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Modified tannins for alkyd based anticorrosive coatings

ABSTRACT

The study of the synthesis of anticorrosive inhibitors, based on chemically modified tannins, and their use in alkyd based coatings to improve anticorrosive properties is presented in this work. Two methods of tannin modification were applied: direct method using ammonium hydroxide, ammonium hydroxide/ammonium chloride buffer or diethylenetriamine (DETA); and a two-step method including tannin modification with epichlorohydrin (ECH) in first step to produce epoxy modified tannin, ET, and further modification with heteroaromatic amines or linseed oil fatty acids (LFA) in second step. The obtained anticorrosive additives were characterized using ATR-FTIR, ^{1}H and ^{13}C NMR spectroscopies and elemental analysis. Epoxy, amino, hydroxyl, acid and iodine values of the synthesized inhibitors were determined according to standard methods. The prepared alkyd coating with tannin inhibitors was tested according to standard SRPS EN ISO 4628 method. Anticorrosive coating containing modified tannin based additive showed increased anticorrosive properties, good adhesion and coverage comparing to the coating with zinc phosphate additive. The alkyd coating films based on ET-LFA and ET modified with 2-amino-5-mercapto-1,3,4-thiadiazole showed best anticorrosive results.

Keywords: *modified tannin, anticorrosion additive, corrosion, alkyd coating.*

1. INTRODUCTION

Development of industrial materials based on bio-renewable resources has recently drawn attention of numerous researchers, due to the reduction of fossil fuels and increasing of environment pollution caused by using of commercial non-biodegradable materials. Thus, various natural monomers, oligomers and polymers, especially resources containing polyphenolic structures (etc. flavonoids, tannins, lignin) for obtaining the high-value biopolymer materials are explored [1]. Tannin is a polyphenolic based biopolymer with numerous -OH groups, the most commonly obtained by extraction from plants. Tannin belongs to a group of the most abundant natural polymers after cellulose, hemicellulose and lignin [2].

The most widely studied tannins are the condensed ones based on the flavan-3-ols, (-)-epicatechin and (+)-catechin by 4-8 or 4-6 linkages, respectively [3]. They were originally used in the skin tanning industry, but thanks to the reactivity of the hydroxyl group and the aromatic ring, tannins easily react with other substances, resulting in materials with improved physical and chemical properties and therefore their wide application. So, today tannins are increasingly used in medicine [4], enology [5], as raw material for the production of chemicals [6], additives [7] as well as polymeric materials for adhesives [8] and construction industry [9].

Corrosion problems have been usually solved by the selection of suitable materials that slow down the oxygen penetration to the metal surfaces. Anticorrosive protection mechanism of metal and steels is most commonly based on layering the organic coatings and paint adhesions on the substrate [10,11]. Many organic compounds have been investigated to explore their corrosion inhibition potential in recent years [12]. The adsorption of protective layer depends mainly on its chemical structure, such as surface functional groups, steric factors, aromaticity, electron density

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at donor atoms and the orbital character of donating electrons [13]. Usually, in protective coatings, tannin is used in combination with commercial corrosion inhibitors such as phosphate salts of zinc, iron and manganese [11,14]. Phosphate or sulphide based coatings are toxic and cause global pollution. So, tannin and its modified products are increasingly used for bio-renewable additives/inhibitors in corrosion protective coatings [6,15].

The aim of this study is investigation of the novel inhibitors obtained from the bio-based natural material tannin and their potential application in the industrial production of the anticorrosive protective coatings. Specific objectives of this study were focused on: (1) the introduction of amino functionalities within the tannin structure in reaction with inorganic nitrogen compounds; (2) the introduction of the epoxy groups onto tannin surface *via* reaction with epichlorohydrin; (3) the introduction of heterocyclic amine moieties *via* epoxy groups, without neat tannin structure transformation; (4) the introduction of linseed oil fatty acids *via* epoxy groups in order to provide higher reactivity and compatibility with alkyd resin matrix; and (5) the evaluation of anticorrosive properties of alkyd resin/modified tannin based coatings.

2. EXPERIMENTAL

2.1. Materials

In this study commercial condensed tannin as standard material and tannin extracted from oak bark were used. Commercial tannins were supplied by Sigma Aldrich. Mild steel standard plate was used in this study. All commercially available chemicals: methanol (CH_3OH), potassium dihydrogen phosphate (KH_2PO_4), potassium hydroxide (KOH), potassium hydrogen carbonate ($KHCO_3$), epichlorohydrin (ECH), sodium hydroxide (NaOH), ethanol (C_2H_5OH), hydrochloric acid (HCl), tetraethyl ammonium bromide (TEAB), ammonium hydroxide ($NH_{3(aq)}$), sodium chloride (NaCl), 2-amino-5-mercapto-1,3,4-thiadiazole, 5-aminoquinoline and 4-aminoquinoline, dimethyl sulfoxide (DMSO), diethylentriamine (DETA), pyridine, *p*-toluenesulfonyl chloride, diethyl ether, allyl chloride, diethylene glycol (DEG), pentaerythritol (PE), trimethylol propane (TMP), phthalic anhydride (PA), tetrabutyltitanate (TBT) and xylene were purchased from Sigma Aldrich. Alkyd resin driers (siccative) calcium, cobalt and zirconium octoate were kindly provided by Interhem Company Ltd. All chemicals were used without further purification. PET (polyethylene terephtalate) flakes as raw material were obtained by the grinding of colorless postconsumer bottles. The ground pieces (approximately 5x5 mm) were washed with acetone and dried at 110 °C for 4 h.

2.2. Isolation of tannin from oak bark

Polyphenol tannins were extracted from oak bark using methanol at room temperature. The extraction was done by mixing the 100 g of dried oak bark with 400 mL CH_3OH for 72 h at room temperature. The extraction mixture was filtered and filtrate was centrifuged for 20 minutes. Afterwards, filtrate was cooled down using an ice bath and 50 mL of 2M KH_2PO_4 were added dropwise until the appearance of white fibrous precipitate. The residue was centrifuged at 1000 rpm for ten minutes and washed with cold CH_3OH. Finally, the obtained product is treated with 0.5M HCl in an ice bath with vigorous stirring for one hour. Neutralization to pH 4 was accomplished by adding a saturated sodium carbonate solution to a tannin solution that was chilled in an ice bath. After the filtration, the tannin powder was dried and used in the further modifications.

2.3. Epoxidation of tannin (ET)

Modification of tannin with ECH was performed as follows: 10 g of extracted tannins were placed into a three-necked reactor equipped with a stirrer, reflux condenser and thermometer and dissolved in 100 mL 10 wt% NaOH whereas the pH was adjusted to 12. Afterwards, the reaction was carried out for 1 h at room temperature. Further on, 43.3 g of ECH and 0.05 g of TEAB were added into the previously obtained mixture solution and the reaction was carried out at 80 °C, for 4 h. After that, the reaction mixture was cooled down to room temperature and then HCl was added in order to adjust pH to 2. The obtained product, epoxy tannin (ET), was then centrifuged and dried in a vacuum oven at 40 °C.

2.4. Isolation of unsaturated fatty acid from linseed oil

Procedure for the isolation of fatty acids from linseed oil (LFA) has been performed analogously to the following publication [16]. In the ethanol solution of linseed oil (LO), KOH was added slowly, so that obtained molar ratio KOH/LO was 3.5/1. The reaction mixture was maintained at temperature below 10 °C for 1h. Then the reaction mixture was heated up to 50°C for another 2h whereas the 2/3 of solvent were evaporated. The obtained slurry was dissolved in distilled water, purified with activated carbon, filtered and then acidified by 10% HCl adjusting the pH to 3. The obtained mixture was held overnight where two layers were formed, upper organic (LFA) which was decanted and the aqueous from which the LFA remains were extracted with 250 mL of ether and merged with LFA from the organic layer. The ether traces were evaporated after the FA solution was dried using sodium sulphate. The obtained mixture of unsaturated fatty acids weighted 180 g.

Obtained value for acid (AV) and iodine value (IV) of LFA corresponded to results shown in literature (AV=200 mg KOH/g and IV=150 g/100 g).

2.5. Modification of Tannin

2.5.1. Modification of tannin by $NH_{3(aq)}$: AT-1 was obtained *via* tannin modification with aqueous solution of ammonia according to previously published procedure [17]. In a 25 mL flask 1 g of tannin extract was dispersed in 1 mL of 25 wt.% $NH_{3(aq)}$. The solution was stirred for 1 h, and left for 24 h in a digestor at room temperature. Further on, the resulting product AT-1 was washed with distilled water and dried at 80 °C.

