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Paal-Knorr kinetics in waterborne polyketone-based formulations as modulating cross-linking tool in electrodeposition coatings

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HIGHLIGHTS

- Waterborne electrodeposition coatings were developed by using a solvent-free and catalyst-free Paal-Knorr curing chemistry
- Electrodeposition bath stability and surface homogeneity were improved by employing sterically hindered diamines for the curing reaction
- Uniform and pin-hole free surfaces were obtained on several metal substrates
- Electrodeposition bath formulations showed stable performance even after being re-used 21 and 56 days later.

GRAPHICAL ABSTRACT

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ABSTRACT

Novel cationic resins were synthesized for a direct application in automotive industry. A previous patent protocol with lower bath toxicity (i.e. no catalyst neither harmful compounds were employed), as compared to the current industrial methods based on polyurethane chemistry, was implemented. This includes the use of aliphatic polyketones as cross-linking agents for epoxy-based resins in electro-deposition (EPD) processes. Cross-linking takes place through the Paal-Knorr reaction of the amino groups on the epoxy-based materials with 1,4-dicarbonyl groups present on the polyketone backbone. The reaction kinetics can be finely tuned by the steric hindrance on both components. This was preliminarily investigated by using 2,5,8-nonanetrione as model compound. The used amines (i.e. 4-aminopiperidine (AP) and 4-aminomethyl piperidine (AMP)) display higher steric hindrance with respect to the primary ones used in the original protocol. Application of these components during electro-deposition coating yields the desired high-quality coating layers on several metallic substrates as shown by optical microscopy and image processing. All the produced coatings scored higher adhesion and chemical resistance rating than the amine-based ones used in the previous protocol (i.e. diethylenetriamine, DETA). Afterwards, the same electro-deposition baths showed to have stable performance even after being re-used 21 and 56 days later.

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1. Introduction

Corrosion prevention of metallic substrates represents a paradigmatic challenge for the use of metals in outdoor applications [1]. In the case of automotive industry, a multi-layer coating is deposited on the metallic frame (body) of a vehicle for such purpose [2]. Since the market requires almost 60 million vehicles per year, the primer surfacer, despite low profit margins, has a high marketing potential of roughly 130,000 t per year [2]. This inner layer is of paramount importance since it must ensure adhesion of the coating to the metal surface and act as binder between the metallic surface and the outer layers (e.g. the primer and the final paint). Electrophoretic deposition of a polymer film is the benchmark technique that encompasses the different materials employed in inner layer production [2]. The deposition process on the metal electrode occurs by appliance of an electrical field to a bath containing high polarity polymer dispersions [3]. This technique is characterized by several advantages, such as high efficiency, no drag-out, and easiness of control and optimization [4]. In this respect, cathodic electrodeposition based on amino-modified epoxy resins and partly blocked organic isocyanates as cross-linkers and a metal salt as curing catalyst (mainly lead and tin-based) [5] ensures outstanding corrosion resistance and adhesion to the metal surface and different dispersions (i.e. solvent-borne and powder coatings). However, the latter formulation involves the use of toxic salts as catalysts, high curing temperatures (160–180 °C) and high stoving losses. Indeed, the weight loss can reach up to 20% on the basis of an air-dried deposited electrocoating film. Although elegant solutions have been proposed to overcome these limitations, such as bis-carbamate epoxy linkers [6] or poly(urethane) dendrimers [7], a cost-effective strategy for producing clear coats in

large scale applications has not yet been developed. Moreover, increasing environmental pressures are impelling the coating industry to reduce the emissions of volatile organic compounds (VOC) [8]. As a consequence, several coating formulations have been adapted for waterborne technologies [9–11]. These are mainly based on acrylic/epoxy materials and, although they present high homogeneity and sufficient corrosion resistance, their VOC content is still considerable (i.e. minimum 50 g/L) and the curing time can last up to several hours.

A waterborne and catalyst-free solution exhibiting relatively milder temperatures (i.e. 120–140 °C) during the curing process was originally conceived by A.A. Broekhuis and P.G. Kooijmans [12]. This alternative system involves the use of aliphatic polyketones (X in Fig. 1) as cross-linking agents through a Paal-Knorr reaction mechanism (E in Fig. 1).

