

FULL PAPER

Synthesis and characterization of fast curing polymeric coating for Iraqi oil tank bases

Zaydoon K. Kuraimed | Qais M. Amoury | Hayder M. Majeed | Huda Q. Jebur | Buthaina Khaleel | Mays Mohammed

Ministry of Oil, Petroleum Research & Development Center, Baghdad, Iraq

The bottom tanks used to store crude oil and derivatives are the most vulnerable to corrosion, because despite the presence of cathodic protection, their contact with corrosive media can cause metal corrosion, which is found in most oil tanks of Iraq. In this study, a resole phenolic resin prepared in an alkaline medium and a plasticizer were used to impart elasticity to the polymer to prepare a self-hardening polymer material with high resistance to acid and temperature up to 170°C. The new synthesized polymers were identified by various spectroscopic methods, such as FTIR, ¹HNMR, ¹³CNMR, and TGA/DTA. The morphology of the polymer surface was also studied by SEM and AFM. This study mainly focused on coat bottom-base oil tanks with fast-curing high-strength polymers. The effectiveness and resistance of synthetic polymers were studied in various tests in acidic and alkaline media. Laboratory experiments showed that the most efficient effective and lowest cost is 1:3 concentration of package 1: package 2 that covers 0.6 mm thickness of metals and resists pressure up to 5226.4N. The economic cost of packaging materials was also studied, and it was found that the cost of a tank bottom covering an area of 706.5 m² was estimated to be 4669.965\$.

***Corresponding Author:**

Zaydoon K. Kuraimed

Email: zaydoon05@yahoo.com

Tel.: + 009647722806989

KEYWORDS

Coating; oil tank bases; corrosion resistance; resole phenolic formaldehyde resin.

Introduction

Crude oil is one of the most important raw materials for the production of energy and crude oil tanks play a strategic role in its storages. Corrosion is considered the most important factor leading to failures of tanks structures [1]. There are many reasons for crude oil tanks to be affected by corrosion. Firstly, general corrosion or pitting occurs when crude oil and high levels of sulfur mix with seawater because the combination forms acidic compounds and an active corrosion cell. Secondly, Crude oil tanks are exposed to a wide range of bacteria that produce corrosive acidic compounds. Thirdly, high temperatures within an oil tank increase corrosion rates,

promote bacterial growth and encourage microbial-influenced corrosion; finally, sludge or scale at the bottom of crude oil tanks may hide pitting and contain harmful microorganisms [2]. Corrosion as a mechanism cannot be prevented entirely as such; it is merely possible to minimize the corrosion rates and the effects of the corrosion [3]. The corrosion rate can be reduced to an acceptable level for a certain system by means of corrosion protection measures, e.g. an appropriate selection of materials, application of the corresponding design principles, suitable coating systems or through cathodic protection [4]. The most difficult problem that comes from the crude oil storage tanks is corrosion, leading to a shortage and loss of

crude oil, which generates environmental pollution and additional economic costs [5]. The phenolic resins may be considered to be the first polymeric products produced commercially from simple compounds of low molecular weight, i.e. they were the first truly synthetic resins to be exploited. Phenolic resins continue to be used for a wide variety of applications, such as moulding powders, laminating resins, adhesives, binders and surface coatings [6]. They are multifunctional polymeric materials with a wide range of commercial applications. Phenolic resins are prepared by reacting phenol or substituted phenols such as resorcinol, cresol, etc., with formaldehyde or other aldehydes such as furfural, acetaldehyde, etc., depending on the reaction conditions, such as pH, phenol and formaldehyde ratio and temperature [7]. Phenolic resins comprise a large family of oligomers and polymers, which are various products of phenols, reacting with formaldehyde [6]. Resorcinol formaldehyde (RF) resin has many applications used as floor and silt coatings, anti-corrosion coatings, adhesives, and graphitization [8]. According to the F/R molar ratio, the RF reaction can produce novolac or resol type resin [9]. The goal of the current work was to develop a resorcinol formaldehyde (RF) layer for the oil tank base in Iraq.

Experimental

Synthesis of RF resins [10]

Synthesis of polymer involves the preparation of two packages which are mixed together.

