



# Amorphous polyamide coating resins from sugar-derived monomers

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**Abstract** In this article, the synthesis of bio-based polyamides for powder coating applications and their evaluation in a solventborne coating system are reported. The  $M_n$  values of the resins were between 3000 and 4000 g mol<sup>-1</sup> and the resins displayed  $T_g$  values from 60 to 80°C. Both amine and carboxylic acid functionalities (total ~0.6 mmol g<sup>-1</sup>) were introduced for curing purposes. The resins were cured with triglycidyl isocyanurate (TGIC) or *N,N,N',N'*-tetrakis(2-hydroxyethyl)adipamide (Primid XL-552). The curing reaction was followed using rheology which indicated that TGIC achieved higher reaction rates and higher gel contents. The DSC analysis of the cured disks showed that all cured samples were amorphous as is desired for the targeted coating application. The resins required a curing temperature higher than 150°C. Aluminum panels were coated using a solventborne approach and the coatings were cured at 180°C during 1 h. Dewetting was observed on all panels. Network formation was adequate for an amine-functional resin cured with TGIC as indicated by solvent resistance testing. In conclusion, the developed bio-

based polyamide resins are promising materials to be used as binder resins in powder coating applications.

**Keywords** Renewable resources, Polyamides, Resins, Amorphous materials, Copolymerization, Network formation

## Introduction

As emission regulations are becoming more stringent, powder coatings are very interesting solvent-free coating systems. Coating of metal substrates with this technique is the largest market but many other materials like wood can also be coated, because curing now can be successfully performed at lower temperatures. Powder coatings have several clear advantages compared to solvent-based coating systems: low emission of volatile organic components, facile, safe application of the coating, very little waste due to reuse of powder overspray, and the curing process produces a hard, tough and durable coating.<sup>1–5</sup>

The dry paint which constitutes a powder coating, consists of a binder resin, a curing agent, pigments, and additives to enhance properties such as flow and to reduce film imperfections.<sup>6,7</sup> The different components are dispersed into the resin using an extruder. The residence time in the extruder is very short (~30 s) to prevent premature crosslinking, which may occur due to the relatively high temperature needed to facilitate flow of the resin. For coating appearance reasons, the final coating needs to be amorphous, so the binders should have a low degree of crystallinity or should be completely amorphous.

Several binder-curing agent combinations exist. Often, the binders in the powder paint are polyesters with a relatively low molecular weight ( $M_n = 2000–6000$  g mol<sup>-1</sup>). These polyesters are typically based on bifunctional monomers, e.g., terephthalic acid, isoph-

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thalic acid, adipic acid, neopentyl glycol, and ethylene glycol, with the addition of a small percentage of trifunctional monomers, e.g., trimellitic anhydride and trimethylolpropane.<sup>8–10</sup> These compounds are derived from petrochemicals. With depleting oil reserves, efforts are made to replace these starting materials with bio-based alternatives to create more sustainable polyesters.<sup>11–16</sup>

Storage of the powder paint imposes requirements on the glass transition temperature ( $T_g$ ) value of the used polymer resin, which has to be significantly higher than ambient temperature. Storage above the  $T_g$  of the powder will cause fusion of the particles, decreasing the ability of the coating to level well or even completely hampering paint application. For these reasons, the binder  $T_g$  value should exceed 60°C. As a consequence, the resulting coating will typically have a  $T_g$  value of more than 70°C due to the curing.

The polyester binders can have either hydroxyl- or carboxylic acid-functionality. The curing agents typically used for bifunctional polyesters must have a functionality of more than two. Triglycidyl isocyanurate (TGIC) has been a widely used curing agent for the curing of carboxylic acid-functional resins.<sup>1,7,17–19</sup> Besides reaction with carboxylic acids, TGIC can also react with hydroxyl groups and amines. However, its use in Europe is declining because of its toxicity. For carboxylic acid-functional resins,  $\beta$ -hydroxyalkylamides have become popular under the trade name Primid.<sup>1,2,7,20</sup> This type of curing agents are non-toxic but can only react with carboxylic acid groups via an oxazolinium intermediate. This reaction cannot be catalyzed.<sup>21,22</sup>

The curing reaction of thermosets can be followed by molecular changes, the disappearance of end groups, the energy required for the reaction, and by measuring material properties. The use of rheological measurements to monitor the extent of crosslinking has been described.<sup>23–27</sup> Sufficient heat will allow the powder paint to flow, after which the viscosity will decrease with increasing temperature. When the curing reaction starts, the viscosity will increase again due to the formed crosslinks. This makes rheological measurements convenient for monitoring the curing as well as assessing the flow of the powder.

