

**NEW ANTIMICROBIAL COATING COMPOSITIONS BASED ON 3,6-DICHLORO BEZO[B]THIOPHENE-2-CARBONYL GLUTAMIC ACID. (DCBTGA) . MODIFIED POLYESTERAMIDE RESINS AS BINDER FOR INDUSTRIAL APPLICATIONS**

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**Abstract**

Thiophene and their derivatives products are some of the oldest and best known class of nitrogen and sulphur containing compounds. In recent years there has been considerable interest in the thiophene -based family of materials due to the wide range of antimicrobial activity properties when incorporated into polymers and their composites. In this research new modified polyesteramide resin compositions which are prepared by partial replacement of phthalic anhydride (PA) with 3,6-dichloro bezo[b]- thiophene-2carbonyl glutamic acid (DCBTGA), as a new source of the dibasic acid and as preservative against microbiological attack with N, N- bis - (2-hydroxyethyl) linseed oil fatty acid amide (HELA) as source of polyol. These new source of dicarboxylic acid materials and new modified polyesteramide resin are confirmed by IR and NMR spectral analysis. The coating performance of the resins is evaluated using international standard test methods (ASTM) and involved the measurement of physico- mechanical properties such as viscosity, drying time, specular gloss, pencil hardness, adhesion, flexibility and The results show that the modification enhances both physico- mechanical and chemical properties The new antimicrobial polyesteramide resins is characterized using standard (Kathon LX biocide) in different excess – OH formulations to reach the best formula against bacteria and fungi. The studies showed promising results as biocide coatings.

**Keywords**–Polyesteramide; 3,6-dichloro bezo[b]- thiophene-2carbonyl glutamic acid (II), antimicrobial, biocide , surface coating.

**Introduction**

Biocides in paint fall into two main categories; those used for wet state protection and those for film protection. Wet state (in-can) biocides may be bactericides and fungicides, which used to protect the coating material until it can be applied. Film biocides, which can be fungicide or algacides, have been incorporated to prevent the growth of fungi and algae on applied surface coatings. Sharif Ahmad et al, have been used it as a starting materials for the development of polyetheramides, polyesteramides, polyesteramide urethanes and polyamide urethanes, as protective coating materials and as an effective antibacterial and biologically safe corrosion protective material [1-6]. Recently microbial activity of

N,N Di-hydroxyethyl-2-thiophenamide (HETA) against *Bacillus subtilis* ATCC 7972, *Staphylococcus Aureus* NCTC 7447, *Escherichia Coli* NCTC 10416, *Pseudomonas aeruginosa* ATCC 10145, *Candida Albicans* IMRU 3669, and *Aspergillus Niger* ATCC 6275 have been discussed and the studies showed promising results as biocidal coatings. Preparation of modified polyesteramides were also considered and found also improved the film performance and durability and lead to substantial antimicrobial growth control [7,8]. Various water-soluble polyesteramide compositions based on 8-hydroxyquinoline as preservative against microbiological attack were also studied [9]. Polyesteramide resins containing pentachlorophenol residue in their structure were prepared and evaluated as antimicrobial growth control [10]. A new modified polyesteramide resins were screened for their anti-bacterial activity against *E. coli*, *Pseudomonas* sp, and *Staphylococcus* sp, and their antibacterial activity was evaluated in the nutrient agar media [11]. A biodegradable polyesteramide was prepared and tested under different conditions where PH =12 and at a temperature of 80 °C. The complete degradation can be realized. [12]. Blends of poly (vinyl chloride) (PVC) and polyesteramides were prepared to improve the impact strength of PVC [13]. Various modified polyesteramide varnishes as antimicrobial growth control were prepared and evaluated as new binder for organic surface coating [14]. Also, new modified polyesteramide compositions based on 2,3-dihydroxypropyl) theophylline, pyromellitimide ring, and N-phthaloylglutamic Acid (NPGA) were prepared and evaluated as vehicles for surface coating, This modification, as expected, improved the film performance and durability and lead to substantial antimicrobial growth control [15-17]. In this work new modified polyesteramide resin compositions are prepared, These modified resins are prepared by partial replacement of N, N- bis - (2-hydroxyethyl) linseed oil fatty acid amide (HELA) with 3,6-dichloro benzo[b]-thiophene-2-carbonyl bis-(2-hydroxy ethyl)-amide (DCBTHEA) as a new source of the polyol source and their antimicrobial as preservative against properties tested.

