Novel Applications of Some Organic Copolymers Derived From Phenolic and Nitrogen-Containing Compounds- A Review

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Abstract

A variety of organic copolymers have been synthesized from phenolic compounds like p-Hydroxybenzoic acid, p-Hydroxybenzaldehyde, p-Hydroxyacetophenone, and also from nitrogen- containing compound like anthranilic acid, aniline, urea, biurate. These copolymers have been studied for various properties like thermal behavior, kinetic parameters, antimicrobial screening, ion-exchange study, polymer composites, photoluminiscence etc. Kinetic parameters of the copolymers derived from phenolic and nitrogen-containing compounds have been studied using Freeman-Carroll (FC) and Sharp-Wentworth (SW). Based on TGA, thermal stability and decomposition temperature have been studied for the copolymers and composites. Higher thermal stability for copolymer composites has been found as compared to the copolymer because the composite has a high activation energy and more residue left out at the end of the decomposition process. The metal ion uptake capacity of the copolymer have been studied by using the batch equilibrium method and is useful for wastewater treatment. The antimicrobial activity of the copolymers have been studied using the agar diffusion method. Polymer composites have been made from copolymers using an ultra-sonication process and exhibit excellent properties in metal ion uptake for wastewater treatment. The present review paper involves the study of novel applications of the copolymer resins derived from phenolic compound and nitrogen-containing compound.

Keywords: Copolymer, Composites, Ion-exchange, Photoluminescence, Composites.

1. Introduction

Phenolic compounds have versatile applications in the food, pharmaceutical, and polymer industries. They exhibit various biological activities like antimicrobial activity, antibacterial activity, antioxidant and anti-inflammatory, and thermal and electrical conductivity. An intra-molecular hydrogen bonding (Fig.1) is observed in phenolic

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compound[1] like protocatechuic acid, O-Nitrophenol, Salicylic acid, and O-Chlorophenol. Primary and secondary amines form hydrogen bonds. Oxygen is more electronegative than nitrogen, so hydrogen bonds in amines are weaker than phenolic compounds. The inter molecular hydrogen bonding (Fig.2) have been observed in anthranilic acid,Diethylamine, Semicarbazide, Di-amino-benzoic acid.

A large number of useful applications like use in electronic devices, use as insulators, adhesives, in aerospace industries, etc. have been noted in Table (3) for phenolic and nitrogen-containing copolymers, These copolymers have high thermal stability, resistant to bacteria, fungi, chemicals and also have electrical insulating properties[2-7]. In recent years copolymers are widely used as semiconducting material. Because of conducting nature, copolymers are used in solid-state physics and chemistry. In addition to the conductivity, copolymers have been extensively used in Photovoltaic Cells, Organic Solar Cells, Sensors, Light Emitting Diodes, Schottky diodes, Field transistors, Electrochemical batteries, Photoconduction, Luminescence, etc.[8]

The electrical conductivity of the copolymers derived from phenol and formaldehyde has been studied by Pekaln and Kolosonov [9,10] who used them in the field of electrochemistry such as electrodes, the field of electronics sensors, etc. Dewar, et. al.[11] have reported copolymer as an industrially useful semiconducting material. Masram and coworkers [12-15] carried out work on the Study of Kinetics, Thermal degradation, and Electrical Conductivity of copolymers derived from Salicylic Acid and Phenylenediamine containing compounds, butylene-diamine-containing compounds, hexamethylenediamine-containing compounds with Formaldehyde

Gurnule et.al.[16] have reported the study of electrical properties of copolymers derived from 2-hydroxy-4-methoxybenzophenone and 1,5-diaminonaphthalene with formaldehyde. They have also studied the electrical conductivity of novel nanoporous o-aminophenol-melamine-containing compounds-formaldehyde copolymer. Phenol-formaldehyde and amino-formaldehyde copolymers have excellent applications and hence various researchers have synthesized copolymers of salicylic acid- hexamethylene-diamine-formaldehyde, containing compounds. Also some combinations of salicylic acid- catechol-formaldehyde, p-hydroxybenzoic acid- semicarbazide -formaldehyde, salicylic acid- thiosemicarbazide-formaldehyde, anthranilic acid, urea-formaldehyde, 4-hydroxyacetophenone-catechol-formaldehyde, salicylic acid-butylenediamine-

formaldehyde, 4-hydroxyacetophenone ethylenedinitrogen-formaldehyde, p-hydroxybenzoic acid- diaminobenzoic acid-formaldehyde, p-cresol- melamine containing compounds-formaldehyde, o-aminophenol melamine containing compounds-formaldehyde have been reported[17-21].