2.5.2. Modification of tannin by $NH_{3(aq)}/NH_4Cl$ buffer: Analogously to method presented in 2.5.1., tannin was modified with a buffer solution ($NH_{3(aq)}/NH_4Cl$) using a procedure described in the literature [17]. In a 25 mL flask, 1 g of tannin was dispersed in 4 mL of buffer solution $NH_{3(aq)}/NH_4Cl$ and stirred for 1h in order to adjust the final pH value to about 9. Then, the mixture was left for 24 h inside the digestor for evaporation of the solvent. The solid, product AT-2, was then washed with distilled water and dried at 80 °C.

2.5.3. Modification of tannin by DETA: 1 g of tannin extract, 10 mL of DMSO and 1.5 mL of DETA were placed into the reactor and reaction was carried out at room temperature with vigorous stirring for 1 h. The obtained viscous liquid was left for 24 h at room temperature and then 0.5 mL C_2H_5OH were added dropwise in order to precipitate the product. The isolated product, AT-3, was vacuum filtered and dried to constant mass.

2.5.4. Reaction of epoxy tannin (ET) with heteroaromatic amine

After the epoxidation, ET was subjected to amination, *i.e.* nucleophilic substitution reaction, using heterocyclic amines: 2-amino-5-mercapto-1,3,4-thiadiazole (A1), 4-aminoquinoline (A2) or 5-aminoquinoline (A3) to obtain anticorrosion additives. According to common procedure, 5 g of ET were dissolved in 30 mL of DMSO and then 9 g of heterocyclic amine (A1, A2 or A3) were added in the reaction mixture. The mixture was kept at room temperature for 30 minutes, afterwards the temperature was increased to 50°C and the reaction was carried out for 3 h. Reaction mixture was maintained for the next 24 h and the obtained products (ETA-1, ETA-2 and ETA-3) were filtered, dissolved in DMSO, precipitated by addition of water, and dried to a constant mass.

2.5.5. Reaction of epoxy tannin with fatty acids isolated from linseed oil

In a three-necked round reactor with provided nitrogen atmosphere, condenser, thermometer and a dropping funnel, 0.5 g of ET and 100 mL of pyridine were charged. Then, 3.5 g of *p*-toluenesulfonyl chloride and 5 mL of LFA mixture were added dropwise into the reactor. After stirring for 3 h, the reaction mixture was centrifuged for 10 minutes, filtered and vigorously washed with distilled water. The obtained product ET-LFA was dried in a vacuum oven at 40 °C to a constant mass and further used in the production of anti-corrosive coatings.

2.6. Synthesis of waste PET based alkyd resin

The glycolysis of waste PET was carried out in a 500 mL four-necked flask equipped with a thermometer, nitrogen inlet tube, a reflux condenser and a mechanical stirrer. DEG was used for PET recycling: 96 g of PET, equivalent to 0.48 mol of the repeating unit in the PET chain, 1.44 mol of DEG and 0.28 mL of TBT were charged to the reactor. The reaction mixture was heated at 210 °C under nitrogen atmosphere for 6 h. At the beginning, the reaction mixture was heterogeneous (solid PET and liquid alcohol) but, after 3-4 h the solid phase was no longer observed and the reaction continued in one single liquid phase. After completion of the glycolysis, reaction mixture was dissolved in dichloromethane and washed two times with 150 mL of distilled water in order to remove excess alcohol. Afterwards, the mixture was filtered with a sintered glass filter (Borosil Glass Works Ltd, porosity grade 3) and dried at 80 °C for 12 h. Then, the formed viscous solution was poured into distilled water, whereas the temperature was maintained at 50 °C. The efficient mixing of the obtained emulsion was necessary (using a mechanical stirrer), over the whole period of addition and thereafter during slow temperature decrease (without external cooling). Approaching the room temperature, the rate of stirring was proportionally decreased, providing separation of the upper aqueous phase. The hydroxyl number (HV) of the glycolyzed product was found to be 317 mg KOH/g.

Alkyd resin, having oil contents of ~48%, based on glycolysis product was synthesized in the next step. The amounts of reactants were calculated using a method based on the alkyd constant value [18]. Synthesis was performed according to the procedure presented in the literature [19]. A four-necked reactor equipped with a stirrer, thermometer, nitrogen inlet tube and Dean-Stark separator for water separation with xylene as azeotropic solvent were used. In a 500 mL glass reactor 80.8 g of glycolysis product, 172 g of LFA, 88.8 g of PA, 28.4 g of PE and TMP were added in the reactor, and the reaction mixture was heated to 220 °C with continual azeotropic water removal. The time-dependent change of acid value (AV) was followed according to a standard method [20], and the reaction product was diluted to 60% of the solid content with xylene when the AV was <15 mg KOH/g.

2.7. Preparation of alkyd based anticorrosive coatings

Alkyd resin based anticorrosive coatings were prepared *via* blending method by mixing of the determined amount of alkyd resin, additives and anticorrosive agent according to composition given in Table 1 (in wt.%).

Table 1. Composition of the anticorrosive alkyd based coatings with commercial and synthesized anticorrosive agents

Tabela 1. Sastav antikorozionih premaza sa komercijalnim i sintetisanim antikorozionim agensima

Component, g	Composition							
	0	1	2	3	4	5	6	7
Alkyd resin (long oil)	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Xylene	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Toluene	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
*Bentone	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Dispersant	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Talc	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
**Anticorrosive additive	0.0	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Zinc Phosphate	6.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
***Pigment	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Ca (5%)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Zr (12%)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Co (6%)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
$CaCO_3$ (20 μm)	36.0	39.5	39.5	39.5	39.5	39.5	39.5	39.5
Anti-skinning agent	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7

*10% Bentone in toluene with 10% ethanol; **anticorrosive additive: coating with AT-1 inhibitor was named Co-AT1, AT-2 (Co-AT2), AT-3 (Co-AT3), ETA-1 (Co-ETA1), ETA-2 (Co-ETA2), ETA-3 (Co-ETA3), and ET-LFA (Co-ETLFA) (coating system); Composition 0 is denoted as Co-1 and represent a comparative sample with addition of Zinc Phosphate; ***Iron oxide was used as pigment

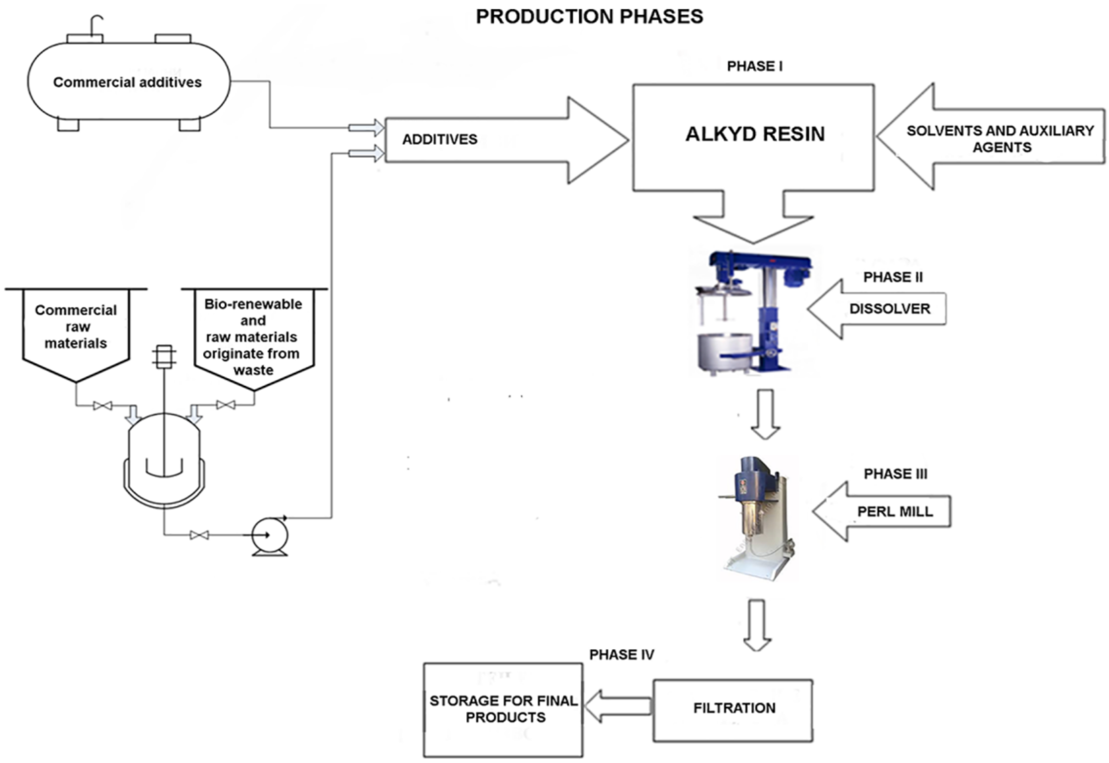

Figure 1. Schematic presentation of production of the alkyd based anticorrosive coatings at industrial level

