

6-1-2009

Section: Chemistry

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How to Cite This Article

AQEEL, SALEM; ABD EL-WAHAB, H.; MAHDY, ABDULSALAM; and ABD EL-HAI, F. (2009) "NEW MODIFIED POLYESTERAMIDE COMPOSITIONS AS VEHICLES FOR SURFACE COATINGS.," *Al-Azhar Bulletin of Science*: Vol. 20: Iss. 1, Article 18.

DOI: <https://doi.org/10.21608/absb.2009.7555>

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NEW MODIFIED POLYESTERAMIDE COMPOSITIONS AS VEHICLES FOR SURFACE COATINGS.

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Abstract

New modified polyesteramide compositions were prepared and evaluated as anticorrosive varnish. The resin prepared by partial replacement of hydroxy ethyl fatty acid amide (HEFA) by polyethylene glycol (PEG) without affecting the resin constants. Primer formulations based on this resin showed good corrosion inhibiting properties.

Keyword: Polyesteramide, Surface coating, Corrosion inhibiting, Polyethylene glycol, Anticorrosive varnish.

Introduction

The main function of organic coating on metal surface is to protect it against corrosion. Corrosion inhibition may be the only reason for painting the metal structures in most cases. Many additives including are used as corrosion inhibitors in protective coatings[1-6].Anticorrosion properties of polyaniline-coated pigments in surface coatings was also studied [7]. Several polyesteramides have been synthesized from seed oils to improve their drying ability, mechanical and corrosion protective efficiency [8-13]. Several modifications have been done including metals and metalloids [14-16], styrene [17], urethane [18], and other groups [19]. The polyesteramide resin itself has good chemical and excellent thermal resistance properties and some of them can be used as an effective antibacterial and biologically safe corrosion protective materials.Cd- and Zn-incorporated polyesteramide based on linseed oil were evaluated for anticorrosive and antibacterial behaviour [20-21]. New modified polyesteramide compositions were prepared and evaluated as vehicles for surface coating, this modification lead to improve the film performance and durability [22]. Anticorrosive primers based on acrylic-modified alkyd resins has been evaluated and showed to have an interesting corrosion inhibiting potential [23].

The aim of the present work is to characterize and evaluate a new anticorrosive polyesteramide resin in protective coating formulations. The anticorrosive polyesteramides were prepared by partial replacement of polyols used in

manufacture of resin by polyethylene glycol (PEG₄₀₀). This replacement would expect to improve the anticorrosive and physicochemical properties of the modified resin.

Experimental

Material used:

Linseed oil fatty acid (LOFA) A product of Echnillon ,Bruxell, Belgique.
Phthalic Anhydride (PA) A product of Avondate laboratories, England.
Diethanolamine (DEA) A product of Merck Germany .

Sulphuric acid, anhydrous sodium carbonate, benzene,glacial acetic acid , and ethyl acetate were obtained from El Nasr Pharmaceutical Co. (Egypt).while xylene and mineral turpentine were obtained from Misr petroleum Co. Egypt.

Polyethylene Glycol (PEG 400): Colorless liquid, a pharmaceutical grade , a product of ASOL, Germany "LIPOXOL 400".

Titanium Dioxide supplied by Clariant-Switzerland

I. Preparation of various modified Polyesteramide Resins;

Preparation of various modified polyesteramides were carried out in two general steps:

A. Preparation of N,N-bis(2-hydroxyethyl)linseed oil fatty acids amide (HELA):

A mixture of freshly distilled diethanolamine, DEA (10.5gm, 0.1 mole) and linseed oil fatty acid (28.0 gm, 0.1 mole) was placed in 250 ml round-bottomed flask fitted with Dean and Stark apparatus. The mixture was allowed to reflux until approximately the theoretical amount of water (1.8ml, 0.1 mole) was collected, indicating the complete formation of *N,N*-bis(2-hydroxyethyl)-linseed oil fatty acids amide (HELA).

B.preparation of PEG₄₀₀- modified polyesteramide resins:

The preparation of various PEG-modified polyesteramide resins based on linseed oil fatty acid was carried out via solvent process in one step reaction. A mixture of hydroxyethyl linseed oil fatty acidamide (HELA),phthalic anhydride(PA),

polyethylene glycol (PEG400) and 15% Xylene was placed in 250 ml round-bottomed flask fitted with Dean and stark apparatus, The content was refluxed until the theoretical amount of water was approximately collected

The prepared resins covered a wide range of oil lengths 55-70% , and hydroxyl content (0, 10, 20, and 30%Excess-OH).within each formulation, the total number of acid and hydroxyl equivalent were kept constant, and the various hydroxyl equivalent (e_B) of each type of Excess-OH resin listed in table (1).