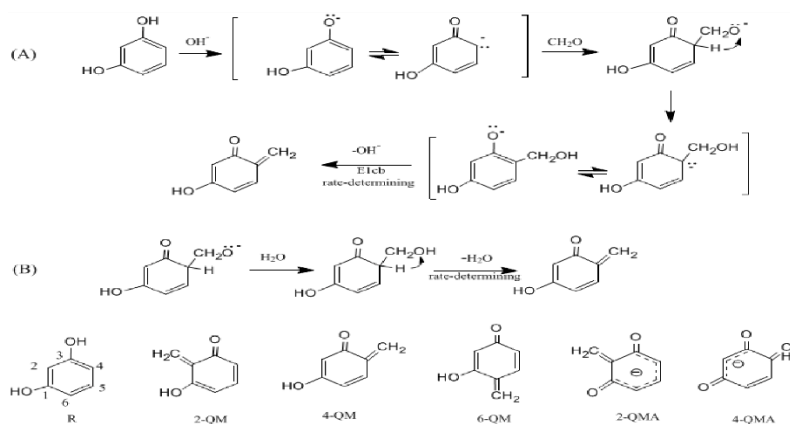
Package 1: Mixing 1 mol of 1,3 di hydroxyl benzene with water in a round bottom flask and heating at 40 °C with stirrer for 20 min and then adding step by step sodium hydroxide until the pH=(6-8) and leaving it for 10 min to cool.

Package 2: Putting 3.67 ml from formalin in a round bottom flask and adding 0.12 g from ethylene diamine with continuous stirring for 10 min.

Package 1 was mixed with Package 2 at ratio 1:1 for 10 min; the result was a thick liquid of polymer.

Results and discussion

This study delved into Resorcinol reaction with formalin solution 35% in basic media of NaOH as catalyst; RF reaction had the same mechanism of the base catalyzed phenol formaldehyde reaction that involved quinonemethide as an intermediate but resorcinol had two hydroxyl groups, so proton dissociation could produce single or double charged anions (divalent anions) in the presence of a base [11]. The mechanism of resorcinol quinonemethides formation is shown in Scheme 1.



SCHEME 1

RF Polymer identification by FT-IR [12]

FTIR spectrum of RF resin showed the appearance of absorption bands at (3400.27) cm^{-1} assigned to the stretching of (O-H), (2918.1, 2850.59) cm^{-1} assigned to the asymmetric and symmetric stretching frequencies of (CH₂), (1521.73, 1604.66) cm^{-1} assigned to stretching (C-C), (1380.94) cm^{-1}

assigned to bending (C-C), (1469.66) cm^{-1} assigned to bending (C-H), and (1257.50) cm^{-1} assigned to stretching (C-O).

Figure 1 shows that the FT-IR spectrum of (resorcinol-formaldehyde) resin indicates that methylation occurs during the reaction, i.e. the presence of absorption band at 3400.27 cm^{-1} attributed to hydroxyl group of (CH₂OH).

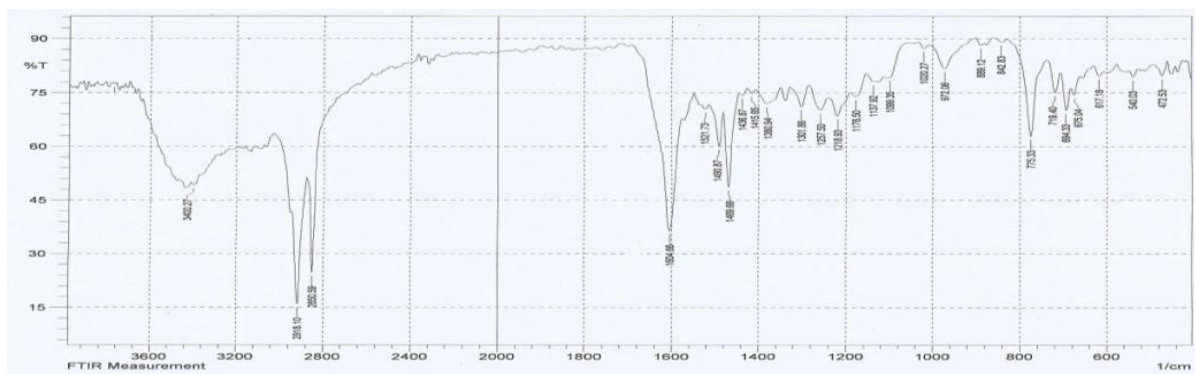


FIGURE 1 The FT-IR of RF polymer

RF Polymer identification by ¹H-NMR

The ¹H-NMR spectrum (δ , ppm) for RF resin showed signal at 6.5-8.1 due to aromatic rings protons, signal at 4.97-5.04 due to methylene

groups (CH₂OH), signal at 3.60-3.90 due to Ether linkage (CH₂OR), and signal at 2.5 due to Hydroxyl OH. Figure (2) shows the ¹H-NMR of RF polymer.