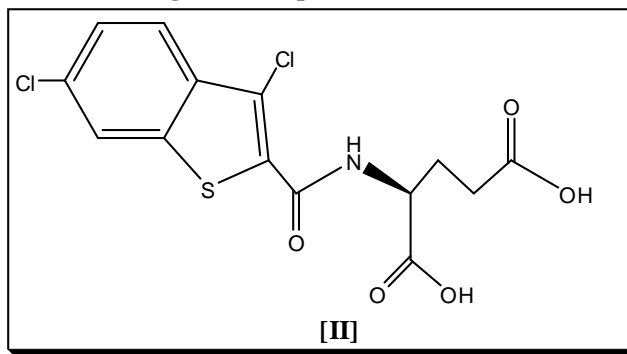
## **Experimental**

### **Materials**

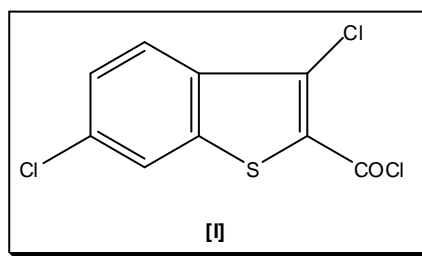
The linseed oil fatty acid (LOFA) used is supplied by Echantillon, Belgium, the phthalic anhydride (PA) by Avondate Laboratories, England and the diethanolamine (DEA) and N-phthaloylglutamic acid are obtained from Sdfine Indian. Sulphuric acid, anhydrous sodium carbonate, benzene, glacial acetic acid and ethyl acetate are obtained from El Nasr Pharmaceutical Company, Egypt. The xylene and mineral turpentine products are obtained from the Misr Petroleum Company, Egypt.

**Methods and techniques**

- 1) **Synthesis of 3,6-dichloro benzo[b]thiophene-2-carbonyl glutamic acid carried out according to two steps .**

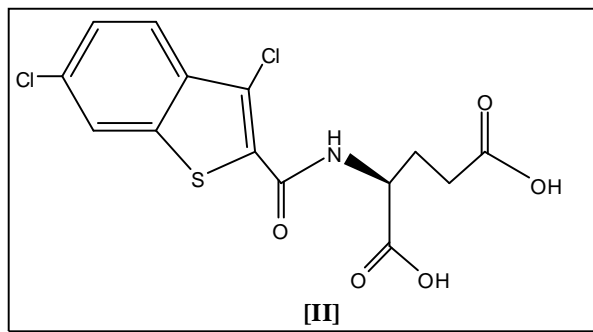


**Step1- synthesis of 3,6-dichlorobenzo[b]thiophene-2-carbonyl chloride [I].**



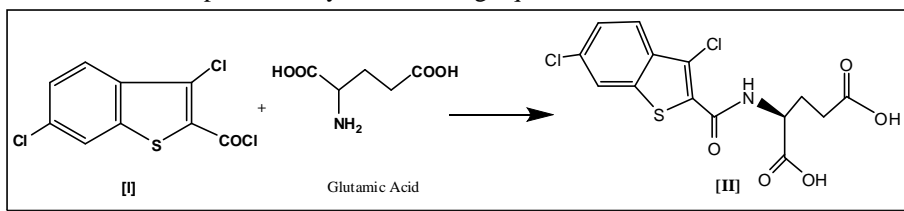
To a mixture of p-chlorocinnamic acid (10 gm 0.055 mol) and pyridine (1 ml), is added (16 ml 0.22 mol.) thionyl chloride dropwise. The mixture was heated in an [(oil-bath) at (125-140 °C)] and stirred at this temperature for an additional 1 hr. The reaction mixture is taken up with 300 ml of dry (n-hexane), heated and decanted from the gummy residue. The yellow solution then solidified to give 6.6 gm (40 % yield) of the product m.p (129-131°C).

**Step 2- Synthesis of 3,6-dichloro benzo[b]thiophene-2-carbonyl glutamic acid [II].**



L-Glutamic acid (8.13 g, 0.055 mol) is suspended in (300 ml.) dioxan and solubilized by the addition of pyridine (9.61 ml.) to the results solution was 3,6-dichlorobenzo[b]thiophene-2-carbonyl chloride 15 gm. (0.056 mol) and the mixture is refluxed for 3 hrs. The reaction mixture is cooled and then poured into crushed ice-water to extract the pyridine-HCl. The precipitate formed is collected on a filter and washed with water deride and further purified by recrystallization from ethanol. The product which white crystals is then dried and weighted as 17 gm. (74% yields), m.p (180-182<sup>0</sup>C).

These reactions represented by the following equation.



### Synthesis of new modified antimicrobial polyesteramide resins carried out according to two steps.

#### Step 1. Synthesis of N,N-bis(2-hydroxyethyl)linseed oil fatty acid amide (HELA)

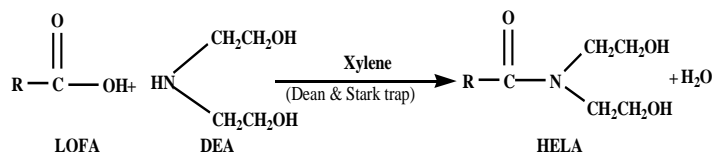
A mixture of freshly distilled diethanolamine (DEA) 11.55g, (0.11mol) and linseed oil fatty acid 28.0g, (0.1mol) is added to a 250 ml round-bottom flask fitted with a Dean and Stark trap. The mixture is allowed to reflux in the presence of 15% xylene until the theoretical amount of water (1.8ml, 0.1mol) is collected, indicating the complete formation of N,N-bis(2-hydroxyethyl)linseed oil fatty acid amide (HELA) this reaction represent as in schem1.