Slika 1. Šematski prikaz proizvodnje alkidnih antikorozionih premaza na industrijskom nivou

Schematic overview of alkyd based anticorrosive coating production at industrial level (50 kg) is shown in Figure 1 (batch of 30 kg; Interhem Company, Belgrade). Analogous technology was applied at laboratory level (0.3 kg). In the first step of anticorrosive coating production, alkyd resins were mixed with components (at amount given in Table 1) in the high speed dissolver, 1300 rpm for 40 minutes, and after addition of alkyd resin, driers and anti-skinning agents mixing was continued for additional 10 min. Afterwards, in the second step fine dispersion of anticorrosive coating was obtained using a pearl-mill by treating of dispersion for 30 minutes at 1840 rpm. The degree of grinding of alkyd coatings was checked using grindometer, and process was adjusted to obtain standard quality of product, while the viscosity was adjusted by addition of xylene. Filtration with polypropylene membrane filter (15 µm) was performed to remove any agglomerates which could create a defect in the anticorrosive coating after application on mild steel base. Production of anticorrosive coatings at industrial level is presented on Figure 1.

2.8. Characterization methods

The chemical structure of extracted and modified tannin was proved by ATR-FTIR method. The ATR-FTIR spectra were recorded in the range 4000-500 cm^{-1} with a resolution of 4 cm^{-1} at room temperature using Nicolet iS10 (Thermo Scientific) spectrometer. ^1H and ^{13}C NMR spectra were recorded at room temperature in DMSO-d_6 using Varian Gemini 2000 spectrometer at 200 MHz for ^1H NMR and 50 MHz for ^{13}C NMR. The chemical shifts were expressed in ppm value referenced to trimethylsilane (TMS). Elemental analyses were performed using a Vario EL III Elemental analyzer.

Epoxy number was determined using 0.4 M HCl in dioxane and titration with solution of silver nitrate in presence of the ammonium thiocyanate as indicator according to the standard method [21]. The epoxy index (EI) was then calculated as follows:

$$\text{epoxy}\ \% = \frac{(B \times N\text{-}b \times n)\text{-}(S \times N\text{-}s \times n)}{10 \times W} + A$$

where: B and S are volumes of silver–nitrate solution labeled in mL for blank and sample respectively; N is the normality of silver nitrate for blank; b and s are the volumes of ammonium–thiocyanate labeled in mL for blank and sample respectively; n normality of ammonium thiocyanate; W is the sample weight labeled in g and A free halide in sample.

Amino value (AmV) was determined by the standard method ASTM D2074-92 [22].

The hydroxyl value (HV) of tannin was determined by the standard method ASTM E1899 [23]. The acid value (AV) was determined by standard method ASTM D3644 [20], and modified method using potassium hydrogen carbonate. The iodine value was determined by the Wijs method.

Coating film applicator was used to obtain consistent dry film thickness. Evaluation of corrosive properties of selected samples was determined according to the standard method in the salt chamber for 48 and 120 h [24]. The plates were covered with one or two 120-240 µm thick layers, of an alkyd based coating. The viscosity measurement was performed using Ford viscosity cup 4 [25]. Hardness was measured by a pendulum hardness tester (Byk PH-5858, BYK-Gardner GmbH, Geretsried, Germany) using a König pendulum according to the standard method [26]. Thickness of the dry film was measured according to ISO 2360 [27]. Blistering, rusting, cracking and delamination were determined according to SRPS EN ISO 4628 [24]. The adhesion of the films was determined according to SRPS EN ISO 2409 [28]. The abrasion was performed according to ASTM D 4060-10 [29]. Volatile organic compound (VOC) were determined using the standard method SRPS EN ISO 11890-1 [30]. Shine was determined using the standard method ASTM D523 – 08 [31]. Impact resistance was determined using the standard method ASTM D2794 − 93 (Re-approved 2010) [32].

The assessment of the blistering grade is made according to the density of the blisters and their size (SRPS EN ISO 4628-2) - Table 2.

Table 2. Blistering assessment according to density and size of blisters

Tabela 2. Bubrenje određeno prema gustini i veličini mehura

Density		Size
ISO	AST	ISO
0	None	1x10 magnification
1	Scarce	
2	Few	visible
3	Medium	up to 0.5 mm 0.5-5 mm
4	Medium-High	>5 mm
5	High	

In order to determine the degree of rusting/corrosion, a series of pictorial standards (Figure 2) must be compared with the painted surfaces. There are also tables showing the percentage area of visible rusting of the surfaces. Corrosion grades are designated by “Ri”. In the table below the areas for each grade of corrosion are shown in Table 3.

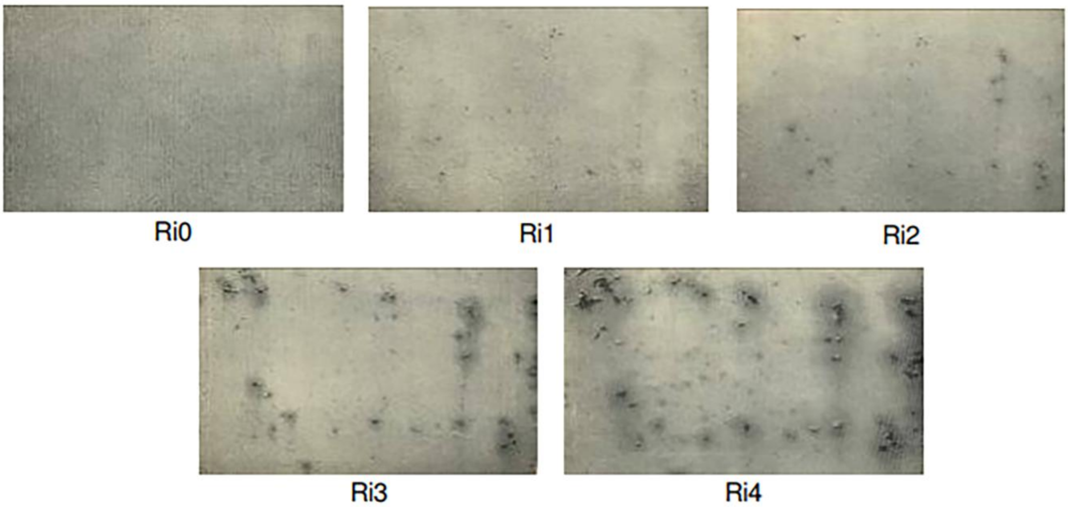

Figure 2. Photographic examples corresponding to ISO 4628-3, to assess the degree of rusting of a painted surface

Slika 2. Antikorozioni premazi različitog stepena korozije u skladu sa ISO 4628-3 standardom

Table 3. Rusting/corrosion assessment

Tabela 3. Određivanje stepena rđe/korozije

ISO	European scale	ASTM	% rusted area
Ri0	Re0	10	0
Ri1	Re1	9	0.05
Ri2	Re2	7	0.5
Ri3	Re3	6	1
Ri4	Re4	4	8
Ri5	Re5	1 a 2	40/50

The assessment of the cracking grade is made according to the density of the cracks and their size (SRPS EN ISO 4628-4), Table 4.

Table 4. Cracking assessment according to density and size of cracks

Tabela 4. Određivanje pukotina prema gustini i veličini pukotine

Rating	Quantity	Size
0	None	Not visible under x10 magnification
1	Very few	Only visible under magnification up to x10
2	Few	Just visible with normal corrected vision (up to 0.2 mm)
3	Moderate number of cracks	Clearly visible with normal corrected vision (larger than 0.2 mm up to 0.5 mm)
4	Considerable number of cracks	Large cracks (larger than 0.5 mm up to 1 mm)
5	Dense pattern of cracks	Very large cracks (generally more than 1 mm wide)

3. RESULTS AND DISCUSSION

The overall reaction of one-step tannin modification with $NH_{3(aq)}$, $NH_{3(aq)}/NH_4Cl$ and DETA, and two-step modification *via* ECH followed by heterocyclic amines (A1, A2 and A3) are shown in Figures 3 and 4, respectively.