This article describes the synthesis of amorphous polyamide resins from sugar-derived monomers (Scheme 1) and their performance is tested in curing

and coating experiments. Polyamides have been selected for their good stability against hydrolysis and solvents. Before applying the resins to aluminum panels, rheology will be used to analyze the binder-curing agent combination. As mentioned, powder coatings are formulated using additives. To make a fair assessment of the properties of the binders investigated, no formulation with additives such as flow agents will be applied.

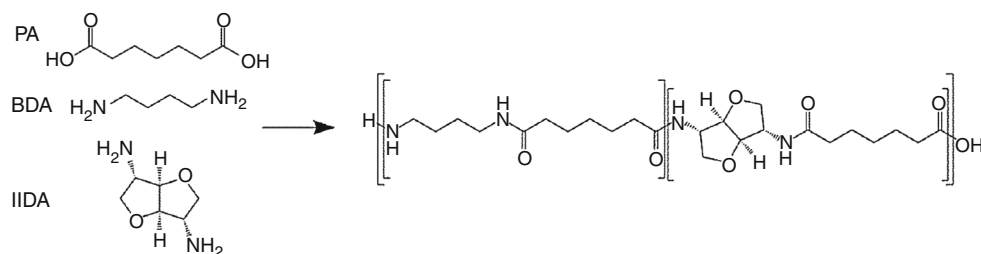
## Experimental section

### Materials

The reactants pimelic acid (**PA**, 98%), butane-1,4-diamine (**BDA**, 99%), and the crosslinker triglycidyl isocyanurate (TGIC) were purchased from Sigma-Aldrich. *N,N,N',N'*-tetrakis(2-hydroxyethyl)adipamide (Primid XL-552, 98%) was obtained from Alfa Aesar. 2,5-diamino-2,5-dideoxy-1,4-3,6-dianhydroiditol (isoidide diamine, **IIDA**,  $\geq 95\%$ ) was synthesized by Wageningen UR Food and Biobased Research.<sup>28,29</sup> Solvents were obtained from Biosolve in AR grade. Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories, Inc. All chemicals were used as received without further purification.

### Methods

<sup>1</sup>H NMR (delay time 5 s, 32 scans, 90°) and <sup>13</sup>C NMR (delay time 1 s, 2000 scans) spectroscopy measurements were performed on a Agilent 400-MR NMR system in DMSO-*d*<sub>6</sub>. Data were acquired using VnmrJ3 software. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS). Rheometry experiments were performed with a TA Instruments AR-G2 using plate–plate geometry, angular frequency  $\omega = 6.283 \text{ rad s}^{-1}$ , strain  $\gamma = 1\%$ . Samples were prepared by mixing 250 mg of resin and crosslinker in a mortar, followed by cold pressing of the mixture to a disk ( $D = 25 \text{ mm}$ ,  $H = 500 \mu\text{m}$ ) at a pressure of 1600 bar. The samples were all subjected to the same temperature pro-time program: heating from 70 to 150°C at a heating rate of 2°C min<sup>-1</sup>, isothermal at



**Scheme 1:** Synthesis of polyamide resins based on pimelic acid (PA), butane-1,4-diamine (BDA), and isoidide diamine (IIDA)