#### Step 2. Synthesis of modified polyesteramide resins.

Polyesteramide resins are prepared through a condensation polymerisation reaction via a solvent process, in a one step reaction. A mixture of a calculated amount of hydroxy ethyllinseed oil fatty acid amide (HELA), as the ingredient source of polyol and phthalic anhydride (PA) replaced partially with 3,6-dichlorobenzo[b]thiophene-2-carbonyl glutamic acid (DCBTGA) as the ingredient source of the dibasic acid added to a 250ml round-bottom flask fitted with a Dean and Stark trap and refluxed in the presence of 10% xylene as showed in the figure represented as in schem2 . The route of esterification are followed by observing the theoretical amount of water liberated. The resins were prepared, covering a wide range of oil lengths and hydroxyl content (0, 10, 20 and 30 % excess-OH). It should be noted that within each set of formulations the total number of acid and hydroxyl equivalent for the various runs are kept constant [18]. Resin characteristic constant and weight changes of the various formulations are illustrated in Tables 1 and2. Alkyd

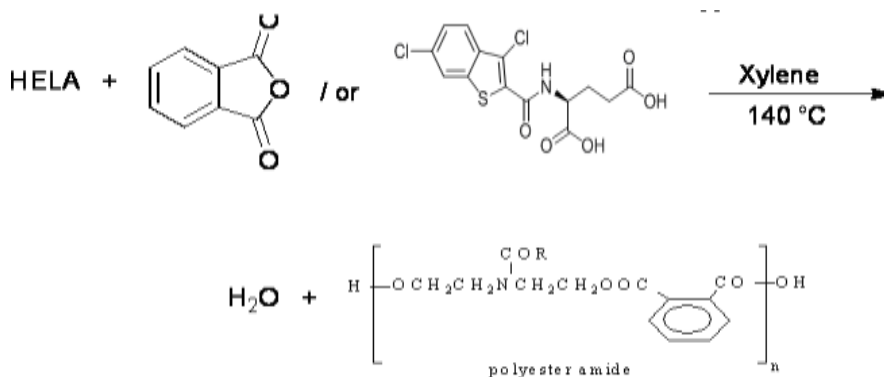
polyesteramide calculations can be used to predict the completed formulation, properties of the resin, the amount of reaction water liberated and the probable risk of gelation. The calculation of water evolved is also useful both as a tool for following the course of esterification reaction and to find the theoretical yield.

**Scheme 1.** Preparation of modified polyester amide resin



Step1- Synthesis of N,N-bis(2-hydroxyethyl) Linseed oil fatty acid amide (HELA)

**Scheme 2 :**



**Step 2- Synthesis of DCBTGA -modified polyesteramides**

**Table1** Resin constants for DCBTGA -modified polyesteramides

Resin No.	Excess – OH (%)	Ingredients	E	F	e <sub>0</sub>	e <sub>A</sub>	e <sub>B</sub>	R	K	H <sub>2</sub> O off (ml)
I <sub>a-d</sub>	0	HELA	184	2	0.260	—	0.260	1.00	1.00	2.3
		DCBTGA	185	2	0.078	0.078	—			
		PA	74.1	2	0.181	0.181	—			
II <sub>a-d</sub>	10	HELA	184	2	0.300	—	0.300	1.10	1.05	2.5
		DCBTGA	185	2	0.082	0.082	—			
		PA	74.1	2	0.191	0.191	—			
III <sub>a-d</sub>	20	HELA	184	2	0.358	—	0.358	1.20	1.10	2.7
		DCBTGA	185	2	0.089	0.089	—			
		PA	74.1	2	0.208	0.208	—			
IV <sub>a-d</sub>	30	HELA	184	2	0.44	—	0.44	1.30	1.15	3.1
		DCBTGA	185	2	0.10	0.10	—			
		PA	74.1	2	0.239	0.239	—			

HELA: Hydroxy Ethyl Linseed Amide; PA: Phthalic Anhydride; 3,6-dichloro bezo[b]- thiophene-2-carbonyl glutamic acid DCBTGA ; E: Equivalent Weight;  $e_A$ : Number of acid equivalent ;  $e_B$ : Number of hydroxyl equivalent;  $e_0$ : Total equivalent present at the start of the reaction; F: Functionality ; K: Alkyl constant ( $m_0/e_A$ ); R: Ratio of total-OH groups to total-COOH groups ( $e_B/e_A$ )