The amination reaction takes place in a one-step procedure (Figure 3). The previous studies show that this reaction under mild conditions and without a catalyst is a regio-selective reaction [33, 34]. The aminated hydroxyl groups lead to oligomerization and cross-linking *via* connections between N and OH within the tannin molecules. Depending on which hydroxyl group of the rings A or C reacts and also due to the formation of imine bonds, several different structures can potentially be formed. Among many possible structures, I and III (Figure 3) are of highest probability to be established [17,33]. The epoxidation and amination of tannins improve the ability of tannins to form complexes which is reflected in better dispersion in various solvents making the obtained corrosion inhibitors suitable for application in metal protective coating compositions. Furthermore, due to the applied modification procedures modified tannin contributes to improved compatibility, adhesion to metal substrate, resistance to abrasion and anticorrosive properties of alkyd based coatings. Presence of nitrogen and oxygen atoms as well as π-electrons in aromatic structure of tannin enable the interaction with polymer matrix and thus better bonding between coating and the metal surface.

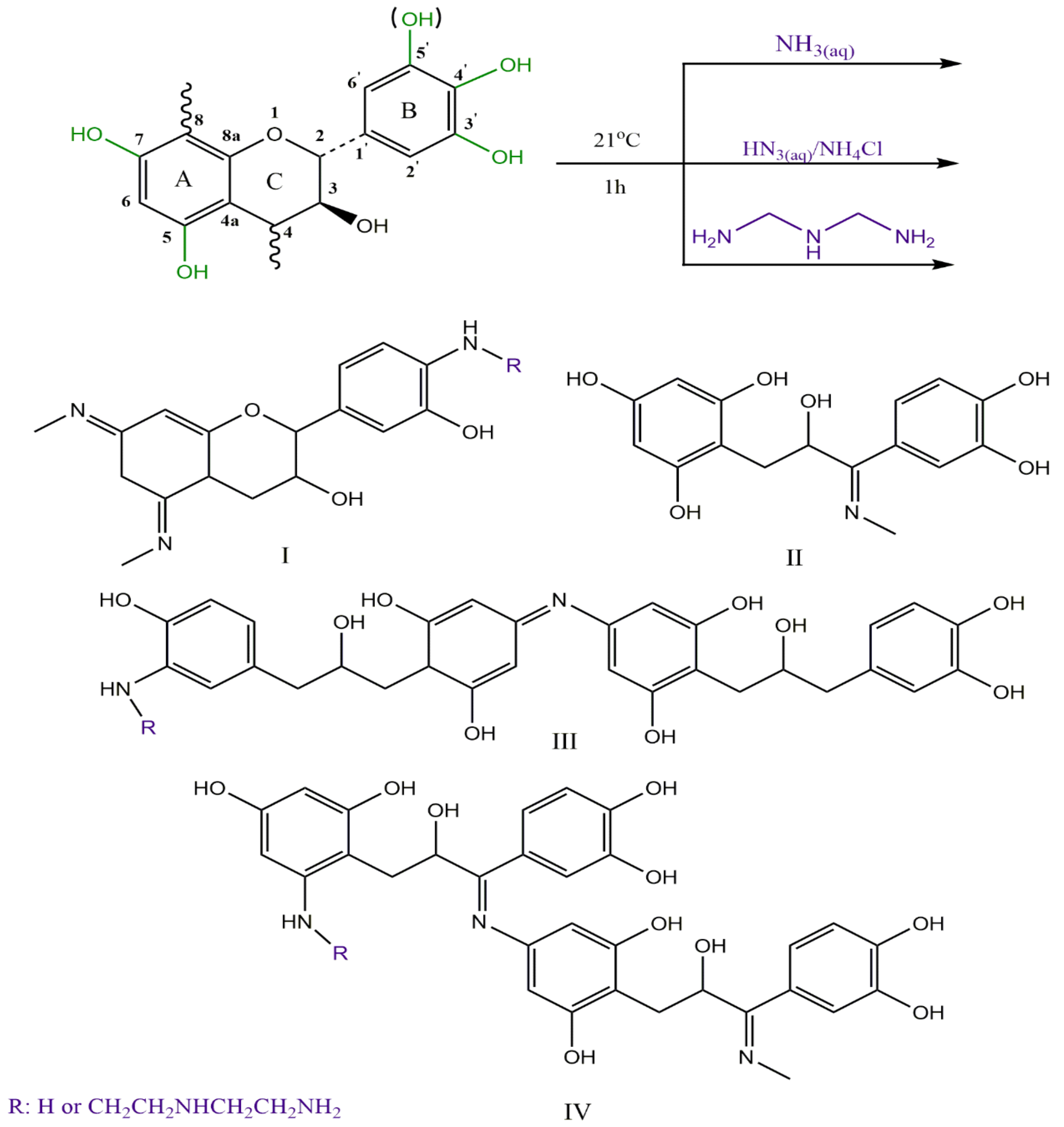

Figure 3. Chemical modifications of tannin with $NH_{3(aq)}$ (AT-1), $NH_{3(aq)}/NH_4Cl$ (AT-2) and DETA (AT-3)

Slika 3. Hemijska modifikacija tanina sa $NH_3(aq)$ (AT-1), $NH_3(aq)/NH_4Cl$ (AT-2) i DETA (AT-3)

Modification procedure presented in Figure 4 includes a two-step process: the first one represents tannin etherification with ECH to form ET, and the second one the reaction between ET and either heterocyclic amine or LFA to form the end-product, *i.e.* anticorrosive inhibitors used for alkyd based coatings production. The epoxidation belongs to S_N2 substitution reactions where epoxy groups from ECH are linked to hydroxyl groups (phenolic) from tannin A or B aromatic ring. In fact, reaction mechanism consists of mixed contribution of S_N2 and epoxide ring opening reactions. Higher reactivity of the ring designated as B, with respect to A ring (Figure 4), is a consequence of the position of OH group and resonance structure [2, 33]. In general, alkaline medium, elevated temperatures and alkyl halides as catalysts favor the epoxidation reaction to produce epoxy tannin at satisfactory yield. Alkyl bromides give greater yields as they are more reactive than alkyl chlorides and less susceptible to dehydrohalogenation than alkyl iodides [2]. In any case, epoxidation is useful due to versatility/reactivity of epoxy ring, and highly desirable even at expected lower reaction yield.

