

The synthesis and characterization of the hydrazone ligand and its metal complexes and their performance in epoxy formulation surface coatings



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ABSTRACT

Hydrazones are present in many of the bioactive heterocyclic compounds that are of wide interest due to their biological applications. This article focuses on the synthesis of the hydrazone ligand and its metal complexes and their potential application as anti-microbial, antifouling and flame retardant additives in epoxy formulations for surface coating application. Selected divalent (Co^{II}) and trivalent (Cr^{III} and Fe^{III}) metal complexes of arylhydrazones, namely *o*-hydroxyacetophenone benzoylhydrazone (HBH) have been isolated and characterized by a combination of elemental analysis, FTIR, ^1H NMR and mass spectra. The ligand and its metal complexes were physically added to an epoxy resin. Experimental coatings were produced on a laboratory scale, and then applied using a brush onto both wood and steel panels. Results obtained from an oxygen index value indicated that the epoxy resin containing the ligand (HBH) and its metal complexes as additives, exhibit a very good flame retardancy effect. The results of the biological activity indicated that the HBH ligand and its metal complexes exhibit a very good antimicrobial and antifouling effect, with the metal complexes showing better results than the ligand. Both physical and mechanical resistance properties were also studied, to evaluate any drawbacks due to the inclusion of the additives. The additives did not affect the flexibility, hardness and adhesion of the epoxy resin formula. The gloss was increased due to the incorporation of the aromatic ring, and the impact strength was also increased due to the incorporation of metal into the epoxy resin formulation.

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1. Introduction

Epoxy coatings are extensively utilized in the protective coatings and flooring markets due to their generally high level of mechanical properties, corrosion protection and chemical resistance. In the last few decades epoxy coatings have evolved from high VOC systems to more environmentally friendly systems e.g. high solids, solvent-free, powder and waterborne coatings [1]. Polymeric materials have replaced many materials in our everyday lives. Although there are numerous advantages associated with polymeric materials there are serious drawbacks, such as poor resistance to fire. Deaths due to fire account for 10 to 20 deaths per million inhabitants in industrialized countries, and the number of people injured is ten times higher [2]. Over time, different strategies have been developed in order to enhance the reaction to fire of these materials. These include the use of inherently

flame retardant polymers [3], modification of the polymer backbone [4,5], or incorporation of flame retardants into the polymers. As inherently flame retardant polymers can lead to high production costs, the modification of already existing systems is still valued by industry. The modification of the polymer backbone by the inclusion of P, Si, B or N elements often provides good fire retardancy properties to the newly synthesized polymer [6]. Unfortunately, epoxy resins tend to burn easily while releasing high quantities of smoke and gas, and one of the traditional solutions is the incorporation of halogen-containing flame-retardants [7]. Therefore, the effort of enhancing the reaction to fire of epoxy resins has been further developed. I have previously reported flame retardant additives containing nitrogen, such as Schiff's base monomer and cyclodiphosph(V) ozone derivatives [8–10]. Epoxy resins are also susceptible to microbial attack when they are exposed to the atmosphere. Generally, microorganisms have been found to cause disbonding and blistering of coatings under various service conditions [11–13]. Paint formulations traditionally containing biocidal species, are used to protect the coating surfaces from marine microorganism [14]. Up until the end of the

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1990s, the most effective anti-fouling paints were based on organotin compounds, mostly tributyltin compounds (TBT-based paints). TBT and its derivatives were found to be harmful molecules to marine eco-systems by Alzieu [15]. Thus, TBT-based paints were completely prohibited and as a consequence promoted research into new ecological paints. One possibility following the prohibition was to develop polymers having biocidal activities which are toxic to marine microorganism [16–20]. In past decades, focus on a versatile hydrazone ligand has increased due to various advantageous properties and the potential for wide applications. Hydrazones are derived from the condensation of *o*-hydroxy, methoxy-aldehydes and ketones with hydrazides. Hydrazone ligands occupied a central role in the development of coordination chemistry. They are potential polynucleating ligands passing azomethine, amide and phenol or methoxy functions, which offer varying bonding possibilities in metal complexes [21,22]. Moreover, Hydrazones have a good potential for biochemical processes and are used as antimicrobial [23], anti-diabetic [24], antimalarial [25], anticancer and potentially mutagenic agents [26]. Also, the presence of fragments such as azomethine, and other structural properties of hydrazones, have made them a good candidate for a new drug development [27]. In addition, the interest in these ligands is due to the fact that the aromatic ring present in them is a constituent of many biological systems. Furthermore, it has been discovered that hydrazones react with transition metals to form coordination compounds with biological activities [28–30]. The most studied amongst the benzoylhydrazones are the benzoylhydrazones of salicylaldehyde (or its substitute), which hesitate in their coordination with the metal ions within a bi- or tri-dentate via C=O, C=N and OH groups forming a five or six chelate ring around the central metal [31]. Based upon this information, the objective of this investigation is to synthesize the hydrazone derivative ligand, *o*-hydroxyacetophenone benzoylhydrazone (HBH) and its metal complexes, to establish whether it has a role in enhancing the antimicrobial and antifouling activity when incorporated physically into an epoxy resin. The work was further extended to study the ligand and its metal complex as a flame retardant additive. The physical resistance and mechanical resistance were also studied to evaluate any drawbacks associated with the additive.