**Table 2 List of hydroxyl equivalent of different runs**

Resin	PA	DBTGA:
A	1.00	0.00
b	0.90	0.10
c	0.85	0.15
d	0.80	0.20

### Measurements

The structure of the prepared 3,6-dichloro bezo[b]- thiophene-2-carbonyl glutamic acid (DCBTGA), was confirmed by the melting point, IR and NMR. The structure of the prepared N,N-bis(2-hydroxyethyl) linseed oil fatty acid amide (HELA) was confirmed by acid value (ASTM D 1639-96) and hydroxyl value (ASTM D 1957- 01). Infrared spectra of the prepared polyesteramide resin is recorded in polymer/KBr pellets using Shimadzu FT-IR 400 spectrometer was also undertaken for confirmation of the polyesteramide resin structure as showed in Figure 1 and tabulated in Table 3. The colour (ASTM D 1544-04) of the prepared polyesteramide and the new modified anti-corrosive polyesteramides resins was undertaken using the ‘Gardner 1953 Standard Colour’, whereas the viscosity [ASTM D4287-00(2010)] is established by the use of Gardner Tubs viscometer.

### Preparation of polyesteramide coatings

The solid content (ASTM D1644-01) of the modified and unmodified polyesteramide resins are adjusted by means of thinning with mineral turpentine to 50% solids for the 0, 10, 20 and 30% excess – OH samples. The resin samples are then filtered and the driers combination added (Co, Zr and Ca-Octoates, 0.04, 1.0 and 0.05% based on metal/solid resin, respectively). The resin material is then applied onto both glass panels (ASTM D3891-02) and steel strips (ASTM D609 - 00) at room temperature by means of a brush.

### Film casting and testing

Glass plates (100×150 mm) coated with the individual resins are utilised to measure the drying schedule, in terms of time of set-to-touch and dry - through times (ASTM D1640-03). In addition, the same coated glass plates are also used to measure the degree of gloss for individual resin coatings (ASTM 523- 08). The measurements are undertaken using a gloss meter set at 20° angle. The chemical resistance (ASTM D 870-02, D 2792-04) of the dried resin coatings to different

solvent media is undertaken on glass panels (25×75 mm). The coated steel strips are utilised to measure the coating film thickness (ASTM D 1005- 07),with this being undertaken using a Model 2100 Minitest microprocessor coating thickness gauge, manufactured by Electro – Physic, West Germany. The thickness of the coatings is found to be 50±5µm. The coated steel strips are also used to measure the mechanical resistance of the coated resin films, with testing undertaken on adhesion strength, by means of the cross-cut method (ASTM D 3359-02), flexibility (ASTM D 522-93),scratch hardness (ASTM D5178-98(2008))and resistance to mechanical damage (impact resistance) (ASTM D 2794-04).

### **Microbiology Assay :**

Test method of antimicrobial activity carried out according to ASTM, D5589-97 (Re-approved 2002).

#### **1.a. Assay medium for antibacterial activity (g/l):**

The nutrient agar medium is used for antibacterial assay. The medium has the following composition:

Pepton; 5.0, beef extract 3.0, NaCl 5.0 and agar 20. The pH of the medium is adjusted at 6.8-7.0 before sterilization.

#### **1.b. Assay medium for anti-yeast activity (g/l):**

Yeast extract-malt extract medium composed of: yeast extract 4.0, malt extract 10.0, cellulose (glucose) 4.0, and agar 20. The PH was adjusted at 7.3 before sterilization.

#### **1.c. Assay medium for antifungal activity (g/l):**

The Dox medium used for antifungal activity. This medium composed of :

Sucrose 20.0, NaNO<sub>3</sub> , 2.0, K<sub>2</sub>HPO<sub>4</sub> 1.0, MgSO<sub>4</sub> . 7H<sub>2</sub>O 0.5, KCl 0.5, FeSO<sub>4</sub>. 5H<sub>2</sub>O 0.001 and agar 20 . The pH is adjusted at 6-6.4 .

### **2. Organism Used :**

Bacteria employed in microbiological assay are Micrococcus lutus NCTC 9341, Staphylococcus aureus NCTC 7447, E.coli Bppol, Salmonella . While fungi are Candida albicans IMRU 366 g, Aspergillus flower, Penicillium citricus and Suserium.

### **3. Preparation of tested sample:**

The tested varnish is brushed on each side of a whatman filter paper (No. 30) and allowed to dry for 24 h. Squares of the coated filter paper of (1.25 in) are made. The square is sterilized by dipping in alcohol and placed centrally on the agar surface in the petri-dishes using a sterile for sepses.