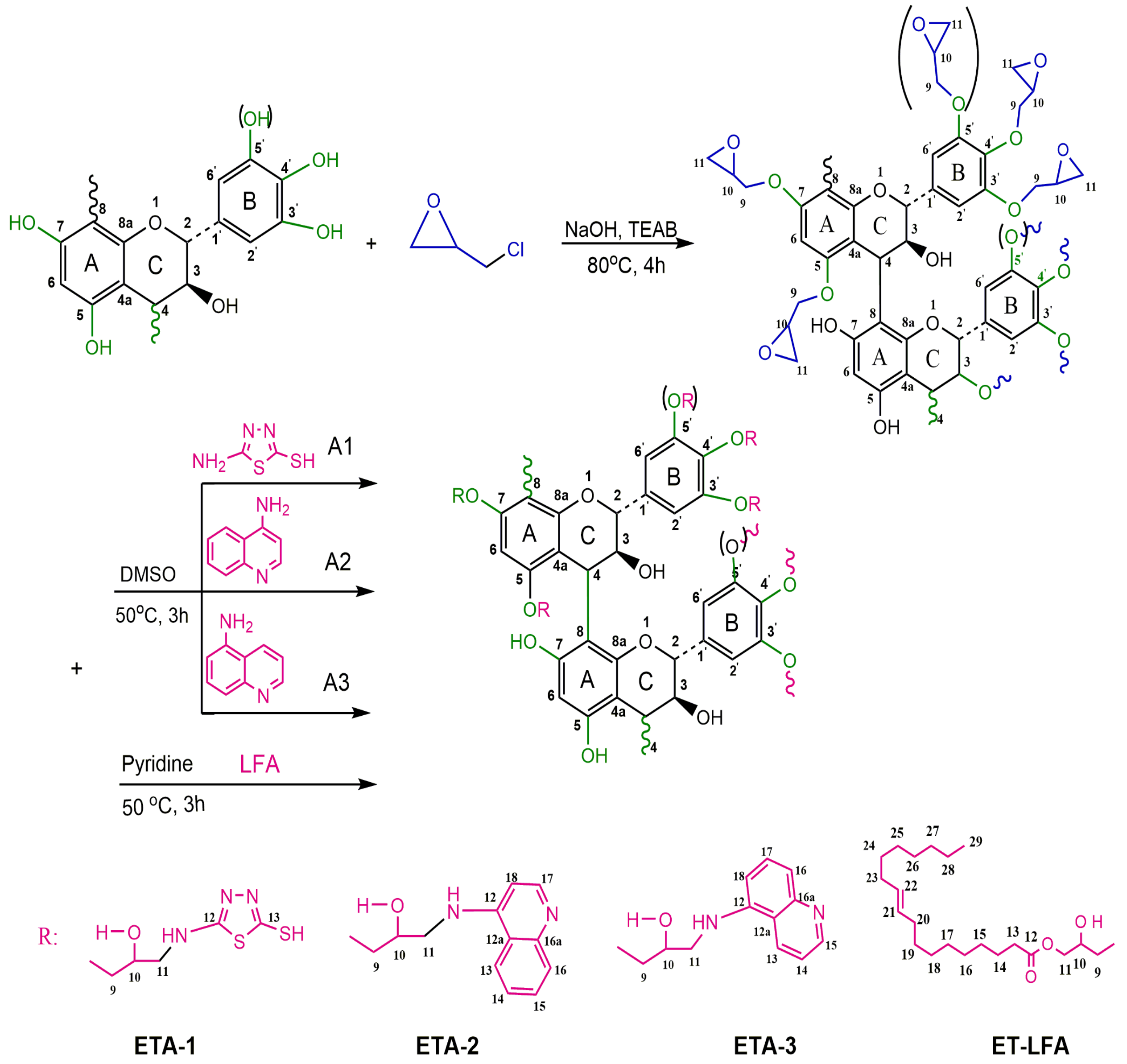

Figure 4. Two-step chemical modifications of tannin with ECH (first step), and heteroaromatic amine (A1-A3) and LFA in second step

Slika 4. Dvostepena hemijska modifikacija tanina sa ECH (prvi korak), i heteroaromatičnim aminima (A1-A3) i LFA u drugom koraku

The usage of epoxy tannins as inhibitors in coatings is limited and requires additional modification *via* introduction of heterocyclic amines which possess inherent anticorrosive capability. The presence of amino groups leads to opening of the epoxy ring by formation of covalent linkage introducing synergetic effects of both, tannin and heteroaromatic moieties. Also, higher stability of resulting anticorrosive agent and higher compatibility with alkyd polymer matrix help in enhancement of final properties of coatings during application. The viscosity of formulated products with respect to the comparative sample (Co-1; Table 1) is similar (change within ±5%).

The HV, AV and amine value (AmV) and the data from elemental analysis of the synthesized inhibitors are presented in Table 5.

Table 5. Results of HV, modified AV, AmV and elemental analysis of the synthesized anticorrosive inhibitors

Tabela 5. Rezultati HV, modifikovanog AV, AmV i elementalne analize sintetizovanih antikorozionih inhibitora

Inhibitor	HV* mg KOH/g	AV* mg KOH/g	AmV mg KOH/g		%C	%H	%O*	N%
AT-1	186	<3	110	Calc.	61.62	6.39	19.31	12.68
				Exp.	61.58	6.23	19.62	12.57
AT-2	177	<3	140	Calc.	63.82	5.71	25.50	4.97
				Exp.	63.51	5.74	25.37	4.99
AT-3	168	<3	160	Calc.	62.78	6.49	22.13	8.60
				Exp.	62.76	6.51	22.15	8.58
ET	280	<3	<10	Calc.	62.83	6.00	31.17	-
				Exp.	63.11	6.03	30.86	-
ETA-1	256	<3	246	Calc.	56.33	5.23	19.16	14.28
				Exp.	56.05	5.20	19.06	14.21
ETA-2	236	<3	216	Calc.	69.56	7.10	14.99	8.35
				Exp.	69.91	7.06	14.92	8.39
ETA-3	248	<3	230	Calc.	68.70	6.16	17.21	7.93
				Exp.	69.04	6.19	17.29	7.89
ET-LFA	268	<3	<10	Calc.	71.30	9.65	19.05	-
				Exp.	71.45	9.71	18.81	-

*HV and AV values were evaluated for synthesis purpose (AV was determined according to modified method using $KHCO_3$ – in case of using KOH AV > 150); The oxygen percent was calculated as the difference to 100%; Iodine value of 126 was obtained for ET-LFA sample.

The values indicate that the number of hydroxyl groups does not change significantly by performing the two-step modification procedure, while low decrease of HV after one-step modification indicates appropriate rearrangement of initial tannin structure. The experimental data of elemental analysis confirm the successfulness of applied transformation. The higher amine content was found in aminated products obtained by one-step procedure which indicates higher extent of modification and basicity of ammonia reacting species.

3.1. Results of the characterization of modified tannins using ATR-FTIR and NMR spectroscopy

In order to confirm the structure of extracted/modified tannins, the FT-IR analysis and NMR spectroscopy were performed. The ATR-FTIR spectra of pristine and modified tannins are presented in Figure 5.

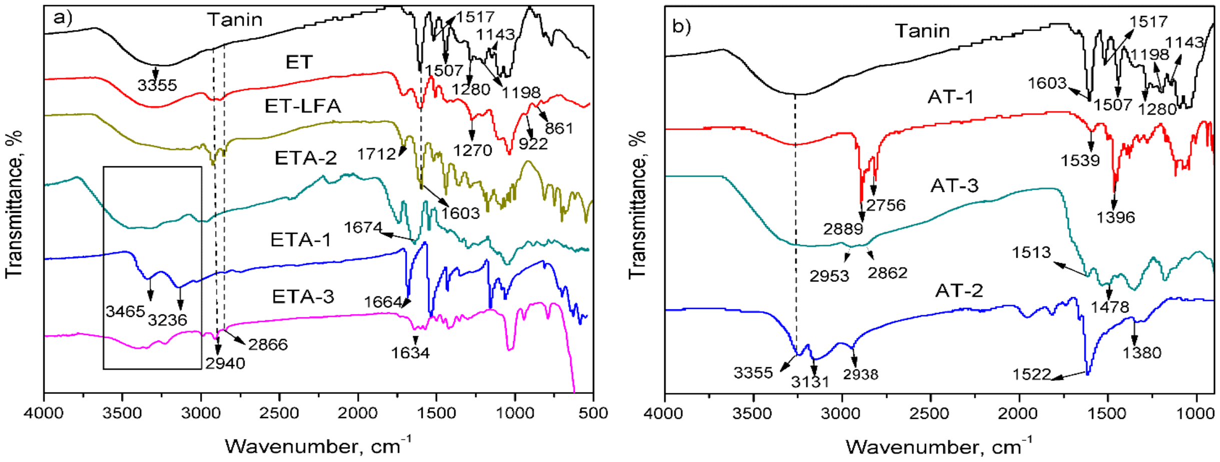

Figure 5. FT-IR spectra of modified tannins inhibitors a) ETA-(1-3) and ET-LFA, and b) AT-(1-3)

Slika 5. FT-IR spektri inhibitora na bazi modifikovanih tanina a) ETA-(1-3) i ET-LFA, i b) AT-(1-3)

The band at 3355-3131 cm^{-1} is related to the presence of O-H and N-H stretching vibrations characteristic for polyphenol extracts and primary and secondary amines obtained by modification with amines (Figure 5a) and aqueous solution of ammonium hydroxide, ammonium buffer $NH_{3(aq)}/NH_4Cl$ and DETA (Figure 5b). Strong signals at 1603, 1517 and 1507 cm^{-1} are assigned for C=C–C vibrations in aromatic A and B rings of tannin. The appearance of the band at 1280 cm^{-1} can be attributed to C-O vibrations in catechol C ring. The peak for C-O vibrations which originates from aromatic A ring, is found at 1198 and 1143 cm^{-1} [35]. After modification with ECH, three new bands, observed at 1270, 922 and 861 cm^{-1}, represent stretching, anti-symmetric and deformation originated from C-O vibration in epoxy ring. The obtained data indicate that epoxy group is successfully attached onto tannin surface.

The two small broad peaks presented at 2940 and 2866 cm^{-1} are assigned to C-H symmetric and asymmetric stretching vibrations of CH_3 and CH_2 groups. The cluster of peaks observed at 1664, 1634 and 1674 cm^{-1} represents the characteristic bands of N-H groups which belong to amine based modifiers. These bands are slightly shifted to 1539, 1522 and 1513 cm^{-1} when the modifications with ammonium, ammonium buffer and DETA (Figure 3b) are employed. The appearance of the amino group was essential for anticorrosion system. Presence of C=O at 1712 cm^{-1} which belongs to ester group proves successfulness of LFA introduction within the tannin structure. The new peaks (Figure 5b)) at 1396 cm^{-1} for AT-1,1380 cm^{-1} for AT-2 and 1478 cm^{-1} for AT-3 indicate presence of C=N group.