150°C for 60 min, heating to 200°C with a heating rate of 5°C min<sup>-1</sup>, and isothermal at 200°C for 15 min. Differential Scanning Calorimetry (DSC) was performed on a TA Q1000 DSC. Approximately 5 mg of polymer or the rheology samples was accurately weighed and sealed into an hermetically closed aluminum pan. Temperature profiles were measured from 0 to 250°C above  $T_m$  and consisted of two heating runs and two cooling runs, at a heating/cooling rate of 10°C min<sup>-1</sup>. TA Universal Analysis software was used for data acquisition and analysis. The value for the  $T_g$  was determined from the inflection point of the curves. Size-exclusion chromatography (SEC) was measured on a system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (40°C), a Waters 2707 autosampler, a PSS PFG guard column followed by 2 PFG-linear-XL (7  $\mu$ m, 8  $\times$  300 mm) columns in series at 40°C. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, Biosolve) with potassium trifluoroacetate (20 mmol L<sup>-1</sup>) was used as eluent at a flow rate of 0.8 mL min<sup>-1</sup>. The molecular weights were calculated against poly(methyl methacrylate) standards (Polymer Laboratories,  $M_p = 580$  g mol<sup>-1</sup> up to  $M_p = 7.1 \cdot 10^6$  g mol<sup>-1</sup>). Samples were prepared in the eluent at a concentration of 2–3 mg mL<sup>-1</sup>. The coating application procedure for panels was determined by several test panels at different conditions and the rheological results. Samples were prepared in duplicate onto a 15-cm and a 12.5-cm chromated aluminum Q-panels. Half of the large panel and the complete smaller panel were rubbed using Scotch-Brite to roughen the surface. The panels were cleaned and degreased using *n*-heptane and ethanol. A solution of resin in dimethylacetamide (DMAc,  $C = 0.16$  g/g) was prepared at 150°C and added to the desired crosslinker ( $r = 1:1.05$   $[2 \cdot AmV + AV]/[v \cdot f_{crosslinker}]$ ). Using a 120- $\mu$ m doctor blade, a film was applied to the panel at 80°C. The coating formulations were cured for 60 min at 180°C under an argon atmosphere. The coated panels were subjected to several tests. The coating thickness was measured with a VF-DC B639 coating thickness gage. The panels were rubbed with a cotton cloth drenched in acetone or ethanol for a maximum of 100 double rubs. The pencil hardness was determined using an Erichsen scratch hardness tester model 291 with Hardmuth Koh-I-Noor 1500 pencils. The panels were subjected to a reverse impact test with a 1 kg weight dropped from 1.00 meter height using a BYK-Gardner PF-5512.

### Synthetic procedures

**A:** **PA** (4.052 g, 25.30 mmol), **BDA** (0.885 g, 10.04 mmol), and **IIDA** (2.203 g, 15.28 mmol).

**B1/B2:** **PA** (2.995 g, 18.70 mmol), **BDA** (0.690 g, 7.83 mmol), and **IIDA** (1.885 g, 13.07 mmol).

**PA**, **BDA**, and **IIDA** were charged to a closed reactor equipped with a double helical ribbon

impeller, two argon inlets, and a distillation setup. Approximately 5 mL of methanol was added and the mixture was stirred under an inert atmosphere without gas flow at a set temperature of 100°C, to allow for oligomerization of the reactants during the initial phase of the reaction. After a day, the inert gas flow through the reactor was allowed to remove the methanol from the reaction mixture. The temperature was slowly increased to 170°C in the course of several hours, while gas flow through the reactor was prevented to retain the volatile **BDA**. After 2 h, the temperature was increased to 230°C and condensate was removed from the system. The condensation setup was removed 2 h later and the pressure was decreased to 3–4 hPa in the reactor. After another 2 h, the products were discharged from the reactor in the liquid state.

Compound **A** was obtained as a brittle, light colored, transparent material with a yield of 3.12 g (50.0 wt% of maximum achievable weight), and two separate fractions with a different composition of monomers (20.6 and 13.9 wt%). **B1** was obtained directly from the reactor as a brittle, greenish, transparent compound (**B1**) with a yield of 1.949 g (39.8%). **B2** was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and was subsequently precipitated from a large excess of acetone and was dried after decantation of the solvent mixture. It was obtained as a brittle, gray-colored, opaque solid with a yield of 2.729 g (55.8%). N.B. samples **B1** and **B2** originate from the same polymerization run, so that the overall yield of the reaction was 95.6%.

**A:** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta_H$  (ppm) 8.10 **IIDA** NH (d, 1.1H), 7.77 **BDA** NH (t, 0.8H), 4.36 **IIDA** bridge CH (s, 1.0H), 4.08 **IIDA** CHNH (t, 1.1H), 3.82 **IIDA** *exo*-CH (q, 1.1H), 3.60 **IIDA** *endo*-CH (dd, 1.1H), 3.00 **BDA** CH<sub>2</sub>NH (d, 1.6H), 2.15 **PA** CH<sub>2</sub>COOH (t, 0.3H), 2.03 **PA** CH<sub>2</sub>COOCH (quin, 3.7H), 1.46 **PA** CH<sub>2</sub>CH<sub>2</sub>CO (quin, 4.0H), 1.35 **BDA** CH<sub>2</sub>CH<sub>2</sub>N (quin, 1.6H), 1.19 **PA** CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> (m, 2H), <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta_C$  (ppm) 172.06, 171.85, 86.04, 71.73, 55.66, 39.52, 38.10, 35.31, 34.94, 30.65, 28.29, 26.67, 25.06, 24.91.