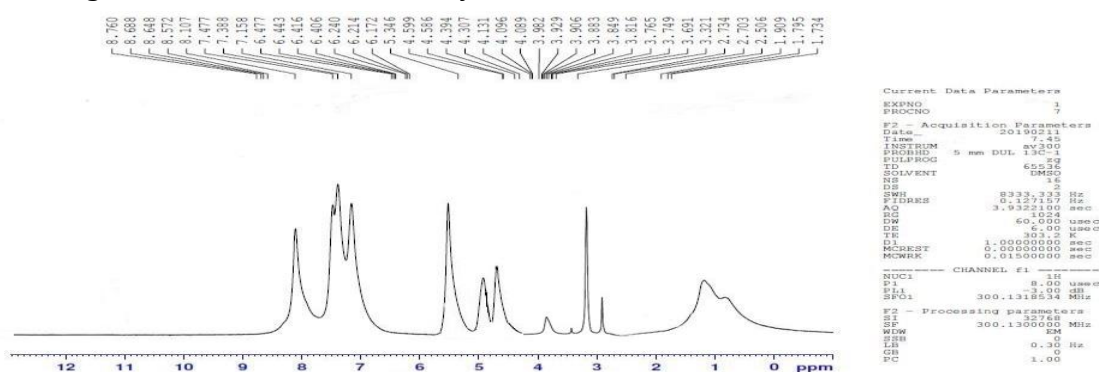


FIGURE 2 The ¹H-NMR of RF polymer

RF Polymer identification by ¹³C-NMR

The ¹³C-NMR spectrum (δ , ppm) for RF resin showed signal at 30 due to Methylene bridge, signal at 55-72 due to methylol groups, signal at 85 due to free formaldehyde, signal at 2.5 due

to hydroxyl group, signal at 92-94 due to hemiformal moiety, signal at 118-123 due to ortho and para free aromatic carbon, signal at 130-135 due to meta aromatic carbon, and signal at 158-162 due to phenolic Carbone. Figure (3) show the ¹³C-NMR of RF polymer.

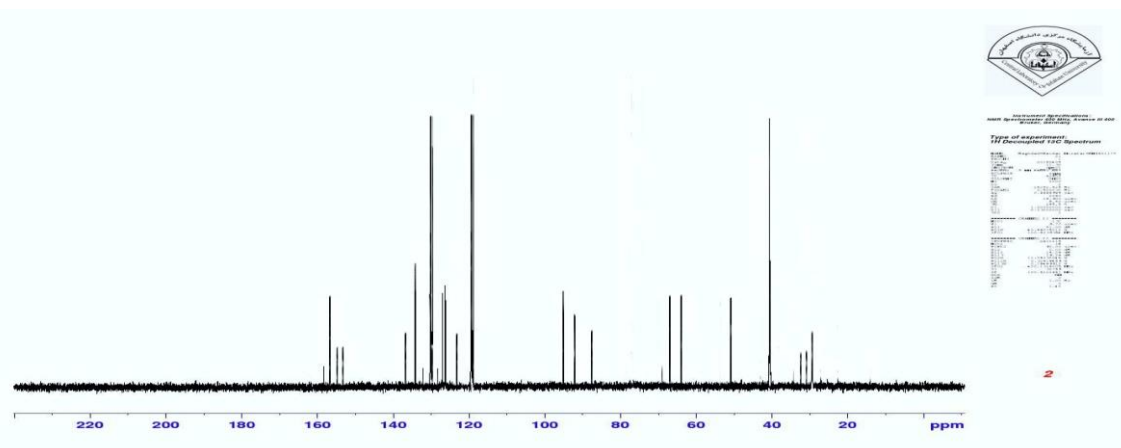


FIGURE 3 The ^{13}C -NMR of RF polymer

Thermogravimetric Analysis (TGA) of RF Polymer

Thermal stability of the synthesized polymer is measured by TGA analysis, in which the weight loss is measured as a function of the ratio of the temperature [13]. Resorcinol-formaldehyde resin is used for TGA from 30 °

C to 800 °C at five different heating rates (2, 5, 10, 20 and 40 °C/min) using a thermogravimetric analyzer under a N_2 atmosphere (Rheometric Scientific TGA 1000, NICEM, University of Baghdad, Baghdad, Iraq). The TGA curing curves for RF resin are shown in Figure 4.