#### 4. Antimicrobial activity :

(a) Method used for bacteria and yeasts under investigation :

Twenty four hours old culture of each of the test bacteria and forty eight hours old culture of each of the test yeasts are used. Five ml of sterile distilled water is added to culture tube and mixed well by a vortex mixer . Five drops of the suspension is used to inoculate 100 ml. Nutrient agar medium (for test bacteria) or 100 ml yeast extract-malt extract medium (for test yeasts) at 45 °C. This was dispensed among Petri dishes in 20 ml. Portions. A coated filter paper discs (13mm) are aseptically put on the surface of the seeded plates with the different test organisms. The plates are left for 2 hours in a refrigerator for diffusion after which the plates are incubated at 30<sup>0</sup>C for 18 hrs.(for bacteria) or 48hrs.( for yeasts). The detection of clear zone around the paper disc is an indication of the antagonistic properties of the coated filter paper disc under study. For each test organism at least 4 discs are used for different concentration (0,10 ,20. and 30% excess-OH) of the varnish under investigation.

(b) Method used for Fungi under investigation :

The spores and mycelia of each of the test fungi (48 hrs. old culture) are streaked on the surface of the plates of Dox medium after pouring and solidification.

The method was preceded as previously described under item

The antimicrobial activity of the coated filter paper disc against a variety of microorganisms, including Gram-Positive, Gram-Negative, Yeasts and fungi is investigated.

#### Results and discussion

In recent years, there has been considerable interest in improving polyesteramide resins. A number of polyesteramide have been developed by the reaction of linseed oil fatty amide with dicarboxylic acids/anhydrides[19]. In the present work, the newly modified antimicrobial polyesteramides resins are obtained by partial replacement of phthalic anhydride with 3,6-dichloro benzo [b]thiophene-2-carbonyl glutamic acid (DCBTGA) as a new source of the dibasic acid source and as preservative against microbiological attack with linseed oil fatty amide (LOFA) as the ingredient source of the polyol . The reaction of LOFA with DEA to give HELA is demonstrated in Scheme 1, which is confirmed by acid and hydroxyl value. The measured acid value was 6mg KOH/g, whilst the theoretical value is 0mg KOH/g, and the measured hydroxyl value is 308 mg KOH/g whilst the theoretical value is 305.72 mg KOH/g, which indicates the complete formation of HELA.

**Spectral analysis of 3,6-dichloro bezo[b]thiophene-2-carbonyl glutamic acid (DCBTGA) (modifier).**



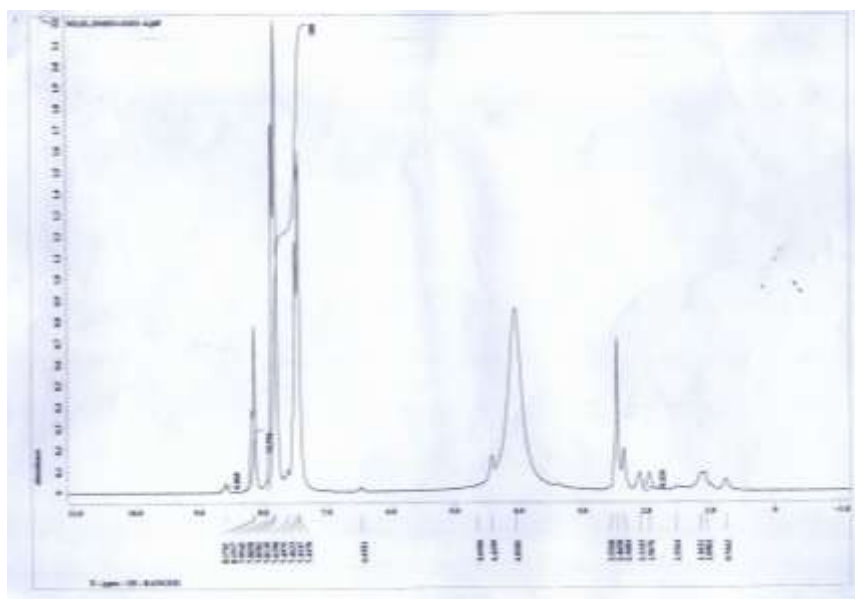
Structural features of 3,6-dichloro bezo[b]thiophene-2-carbonyl glutamic acid [II] are confirmed by IR spectroscopy which tabulated in table3 and  $^1\text{H}$ NMR spectrum which represented in fig 1.

**Table 3. IR spectral showed the following data.**

Functional group	IR peak ( $\text{cm}^{-1}$ )
OH,NH	3394
CH aromatic	3072
CH aliphatic	2923
COO ester carbonyl	1698
Ring stretching vibration of aromatic nuclei	821

**$^1\text{H}$ NMR spectrum showed the following data.**

$^1\text{H}$ NMR spectrum of 3,6-dichlorobezo[b]thiophene-2-carbonyl glutamic acid [II] in Damso-d<sub>6</sub> gave signals peaks at ( $\delta$ , ppm): 1.20 (t, 2H, CH<sub>2</sub>), 2.11(t, 2H, CH<sub>2</sub>), 4.46 (t, 1H, CH), 6.50 (hump, 1H, NH), 7.48-8.24 (CH-Ar.), 8.60 (hump, 2H, 2COOH), as showed in the (fig.1).