**B1:** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta_H$  (ppm) 8.09 **IIDA** NH (d, 1.2H), 7.75 **BDA** NH (t, 0.8H), 4.36 **IIDA** bridge CH (s, 1.2H), 4.22 **IIDA** (monomer) bridge CH (s, 0.1H), 4.08 **IIDA** CHNH (t, 1.2H), 3.82 **IIDA** *exo*-CH (q, 1.1H), 3.60 **IIDA** *endo*-CH (dd, 1.2H), 3.00 **BDA** CH<sub>2</sub>NH (d, 1.6H), 2.82 **BDA** CH<sub>2</sub>NH<sub>2</sub> (d, 0.1H), 2.21 **PA** CH<sub>2</sub>COOH (t, 0.1H), 2.05 **PA** CH<sub>2</sub>COOCH (quin, 3.9H), 1.46 **PA** CH<sub>2</sub>CH<sub>2</sub>CO (quin, 4.0H), 1.35 **BDA** CH<sub>2</sub>CH<sub>2</sub>N (quin, 1.6H), 1.19 **PA** CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> (m, 2H), <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta_C$  (ppm) 172.05, 171.84, 86.04, 71.73, 55.66, 39.52, 38.10, 35.29, 34.94, 28.29, 26.67, 25.09, 24.91.

The frequencies of **B2** are identical to **B1** except the ratio between  $\delta_H = 3.00$  and 2.82 ppm, and the presence of a contamination at  $\delta_H = 5.2$  ppm.

## Results and discussion

### Resin synthesis and properties

The resins were successfully synthesized following an improved procedure compared to our previously published work.<sup>30</sup> The polyamides were obtained as brittle compounds. However, the resin colors differ from each other (see Fig. SI3). Most likely, the greenish color of **B1** originates from metal ions leached from the impeller. Both **A** and **B1** are highly transparent, glassy materials which indicates that they are largely amorphous. The precipitation of **B2** yields an opaque material indicating that an ordered phase is present that scatters light at its boundaries with the amorphous matrix.

The polyamide resins were analyzed in terms of their molecular weights and compositions using SEC and NMR techniques (see Table 1). Optimization of the synthesis resulted in polyamides with  $M_n$  values ranging from 3100 to 3800 g mol<sup>-1</sup> as calculated from NMR data. SEC results show an overestimation of the molecular weights compared to NMR measurements with dispersities between 2.1 and 2.8.

The resins were analyzed using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (see Fig. 1; Table 1) and the resonances have been assigned. For all three compositions, the resonance of the CH<sub>2</sub> protons adjacent to unreacted carboxylic acid moieties (i.e., end groups) could be observed at  $\delta = 2.2$  ppm. For **A**, only these carboxylic end groups were observed, while for **B1** and **B2** a signal was also observed for the proton next to an amine end group in **IIDA** (e') at  $\delta = 4.2$  ppm. This indicated that the excess amount of **IIDA** used for the synthesis of **B1** and **B2** was incorporated and resulted in amine end groups. End groups formed by **BDA** accounted for less than 20% of all amine end groups in **B1** and **B2**. The different ratio of end group signals for **IIDA** and **BDA** with respect to their copolymer ratio is due to the higher reactivity of the **BDA** amine groups. Therefore, more **BDA** was incorporated into the backbone of the polymers compared to **IIDA**. In the spectrum of **B2**, a resonance was observed at  $\delta = 5.2$  ppm. This signal could not be assigned. The <sup>13</sup>C NMR spectra were very clean. All signals could be assigned to the expected polyamide structures.

The acid value (*AV*) and amine value (*AmV*) were calculated from NMR data rather than potentiometric end group titration due to the limited amount of resins available for analysis. (See Supplementary Information). With optimized NMR measurement settings and data analysis, the resulting error is around 10%. The end groups of the polymers were controlled by the feed ratio between **PA**, **BDA**, and **IIDA**. Polyamide **A** was carboxylic acid functional, while polyamides **B1** and **B2** were predominantly amine functional as determined by NMR spectroscopy. The lower *AV* and *AmV* of **B2** compared to **B1** were expected due to the precipitation step. This was caused by the fact that the shortest chains in **B2** could remain in solution in the mixture of HFIP (solvent) and acetone (non-solvent, large excess) used for precipitation. The total functionality for these polyamides is in a suitable range for powder coating resins (target: ~0.50–0.70 mmol g<sup>-1</sup>).