The complete reaction scheme depicted in Fig. 1 pertains to the preparation of a resin (VIII) by coupling a flexibilizer (III), in turn produced by modification of an epoxy component (I) with a di-amine (II), to a partially protected amine (VI) via a low molecular weight glycidyl-ether end-capped (VII) epoxy resin as coupling agent. The final step (D) of the procedure is constituted by the amine de-protection (IX) with lactic acid followed by the curing reaction (E) of the in situ generated and partly protonated amino groups with aliphatic polyketone (X) through the Paal-Knorr mechanism [13].

The latter implies the reaction of the free primary amino group with 1,4-dicarbonyl moieties yielding a pyrrole ring, with the only by-product being water, which is absorbed in the aqueous reaction resin dispersion medium.

The practical advantage of this approach is the use of the polyketone oligomers as cross-linkers, already being used for the same purposes in coatings [14], wood [15,16] and electronic adhesives [17].

Fig. 1. Synthesis of cationic resin: flexibilizer (A), ketimine (B), protected resin (C), de-protected cationic resin (D) and resin dispersion and cross-linking (E).

As such, the proposed system already fulfils most of the criteria outlined above except for two crucial (conceptually linked) factors. The reaction kinetics for the cross-linking of the two dispersed components E (Fig. 1) is actually too fast (relatively high conversion being achieved in a few minutes at elevated temperatures), which even at low temperatures seriously affects the stability of the resin-bath (e.g. the resin-dispersion prior to deposition) and causes premature cross-linking and coagulation of the resin system. This phenomenon caused a reduction in the surface tension of the layer and allows the encapsulation of gas bubbles produced during the electrophoretic process.

A possible solution to this problem can be found by an in-depth analysis of the reaction mechanism. The Paal-Knorr reaction, as already reported in the literature [13,18], is sensitive to steric hindrance on the carbon adjacent to the amino group. In this respect, the use of more sterically hindered amino groups instead of those present in V (Fig. 1) should allow modulation of the cross-linking kinetics, and, as a result, the stability of the resin dispersion prior to its use in the actual coating application.

In this study, we aim at presenting the proof of principle for this idea by testing different amino compounds. In particular, we planned to investigate the corresponding kinetics in the Paal-Knorr reaction with model compounds and subsequently employ the most promising ones in real lab-scale electro-deposition coatings on stainless steel (QD and R) panels and chromated (AL) and not-chromated (A) aluminium ones. The stability of the electrodeposition bath was then evaluated by using the original bath for newly synthesized coatings after 21 and 56 days.

2. Experimental conditions

2.1. Materials

Methyl isobutyl ketone (MIBK, Fluka, $\geq 98\%$), diethylenetriamine (DETA, Fluka, $\geq 97\%$), 4-(aminomethyl)piperidine (AMP, Aldrich, 96%), 4-aminopiperidine (AP, Aldrich, 99%), 1,6-hexanediamine (HDA, Aldrich, 98%), 2,5,8 nonanetrione (Sigma-Aldrich, 99%), bis(aminomethyl)norborene (TCI Europe, mixture of isomers, 98%), m-xylylenediamine (Sigma-Aldrich, 99%), 4,4'-methylenebis(cyclohexylamine) (Sigma-Aldrich, mixture of isomers, $>98\%$), 3-Aminomethyl-3,5,5-trimethylcyclohexylamine (isophorone-diamine, Sigma Aldrich, $>98\%$), Cardura E10 (Resolution Europe BV, batch no. HCPD0036), methyl ethyl ketone (MEK, Acros, 99%), Epikote 1001 (Resolution Europe BV, batch no. FBES 1121, M_n 880), 2-butoxyethanol (Fluka, $\geq 98\%$), ethanolamine (Aldrich, $\geq 98\%$), dichloromethane (Aldrich, 99%), lactic acid (SAFC, 85% FCC), toluene (Sigma-Aldrich, 99%) were purchased and used without further purification.

Alternating polyketones with 0% (PK0, 100% propene-CO copolymer; M_w -1680) and 30% ethene (PK30, 30%-ethene, 70%-propene-CO ter-polymer; M_w -3970) based on the total olefin content were synthesized according to a reported procedure [19].

2.2. Paal-Knorr kinetics model compound

0.117 g (2.0 mol) of 2,5,8-nonanetrione were reacted with the respective equimolar amount of diamine to form a bis-pyrrole. The reaction was carried out in toluene (25% m/m nonanetrione in toluene) and the solution was refluxed on a hot plate using a magnetic stirrer. A potentiometric titration method previously described in literature [13] was employed by using 702 SM Titrimetrohm with an automatic burette of 10 mL capacity.