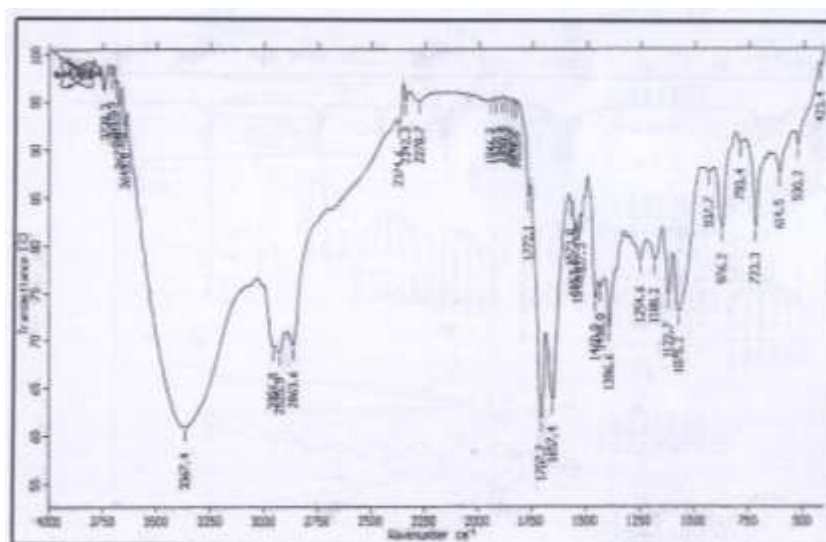
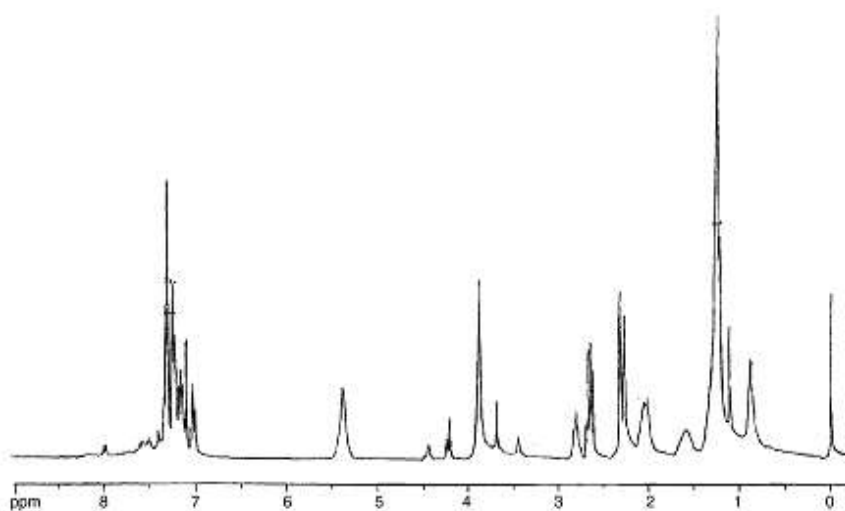
**Figure 1  $^1\text{H}$ NMR spectrum of 3,6-dichlorobezo[b]thiophene-2-carbonyl bis-(2-hydroxy ethyl)-amide (DCBTHEA).**

#### **Spectral analysis of polyesteramide resin.**

The spectral analysis of the resin shows the presence of both ester and amide linkages in the polymer backbone. This has been confirmed by both FT-IR and  $^1\text{H}$ NMR spectral analyses, as showed in figure 3,4. The key peaks of the IR spectra of polyesteramide are shown in Table4, which indicates the presence of both ester and amide groups, confirming the formation of polyesteramide.

**Table 4. FTIR spectra of DCBTGA polyesteramide resin**

Functional group	IR peak ( $\text{cm}^{-1}$ )
OH	3394
CON amide carbonyl	1657
COO ester carbonyl	1707
C-N	1460
CH aliphatic	2863-2956
Ring stretching vibration of aromatic nuclei	723

**Figure 3. I.R. Spectrum of DCBTGA modified polyesteramide resin****Figure 4. <sup>1</sup>H NMR Spectra of polyesteramide resin**

$^1\text{H}$  NMR spectra Fig.(2) shows characteristic peaks for  $\text{CH}_2$  attached to free hydroxyl, amide nitrogen and amide carbonyl at 3.491 ppm, 3.745–3.56 ppm and 2.3–2.26 ppm, respectively, while those in the aromatic region at 7.8–6.9 ppm for ring protons of PA.