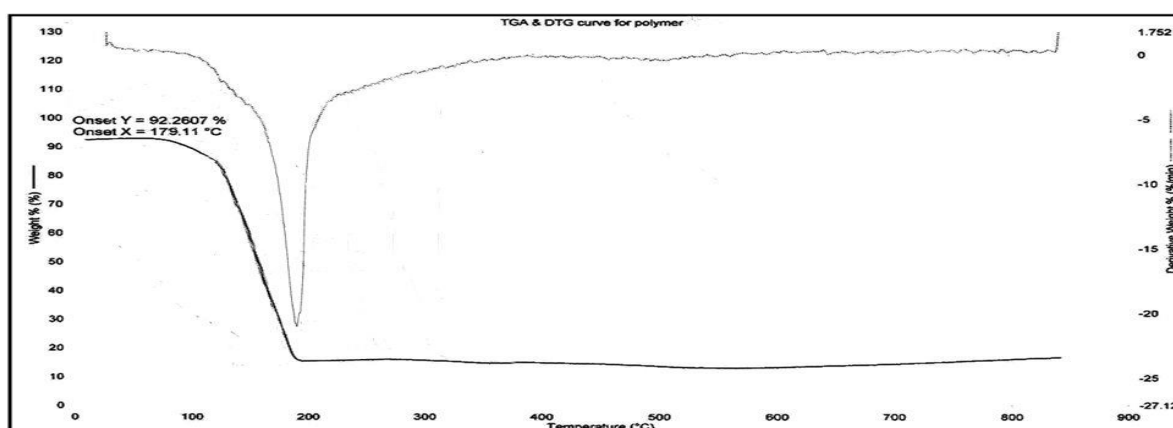


FIGURE 4 TGA of RF polymer

Scanning electron microscopy (SEM) of RF Polymer

The fracture surface morphologies of the RF polymer coatings were inspected by scanning

electron microscopy (SEM). The SEM micrographs of the polymer had a smooth surface (Figure 5); no evidences for phase separation could be found; therefore, the polymers were homogeneous.

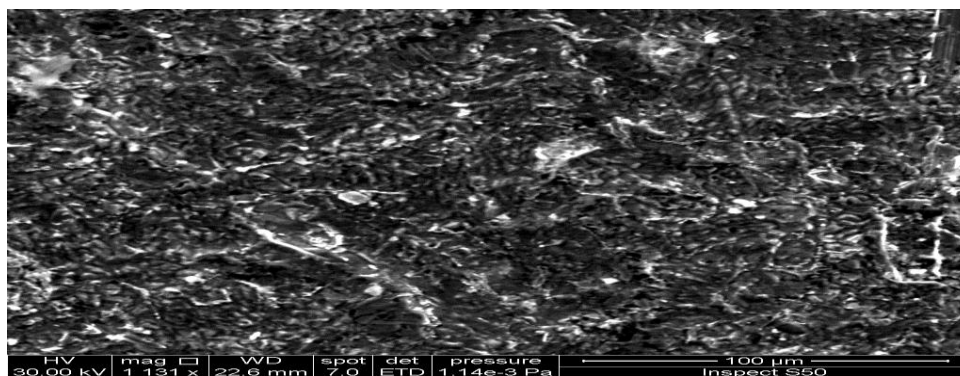


FIGURE 5 The SEM of RF polymer

Atomic force microscopy AFM of RF Polymer

For studying the mechanical properties and molecular composition of the synthesized RF

polymer, AFM analysis was used. Figure (6 a,b,c,d,e,f) shows the polymer surface by AFM.

