Chapter 6

The kinetics of Paal-Knorr reaction in polyketone-based materials as tuning tool for electro-deposition coatings

Abstract

Novel cationic resins were synthesized for a direct application in automotive industry. A previous patent protocol with low bath toxicity (i.e. no use of catalyst or highly harmful compounds) compared to the current industrial methods based on polyurethane chemistry was implemented. This comprises the use of aliphatic polyketones as crosslinking agents for epoxy-based resins in electro-deposition processes. Cross-linking takes place through the Paal-Knorr reaction of the amino groups on the epoxy-based materials with the 1,4-dicarbonyl ones 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 included 4-aminopiperidine (AP) and 4-aminomethyl piperidine (AMP), both displaying 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. Moreover, it reduces undesirable side reactions and avoids pin-holes formation.

Several parameters have been considered, such as electrode distance, potential, electro-deposition time and temperature and curing times have been adjusted in order to optimize the annealing stage. All the produced coatings scored a higher adhesion and chemical resistance rating than the amine-based ones used in the previous protocol (i.e. diethylenetriamine, DETA). Afterwards, the coatings have been tested on different metallic substrate and the same electro-deposition baths have been re-used after 21 and 56 days in order to check their stability.
6.1 Introduction

The corrosion of metal layers in outdoor applications remains an ongoing subject of investigation [1-3]. The dimension and gravity of the problem is paradigmatic in the automotive industry, where it is common practice to apply a multi-layer coating to the metallic frame (body) of a vehicle [4]. In particular, the first coating, i.e. the 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). Nowadays, the automotive market requires an average of 1 million tons of material per year for the production of car paints, including clear coats, primer surfaces, base coats and electrodeposition coatings [5]. The latter, being widely used as the outer layer, consists of stimulating deposition on one of the electrodes by application of an electrical field on water-borne charged polymer dispersions [6-8]. This technique is characterized by several advantages, such as a high efficiency, no drag-out, and easiness of control and optimization [9]. However, the resin systems applied in the majority of industrial applications involves partly blocked organic isocyanates as cross-linkers and a metal salt as curing catalyst (mainly lead and tin-based) [10]. Despite the outstanding corrosion resistance and adhesion to the metal surface of the final coating, the polyurethane cross-linkers display several drawbacks. Besides the well-known environmental issues connected with these chemicals and their preparation (ultimately requiring the use of phosgene), both the isocyanates and the catalyst are toxic and dangerous for human health, they require relatively high curing temperature (160-180°C) and are characterized by high stoving losses.

A first step [11] towards a successful study of an alternative system involves the use of aliphatic polyketones (X in Figure 6.1) as cross-linking agents through a Paal-Knorr reaction mechanism (E in Figure 6.1).
Figure 6.1. Total synthesis of cationic resin: flexibilizer (A), ketimine (B), protected resin (C), de-protected cationic resin (D) and resin dispersion and cross-linking (E)
The complete reaction scheme (Figure 6.1) involves the preparation of a resin (VIII) by coupling a flexibilizer (III), in turn prepared by modification of an epoxy component (I) with a di-amine (II), to a partially protected amine (VI) with the help of low molecular weight glycidyl-ether end-capped (VII) epoxy resin. 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 [12].

The latter implies the reaction of the free primary amino group with two carbonyl moieties yielding a pyrrole ring, the only by-product being water, which is absorbed in the aqueous reaction resin dispersion medium. The reaction proceeds in relatively mild conditions (120-140°C), its kinetics being fast enough to make the use of a metal catalyst unnecessary. The practical advantages of this approach are testified by the use of the same polyketone oligomers as cross-linkers for applications such as coatings [13,14], wood [15] and electronic adhesives [16].

As such, the proposed system fulfills already 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 (Figure 6.1) 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. The latter causes the formation of gas bubbles between the metal surface and the coating during the ultimate electro-deposition and curing 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 [12,17], 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 (Figure 6.1) should allow the fine-tuning of the cross-linking kinetics, and, as a result, of 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 plan 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 different metal substrates.

