suggested that formaldehyde reacts in alkaline solution as methylene glycol or undergoes acetal addition with subsequent rearrangement of the hemiformal. The similar suggestions

were also made by Tollens et al. and Baekeland. A perusal of literature, however, suggests that very scarce reports were available on the use of substituted monomers such as.

Herein, we reported the synthesis and characterization of novolacs based on substituted phenols and substituted aromatic aldehyde, as shown in scheme 1. The resins thus obtained were cured with HMTA at elevated temperature.



2. RESULT AND DISCUSSIONS

2.1. Material

All the chemicals used were of analytical grade. Conventional methods purified the solvents and monomers. H₂SO₄ having density = 1.84 g / ml and HCl (density = 1.21 g /ml) were used as acid catalysts.

2.2. Synthesis and curing of phenol-aldehyde resins

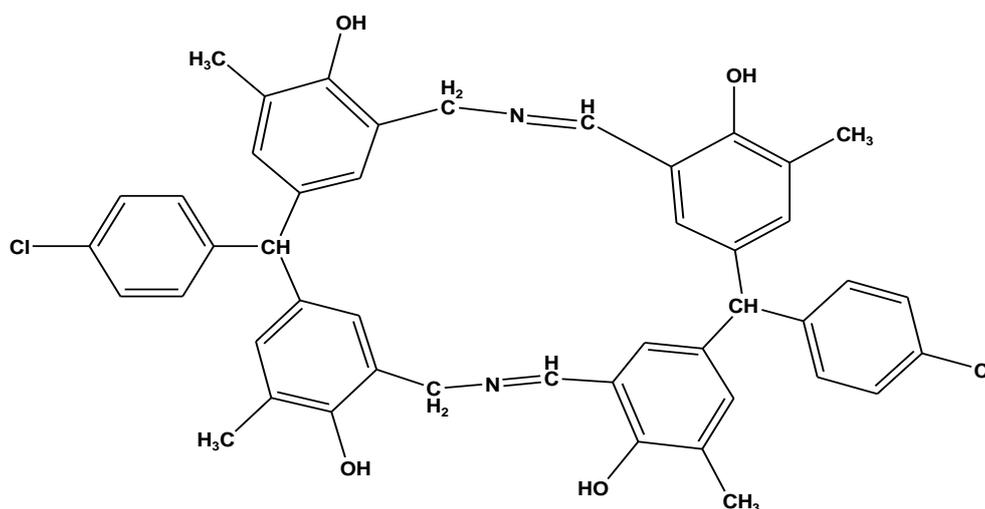
A series of novolacs were synthesized via a condensation reaction between appropriately substituted phenols and substituted aromatic aldehydes. The reactions are catalyzed by dilute hydrochloric acid/sulfuric acid to get linear novolacs.

2.2.1 Synthesis and curing of the *o*-cresol-*p*-chlorobenzaldehyde resin

In a typical reaction, 16 g of *o*-cresol, 9g of *p*-chlorobenzaldehyde were mixed in the round bottom flask. The color of the solution was pale yellow. To this mixture 0.5 ml H₂SO₄ was added. The color of the solution was deep red. The solution was heated for 2h on a water bath at 100⁰ C. This reaction mixture poured in cold water and washed liberally with distilled water for removing sulfate ions from the mass. This resin was dried in vacuum oven till we get constant weight. The color of resin was dark red, and the melting point was 80⁰c. The yield of the thermoplast was 75 %. *O*-cresol reacts with *p*-chlorobenzaldehyde to give

condensation product. This reaction is catalyzed by sulphuric acid to give linear novolacs. Characterization: FTIR of uncured resin shows characteristic peaks at 1693.85, 1488.34, 1261.99, 1161, 820.39, 754.64 cm^{-1} . The $^1\text{H-NMR}$ spectrum shows peaks at δ 2.7 (CH_2), 2.2 (CH), 5.5 (phenolic), 6.6-7.0 (aromatic ring)

Curing of *o*-cresol-*p*-chlorobenzaldehyde (novolac) resin was carried out with hexamine 500mg of resin and 40mg of hexamine was heated at 200°C or 25 minutes. This temperature was maintained throughout the reaction. The mixture of resin and HMTA melted to red liquid which turned to brown solid (cured) product. This cured resin is insoluble and infusible. The cured resin was washed with acetone for removing impurities and uncured resin; after drying, the pure cured resin is obtained. In *o*-cresol-*p*-chlorobenzaldehyde resin due to the presence of free ortho-para positions, the reaction with urotropine results in the formation of azomethine linkage between two phenol moieties. Characterization: FTIR of cured resin shows characteristic peaks at 1587.85, 1248.99, 1153 cm^{-1} . Since the temperature required for curing is very high, some of the aldehyde moieties break at para position and react with



urotropin, so the expected structure of cured resin of *o*-cresol-*p*-chlorobenzaldehyde resin is represented below.