Copolymers derived from phenolic and nitrogen-containing compounds show antimicrobial activity[22-23] (inhibitory activity) against some bacteria such as C. Albicans, S. Typhi, S. Aureus A. Niger, and E. Coli, S. Subtilis, pathogens.

Versatile properties of phenolic compounds have been studied including resistance to high temperatures and excellent thermal insulators, phenolic compounds are resistant to corrosion and exhibit fire-toxic smoke properties[24-30]. Phenolic copolymers are used for various composite manufacturing processes such as filament winding, resin transfer molding, injection molding, and compression molding. Phenolic copolymers provide easy processability, tight tolerances, reduced machining, and high strength[31]. Copolymers derived from phenolic and nitrogen-containing compounds also exhibit excellent photoluminescence properties and have been used in semiconductor devices. This shows that the synthesized coordination polymer can be used as a photoluminescence material for various applications & also as a supporting material for light-emitting devices[32].

A review of some organic copolymers derived from phenolic and nitrogen-containing compounds includes novel applications of copolymer resins like thermal resistance materials, fireproofing materials, molding materials, binders, a Semiconductor, antibacterial materials, antifungal agents, wastewater treatment, Photoelectronic devices, fluorescence sensors, probes, Light emitting, luminescent sensors, Multicolor light emitting device OLEDs.

2.Synthesis of Copolymer Resins

Copolymer resins have been synthesized from phenolic compounds and nitrogen-containing compounds mentioned in Table 1 by using the condensation method with formaldehyde using varied molar ratios of reacting mixture. The reaction has sped up using HCl as a catalyst and heated with occasional shaking at temperature ranges from 125-140 ^{0}C for 5-7 h.[18-20]. The colored copolymer has been separated and then washed with warm water and methanol to avoid unreacted monomers. The synthesis of p-CPBF-II using phenolic and nitrogen-containing

compound by condensation method is shown in Fig.3**.** The yield of the copolymer is 90-95% for all the copolymer resins.

3. Properties and Applications of Copolymers

Various properties and applications have been studied for copolymers derived from phenolic and nitrogen-containing compounds. Some of the important properties and applications are given below.

3.1 Thermal Stability

Copolymers derived from phenolic and nitrogen-containing compounds show thermal stability and hence can be used as thermal resistance materials, fireproofing agents, molding materials, and binders. It has been further supported based on low values of frequency factor (Z) and slow rate of the decomposition reaction of the copolymer. The thermal stability of the copolymers at high temperatures have studied based on decomposition reactions started at higher temperatures[18,20-23.] The thermogravimetric analysis method is mostly used to determine the thermal stability of the copolymers. Thermal methods of analysis is an experimental method for determining the thermal stability of the copolymers by measuring changes in physicochemical properties with continuously increasing temperature with time. The thermogravimetric analysis (TGA) of the novel copolymers has also been studied in a stationary atmosphere over a heating rate of 10^0C/min. In the present investigation, thermo-gram of copolymers synthesized from phenolic and nitrogen-containing compounds have been studied with % weight loss of the material (copolymer resin) as a function of temperature and also time. From thermo-grams, activation energy (Ea) have been calculated by adopting an analytical method proposed by Freeman-Carroll (FC) and Sharp-Wentworth(SW)[12-18] as given in Table 2. These methods help to decide the thermal stability of the copolymer resins and also the order of reaction (n), activation energy, entropy, Frequency factor, etc.[26-28].

3.2 Electrical Conductivity

The copolymers synthesized from phenolic and nitrogen-containing compounds have shown good electrical conductivity and can be used as semiconductors[12]. Most of the copolymers derived from phenolic and nitrogen-containing compounds have shown good electrical conductivity and are measured within the range of 303-423 K temperature in their pellets form. The conductivity is further supported based on low activation energy and delocalization of π-

electron in polymer chain[13-14]. Experimentally electrical conductivity of the copolymers have determined by making pellets of the finely powdered copolymer in a steel die isostatically at 5-10 tonnes/2inch($1cm^2$). Colloidal graphite in acetone has been applied in thin layer form on both sides of the pellets. At room temperature, all pellets have been dried in a vacuum for 6 h. To avoid any leakage across the border precaution has been taken not to apply very high voltages[12-14,16,17]. The rate (slow) of heating have maintained at 1 to 10 ^{0}C / min. during the entire process. The two probes (terminals) method has been used to measure the resistance of the sample pellets. Resistivity (ρ) have calculated using the relations between the resistance of the pellets, surface, and thickness area of pellets as shown in equation (1).