Table(1) The resin characteristic constants of various PEG-modified polyesteramide.

Ex-OH	e_o	e_A	e_B	R	H ₂ O ml off
0%	0.519	0.259	0.260	1.00	2.3
10%	0.573	0.273	0.300	1.10	2.3
20%	0.650	0,298	0.352	1.20	2.3
30%	0.779	0.339	0.440	1.30	2.3

e_o :Total Equivalents Present at the start of reaction, e_A : Number of acid equivalents, e_B : Number of Hydroxyl Equivalent, R : Ratio of total-OH equivalent to total-COOH equivalent(e_B / e_A),

Table (2)list of hydroxyl equivalent of various modifications.

Number	HELA	PEG-substitution
*A	1.00	00.0
B	0.90	0.10
C	0.80	0.20
D	0.70	0,30

*: Unmodified formulations

Methods of evaluation:

Methods of testing and evaluation were performed according to the American Standard for Testing Methods (ASTM) and including, acid value [24], solid content [25], preparation of test panels [26], drying time [27], viscosity [28], color [29], The pencil hardness [30], film thickness [31], adhesion [32], Gloss [33], flexibility [34], chemical resistance [35-38] and corrosion resistance [39-43].

Results and Discussion

New modified polyesteramide resins were described through the partial replacement of *N,N*-bis(2-hydroxyethyl)linseed oil fatty acids amide (HELA) by polyethylene glycol (PEG400-modifier), such modification is expected to lead to better film performances .

The structure of resin prepared can be confirmed by FTIR fig(1) , which shown the following peaks:

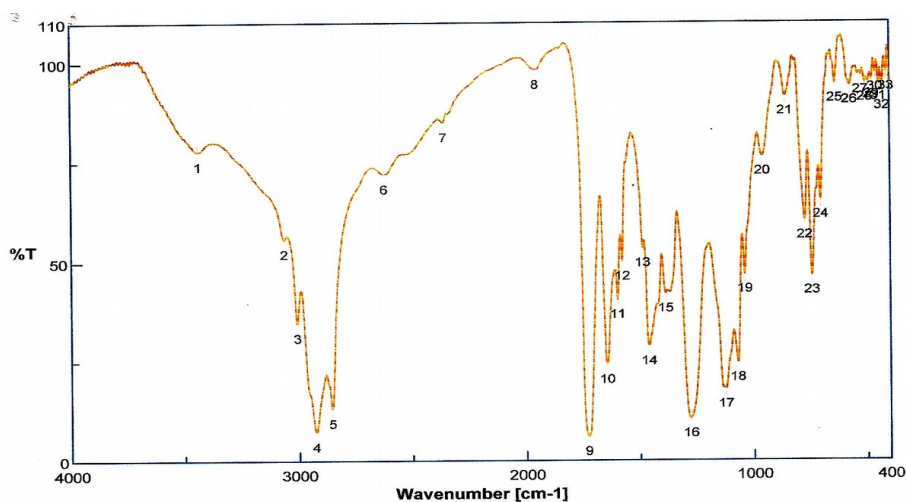


Fig (1): IR Spectra of PEG400 – modified polyesteramide

Functional group	IR peak (cm ⁻¹)
OH	3430
CON amide	1645
COO ester carbonyl	1728
C-N	1455
CH ₂ symmetric	2855
CH ₂ a symmetric	2925
Ring stretching vibration of aromatic nuclei	705

While ^1H NMR spectra Fig.(2) shows characteristic peaks for 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 and 5.35 ppm are characteristic peaks for OH alc.