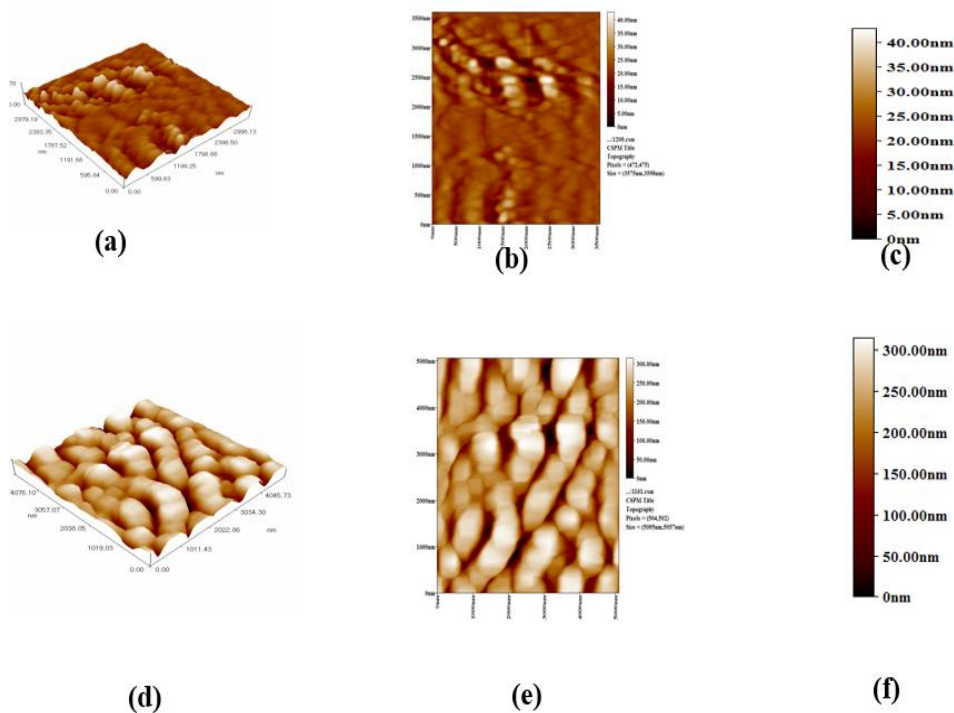
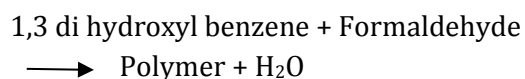


FIGURE 6 The AFM 3D diagram of RF polymer

Time effect on curing of coating polymer



The weight of polymer changed after the curing because first one containing water evaporated after curing the polymer and the second condensation of polymer gave water as aside product.

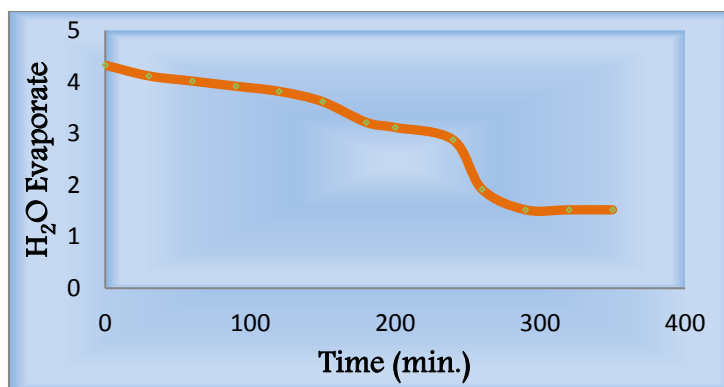


FIGURE 7 The time effect on curing of coating polymer

Temperature effect on curing of coating polymer

The temperature change was studied over time, where it was observed that the behavior

of the coating polymer with the change of temperature was inversely proportional to the time, so when the higher temperatures increased, the time of curing decreased.