6.2 Experimental

6.2.1 Materials
Methyl isobutyl ketone (MIBK; Fluka, ≥ 98%), diethylenetriamine (DETA; Fluka, ≥ 97%), 4-(aminomethyl)piperidine (AMP; Aldrich, 96%), 4-aminopiperidine (AP; Aldrich, 99%), 1,6-hexanediameine (HDA; Aldrich, 98%), 2,5,8 nonanetrione (Sigma-Aldrich, 99%),
bis(aminomethyl)norbornane (TCI Europe, mixture of isomers, 98%), m-xylylenediamine (Sigma-Aldrich, 99%), 4,4′-methylene-bis(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, Mn 880), 2-butoxyethanol (Fluka, ≥98%), ethanolamine (Aldrich, ≥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 co-polymer; Mw-1680) and 30% ethene (PK30, 30%-ethene,-70%-propene-CO ter-polymer; Mw-3970) based on the total olefin content were synthesized according to a reported procedure [18].

### 6.2.2 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 [17] was employed by using 702 SM Titrino Metrohm with an automatic burette of 10 mL capacity.

### 6.2.3 Synthesis of cationic resins

Ketimines (VI in Figure 6.1) were synthesized according to the procedure described in literature [11]. 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; conversions 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 flexibiliser (A in Figure 6.1) and the final step to the cationic resins (C in Figure 6.1) have been carried out by following the same supra-mentioned protocol [11].

Flexibilizer $^1$H NMR: 1.5 (m, 4H, NH-CH$_2$-CH$_2$), 4.1 (m, 4H, CH$_2$-CH$_2$-CHOH-CH$_2$), 1.0 (CH$_3$-CH$_2$), 1.7 (CH$_2$ Aliph.), 1.3 (CH$_3$-CH), 2.8 (CH$_2$OH-CH$_2$-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

### 6.2.4 Electro-deposition bath set-up

The employed electro-deposition lab-scaled equipment is depicted in Figure 6.2. Two Q-panels were connected with PVC rods and rinsed with dichloromethane.

Then they were immerged 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 during the analysis of different substrate for the present cathodic electrodeposition (Figure 6.2).

![Figure 6.2. Schematic representation of the lab-scaled electrodeposition setup](image)

The electro-deposition bath has been set-up using the same ratios between cationic resin (VIII in Figure 6.1), lactic acid, 2-butoxyethanol and polyketone (IX in Figure 6.1) in water solution as described in the previous protocol [11]. The same holds for the weight ratios of ketimine, di-epoxy and flexibilizer in reaction step C (Figure 6.1) for all different di-amine analyzed. 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 atmospheric pressure, different temperatures (120 - 160°C) and different curing times (20 - 110 min).

### 6.2.5 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)

$^1$H-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 Achrostigmat 10x/0.25 and Zeiss Achrostigmat 20x/0.45 lenses respectively.

The coatings thickness on the QD and R type Q-panels was measured in accordance with the ASTM D1186 [19] 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 [20] standard using a CM-8828 Refinishing Gauge.

Solvent resistance of the coatings was measured in accordance with the ASTM D5402 standard [21], 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 [22].

6.3 Results and discussion

The aim of this study was to design 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 will be discussed in the next paragraphs. The first paragraph discusses the reaction kinetics for some selected di-amines, which will be followed by the evaluation of the new resin performance in the coating process and as final cured coating.

6.3.1 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-trione) and several di-amines (Figure 6.3). The amount of unreacted amine as function of time was determined by potentiometric titration.
Figure 6.3. 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 toluene refluxing temperature

The results show that the Paal-Knorr reaction is affected by steric hindrance at the $\alpha$- and $\beta$-position relative to the primary amine groups. Di-amines with un-substituted carbons in the $\alpha$-position to the amino group (i.e. m-xylylenediamine, norbornanedimethylamine and 4-aminomethylpiperidine (AMP)) clearly display faster kinetics than isophoronediamine and 4,4'-methylene-biscyclohexylamine (the latter two are characterized by more steric hindrance in the $\alpha$- or $\beta$-positions).

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-cyclohexanediame (employed in the kinetic study), but it still satisfying to the main requirements for the next electrodeposition studies.