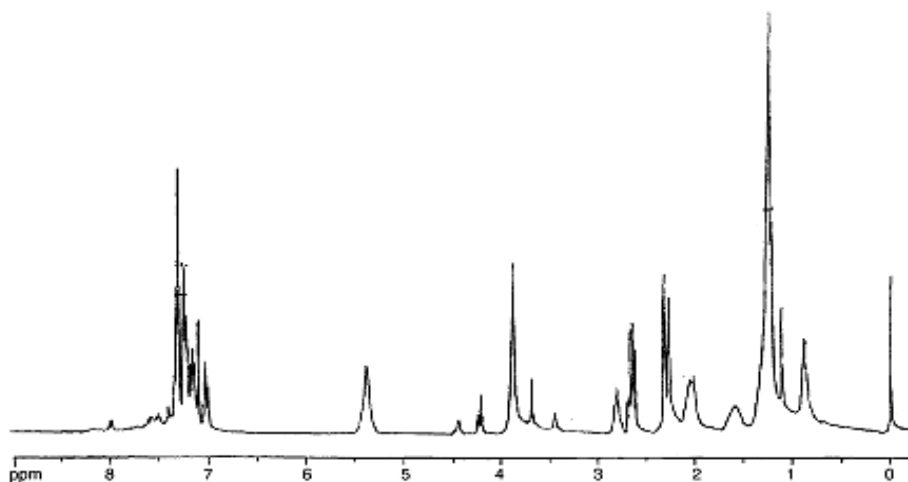


Fig. (2) ^1H NMR Spectra of polyesteramide resin

Physical-mechanical characterization of the modified polyesteramid resin

During the course of preparation, the amount of collected water in the trap was observed against the time of reaction and the obtained data are graphically represented in fig.(3) which indicate that the time of reaction increase with increase the modifier percent. The effect of the modifier (PEG 400) on physical properties such as color, viscosity, air and stove drying time are represented in table (4) while the mechanical properties such as gloss , scratch hardness, adhesion and flexibility (bend) are represented in table(5).

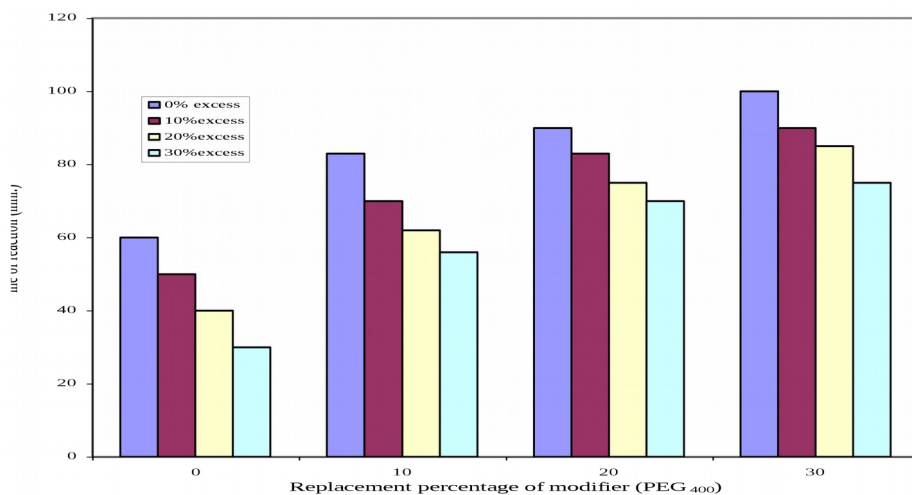


Fig.(3) Effect of modifier on time of reaction at 0%, 10%, 20% and 30% excess-OH for modified polyesteramide resin

Table (4) Effect of PEG₄₀₀ (Modifier) on physical properties of modified polyesteramide resin

Resin No.	Excess – OH %	Replacement % of PEG 400	Color (Gardner)	Viscosity (Gardner)	Air drying time (h)	Stoving at 120°C (min.)
Ia	0	0	>18	E	2	30
Ib		10	>18	K	3	35
Ic		20	18<	M	5	45
Id		30	18<	O	8	55
IIa	10	0	18<	F	4	55
IIb		10	18<	M	6	65
IIc		20	18<	P	9	75
IId		30	18<	Q	12	85
IIIa	20	0	18<	H	5	75
IIIb		10	18<	N	6	85
IIIc		20	18<	Q	10	95
IIId		30	18<	R	13	100
IVa	30	0	18<	K	7	95
IVb		10	18<	R	9	110
IVc		20	18<	S	12	125
IVd		30	18<	T	14	135

Table (5) Effect of PEG₄₀₀ (Modifier) on mechanical properties of cured modified polyesteramide