2.3. Synthesis of cationic resins

Ketimines (VI in Fig. 1) were synthesized according to the procedure described in literature [12]. The reactions of AMP and AP with MIBK

have been carried out in the presence of molecular sieves (3 Å pellets, 3.2 mm diameter) to remove from the reaction equilibrium the produced water. Reaction yields were evaluated by GC/MS at reaction times of 90, 200 and 4600 min. The reaction between DETA and MIBK required 420 min till full conversion.

The synthesis of the flexibilizer (A in Fig. 1) and the final step to the cationic resins (C in Fig. 1) have been carried out by following the same supra-mentioned protocol [12] (Fig. SI-1).

Flexibilizer ^1H NMR: 1.5 (m, 4H, $\text{NH}-\text{CH}_2-\text{CH}_2$), 4.1 (m, 4H, $\text{CH}_2-\text{CHOH}-\text{CH}_2$), 1.0 (CH_3-CH_2), 1.7 (CH_2 Aliph.), 1.3 (CH_3-CH), 2.8 ($\text{CH}_2\text{OH}-\text{CH}_2-\text{NH}$).

Cationic resin elemental analysis: Calcd. N 2.53, O 13.37, C 75.22, H 8.88, Found. N 2.56, O 16.37, C 72.86, H 8.21.

2.4. Electro-deposition bath set-up

Two QD-panels were connected with PVC rods, rinsed with dichloromethane and dried under N_2 atmosphere. Afterwards, they were immersed in the electro-coating solution and the rods connected with the power supply and different voltages were applied. The anode was always a QD type while the cathode was varied according to the type of substrate employed in the cathodic electrodeposition process.

The electro-deposition bath has been set-up using the same ratios between cationic resin (VIII in Fig. 1), lactic acid, 2-butoxyethanol and polyketone (IX in Fig. 1) in water solution as described in the previous protocol [12]. The same holds for the weight ratios of ketimine, diepoxy and flexibilizer in reaction step C (Fig. 1) for all different diamine analysed.

The potential has been individually tuned according to the acidity of the resulting protonated nitrogen moieties. Indeed, since electro-deposition is a charge-transfer limited phenomenon, more acid proton groups will need lower potential to achieve the same coating thickness.

Depending on the observed kinetics, curing has been carried out in oven at 1 bar by using different temperatures (120–160 °C) and different curing times (20–110 min).

2.5. Methods

The GC/MS of ketimine based on DETA was performed on a HP 5890 series II Plus GC system, using a SolGel-1 ms column, with a length of 30 m, an inner diameter of 0.25 mm and a 0.25 μm film. Tetrahydrofuran (THF) was used as the carrier phase. A HP 5972 series Mass Selective Detector was used as the mass spectrometer.

The GC/MS of the other ketimines was performed on a HP 6890 series GC system, using a HP5 column (5% phenylmethylsiloxane) with a length of 30 m, an inner diameter of 0.25 mm and a 0.25 μm film. THF was used as the carrier phase. A HP 5973 Mass Selective Detector was used as the mass spectrometer. (T_{inj} 275 °C) ^1H NMR spectra were collected at room temperature using a Varian Oxford 200 MHz using CDCl_3 as the solvent.

Elemental analysis was carried out on a Euro EA CAP 4012.

Coatings were examined with a Zeiss Axioskop microscope, using the ZEISS Achrostatigmat 10 $\times$ /0.25 and Zeiss Achrostatigmat 20 $\times$ /0.45 lenses respectively.

The coatings thickness on the QD and R type Q-panels was measured in accordance with the ASTM D1186 standard using a CM-8828 Refinishing Gauge. The thickness of coatings on the AL and A type Q-panels was measured in accordance with the ASTM D1400 standard using a CM-8828 Refinishing Gauge.

Solvent resistance of the coatings was measured in accordance with the ASTM D5402 standard, using cotton cloth and methyl ethyl ketone (Acros, 99%) as the solvent. The strength index (n) for the coatings is defined as a normalized value of the coating solvent resistance in relation to its thickness.

Adhesion of the coatings was measured by the tape test in accordance with test method B described in the ASTM D3359 standard.

Table 1
Overall experimental conditions used for the electro-deposition experiments.