Indeed, bis-cyclohexanediame 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 achieved by using compounds with one primary and one secondary amino group.
groups, 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 \( \alpha \)-position to the primary amine. Both indeed contain a secondary amino group, but their primary amino group is linked to a primary and secondary carbon, respectively. The two new systems were then compared with the PK0 and PK30 with DETA di-amine as reference systems.

**6.3.2 Effect of physical parameters in electro-deposition bath: time, applied potential and electrode distance**

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 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 6.1). Indeed, the overall charge density of the amine-modified epoxy resin and their diffusion parameters are remarkably different.

<table>
<thead>
<tr>
<th></th>
<th>Electrode distance (cm)</th>
<th>Electrodeposition time (min)</th>
<th>Applied voltage (V)</th>
<th>Curing temperature (°C)</th>
<th>Curing time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMP-30</td>
<td>3</td>
<td>2</td>
<td>50</td>
<td>140</td>
<td>45</td>
</tr>
<tr>
<td>AP-30</td>
<td>3</td>
<td>2</td>
<td>100</td>
<td>140</td>
<td>75</td>
</tr>
<tr>
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<td>3</td>
<td>2</td>
<td>150</td>
<td>140</td>
<td>30</td>
</tr>
<tr>
<td>DETA-0</td>
<td>3</td>
<td>2</td>
<td>150</td>
<td>140</td>
<td>30</td>
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</table>

Table 6.1. Overall experimental conditions used for the electrodeposition experiments

The index was found to decrease as function of the electrode distance for the three employed systems (Figure 6.4) at 2 minutes electrodeposition time and 150 V.
The indices for the three employed systems clearly seem to depend on the reactivity of the system. A better performance of AMP-30 with respect to DETA is observed which is in agreement with the corresponding reaction kinetics (vide supra). The fact that steric hindrance plays a dominant role here is further confirmed by using two different polyketones, differing in their ethylene content (30% for DETA-30 and 0% for DETA-0 in Figure 6.4) and thus in their relative steric hindrance along the backbone (the latter generally decreases with increasing ethylene content[17]).

By analyzing the coating thickness at different electrodeposition time (d=3 cm, different V), it appears more clear that DETA-0 and AMP-30 coatings displayed constant thickness values at different times while DETA-30 coatings results to be thicker for longer electrodeposition times. The overall thickness follow this order DETA-30>DETA-0>>AMP-30.
Figure 6.5. Variation of thickness in coatings produced by DETA-30, DETA-0 and AMP-30 at different deposition times (3 cm electrode distance, different employed potential according to amine type)

This is not surprising if one takes into account [23-25] that electro-deposition is a resistivity-limited phenomenon. As a consequence the polymeric coatings thickness increases till the layer resistivity formed around the electrode counter-balances the applied voltage. The thickness of the DETA coatings produced by using more sterically hindered polyketone PK0 (DETA-0) reached, at the same electro-deposition times, lower thickness in comparison with the one obtained with PK30 (DETA-30), probably because of the presence of the methyl groups along the backbone. The strength index vs. applied potential of DETA-30, AMP-30 and AP-30 coatings (Figure 6.6) showed that the first is remarkably affected by the potential while the latter two displayed more stable behavior.
Figure 6.6 Strength index of electro-deposition coatings synthesized with DETA-30, AMP-30 and AP-30 compounds (i.e. in the presence of PK30 as cross-linker) at different applied voltage with 2 minutes electrodeposition time and 3 cm electrode distance.

These results might be correlated with the protonation degree of the three resins. Indeed, a pH of 4.5 is used during electrodeposition and, at this pH value, part of the amino group pendant on the cationic resins are protonated and responsible of the macromolecule migration and deposition on the cathode [26]. Since AMP and AP display a lower PKa than DETA, the electrodeposition process of the former is more gradual and less susceptible to potential variations.

Such control in the deposition kinetic is highly desirable in order to achieve good homogeneity between the cross-linker and the cationic resin in the final coating. Moreover, Figure 6.6 indicates a comparable strength index of AP-30 and DETA-30 coatings while AMP-30 scored higher values.

It is important to notice that in the general framework of physical parameters optimization, lower coating thickness was obtained for AP-30 and AMP-30 coatings compared to DETA-30 and DETA-100 ones, but with comparable, if not superior, properties in terms of adhesion and chemical resistance.