The results of the ^{1}H and ^{13}C NMR analysis for all products are as follow (numbering of atoms and ring of interest are given on Figures 3 and 4):

AT-1: ^{1}H-NMR (DMSO-d$_6$; δ/ppm): 1.80-3.25 (8H, s, N-$\underline{H}$), 3.50 (3H, dd, $C_{4,8}\underline{H}$), 5.10 (1H, s, C_{ring}-O$\underline{H}$), 6.63 (1H, s, B_{ring}-O$\underline{H}$), 3.33-3.52 (3H, dd, $3C_{4a,6}\underline{H}$), 4.20-4.70 (2H, m, $2C_{2,3}\underline{H}$), 6.70-7.20 (3H, m, $C_{2',5',6'}\underline{H}$). ^{13}C-NMR (δ/ppm): 30 (C_4), 65 (C-N), 130 ($C_{1'}$), 117 ($C_{2'}$, $C_{5'}$, $C_{6'}$), 140 ($C_{3'}$ and $C_{4'}$), 169 (C_7), 189.5-190 (C_9) [17].

The spectra of the product AT-2 [17] were similar to one obtained for AT-1.

AT-3 ^{1}H-NMR (DMSO-d$_6$; δ/ppm): 1.80-3.25 (8H, s, N-$\underline{H}$), 2.89-3.28 (8H, dd, $4C\underline{H_2}$), 3.50 (3H, dd, $C_{4,8}\underline{H}$), 5.10 (1H, s, C_{ring}-O$\underline{H}$), 6.63 (1H, s, B_{ring}-O$\underline{H}$), 3.33-3.52 (3H, dd, $3C_{4a,6}\underline{H}$), 4.20-4.70 (2H, m, $2C_{2,3}\underline{H}$), 6.70-7.20 (3H, m, $C_{2',5',6'}\underline{H}$). ^{13}C-NMR (δ/ppm): 30 (C_4), 65 (C-N), 52.60 and 52.80 (4C from CH_2 in DETA), 130 ($C_{1'}$), 117 ($C_{2'}$, $C_{5'}$, $C_{6'}$), 140 ($C_{3'}$ and $C_{4'}$), 169 (C_7), 189.5-190 (C_9) [17].

ET: ^{1}H-NMR (DMSO-d_6; δ/ppm): 2.87 (10H, m, $5C_{11}\underline{H_2}$), 3.34 (5H, m, $5C_{10}\underline{H}$), 3.53-3.73 (11H, m, $5C_9\underline{H_2}$ and C_{ring}-$C_4\underline{H}$), 4.96 (1H, d, C_{ring}-$C_2\underline{H}$), 5.10 (1H, s, C_{ring}-O$\underline{H}$), 5.32-7.31(4H, m, C_{ring}-$C_3\underline{H}$, A_{ring}-$C_6\underline{H}$, B_{ring}-$C_{2',6'}\underline{H_2}$); ^{13}C-NMR (DMSO–d_6; δ/ppm): 40.77 (C_4), 48.2 ($5C_{11}$), 56.57 ($5C_{10}$), 76.67 ($5C_9$), 78.04 (C_3), 89.73 (C_2), 93.73 (C_6), 99.01 (C_5), 111.05 ($C_{2'}$ and $C_{6'}$), 115.52 (C_{4a}), 121.93 (C_8), 136.10 ($C_{1'}$), 142.10 ($C_{4'}$), 159.55 ($C_{3'}$ and $C_{5'}$), 161.52 (C_7 and C_{8a}).

ETA-1: ^{1}H-NMR (DMSO-d$_6$; δ/ppm): 2.24 (5H, s, C_{10}-O$\underline{H}$), 3.41 (10H, dd, $5C_{11}\underline{H_2}$), 3.53-3.73 (11H, m, $5C_9\underline{H}_2$ and C_{ring}-$C_4\underline{H}$), 4.21 (10H, s, $5C_{10}\underline{H_2}$), 4.25 (5H, s, 5NH), 4.96 (1H, d, C_{ring}-$C_2\underline{H}$), 5.10 (1H, s, C_{ring}-O$\underline{H}$), 5.32-7.31(4H, m, C_{ring}-$C_3\underline{H}$, A_{ring}-$C_6\underline{H}$, B_{ring}-$C_{2',6'}\underline{H_2}$), 14.00 (5H, s, 5S$\underline{H}$); ^{13}C-NMR (DMSO–d$_6$; δ/ppm): 35.2 ($5C_{11}$), 40.77 (C_4), 63.04 ($5C_{10}$), 76.67 ($5C_9$), 78.04 (C_3), 89.73 (C_2), 93.73 (C_6), 99.01 (C_5), 111.05 ($C_{2'}$ and $C_{6'}$), 115.52 (C_{4a}), 121.93 (C_8), 136.10 ($C_{1'}$), 142.10 ($C_{4'}$), 159.55 ($C_{3'}$ and $C_{5'}$), 161.52 (C_7 and C_{8a}), 180.62 ($5C_{13}$), 195.40 ($5C_{14}$).

ETA-2: ^{1}H-NMR (DMSO-d_6; δ/ppm): 2.24 (5H, s, C_{10}-O$\underline{H}$), 3.41 (10H, dd, $5C_{11}\underline{H_2}$), 3.53-3.73 (11H, m, $5C_9H_2$ and C_{ring}-C_4H), 4.21 (10H, s, $5C_{10}\underline{H_2}$), 4.25 (5H, s, 5NH), 4.96 (1H, d, C_{ring}-$C_2\underline{H}$), 5.10 (1H, s, C_{ring}-O$\underline{H}$), 5.32-7.31(4H, m, C_{ring}-$C_3\underline{H}$, A_{ring}-$C_6\underline{H}$, B_{ring}-$C_{2',6'}\underline{H_2}$), 7.60-7.90 (4H, dd, $4C_{14,15,16,18}\underline{H}$), 8.50-9.20 (3H, m, $C_{13,17}\underline{H}$); ^{13}C-NMR (DMSO–d_6; δ/ppm): 35.2 ($5C_{11}$), 40.77 (C_4), 63.04 ($5C_{10}$), 76.67 ($5C_9$), 78.04 (C_3), 89.73 (C_2), 93.73 (C_6), 99.01 (C_5), 111.05 ($C_{2'}$ and $C_{6'}$), 115.52 (C_{4a}), 118.9 ($5C_{18}$), 119.12 ($5C_{12a}$), 121.93 (C_8), 123.94 ($5C_{13}$), 127.82 ($5C_{14}$), 131.28 ($5C_{15}$ and $5C_{16}$), 135.12 ($5C_{12}$), 136.10 ($C_{1'}$), 142.10 ($C_{4'}$), 147.80 ($5C_{16a}$), 153.17($5C_{17}$), 159.55 ($C_{3'}$ and $C_{5'}$), 161.52 (C_7 and C_{8a}).

ETA-3: ^{1}H-NMR (DMSO-d_6; δ/ppm): 2.24 (5H, s, C_{10}-O$\underline{H}$), 3.41 (10H, dd, $5C_{11}\underline{H_2}$), 3.53-3.73 (11H, m, $5C_9H_2$ and C_{ring}-C_4H), 4.21 (10H, s, $5C_{10}\underline{H_2}$), 4.25 (5H, s, 5NH), 4.96 (1H, d, C_{ring}-$C_2\underline{H}$), 5.10 (1H, s, C_{ring}-O$\underline{H}$), 5.32-7.31(4H, m, C_{ring}-$C_3\underline{H}$, A_{ring}-$C_6\underline{H}$, B_{ring}-$C_{2',6'}\underline{H_2}$), 7.40-7.80 (3H, dd, $4C_{16,17,18,}\underline{H}$), 8.40-9.05 (2H, m, $C_{16,17,18}\underline{H}$); ^{13}C-NMR (DMSO–$d_6$; δ/ppm): 35.2 ($5C_{11}$), 40.77 ($C_4$), 63.04 ($5C_{10}$), 76.67 ($5C_9$), 78.04 ($C_3$), 89.73 ($C_2$), 93.73 ($C_6$), 99.01 ($C_5$), 111.05 ($C_{2'}$ and $C_{6'}$), 115.52 (C_{4a}), 118.9 ($5C_{18}$), 119.12 ($5C_{12a}$), 121.93 (C_8), 123.63 ($5C_{14}$), 125.84 ($5C_{13}$), 127.28 ($5C_{16}$ and $5C_{17}$), 131.80 ($5C_{16a}$), 135.12 ($5C_{12}$), 136.10 ($C_{1'}$), 142.10 ($C_{4'}$), 152.36 ($5C_{15}$), 159.55 ($C_{3'}$ and $C_{5'}$), 161.52 (C_7 and C_{8a}).