$$\rho = R\,(A/l) \quad \text{.....(1)}$$

Where, R= resistance of the pellets, A = Surface area of pellets & l = Thickness of pellets

The electrical conductivity(σ) may vary exponentially with the absolute temperature according to the well-known Wilson's exponential relationship (2) which is given below.

$$\sigma = \sigma^0 \exp\,[-Ea/kT\,] \quad \text{.....(2)}$$

The modified relationship (3) is given as:

$$\text{Log}\ \sigma = \log\sigma 0 + -Ea/2.303kT \quad \text{.....(3)}$$

3.3 Antimicrobial Activity

Copolymers synthesized from phenolic and nitrogen-containing compounds exhibit antimicrobial activity against microorganisms, bacteria, and pathogens[18-19]. It is then used as antimicrobial copolymers. The antimicrobial activity of the copolymers is due to the presence of a function group containing nitrogen(amide), oxygen(hydroxyl), and sulfur (thio). Experimentally an agar diffusion method[20-23] has been used to know the antimicrobial properties of the copolymers.

3.3.a. Antibacterial analysis: Antimicrobial screening of the copolymers have been studied by using the agar diffusion method. The test bacterial pathogen like B. subtilis, E.Coli, S.Typhi Klebsiella species, S. Aureus, C. Albicans, C. Tropicals, and A. Niger microorganisms have been used for antibacterial screening of the copolymers. The agar plates of the above media have been prepared along with wells. The agar plates were then incubated at 37ºC for 24 h and recorded the diameter of inhibition zones. These were tested at different concentrations to test their efficacy in inhibiting the growth of human pathogens[18].

The antimicrobial activity of the copolymers have been checked using varied concentrations screened 0.0625, 0.125, 0.25, 0.5, 1.0, and 2.0 mg in DMSO. Gentamycin was used as standard antibiotic. The 20 mg sample was dissolved to prepare the above concentrations. The stock Sample was prepared in 20 mg/ml Concentration. The Media Used (Nutrient broth) for the above analysis is Peptone-10 g, NaCl-10g and Yeast extract 5g, Agar 20g in 1000 ml of distilled water. The S. Aureus (MRSA), B. Subtilis, E.Coli (ETEC), S. Typhi Klebsiella species, S. Aureus, and C. Tropicals bacteria were used for antimicrobial analysis[20-23].

3.3.b. Antifungal analysis: The copolymers have been analyzed with 0.0625, 0.125, 0.25, 0.5, 1.0, and 2.0 mg concentration in DMSO. Amphotericin was used as standard Antibiotic. The 20 mg sample has been dissolved to prepare the above concentrations. The Stock Sample was prepared in 20 mg/ml Concentration. The A.Niger, Candida albicans fungi were used for antifungal analysis[18,23].

3.4 Ion-Exchanger for Waste Water Treatment

The copolymers derived from phenolic and nitrogen-containing compounds have also been found suitable and more convenient for the removal of traces of heavy toxic metal ions present in industrial wastewater, domestic water treatment, and nuclear waste treatment. The toxic heavy elements present in wastewater are a serious issue and it creates health-related problems like skin infections, stomach infections, kidney damage, and damage to the nervous system and so on[24]. Therefore, the synthesis of a chelating ion-exchange copolymer has been performed by various researchers from phenolic compounds and nitrogen-containing compounds to assess the ion-exchange characteristics of the copolymer. Ion-exchange process is an efficient and eco-friendly extraction technique for the separation of metal ions and recovery of toxic heavy metal ions from industrial wastes, tannery effluents, sewages, etc[25-30]. The copolymers derived from phenolic and nitrogen-containing compounds are used as ion-exchanger for the removal and pre-concentration of hazardous metal ions such as Cr^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+} Co^{2+}, etc. found in natural water samples using batch equilibrium method[31,33]. The ion-exchange techniques have been studied by evaluating the following experimental steps.