2.2.2 Synthesis and curing of the *m*-cresol-anisaldehyde resin

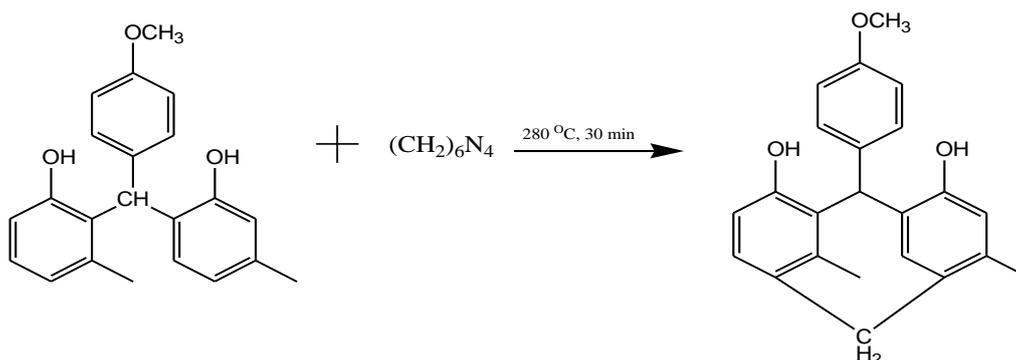
The monomer 20g of *m*-cresol was mixed with 15g of anisaldehyde in a round bottom flask. The color of the solution was pale yellow. To this mixture, 1mL of dilute HCl was added which changes the color to deep red. The solution was refluxed for half an hour at 100 C.

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This reaction mixture was poured into cold water and washed liberally with distilled water for removing the chloride ions. After washing, the resin is dried in vacuum oven till constant weight. The color of the resin was dark red, and a melting point of the resin was 100° C. the yield of the thermoplast 64%. Characterization: FTIR of uncured resin shows characteristic peaks at 1691.85, 1480.34, 1251.99, 1141, 830.39, 744.64 cm^{-1} . The $^1\text{H-NMR}$ spectrum shows peaks at δ 2.6 (CH_2), 2.3 (CH), 5.3 (phenolic), 6.5-7.2 (aromatic ring)

Curing of m-cresol-anisaldehyde resin was carried out with urotopine. 500 mg of m-cresol-anisaldehyde resin and 50 mg (10%) of hexamine was heated to 280 C for 30 minutes. The temperature was maintained throughout the reaction. The mixture of resin and HMTA melted to yellow liquid which turned to brown solid (cured) product. This cured resin was washed with acetone for removing impurities and uncured resin. After drying, the pure cured resin is obtained. The linear novolacs type m-cresol-anisaldehyde resin could not be cross-linked without the addition of a cross-linking agent. FTIR of cured resin shows characteristic peaks at 1585.85, 1243.99, 1253 cm^{-1} . The reaction involved in cross-linking is represented in scheme below.



2.2.3 Synthesis and curing of the o-cresol-paraformaldehyde resin

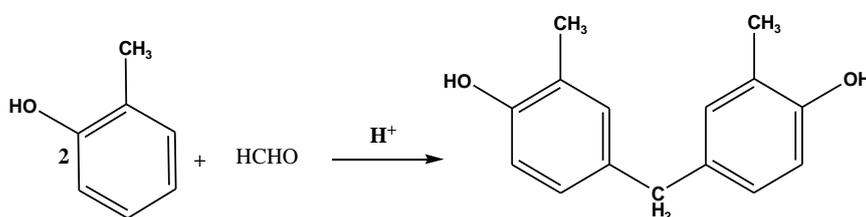
8 g of m-cresol was mixed with 6 g of paraformaldehyde in a round bottom flask. The color of the solution was pale yellow. To this mixture, 0.5 mL H₂SO₄ was added; the color of the solution changes to deep red. The solution was refluxed for 25 minutes. This reaction mixture was poured in cold water and washed liberally with distilled water for removing sulfonate ions from the acid. After wash, the resin is dried in vacuum oven till constant weight. The color of the resin was dark brown, and a melting point of the resin was 140 C. The yield of thermoplast is 70%. Characterization: FTIR of uncured resin shows characteristic peaks at

1693.85, 1488.34, 1261.99, 1161, 820.39, 754.64 cm^{-1} . The $^1\text{H-NMR}$ spectrum shows peaks at δ 2.7 (CH_2), 2.2 (CH).

Curing of o-cresol-paraformaldehyde resin was carried out with urotropin (HMTA), 500 mg of novolacs resin and 50 mg of hexamine were heated upon hot plate at 280 C. With continuous mixing, the mixture of resin and HMTA melted to yellow liquid which turned to brown solid (cured product). This temperature was maintained throughout the reaction. This cured resin is washed with acetone for removing impurities and uncured resin after drying pure cured is obtained. By this reaction, it was concluded that primary reaction between a novolacs and hexamine leads to a complex structure containing amine linkage. These linkages break down to give methylene links. FTIR of cured resin shows characteristic peaks at 1585.85, 1247.99, 1151 cm^{-1} .