2. Experimental

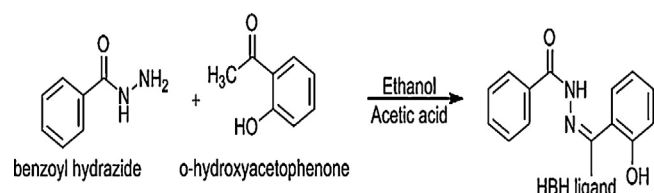
2.1. Materials

All chemicals and solvents utilized were Analar quality from Merck or BDH and used as received without further purification.

2.2. Methods and techniques

2.2.1. Synthesis of *o*-hydroxyacetophenone benzoylhydrazone (HBH)

Benzoylhydrazide (BH) was prepared following the method described in the literature [32,33]. The ligand was prepared using the recipe described elsewhere [34] as follows. Benzoylhydrazide (3.0 g, 0.022 mol) was dissolved in absolute ethanol (50 ml) and the resulting solution was then added to an ethanolic solution (50 ml) of *o*-hydroxyacetophenone (2.99 g, 0.022 mol). The reaction mixture was prolonged under reflux for 2 h in the presence of 2–3 drops of glacial acetic acid. The separated product was filtered, washed with ethanol, crystallized using ethanol and finally dried in the oven at 80 °C for 24 h. The resulting ligand, having the chemical formula C₁₅H₁₄N₂O₂ is shown in Scheme 1. The synthesized hydrazone (HBH) is insoluble in petroleum ether and soluble in most common organic solvents, e.g. alcohol, acetone, benzene, chloroform, DMF and DMSO.



Scheme 1. Synthesis of *o*-hydroxyacetophenone benzoylhydrazone (HBH) ligand.

2.2.2. Synthesis of metal complexes of HBH ligand

All the isolated solid complexes were prepared by mixing equimolar amounts of HBH ligand and metal(II) acetates [M=Cr(II) and Co(II)] in 100 ml ethanol. Fe(III) chloride was utilized to prevent separating the iron complex. The reaction mixture was refluxed on a hot plate for 3 h. Coloured crystalline solids were isolated by concentrating the solutions by approximately half and then filtering hot. The complexes obtained were washed repeatedly with hot ethanol and finally dried in the oven at 80 °C for 24 h. The complexes retain their colours for a considerable time, and are insoluble in water and petroleum ether, but soluble in DMF and DMSO.

2.3. Instrumental analysis

The physical measurements were carried out using the methods and appliance models reported earlier [35]. The elemental analysis for carbon, hydrogen and nitrogen content was performed using a Perkin Elmer 2400 instrument in the Microanalytical Unit of Cairo University, Egypt. Metal content (%wt) was estimated complexometrically by EDTA, using xylenol orange as an indicator and solid examine as a buffer (pH = 6). FTIR spectra of the HBH ligand and of the complexes were recorded using KBr pellets on a Bruker (Vector 22) single beam spectrometer at a spectral resolution of 2.0 cm⁻¹. The ¹H NMR spectra for the ligand was recorded on a Varian Mercury VX-300 NMR spectrometer at 25 °C using DMSO solvent and TMS as an internal standard. The Mass spectra of the HBH was recorded on a Shimadzu-GCMS-Q5050 instrument using the direct inlet system [33].

2.4. Preparation of epoxy paint films containing HBH ligand and its metal complexes for surface paint

The epoxy paint compositions were prepared by means of incorporating *o*-hydroxyacetophenone benzoylhydrazone (HBH) ligand and its metal complexes, in the ratio of 1.0 1.5 and 2.0 wt.% into epoxy paint. The composition of epoxy paint is tabulated in Table 1. The samples of different molar ratio were then applied to both steel and glass panels by means of a brush. All efforts were made to

Table 1
Epoxy resin composition.

Component	wt.%
Epikote™ resin 1001-X-75 included aliphatic amine (base: hardener, 87: 13%)	18.4
Nonyl phenol	2.9
Aromatic hydrocarbon solvent	3.9
Mixtures of fine 65–75 μm	
Talc	15.0
TiO ₂	6.0
CaCO ₃	20.0
BaSO ₄	15.0
Modified polyamide thix agent	2.0
Methoxy propanol	5.5
Aromatic hydrocarbon solvent	11.3
HBH and its metal complexes	1.0–2.0

Viscosity: M–N (Gardner), colour: >18 (Gardner), solid content: 65 ± 2%.

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