The molar ratio between **IIDA** and **BDA** was targeted at 60:40 to obtain amorphous polymers with an expected  $T_g$  value of 70°C. The obtained polymers have a ratio of 66:34 between the respective diamines, which is fairly close to the aim. Evaporation of part of the relatively volatile **BDA** explains the observed discrepancy. The polyamide resins have been thermally characterized with DSC. The results are reported in Fig. SI1 and Table 1. During the first heating run, all three polyamides showed a moderate melting endotherm between 100 and 200°C with  $\Delta H_{m,1}$  ranging from 10 to 17 J g<sup>-1</sup>. This indicated that some ordered phases were present in the polymers after uncontrolled cooling due to collection of the material from the melt. Furthermore, **B2** showed a sharp melting peak at 238°C. This can be explained by crystallized short PA-4,7 segments, which together with the observation of an increased ratio of **IIDA** chain ends in <sup>1</sup>H NMR suggests that the molecular composition was not completely random. The  $T_g$  values determined from the first heating trace were between 45 and 58°C, which is well above room temperature. However, the 45°C for **B2** was unexpectedly low in this first run, which was probably caused by the presence of some residual solvent from the work-up procedure.

The cooling runs showed no crystallization phenomena for these polyamides, which therefore remained

**Table 1: SEC, <sup>1</sup>H NMR, and DSC results for polyamide resins A, B1, and B2**

Polymer	SEC <sup>a</sup>		<sup>1</sup> H NMR <sup>b</sup>					DSC <sup>c</sup>
	$M_n$ (g mol <sup>-1</sup> )	$\bar{D}$	$M_n$ (g mol <sup>-1</sup> )	<i>AV</i> (mmol g <sup>-1</sup> )	<i>AmV</i> (mmol g <sup>-1</sup> )	$X_{\text{feed}}^d$	$X_{\text{copolymer}}^d$	$T_g$ (°C)
<b>A</b>	8030	2.8	3130	0.64	0	100/60/40	100/51/34	71
<b>B1</b>	8760	2.3	3110	0.17	0.47	100/70/42	100/63/41	64
<b>B2</b>	10,700	2.1	3720	0.13	0.41	100/70/42	100/62/40	89

<sup>a</sup> Number-average molecular weight and  $\bar{D}$  measured by SEC in HFIP against PMMA standards

<sup>b</sup> <sup>1</sup>H NMR performed in DMSO-*d*<sub>6</sub>

<sup>c</sup> DSC recorded at 10°C min<sup>-1</sup>, data extracted from the second heating run