ET-LFA: ^{1}H-NMR (DMSO-d_6; δ/ppm): 0.90-1.30 (85H, m, $5C_{20,23-29}\underline{H_{17}}$), 1.35-160 (30H, dd, $5C_{17-18}\underline{H_2}$, $5C_{19,16}\underline{H_2}$, $5C_{14-15}\underline{H_2}$), 2.32 (5H, d, $5C_{13}\underline{H}$), 3.65 (1H, d, C_{ring}-$C_4\underline{H}$), 4.20-4.54 (25H, dd, $5C_{9-11}\underline{H_5}$), 4.96 (1H, d, C_{ring}-$C_2\underline{H}$), 5.10 (1H, s, C_{ring}-O$\underline{H}$), 5.32-7.31(4H, m, C_{ring}-$C_3\underline{H}$, A_{ring}-$C_6\underline{H}$, B_{ring}-$C_{2',6'}\underline{H_2}$); 5.43 (15H, s, 5C$\underline{H}$=C$\underline{H}$ and 5O$\underline{H}$);

^{13}C-NMR (DMSO–d_6; δ/ppm): 20.1 (5C$_{29}$), 24.0 (5C$_{28}$), 25.9 (5C$_{14}$), 30.09 (5C$_{15-19}$ and 5C$_{24-27}$), 34.2 (5C$_9$,5C$_{13}$,5C$_{20}$ and 5C$_{23}$), 68.1 (5C$_{10}$), 72.3 (5C$_{11}$), 78.04 (C$_3$), 89.73 (C$_2$), 93.73 (C$_6$), 99.01 (C$_5$), 111.05 (C$_{2'}$ and C$_{6'}$), 115.52 (C$_{4a}$), 121.93 (C$_8$), 136.10 (C$_{1'}$), 142.10 (C$_{4'}$), 159.55 (C$_{3'}$ and C$_{5'}$), 161.52 (C$_7$ and C$_{8a}$).

In general complex NMR spectra were obtained, and presented results relate to analysis of obtained spectra which emphasize structure modification in the course of applied syntheses methods. Comparison of NMR spectra of synthesized inhibitors, isolated tannin and commercial tannin help in confirmation of material structure and peak assignments.

3.2. Determination of epoxy content

Epoxy content is expressed through the epoxy groups present in ET and amounted to 8.2%. The presence of the epoxy groups within the amino modified materials is difficult to define due to reactions between epoxy and amino/carboxyl groups from amines and fatty acids isolated from linseed oil used for tannin modification, respectively.

3.3. Rusting test of anticorrosive properties of formulated products

In order to better understand the influence of alkyd anti-corrosion coatings with additives based on modified tannins, synthesized inhibitors were used in a three layer protective system (Table 6) and one controllable three in one (3 in 1) system with incorporated anticorrosive agents. They are also tested using a standard or modified method/equipment to determine corrosion degree in the wet and salt chamber.

Table 6. Definition of three-layers and limits of thickness of dry film (TDF) of obtained coatings

Tabela 6. Opis troslojnog premaza i debljina suvod filma (TDF) dobijenih premaza

	Type of coating	TDF*, µm
1. layer	Anticorrosive	40-70
2. layer*	Intermediary	40-50
3. layer**	Top coat (Gloss coat)	20-30
Total thickness of dry film:		100-150

* Thickness of dry film was measured according to ISO 2360; Intermediary coat was produced according to composition Co-1 presented in Table 1 by excluding zinc phosphate; Top coat was based on Co-1 by excluding all filler and pigment from composition.

Physico-chemical and mechanical properties, adhesion and elasticity of alkyd resin anticorrosive coatings before anticorrosive testing were examined, and obtained results are given in Table 7.

Table 7. Physico-chemical properties of the prepared plate with anticorrosive coatings

Tabela 7. Fizičko hemijske osobine pripremljenih ploča sa antikorozionim premazima

Coating /properties	Co-1	Co-AT1	Co-AT2	Co-AT3	Co-ET	Co-ETA1	Co-ETA2	Co-ETA3	Co-ETLFA
Thickness, µm	129	127	120	128	129	125	120	128	128
Viscosity, Ford 4	173	175	185	188	175	180	184	180	171
Density, g/cm^3	1.60	1.52	1.56	1.55	1.52	1.53	1.55	1.54	1.50
Hardness, s	66	72	77	81	69	82	68	67	85
Gloss, %	84	74	75	72	79	76	75	78	82
Abrasion, 0-good, 5-bad	0	0	0	0	0	0	0	0	0
Adhesion 0-good, 5-bad	0	0	0	0	0	0	0	0	0
VOC, g/L	255	255	251	255	253	255	251	253	253
Bending, 0-good, 5-bad	0	0	0	0	0	0	0	0	0
fineness of a paint's grind,µm	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Coverage, 0-good, 5-bad	0	0	0	0	0	0	0	0	0
Impact Resistance	> 30	> 30	> 30	> 30	> 30	> 30	> 30	> 30	> 30
Elasticity, mm	7.4	7.6	7.5	7.7	7.6	7.8	7.6	7.7	7.9

The thicknesses of the anticorrosive films are from 120 to 129 µm. On the basis of the obtained results it can be concluded that anticorrosive coatings meet the requirements defined by the standards. In order to select anticorrosive agents the preliminary tests were performed for all protective coatings (Table 7) with respect to rusting and adhesion (120 h exposure) to select the most potential ones. Obtained results are given in Table 8.

Table 8. Anticorrosive properties of all anticorrosive coating applied in a three layer system (Test duration: 120 hours)

Tabela 8. Antikoroziona svojstva svih antikorozionih premaza u troslojnom sistemu (Trajanje ispitivanja 120 sati)

Coating/properties	Co-1	Co-AT1	Co-AT2	Co-AT3	Co-ET	Co-ETA1	Co-ETA2	Co-ETA3	Co-ETLFA
SRPS EN ISO 4628-3 (rusting)	Ri2	Ri2	Ri2	Ri1	Ri2	Ri1	Ri1	Ri2	Ri1
SRPS EN ISO 2409 (adhesion)	2	1	2	1	2	1	2	1	1

Preliminary results of anticorrosive tests showed the best properties of Co-AT3, Co-ETA1 and Co-ETLFA coating.

As the coatings Co-ETA1 and Co-ETLFA showed better properties, in further studies synthesized anti-corrosive agent ET-A1 and ET-LFA was used as a three-layer system as it is given in Table 6. The anticorrosive properties of the three-layer coating either without (Co-1 as reference) and with modified tannin anticorrosive agents (Co-ETA1 and Co-ETLFA) formed by three layers coatings was comparatively studied with one pot system (3 in 1). Three in one system should justify the idea of simplified application procedure and anticorrosive properties of obtained coating with respect to more operationally complex three layer coating. The characteristics of the prepared protective systems after the exposure to wet chamber are tabulated in Tables 9 and 10.

Table 9. Anticorrosive properties of Co-ETA1 (three layer coating)

Tabela 9. Antikoroziona svojstva Co-ETA1 (troslojni premaz)

Evaluation after testing according to SRPS ISO 6270-1	Plate 1	Plate 2	Plate 3
SRPS EN ISO 4628-2 (blistering)	0	0	0
SRPS EN ISO 4628-3 (rusting)	Ri0	Ri0	Ri0
SRPS EN ISO 4628-4 (cracking)	0	0	0
SRPS EN ISO 4628-5 (delamination)	0	0	0
Thickness of dry film, μm	120	125	124
SRPS EN ISO 2409 (adhesion)	0	0	0

During 48 h exposure in a wet chamber, plates covered with protective coatings Co-ETA2 and Co-ETLFA did not show noticeable rusting and color change, whereas plates with standard additive, Co-1, suffered a mild film deterioration and hardly noticeable surface roughening. While examining plates with Co-ETA2 and Co-ETLFA there were no film defects observed as blistering, rusting, cracking or flaking according to SRPS EN ISO 6270-1 standards.

Table 10. Anticorrosive properties of Co-ETLFA (three layer coating)

Tabela 10. Antikoroziona svojstva Co-ETLFA (troslojni premaz)

Evaluation after testing according to SRPS ISO 6270-1	Plate 1	Plate 2	Plate 3
SRPS EN ISO 4628-2 (blistering)	0	0	0
SRPS EN ISO 4628-3 (rusting)	Ri0	Ri0	Ri0
SRPS EN ISO 4628-4 (cracking)	0	0	0
SRPS EN ISO 4628-5 (delamination)	0	0	0
Thickness of dry film, μm	128	120	125
SRPS EN ISO 2409 (adhesion)	0	0	0

The characteristics of the prepared protective systems Co-ETA1 and Co-ETLFA (three layer coatings) after appropriate time of exposure to a salt chamber are tabulated in Tables 11 and 12 (48 h), and Tables 13 and 14 (120 h).