3.5 Polymer Composites

The polymer composites derived from the phenolic compound and nitrogen-containing compounds exhibit excellent ion exchange properties for wastewater treatment and management[31,32]. Experimentally it has been synthesized from copolymers and activated

charcoal in a 1:2 ratio. The copolymer was dissolved in 25 ml of DMF and the activated charcoal was added to it and subjected to ultrasonication for 3 h with constant stirring for 24 h. Finally, the obtained black-colored composite was dried in an air oven at 70°C for 24 h[31,32]. The polymer composites exhibit excellent properties in metal ion uptake for wastewater treatment. Higher thermal stability and decomposition temperature have been found in polymer composites as compared to copolymers[33-38].

3.6 Photo luminescent copolymers

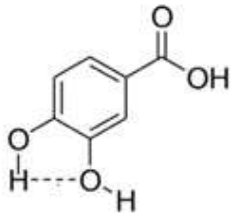
The copolymer synthesized from phenolic and nitrogen-containing compounds exhibit photoluminescence properties and can be used as fluorescence sensors, probes, Light emitting, photoelectronic devices, luminescent sensors, Multicolor light emitting device OLEDs. The copolymers also worked as ligands as it contains oxygen and nitrogen as donor atoms. When such a copolymer reacts with transition metal ions like Cu^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, and Zn^{2+}, co-ordination polymer complex formation takes place in a 2:1 molar ratio. The photoluminescence properties of copolymers derived from phenolic and nitrogen-containing compounds having copolymer metal complex samples have been recorded in photoluminescence spectra[39-43].

4. Conclusion

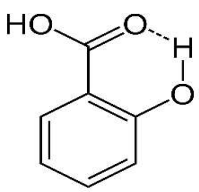
Copolymers in the review study have been synthesized from phenolic and nitrogen-containing compounds by poly-condensation method. The kinetic parameters of the copolymers derived from phenolic and nitrogen-containing compounds have been studied using Freeman-Carroll (FC) and Sharp-Wentworth (SW). On the basis of TGA, thermal stability and decomposition temperature have been studied for the copolymers and composites. Higher thermal stability for copolymer composites have been found as compared to the copolymer, because composite has high activation energy and more residue left out at the end of decomposition process. Metal ion uptake capacity of the copolymer have been studied by using batch equilibrium method and useful for wastewater treatment. Antimicrobial activity of the copolymers have studied using agar diffusion method. Copolymers derived from phenolic and nitrogen-containing compounds shows antibacterial activity for certain bacteria and fungi. Polymer composites made from copolymers using ultra sonication process exhibit excellent properties in metal ion uptake for wastewater treatment. Copolymers derived from phenolic and nitrogen-containing compounds have ranked as thermally stable material, semiconductor, ion-exchanger in wastewater treatment also exhibit antimicrobial and photoluminescence properties. The copolymers also exhibit photoluminescence properties and used in photo-electronic devices,

fluorescence sensors , probes, Light emitting, luminescent sensors, Multicolor light emitting device OLEDs.

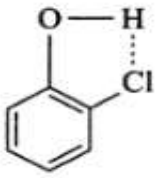
Figures



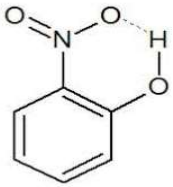
Structure-I: Protocathechuic acid



Structure-II: Salicylic Acid

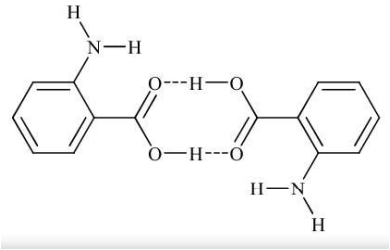


Structure-III: O-Chlorophenol

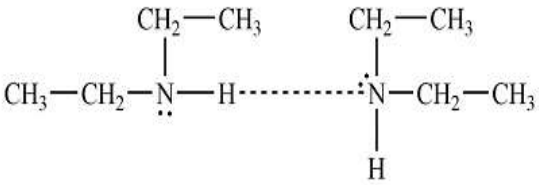


Structure-IV: O-Nitrophenol

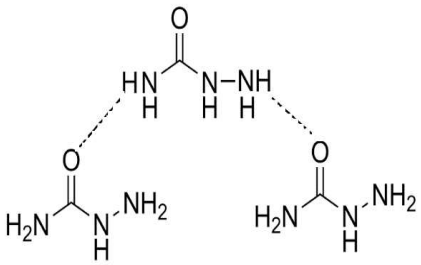
Fig.1: Intra-molecular hydrogen bonding in phenolic compounds.