<sup>d</sup> PA/IIDA/BDA

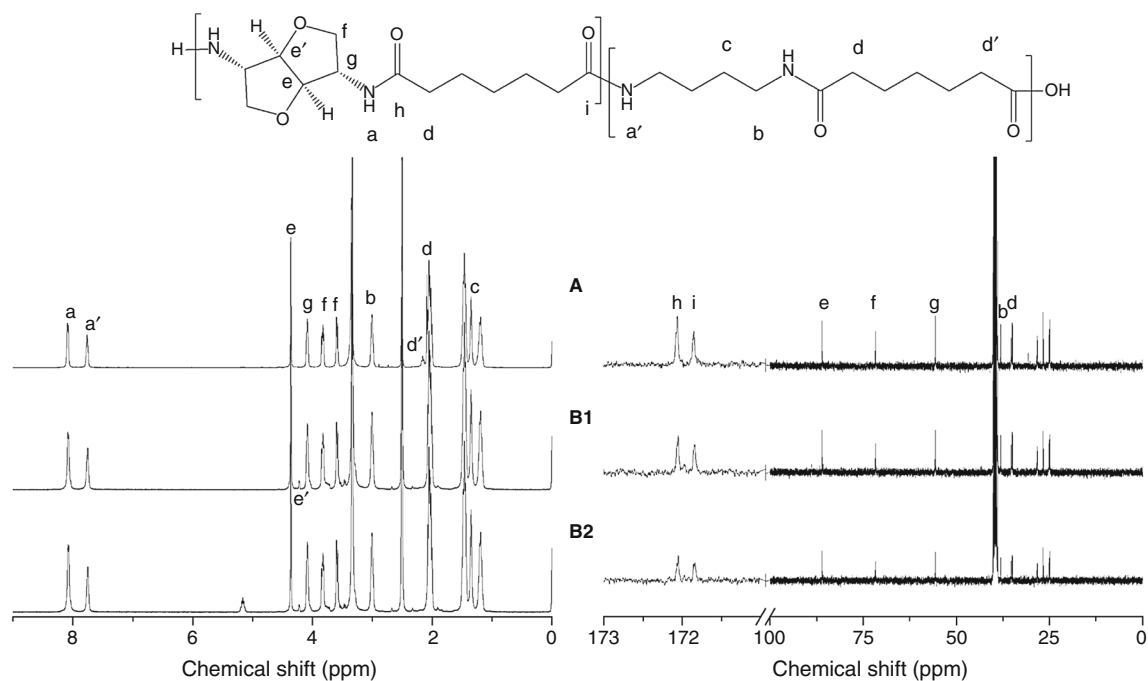


Fig. 1:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and assignment for polyamides **A**, **B1**, and **B2** recorded in  $\text{DMSO-}d_6$

Table 2: Properties of rheology samples: stoichiometric balance  $r$ , critical point of gelation  $p_c$ , and gel content after the experiment

Resin	Curing agent	$r$	$p_c$	Gel content (wt%)
<b>A</b>	TGIC	0.96	0.72	97
<b>A</b>	Primid	0.94	0.60	27
<b>B1</b>	TGIC	0.95	0.47	66
<b>B1</b>	Primid	0.92	0.60	12

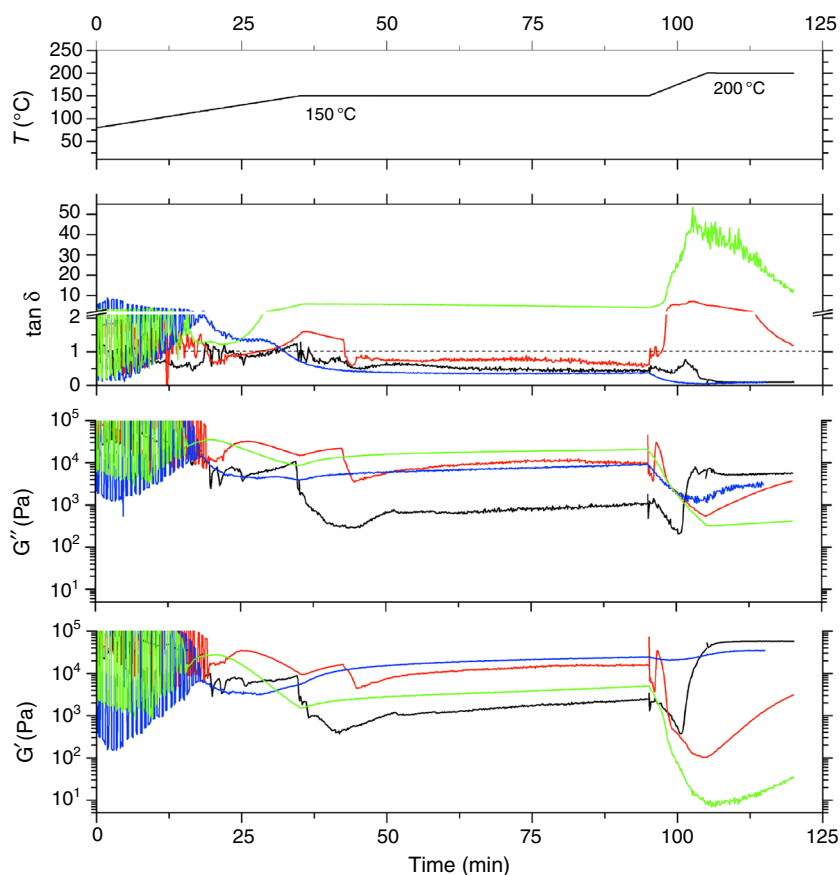
amorphous. In the second heating run, the  $T_g$  values showed some spread despite the polymers having similar  $M_n$  values. The  $T_g$  value of **A** was similar to the value expected, while **B1** was about  $6^\circ\text{C}$  lower and **B2** much higher at a value of  $89^\circ\text{C}$ . The large difference in the  $T_g$  values for **B2** and **B1** is caused by the higher  $M_n$  value for **B2** after precipitation, and the evaporation of the solvent that effected its first heating run. All values exceeded the requirement of  $60^\circ\text{C}$  for a powder coating resin.