Resin No.	Gloss at 20 °		Flexibility		Adhesion		Scratch hardness (Kg)	
	A	S	A	S	A	S	A	S
Ia	93	97	Pass	Pass	4B	4B	<1	<1
Ib	93	96	Pass	Pass	4B	4B	1<	1<
Ic	92	95	Pass	Pass	4B	4B	1<	1.2<
Id	91	93	Pass	Pass	4B	4B	1.3<	1.4<
IIa	95	96	Pass	Pass	4B	4B	<1	<1
IIb	88	92	Pass	Pass	4B	4B	1<	1.4<
IIc	86	90	Pass	Pass	4B	4B	1.2<	1.6<
IId	80	88	Pass	Pass	4B	4B	1.4<	1.6<
IIIa	95	99	Pass	Pass	4B	4B	<1	<1
IIIb	87	92	Pass	Pass	4B	5B	1<	1.2<
IIIc	84	90	Pass	Pass	4B	4B	1.2<	1.5<
IIId	82	86	Pass	Pass	4B	4B	1.5<	1.7<
IVa	94	98	Pass	Pass	4B	5B	<1	<1.4
IVb	83	90	Pass	Pass	4B	5B	1<	1.5<
IVc	82	90	Pass	Pass	4B	4B	1.2<	1.6<
IVd	80	85	Pass	Pass	4B	4B	1.5<	2.0<

A: air dried film, S: stove dried film.

From the data recorded in table (4) & (5), the following conclusions were drawn:

- All modified and unmodified polyesteramide showed transparent and homogenous appearance.
- The color of the prepared modified polyesteramide resins were dark brown due to the presence of nitrogenous base.
- Varnish viscosity increase through modification with low molecular weight grade of polyethylene glycol.
- Air and stove drying time increase through modification.
- Gloss of cured films decrease through modification due to the partial replacement of aromatic with aliphatic compound.
- All cured films passed successfully flexibility (bend), adhesion, pinhole and stripping test.
- The modifier has slight effect on the cured film hardness; the purpose of this test is to assess the ability of the surface coating to withstand scratching.
- The mechanical properties of stove dried films are relatively better than the corresponding air dried films.

Evaluation of PEG400 –modified polyesteramide as corrosion inhibitor

The work was extended to include the utilization of PEG400 modified polyesteramids as binder and titanium dioxide nano particles as a white pigment in some primer formulations this amin containing resin would expect to improve the corrosion resistance through its effect on the entire surface of metal when present in sufficient concentration. these types of corrosion inhibitors work via decreasing the permeability of coating to water. oxygen and aggressive ions (such as chloride , sulphates) improving adhesion .Also the adsorption of resin through its hydroxyl function onto the metal surface increase the corrosion inhibition.

Five primer formulations based on PEG modified PEA (0,10,20,30 and 50% replacement). containing a deferent ratio from TiO₂ nano particle as a pigment, were prepared (table 5).

Table (5) Percent composition of the anticorrosive primer formulations.

Ingredient	Formulation no.				
	I	II	III	IV	V
Type of PEA	Unmodified	10% PEG	20% PEG	30%PEG	50%PEG
PEA %	30	30	30	30	30
TiO ₂ %	15	15	15	15	15
Talc	20	20	20	20	20
Zinc.phosphate	20	20	20	20	20
Solvent	11	11	11	11	11
Additives	02	02	02	02	02
Drier	02	02	02	02	02
	100	100	100	100	100

The primers then evaluated on actual coated steel panels by subjecting to salt spray machine for 500 hr. at room temperature . the corrosion was monitored via three techniques :-

- 1- Determination of blistering (size and frequency).
- 2- Determination of scribe failure.
- 3- Determination of degree of rusting.

The data obtained are listed in table (6) and can be clearly showed in figure (4).

The main conclusions derived from these data are. The presence of modifier(PEG400) in polyesteramide molecule increase the corrosion resistance (formulation 2,3,4), but at higher substitution the corrosion resistance fal down which may be du to the partial solubility of modified resin in water.

Table(6) Evaluation of corrosion resistance of the painted films

Formula No.	Modification %	Blistering**		Scribe failure rating***	Rust grade*
		Size	Frequency		
1	Blank	4	MD	3	4
2	10% PEG	7	M	7	8
3	20% PEG	9	F	9	9
4	30%PEG	9	F	9	9
5	50%PEG	2	MD	4	3

* Rusting is rated on scale from 10 to 0 , with 10 being no rusted and 0 being sever rusting.

** Blistering is graded also on scale from 10 to 0 , with 10 for no blistering and 0 for the largest blisters . Blistering frequency is denoted by F,M,MD and D (Few, Medium , Medium dense ,and Dense).

*** Scribe failure is also rating on scale from 10 to 0 , with 10 being zero (mm) form the scribe and 0 is 16(mm) from the scribe .



1 2 3 4 5

Fig(4). The corrosion inhibition of PEG – modified polyesteramide primers .

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