	Electrode distance (cm)	Electrodeposition time (min)	Applied voltage (V)	Curing temperature (°C)	Curing time (min)
AMP-30	3	2	50	140	45
AP-30	3	2	100	140	75
DETA-30	3	2	150	140	30
DETA-0	3	2	150	140	30

Imaging analysis of the coatings were carried out by using Image J, a Java-based image processing program developed at the National Institute of Health which is mainly used in live-cell imaging [20]. This software has been used to calculate the distribution of pixel intensity and the variation of pixel intensity along one dimension of the produced coatings.

2.6. Electrodeposition coating optimization

The physical parameters of the electro-deposition bath are expected to affect the overall performance in terms of coating quality. The strength index (*n*) of the coating and the adhesion has been measured as a function of electrode distance, deposition time and applied deposition potential.

For each of the coating types employed in the following experiments (DETA-0, DETA-30, AMP-30 and AP-30), the setting of the experimental parameters were individually optimized in order to get a stable and homogeneous coating dispersion (Table 1). Indeed, the overall charge density of the amine-modified epoxy resin and their diffusion parameters are remarkably different.

By considering the different kinetics of the employed amines (see Section 3.1) as well as the performance in terms of adhesion and chemical resistance, the curing parameters (i.e. time and temperature) were adjusted (Table 1).

3. Results and discussion

The aim of this study was the design of novel resin chemistry that provides controllable reactivity in polyketone based electro-deposition coating dispersions, while maintaining excellent coating performance. The sequential steps followed to achieve this goal and to optimize the deposition process have been omitted in the discussion. The first paragraph discusses the reaction kinetics for some selected di-amines, which will be followed by the evaluation of the obtained coatings in terms of adhesion, thickness, chemical resistance and homogeneity. This was determined by image processing of the final coatings.

Fig. 2. Conversion data for the reaction of 2,5,8-nonanetrione with sterically hindered primary amines in the presence of 25% m/m ratio of 2,5,8-nonanetrione at 110 °C (toluene reflux).

Fig. 3. 10× microscope images of cationic resins synthesized by DETA-30, DETA-0, AP-30 and AMP-30 amines coated on QD stainless steel substrate (*t* = 2 min, *d* = 3 cm, *V* and curing time varied with amine type (Table 1), curing temperature 140 °C).

3.1. Paal-Knorr kinetics

In order to assess a proper qualitative relations between amine steric hindrance and Paal-Knorr reactivity to be used during the curing stage, a kinetic study has been performed using a model 1,4-dicarbonyl compound (i.e. 2,5,8-nonane-tri-one) and several di-amines (Fig. 2). The amount of un-reacted amine as function of time was determined by potentiometric titration.

The results show that Paal-Knorr reaction is affected by steric hindrance at the α- and β-position relative to the primary amine groups. Di-amines with un-substituted carbons in the α-position to the amino group (i.e. m-xylylenediamine, norbornanedimethylamine and 4-aminomethylpiperidine (AMP)) clearly display faster kinetics than isophoronediamine and 4,4'-methylene-bis-cyclohexylamine (the latter two are characterized by more steric hindrance in the α- or β-positions). This study is in agreement with what observed in a previous publication of our group [13], as increasing steric hindrance at the α- and β-position relative to the primary amine groups lowers the Paal-Knorr conversion rate.

Taking the supra-mentioned reactivity differences into consideration, it was decided to test the stability of the dispersion and the quality of the coating for two selected amines. Each represents one of the two types identified above: 4-aminomethylpiperidine as a non-hindered diamine (AMP) and 4-aminopiperidine (AP) as hindered structure comparable to the bis-cyclohexanediamine (employed in the kinetic study), but still in agreement with the main requirements for the next electrodeposition studies. Indeed, bis-cyclohexanediamine cannot be directly used because one primary amino group needs to be selectively protected in order to further react during the Paal-Knorr curing reaction while the other is reacting with the bisphenol A resin. Thus a difference in reactivity between the two amino groups is compulsory and it can be

Fig. 4. Pixel intensity variation (left) and distribution along the panel length (right) of cationic resins synthesized by DETA-30, DETA-0, AP-30 and AMP-30 amines coated on QD stainless steel substrate (*t* = 2 min, *d* = 3 cm, *V* and curing time varied with amine type (Table 1), curing temperature 140 °C).

Table 2

Property description of optimized coatings synthesized by DETA-30, DETA-0, AP-30 and AMP-30 amines on QD stainless steel substrate ($t = 2$ min, $d = 3$ cm, V and curing time varied with amine type (Table 1), curing temperature 140°C).