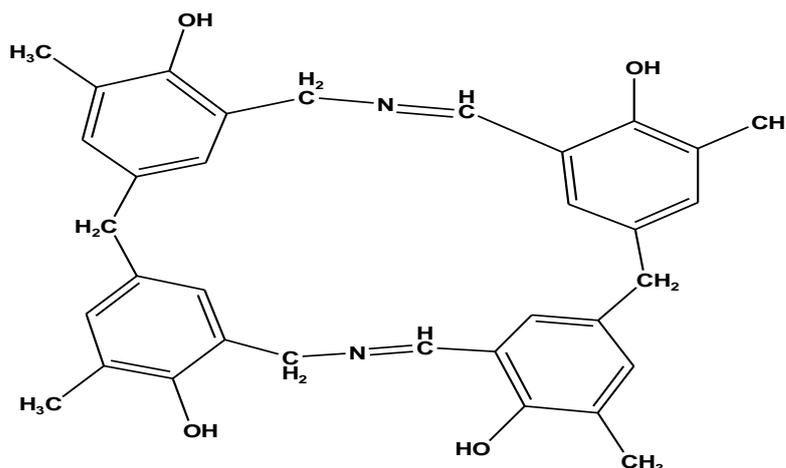
2.2.4 Synthesis and curing of the hydroquinone-anisaldehyde resin

11 g of hydroquinone was mixed with 6.5 g of anisaldehyde in a round bottom flask. The color of the solution was pale yellow. To this mixture, 0.5 mL H_2SO_4 was added; the color of the solution changes to pale yellow. The solution was refluxed for 2 h on a water bath at 100 C. This reaction mixture was poured into cold water and washed liberally with distilled water for removing sulfonate ions from the acid. After wash, the resin is dried in vacuum oven till constant weight. The color of the resin was dark brown, and a melting point of the resin was 105 C. The yield of thermoplast is 76%. Characterization: FT-IR of uncured resin shows characteristic peaks at 3422.98, 1636.29, 1507.26, 1483.85, 1325.40, 1116.53, 818.55 cm^{-1} . The $^1\text{H-NMR}$ spectrum shows peaks at δ 2.2 (CH_3), 3.9 (CH_2), 5.2 (phenolic), 6.6-7.0



(aromatic ring)

Curing of hydroquinone-anisaldehyde resin was carried out with hexamine. 500 mg of hydroquinone-anisaldehyde resin and 50 mg (10%) of hexamine was heated to 200 C for 20 minutes. The temperature was maintained throughout the reaction. The mixture of resin and HMTA melted to red liquid which turned to red solid (cured) product. This cured resin was washed with acetone for removing impurities and uncured resin. Characterization: FT-IR of cured resin shows characteristic peaks at 1597.12, 1387.56, 3375.12 cm^{-1} . After drying, pure cured resin is obtained (shown below).



2.3 Biocidal activity of phenol-Aldehyde resins

RESIN NAME	TEST CONCENTRATION	ALTERNARIA ALTERNATE	ARTHROBOTRYS SP.
<i>o-cresol-parachlorobenzaldehyde resin</i>	1000 ppm	0.8 mm	0.6 mm
	500 ppm	0.6 mm	0.4 mm
	250 ppm	0.1 mm	0.2 mm
<i>o-cresol-paraformaldehyde resin</i>	1000 ppm	1.0 mm	0.6 mm
	500 ppm	0.5 mm	0.5 mm
	250 ppm	0.2 mm	0.4 mm
<i>m-cresol-anisaldehyde resin</i>	1000 ppm	1.5 mm	0.8 mm
	500 ppm	0.6 mm	0.3 mm
	250 ppm	0.2 mm	0.2 mm

To understand the biocidal potential of the resins, three resins namely *o-cresol-parachlorobenzaldehyde*, *o-cresol-paraformaldehyde*, and *m-cresol-anisaldehyde* were put under test. As visible from the table all the three resins show an appreciable degree of biocidal effect on the pathogenic organisms

CONCLUSIONS

A series of Phenol-Aldehyde novolac resins were synthesized by the reaction of phenols and aromatic aldehydes (2:1 ratio) in acidic medium. The afforded resins were further cured with hexamethyltetraamine (HMTA). They were characterized by spectroscopic and thermal analysis. Biocidal properties of the products were also investigated.

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REFERENCES

1. L. H. Baekeland, "U. S. Patent," 88677, 1907.
2. I. Poljanšek and M. Krajnc, "Characterization of phenol-formaldehyde prepolymer resins by in line FT-IR spectroscopy," *Acta Chim. Slov.*, vol. 52, no. 3, pp. 238–244, 2005.

3. M. Wang, M. Leitch, and C. (Charles) Xu, "Synthesis of phenol-formaldehyde resol resins using organosolv pine lignins," *Eur. Polym. J.*, vol. 45, no. 12, pp. 3380–3388, 2009.
4. J. E. Shafizadeh, S. Guionnet, M. S. Tillman, and J. C. Seferis, "Synthesis and characterization of phenolic resole resins for composite applications," *J. Appl. Polym. Sci.*, vol. 73, no. 4, pp. 505–514, 1999.