#### **Physical-mechanical characterisation of the new modified antimicrobial polyesteramides resin**

During the course of the preparation of the resin, the effect of the 3,6-dichloro benzo[b]-thiophene-2-carbonyl glutamic acid (DCBTGA), on the physical properties such as colour, viscosity, air drying time, were determined as in Table 5. The effect on the mechanical properties such as gloss, flexibility (bend), adhesion, scratch hardness are also determined and represented in Table 6. The new modified antimicrobial polyesteramide compositions, gave a very clear transparent and homogenous appearance. The colour of resins are observed to be dark brown due to the presence of nitrogenous base while the viscosity of resins increase with an increase in the percentage of both 3,6-dichloro benzo- thiophene-2-carbonyl glutamic acid (DCBTGA), and excess hydroxyl content. The drying time is observed to be proportional with both 3,6-dichloro benzo[b]- thiophene-2-carbonyl glutamic acid (DCBTGA), and excess hydroxyl content. The results indicate that the modified films show outstanding performance, compared to unmodified films, The gloss results for the resins increases through modification, which may be attributed to the incorporation of dicarboxylic acid containing a DCBT ring within the resin structure. The presence of the repeating units of ester (-COOR) in the polymeric chain of polyesteramide improved the ease of application, as well as enhancing the hardness properties. The flexibility test for the coated panel, carried out at the mandrel diameter of 6mm, show no evidence of cracks or de-laminating of the coating film. This high flexibility of the coating is attributed to the resin being composed of a polyester backbone. The cross-hatch test, carried out to determine the adhesion of the coating, clearly indicates that the modified coating has very good adhesion properties. No delaminating or detachment, of coatings at the edges, and within the square lattice, is observed. Improvement of the mechanical properties appears to be due to the combination of amide groups, which results in poly (amide), containing a benzene and thiophene ring within the resin structure.

#### **Chemical resistance of the new modified antimicrobial polyesteramide resin**

The chemical resistance testing of the new modified anti-microbial polyesteramide resins are undertaken on glass panels (25×75mm). From the data in table 5, it can be observed that an increase the levels of 3,6-dichloro benzo[b]-thiophene-2-carbonyl glutamic acid (DCBTGA), lead to a substantial improvement in

the films resistance towards alkali and acid. This may well be attributed to the introduction of the DCBT ring within the resin structure. However, 3,6-dichloro benzo[b]- thiophene-2-carbonyl glutamic acid (DCBTGA) does not appear to affect the solvent and water resistance properties, since all the examined films showed excellent performance within the experimental time of 30 days.

**Table 5. Varnishes characteristics data**

Resin No.	Excess-OH (%)	Replacement (%) of DCBTGA	Viscosity (Gardner Tubs )	Air Drying (HD)Time (hr)	Color (Gardner)
<b>Ia</b>	0	0	F	3	>18
<b>Ib</b>		10	H	2.5	>18
<b>Ic</b>		15	K	2.5	>18
<b>Id</b>		20	N	2.5	>18
<b>IIa</b>	10	0	G	2.15	>18
<b>IIb</b>		10	H	2	>18
<b>IIc</b>		15	K	1.4	>18
<b>IId</b>		20	N	1.4	>18
<b>IIIa</b>	20	0	H	2.5	>18
<b>IIIb</b>		10	L	2.4	>18
<b>IIIc</b>		15	N	2.1	>18
<b>IIId</b>		20	O	2	>18
<b>IVa</b>	30	0	J	3	>18
<b>IVb</b>		10	M	3	>18
<b>IVc</b>		15	P	2.5	>18
<b>IVd</b>		20	T	2.3	>18

**Antimicrobial Activity 3,6-dichloro bezo[b] thiophene-2-carbonyl bis-(2-hydroxy ethyl)-amide (DCBTHEA)-Modified Polyesteramide Resins:**

Table 7. showed the activity of 3,6-dichloro benzo- thiophene-2-carbonyl glutamic acid on some representatative microorganisms. Bacterial resistance of various excess hydroxyl of 3,6-dichloro benzo- thiophene-2-carbonyl glutamic acid .modified polyesteramide showed that Micrococcus luteus ATCC 9341 and Staphylococcus aureus NCTC 7447 is largely affected by modification with 3,6-dichloro benzo- thiophene-2-carbonyl glutamic acid Where Escherichia coli and Salmonella is lowest affect... The fungi resistance of various excess hydroxyl 3,6-dichloro benzo[b]- thiophene-2-carbonyl glutamic acid modified polyesteramides showed that Candida albicana, IMRU 3669, Aspergillus flower , Penicillium

citricus and Suserium are improved by increasing the modifier percent (DCBTGA) as shown in figure 4 .