Coating	Average pixel intensity	Dev St	Dev St (%)	Thickness (μm)	Adhesion rating	Strength index (n)
DETA-30	84.026	15.32	18.23	37.7 ± 2.7	4.5	1.06
DETA-0	59.553	7.346	12.34	25.7 ± 2.4	4.5	1.95
AMP-30	51.793	5.068	9.785	11.6 ± 1.1	5	2.16
AP-30	87.741	9.281	10.58	30.6 ± 2.2	5	0.95

achieved by using compounds with one primary and one secondary amino group, such as in the case of AMP and AP compounds. AMP and AP display the same chemical surroundings (i.e. the presence of a piperidine ring), but represent different levels of steric hindrance in the α -position to the primary amine. The two new systems were then compared with the PK0 and PK30 with DETA di-amine as reference systems.

3.2. Imaging analysis of electrodeposition coatings

The morphology of the optimized electrodeposition coatings synthesized by DETA (by using PK0 and PK30 as cross-linkers), AMP-30 and

AP-30 amino-modified epoxy resins were analysed by optical microscope (Fig. 3).

As a result, the coating morphology of the four different amines (DETA-0, DETA-30, AMP-30 and AP-30) is strikingly different. The coatings with the two sterically hindered amines (AMP-30 and AP-30) showed a radical improvement in morphology with respect to the one based on DETA-30 and DETA-0. The coatings prepared with a fresh resin of DETA-30 and DETA-0 showed remarkable roughness and scarce homogeneity. In addition, the appearance of bubbles caused by the electrochemical formation of hydrogen and resin instability further affected the coating homogeneity, which results in an inadequate protection of the metallic substrate from corrosion [21]. On the other hand, freshly prepared AP-30 and AMP-30 based resins produced a uniform coating, with few visible imperfections or pinholes. This phenomenon can be easily correlated with the lower cross-linking kinetic rate of the two more sterically hindered amines (AMP and AP) (Fig. 2) which do not cause any reduction in the surface tension of the layer, thus air bubbles are not being encapsulated in the coating during the electrodeposition process.

Furthermore, the colorimetric distribution of pixel intensity (i.e. calculated by image processing of the coating snapshots) can be related to the coating smoothness and uniformity.

AMP-30 and AP-30 resins scored lower standard deviation in pixel intensity distribution compared than the DETA-30 and DETA-0

Fig. 5. $10\times$ microscope images of cationic resins synthesized by DETA-30, DETA-0, AP-30 and AMP-30 amines coated on R stainless steel panels as well as AL and A aluminium ones ($t = 2$ min, $d = 3$ cm, V and curing time varied with amine type (Table 1), curing temperature 140°C).

homologue (Fig. 4 left, Table 2) which confirms the previous results in morphology analysis by optical microscopy and indirectly validates our proof of concept.

The same trend is observed if the average of pixel intensity is monitored along the panel length (Fig. 4 right) which shows rather uniform intensity pattern for AMP-30, AP-30 and DETA-0 compared to the DETA-30 resins.

Hence, an increase in coating homogeneity is achieved by using DETA and polyketone at high propene content as cross-linker. However, its kinetic is still too fast to observe a pinhole free surface. On the other hand, AMP-30 and AP-30 coatings showed better morphology, which contributes to a relative higher adhesion (Table 2). In particular, AMP-30 resins presented lower thicknesses, but comparable adhesion and chemical resistance properties.

3.3. Imaging analysis of coatings on different metallic substrates

In order to assess the versatility of such electro-deposition process, four diverse electrode substrates were tested.

QD and R panels were used as stainless steel material with different roughness (<20 and 25–65 μ inches) as well as two types of aluminium panels, chromated (AL) and not chromated (A). The morphology of the coatings analysed by optical microscopy (Fig. 5) displayed an increased homogeneity and smoothness for all substrates by using AMP-30 and AP-30 cationic resins compared to DETA-30 and DETA-0 ones.

In particular, the chromate and not-chromated aluminium panels presented similar morphology characteristics as previously described by using QD stainless steel panels. Indeed, all the DETA-30 and DETA-0 coatings showed formation of bubbles and pin-holes, which

consequently reduced the adhesion and the chemical resistance of the analysed coatings (Fig. SI-3).

Furthermore, coatings produced on R stainless steel substrate displayed a heterogeneous surface for all amines. This can be certainly attributed to the higher roughness of the panel compared to the other three substrate materials.