6.3.3 Effect of different curing times and temperatures

Curing time and temperature will affect the coating quality in terms of mechanical properties, such as wear-resistance and adhesion. Cationic resin synthesized by DETA-30, DETA-0, AMP and AP in the presence of PK30 as cross-linker, at different curing times and temperatures (Figure 6.7 a and b respectively) showed that AMP-30 and AP-30 coating need longer curing time in order to achieve the same performance in terms of coating durability.
Figure 6.7. Strength index of coatings synthesized by diverse amine compounds at different curing time (a) with curing temperature of 140°C and different curing temperatures (b) with curing time of 75 min for AP-30, 30 min for DETA-30 and DETA-0, 45 min for AMP-30

This is in perfect agreement with the kinetics on model compounds (vide supra). On the other hand, AMP-30 coating showed an outstanding strength index at 45 minutes, which is longer than all other examined coatings. Moreover, longer curing time causes an overall slight increase of strength index for the three resins characterized by steric hindrance (i.e. DETA-0, AMP-30 and AP-30) while DETA-30 was not significantly affected.
Data for strength against cure time (at constant temperature of 140°C) and those for strength against cure temperature show that better strength data are achieved for better cured resins. Longer reaction times and higher temperatures result in better strength performance for each system and stipulate the differences in reactivity between the systems. The reactivity follows the sequence (high to low): DETA-30 > DETA-0 > AMP-30 > AP-30.

All the displayed results might be explained as a consequence of slower kinetics for AMP-30 and AP-30 with the respect to DETA-30, thus confirming the validity of the original hypothesis (i.e. fine tuning of the coating properties by control of the reaction kinetics).

### 6.3.4 Effect of 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 μinch) as well as two types of aluminum panels, chromated (AL) and not chromated (A) (Figure 6.8).

**Figure 6.8.** Strength index performance of cationic resins synthesized by DETA-30, AP-30 and AMP-30 amines in the presence of PK30 as cross-linker and coated on different metal substrates (t=2 min, d= 3 cm, V and curing time varied with amine type (Table 6.1), curing temperature 140°C)

AMP-30 coatings resulted in higher strength index in all materials, except when using AL panels. By using the latter, the strength index of the three cationic resin coatings did not vary. While DETA-30 reached the highest strength index with AL substrate, AMP-30 showed its best result with R panel and AP strength index did not vary by using diverse electrodes. Although the reason for such differences at the molecular level are yet to be investigated, one might notice that not only the newly synthesized AMP-30 and AP-30 coatings did not reduce the DETA-30 coating versatility but the overall
performance in all substrates are evidently improved.

### 6.3.5 Electro-deposition bath stability

The previous electro-deposition dispersions used for the coatings during the process optimization phase have also been tested after 21 and 56 days (Figure 6.9) in order to check their stability.

![Figure 6.9](image)

**Figure 6.9.** From the top to the bottom, optical microscope (20X) and visual coating images of DETA-30, AP-30, AMP-30 (in the presence of PK30 as cross-linker) (experimental conditions listed in Table 6.1) (Samples a – c based on resin stored for 56 days)

As a result, the coating morphology of the three different amines (DETA-30, AMP-30 and AP-30) is strikingly different. The coatings with the two sterically hindered amines showed a radical improvement in morphology with respect to the one based on DETA-30. The coating prepared with a fresh resin of the latter appeared quite irregular and different thickness values were indeed measured in different regions proving its intrinsic roughness. In addition, the appearance of bubbles caused by the electrochemical formation of hydrogen and resin instability affected the coating homogeneity and is not expected to ensure an adequate protection towards corrosion processes at the metal substrate [27]. Freshly prepared AP-30 and AMP-30 based resins produced a uniform coating, with few visible imperfections or pinholes. Retaining of the morphological properties were actually observed by optical microscope and visually after re-usage of the stored AMP-30 and AP-30 electrodeposition baths after 28 days and 56 days (Figure 6.9).

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

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

In first instance, we proved the sensibility of the curing reaction (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.

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 not highly toxic electro-deposition bath formulations.
6.5 References