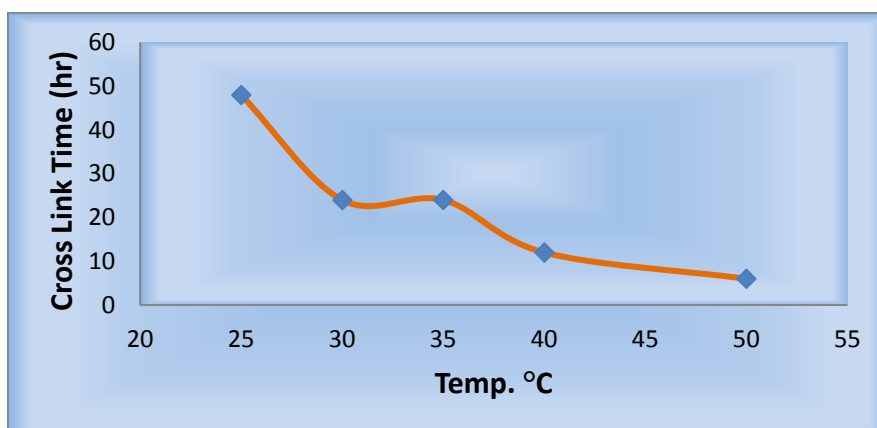


FIGURE 8 The temperature effect on curing of coating polymer

Mechanical resistance of coating polymer

The Table 1 shows the behavior of the prepared polymer towards the influence of the compression factor, which is one of the most important mechanical factors that has a direct

impact on the behavior of resin molecules once exposed to external pressure. The results showed the success of the packing material with a thickness of (0.6 mm) and economical cost less than the economic cost of thickness (0.8 mm).

TABLE 1 The behavior of the prepared polymer towards the influence of the compression factor

Thickness (mm)	0.2	0.3	0.4	0.6	0.8
Applied Force (N)	16.6	80.2	85.7	5226.4	5230
Note	Break	Break	Break	Over Load	Over Load

Temperature resistance of coating polymer

Direct contact: Samples of the final resin were subjected to direct heating at a temperature of 50-150 °C. The results showed the stability of

the thermal resistance of the material up to 140 °C. where the material faces distortion and failure at the temperature 149 °C. Table 2 below shows the resin's behavior towards temperature change.

TABLE 2 The resin's behavior towards temperature change

Temp. °C	Mole Ratio	Resin Behavior			
		Time min	1:1	1:2	1:3
50		30	*R	R	R
		60	*F	F	R
		120	R
		180	R
100		30	R
		60	R
		120	R
		180	R
120		30	R
		60	R
		120	R
150		30	F

*R: resistance *F: failure

Indirect contact: Samples of the final resin were subjected to heating in the presence of a fluid (silicon oil) at a temperature ranging from 50 to 200 °C. Failure appeared on the

resin at 179 °C as the material reached the state of mechanical dissociation. Table 3 below shows the resin's behavior towards fluid temperature change.

TABLE 3 The resin's behavior towards fluid temperature change

Temp. °C	Mole Ratio	Resin Behavior			
		Time min.	1:1	1:2	1:3
50		30	R	R	R
		60	F	F	R
		120	R
		180	R
100		30	R
		60	R
		120	R
		180	R
120		30	R
		60	R
150		120	R
		30	R
180		30	F

The diagrams below (Figures 9 and 10) show the thermal stability of the prepared polymer in case the material is exposed to a

temperature of 140 °C by direct contact and indirectly 170 C by contact with the heating source.

Technical and economic feasibility

After the mathematical analysis of the cost of production of coating material, it was applied to a specific area. The results proved that the coating of an area of 7.1 cm² cost \$ 0.43

provided that thickness of the coating layer was 0.6 mm. Table (5) shows the economic costs of preparing resin for the packaging of the tanks with the change in surface area (Cost (\$) = 6.61 Area (m²).

TABLE 5 The economic costs for the packaging of the tank bases with RF coat

Cost \$	Area m ²	Diameter (m)
0.467	0.07063	3x 10 ⁻²
518.8	78.5	10
1167.45	176.62	15
2075.54	314	20
3243.06	490.63	25
4669.965	706.5	30

Conclusion

The current study presented the following results:

- The polymer prepared is self-curing and is of great importance to the petroleum industry to prevent corrosion in oil tank bases;
- The prepared polymer, due to its adhesion properties, qualifies it to be used in the fields of thermal insulation;
- The prepared polymer is highly efficient in resisting solvents and acidic media;
- The prepared polymer is able to withstand high compression up to 5000 N at 0.6 mm and above. The resistance of the encapsulation resin to the temperature reaches 170 ° C; and
- The RF coating was observed to have good adhesion and cohesive strength before and after exposure to the crude oil solution.

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