On the other hand, AP-30 coatings did not show any pinhole formation and the microscopy images showed a substantially improved morphology even on the previously mentioned panel.

The same results were obtained when observing the pixel intensity distribution (Fig. 6 A), which showed the lowest standard deviation in pixel intensity for AP-30 coatings for all panels but QD ones.

On the other hand, the strength index did not follow the same trend, displaying the highest value of strength index for AMP-30 coatings in all panels, except when using AL ones (Fig. 6 B). Indeed, DETA-30 scored the highest strength index with AL substrate, probably suggesting that primary amino groups do interact better with a chromate surface by forming chelation with the metal itself [22].

This enhances the versatility of our approach, which can identify and select the appropriate amine in order to obtain the best coating performance for different metal substrates.

3.4. Electro-deposition bath stability

As both coatings produced by AMP and AP di-amines showed similar morphologies with all the analysed substrates (Figs. 3 and 5), only AMP coatings were selected for testing the electrodeposition bath stability, although in principle both di-amines could be successfully employed as primer surface polymer.

Retaining of the morphological properties was actually observed by optical microscope and visually after re-usage of the stored DETA-30,

Fig. 6. Pixel intensity standard deviation from imaging analysis (A) and strength index performance (B) of cationic resins synthesized by DETA-30, DETA-0, AP-30 and AMP-30 amines coated on different metal substrates ($t = 2$ min, $d = 3$ cm, V and curing time varied with amine type (Table 1), curing temperature 140 °C).

Fig. 7. 10 $\times$ microscope images of cationic resins synthesized by DETA-30, DETA-0 and AMP-30 amines coated on QD panels ($t = 2$ min, $d = 3$ cm, V and curing time varied with amine type (Table 1), curing temperature 140 °C) after re-usage of the stored electrodeposition baths 21 days and 56 days later.

Fig. 8. Pixel intensity standard deviation from imaging analysis of cationic resins synthesized by DETA-30, DETA-0 and AMP-30 amines coated on different metal substrates ($t = 2$ min, $d = 3$ cm, V and curing time varied with amine type (Table 1), curing temperature 140°C) after re-usage of the stored electrodeposition baths 21 days and 56 days later.

DETA-0 and AMP-30 electrodeposition baths 21 days and 56 days later (Fig. 7).

The distribution of the pixel intensity (Fig. 8) follows the same trend, once again confirming the stability of the electrodeposition bath produced by AMP coating, with the exception of DETA-30 coatings after 56 days which scored the lowest deviation standard.

However, an equally good chemical resistance does not support such result, since DETA-30 scored 0.94 as strength index, which is roughly the half of what observed with DETA-0 and AMP coatings (i.e. 2.08 and 2.06 respectively). This can probably suggest that most of the cross-linking in the DETA-30 electrodeposition bath already occurred in situ, as already observed during the coating processing.

Therefore the coating presents a lower cross-linking degree, which enhances its coating homogeneity, i.e. the coating is more ductile and consequently ensures relatively high homogeneity. On the other hand, lack of cross-linking negatively affects its chemical resistance.

Such result is indicative of higher bath stability of AMP-30 coatings compared to DETA-30 and DETA-0 ones and confirms our first hypothesis of a possible tuning by steric hindrance of the amino group in Paal-Knorr curing mechanism for electrodeposition baths.

4. Conclusions

Novel polyketone-based resins were tested in electro-deposition process for automotive applications in order to implement a previous protocol based on diethylentriamine (DETA) modified epoxy coatings.

In first instance, we proved the sensibility of the curing reaction to steric hindrance (Paal Knorr mechanism) through a relatively simple model compounds study. As a consequence, higher sterically hindered (i.e. 4-aminopiperidine, AP and 4-(aminomethyl)piperidine, AMP) amino coatings were successfully prepared and compared to the previous study.

The displayed coatings showed higher bath stability and negligible formation of pin-holes on the coating surfaces even 56 days after the preparation of the bath, thus exhibiting an excellent shelf-life as well as relatively high versatility for different metal substrate. Moreover, image processing showed for all AMP-30 and AP-30 coatings the highest homogeneity and smoothness among the employed di-amines.

The proposed system represents a perfect and desirable alternative to the several coating formulations used in electro-deposition process for automotive applications and a firm, green-oriented perspective for catalyst-free and non-toxic electro-deposition bath formulations.

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