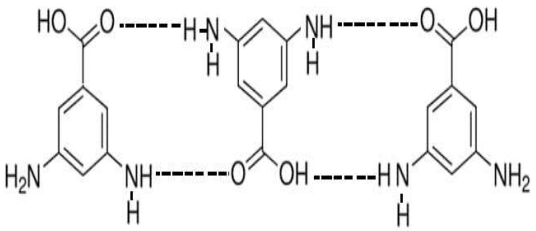
Structure-V: Anthranilic acid



Structure-VI: Di-ethylamine



Structure-VII: Semicarbazide



Structure-VIII: Di-amino-benzoic acid

Fig. 2: Intermolecular hydrogen bonding Nitrogen-containing compounds.

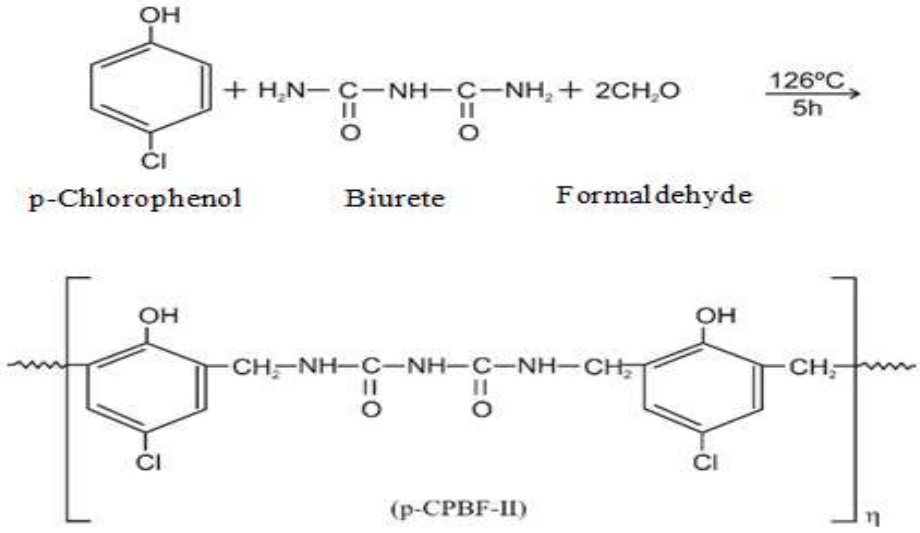


Fig. 3: Synthesis of p-CPBF-II using phenolic and nitrogen-containing compound by condensation method.

Tables

Table-1: List of some phenolic and nitrogen-containing compounds for the synthesis of copolymer resins.

Sr. No	Phenolic Compounds	Nitrogen-containing compounds
1	Salicylic acid	Phenylenediamine
2	Salicylic acid	Butylenediamine
3	Salicylic acid	Hexamethylenediamine
4	*p*- Hydroxybenzoic Acid	Diaminobenzoic Acid
5	2-Hydroxy 4-Methoxybenzophenone	1,5-diaminonaphthalene
6	o-Aminophenol	Melamine
7	*p*- Hydroxybenzoic Acid	Anthranilic acid + Urea
8	4-Hydroxyacetophenone	Ethylenediamine
9	Salicylic acid	Thiosemicarbazide
11	p-Hydroxybenzoic acid	Semicarbazide
12	p-Cresol	Melamine

Table-2: Thermo analytical methods and important equations

Thermoanalytical Method	Equations
Freeman-Carroll Method	$\Delta \log (dw / dt)] / \Delta \log Wr = (-Ea / 2.303R) . \Delta (1/ T) / \Delta \log Wr + n$
Sharp -Wentworth Method	$\log [(dc/dT)/ (1-c)] = \log (A/\beta) - [Ea/2.303R]. 1/T$

Table-3. Properties and applications of copolymer resins derived from phenolic and nitrogen-containing compound.

Sr. No	Properties of copolymers	Applications
1	Thermal Stability	Thermal resistance materials, Fireproofing agent, Molding material, Binder(adhesive)
2	Electrical Conductivity	As a Semiconductor, In aerospace industries.
3	Antibacterial Activity	Antibacterial material, Antifungal agent, Coating material.
4	Ion-Exchange	Wastewater treatment, Removal of toxic heavy elements
5	Polymer Composites	Wastewater treatment, Engineering Use.
6	Photoluminiscence	Photoelectronic devices , fluorescence sensors , probes, Light emitting, luminescent sensors, Multicolor light emitting device OLEDs. Organic Solar Cells,

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