**Table 6 . Effect of DCBTGA on mechanical and chemical properties of cured modified polyesteramide**

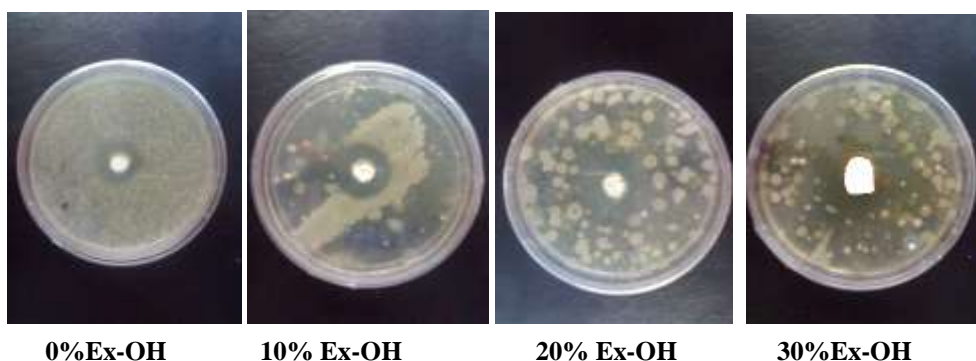
Resin No	Gloss at 20 °		Flexibility	Adhesion	Scratch hardness 1Kg	Water Resistance Per(day)	Alkali ** Resistance Per (day)	Acid * Resistance Per (day)	Solvent Resistance Per (day)
Ia	85		Pass	5B	>1.5	>30	1	12	>30
Ib	90		Pass	5B	<2	>30	1	18	>30
Ic	92		Pass	5B	<2	>30	2	18	>30
Id	95		Pass	5B	<2	>30	3	24	>30
IIa	90		Pass	5B	>2	>30	1	18	>30
IIb	95		Pass	5B	>2	>30	1	24	>30
IIc	95		Pass	5B	<2	>30	3	24	>30
IIId	102		Pass	5B	<2	>30	5	30	>30
IIIa	100		Pass	5B	>2	>30	2	24	>30
IIIb	102		Pass	5B	>2	>30	3	24	>30
IIIc	102		Pass	5B	<2	>30	5	30	>30
IIId	100		Pass	5B	<2	>30	7	30	>30
IVa	89		Pass	5B	>2	>30	2	24	>30
IVb	95		Pass	5B	<2	>30	3	30	>30
IVc	98		Pass	5B	<2	>30	5	30	>30
IVd	100		Pass	5B	<2	>30	7	30	>30

**Table 7. Biocides activity of DCBTGA modified polyesteramide**

Microorganisms	(0 % excess OH).	(10 % excess OH).	(20 % excess OH).	(30 % excess OH).
<b>Micrococcus luteus ATCC 9341</b>	+ve	++Ve	+++Ve	++++Ve
<b>Staphylococcus aureus NCTC 7447</b>	+Ve	++Ve	+++Ve	++++Ve
<b>Escherichia coli</b>	-ve	+Ve	+Ve	+Ve
<b>Salmonella</b>	-Ve	+ve	++Ve	++V
<b>Candida albicans IMRU 3669</b>	-Ve	+Ve	++ve	+++Ve
<b>Aspergillus flower</b>	-Ve	+Ve	++Ve	++Ve
<b>Penicillium citricus</b>	-Ve	+Ve	++Ve	++V
<b>Suserium</b>	-Ve	+Ve	++Ve	+++Ve

**Table 8. Rating the results according to the following:**

-ve	=	No Inhibition Zone
+ve	=	Weak Inhibition Zone (10-19mm.)
++ve	=	Moderate Inhibition Zone (20-26mm.)
+++ve	=	Good Inhibition Zone (27-35mm.)
++++ve	=	Very Good Inhibition Zone More than 35mm.

**Figure 5. Showed the photos of the biological activity of DCBTGA modified polyesteramide resins.**

### Conclusion

The successful modification of polyesteramide resin by the partial replacement of phthalicanhydride(PA) as dibasic acid source by 3,6-dichloro bezo[b]-thiophene-2-carbonyl glutamic acid with Hydroxyl ethyl linseed oil fatty acid amide (HELA) as the ingredient source of the polyol has been achieved with the time of reaction and curing time being the only minor drawbacks. The modified resin shows enhanced physico-mechanical properties such as gloss and scratch hardness. It is also observed that the modified resin showed better film performance in terms of chemical resistance to acid and alkali. The antimicrobial activity of the DCBTGA modified polyesteramide resins, incorporated within different Ex-OH formulations, also improved with increased levels of the modifier. This improvement may be attributed to (i) the combination of amide groups, which results in poly (amide), containing a Benzothiophen(BT) ring within the resin structure; (ii) the presence of Chlorine, Sulphur, Nitrogen, benzene and thiazoline heterocyclic ring in the polymeric chain of the modified polyesteramide.

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