Table 11. Anticorrosive properties of Co-ETA1 (test duration: 48 hours)

Tabela 11. Antikoroziona svojstva Co-ETA1 (trajanje testa 48 sati)

Evaluation after testing according to SRPS ISO 9227	Plate 1	Plate 2	Plate 3
SRPS EN ISO 4628-2 (blistering)	1	0	1
SRPS EN ISO 4628-3 (rusting)	Ri1	Ri0	Ri0
SRPS EN ISO 4628-4 (cracking)	0	1	0
SRPS EN ISO 4628-5 (delamination)	0	0	0
Thickness of dry film, μm	130	132	129
SRPS EN ISO 2409 (adhesion)	0	1	0

Table 12. Anticorrosive properties of Co-ETLFA (test duration: 48 hours)

Tabela 12. Antikoroziona svojstva Co-ETLFA (trajanje testa 48 sati)

Evaluation after testing according to SRPS ISO 9227	Plate 1	Plate 2	Plate 3
SRPS EN ISO 4628-2 (blistering)	0	0	0
SRPS EN ISO 4628-3 (rusting)	Ri0	Ri1	Ri0
SRPS EN ISO 4628-4 (cracking)	0	1	0
SRPS EN ISO 4628-5 (delamination)	1	0	0
Thickness of dry film, μm	125	128	131
SRPS EN ISO 2409 (adhesion)	0	1	0

Table 13. Anticorrosive properties of Co-ETA1 (test duration: 120 hours)

Tabela 13. Antikoroziona svojstva Co-ETA1 (trajanje testa 120 sati)

Evaluation after testing according to SRPS ISO 9227	Plate 1	Plate 2	Plate 3
SRPS EN ISO 4628-2 (blistering)	1	1	1
SRPS EN ISO 4628-3 (rusting)	Ri1	Ri1	Ri1
SRPS EN ISO 4628-4 (cracking)	0	1	1
SRPS EN ISO 4628-5 (delamiantion)	1	0	0
Thickness of dry film, μm	135	137	133
SRPS EN ISO 2409 (adhesion)	1	1	1

Table 14. Anticorrosive properties of Co-ETLFA (test duration: 120 hours)

Tabela 14. Antikoroziona svojstva Co-ETLFA (trajanje testa 120 sati)

Evaluation after testing according to SRPS ISO 9227	Plate 1	Plate 2	Plate 3
SRPS EN ISO 4628-2 (blistering)	0	1	1
SRPS EN ISO 4628-3 (rusting)	Ri0	Ri1	Ri1
SRPS EN ISO 4628-4 (cracking)	0	1	1
SRPS EN ISO 4628-5 (delamination)	1	0	0
Thickness of dry film, μm	130	133	132
SRPS EN ISO 2409 (adhesion)	0	0	1

After the exposure of 120 h the obtained results (Tables 13 and 14), compared to the results for standard plate Co-1 and alkyd paint 3 in 1 (data not presented) showed that the both three layer and 3 in 1 system satisfies standard requirements while the basic alkyd paint Co-1 is not adequate to be used as anticorrosive paints. Test sample Co-1 shows noticeable film destruction with intensive rusting, and these results indicate significance of added anticorrosive agents.

The tests for thickness of blistering, adhesion and cracking show better results for anticorrosive three layered system Co-ETA1 and Co-ETLFA showed good anticorrosive properties, while three in one, shows appropriate adhesion failure and blistering. Therefore, it can be concluded that the anticorrosive system 3 in 1 does not meet the requirements of the standards, and that the three layer coating system and the final rapid-drying paint meet the requirements prescribed by the standards.

Corrosion inhibition of those synthesized tannin based additives may be explained by chemical structure of the prepared compounds. Namely, tannin itself is a biopolymer with an aromatic structure and his pK_a value does not exceed more than 7 as a result of plenty hydroxy groups bounded on benzene rings. That is a very low value and tannin itself could not be used as a corrosion inhibitor. Conversely, amines with low molecular weight lack in dispersity, especially amines which have good solubility in water. Alkyd based amino modified tannin anticorrosive coating have both benefits. Tannin matrix disperses the amine functional group and at the same time creates a passivating layer which impacts diffusion of oxygen resulting in inhibition of the cathode half–reaction (oxygen reduction). Free electron couples on nitrogen atoms from amine functional group also affect the oxidation of the metal for they participate in creation of the metal complex which precipitates on the metal surface slowing the rate of the metal oxidation. Nevertheless, anticorrosive additives ETA(1-3) and ETA-LFA showed good compatibility and easy procesability in the course of grinding process. Synthesized materials act as processing aids, and ET-LFA have high gloss comparable to Co-1 coating. Considering Co-ETLFA, anticorrosive potential of LFA modifying structure contribute to better adhesion, structural integrity and improvement of film hydrophobicity. In this case presence of LFA modifying agent contribute to better dispersibility in alkyd media, participate in cross-linking reactivity causing increased film homogeneity and network density which behave as a good protective barrier for oxygen, water and ion transport.

Study on anticorrosive properties of nine anti-corrosive agents in alkyd based coatings showed diversity of physico-chemical and anticorrosion potential. In this sense, the choice of anti-corrosive agent and metal protection system could not be analyzed and selected according to presented results but techno-economic analysis would also be the decisive criteria in determining the efficiency of production/implementation of a particular protection system. A preliminary techno-economic analysis shows that the use of anticorrosive agents ET-LFA and ETA-1 is more functional, and in further testing and production at the industrial level, the aforementioned anti-corrosion additive will be used and studied in detail.

4. CONCLUSION

The effect of natural tannin polymers modified with ($NH_{3(aq)}$), ($NH_{3(aq)}$)/NH_4Cl buffer, DETA in one step modification, and heterocyclic amines and fatty acids of linseed oil in a two steps process on corrosion resistance of alkyd based coatings was studied. Synthesized inhibitors have shown high resistance and significant inhibiting effect, and the best properties were obtained using ET-LFA and ETA-1 inhibitors. Coatings with the addition of new inhibitors showed better adhesion, abrasion, gloss, and viscosity, and have proven to have good anti-corrosion properties. Additionally, processability of alkyd coating with added synthesized anticorrosive agents was similar/better to/than coating with zinc-phosphate addition, while Co-ETLFA was easily milled even for shorter time.

Synthesized inhibitors were applied in two different protective systems: three layer system and comparative three in one system, whereas the former one was found to possess better anticorrosive performance.

Anticorrosive tannin modified compounds represent synergetic inhibitors due to effect of both tannin basic structure and modifying reagent. These compounds represent noble biopolymer corrosion inhibitors and further researches should be pointed towards optimizing the synthesis itself, detail study on anticorrosive mechanism and finding the defects of those coatings so they could be eliminated or mitigated.

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IZVOD

PRIMENA MODIFIKOVANIH TANINA U ANTIKOROZIONIM ALKIDNIM PREMAZIMA

U ovom radu prikazana je sinteza antikorozionih aditiva na bazi hemijski modifikovanog tanina i njihova primena u alkidnim premazima u cilju poboljšanja antikorozionih svojstava. Prikazane su dve metode modifikacije tanina: direktna modifikacija tanina primenom amonijum-hidroksida, amonijum-hidroksid/amonijum-hlorid pufera ili dietilentriamina (DETA); i dvostepena modifikacija tanina koja u prvom stupnju uključuje modifikaciju epihlorhidrinom sa ciljem da se dobije tannin sa epoksi terminiranim funkcionalnim grupama, ET, i modifikaciju ET tanina sa heteroaromatičnim aminima ili masnim kiselinama izolovanim iz lanenog ulja (LFA) u drugom stupnju. Sintetisani antikorozioni aditivi su okarakterisani primenom ATR-FTIR, ^{1}H i ^{13}C NMR spektroskopija, i elementalnom analizom. Sadržaj epoksi, amino, hidroksilnih i karboksilnih grupa i vrednost jodnog broja sintetisanih aditiva određen je prema standardnim metodama. Alkidni premazi koji sadrže antikorozione aditive na bazi modifikovanog tanina ispitani su prema standardnoj SRPS EN ISO 4628 metodi. Antikorozivni alkidni premazi na bazi modfikovanih tanina pokazali su poboljšane antikorozione karakteristike i adheziju u poređenju sa alkidnim premazom na bazi cink-fosfata. Alkidni premazi koji sadrže dvostepeno modifikovani tanin sa LFA i 2-amino-5-merkapto-1,3,4-tiadiazolom pokazali su najbolje antikorozione karakteristike.

Ključne reči: *modifikovani tanini, antikorozioni aditivi, korozija, alkidni premazi*

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