### Rheology

Ultimately, the polyamides described in this paper are intended to replace petrochemistry-based resins used in powder coatings. Therefore, the synthesized resins were analyzed in terms of their curing behavior with two well-known curing agents: triglycidylisocyanurate (TGIC, a trifunctional epoxy compound) and  $N,N,N',N'$ -tetrakis(2-hydroxyethyl)adipamide (Primid XL-552, a tetrafunctional  $\beta$ -hydroxy alkamide). TGIC

is capable of reacting with both acid- and amine-functional resins, while the activated OH-groups of Primid will only react with acid functionalities. Crosslinking using Primid results in the release of water molecules as condensate. Resin **A** is expected to perform slightly better with Primid due to its higher functionality, while the resins **B1** and **B2** should, in principle, form a more dense network with TGIC than with Primid because of the presence of amine groups.

To follow the curing reactions between the crosslinkers and the resins, a rheometer was used. Sample disks were prepared by cold pressing the resins **A** and **B1** and one of the crosslinkers at high pressure (1600 bar) and room temperature. The compositions of the samples are reported in Table 2. The higher amine value of **B1** compared to that of **A** ( $0.47$  vs  $0$   $\text{mmol g}^{-1}$ , respectively) results in a significantly lower point of gelation ( $p_c$ ) when TGIC is used. The presence of amine groups effectively increased the functionality of the polymer chain ( $f_{e0}$ ) from 2.0 (with Primid) to 3.7 (with TGIC). This is likely to result in differences in the final crosslink density and hence the toughness and



**Fig. 2:**  $\tan \delta$ ,  $G'$ , and  $G''$  as function of time for experiments **A** + TGIC (black), **A** + Primid (red), **B1** + TGIC (blue), and **B1** + Primid (green) as noted in Table 2 with angular frequency  $\omega = 6.283 \text{ rad s}^{-1}$ , strain  $\gamma = 1\%$ . Sample disks 1 and 2 were not perfectly circular (Color figure online)

hardness of the final coating. When Primid XL-552 was used, a different phenomenon occurred. While for resin **A** all the end groups (i.e., carboxylic acid groups) can be fully crosslinked, for polyamide **B1** only the carboxylic acid groups can react, while the amine end groups remain as dangling chains. Because the  $AmV$  is higher than the  $AV$ , the largest fraction of the polymers will bear two amine groups, i.e., one at both ends. Most of the remaining chains will have one amine group and one carboxylic acid group. This results in polymers that will have reacted only once, and chains that were not crosslinked (i.e., bearing two amine groups) and remained as free chains in the network.

Sample disks were loaded in the rheometer at 70°C and the curing reaction was followed during a temperature program (see Fig. 2). Unfortunately, some samples (**A** + TGIC, **A** + Primid) had defects at the edges which will affect the measurement. The measured viscosities and moduli will be lower than their actual values. An insufficient amount of material remained to prepare new samples, so the results should be considered in a qualitative and not in a quantitative manner. The samples were heated gradually to 150°C and kept at this temperature for 60 min to cure. Subsequently,

the temperature was increased to 200°C to assess the crosslinking in the system.

During heating, all samples behaved as solids until roughly 20 min ( $T = 110^\circ\text{C}$ ), at which point the graphs smoothed out as the material started to flow well above  $T_g$ . For **A** + TGIC and **A** + Primid, fluctuations were observed in the first fifty minutes of the experiments. This is attributed to trapped air pockets that originate from the more coarse samples and macroscopic inhomogeneity resulting from sample preparation. Both samples were submitted to a trial experiment with a similar but different temperature profile in which these unexpected fluctuations were not observed.

Figure 2 shows the  $G'$ ,  $G''$ , and  $\tan \delta$  of the rheological experiments. When  $G''$  is larger than  $G'$ , the system behaves predominantly as a viscous liquid. At  $G' > G''$ , the system is behaving mostly like an elastic solid. Therefore, at  $G' = G''$ , or  $\tan \delta = 1$ , the system transfers from liquid to solid behavior. This crossover point is regarded as the gel point.<sup>31</sup> **A** + TGIC, **A** + Primid, and **B1** + TGIC showed  $\tan \delta < 1$  during the isothermal curing at 150°C and became crosslinked gels. **B1** + Primid remained a viscous liquid. Upon heating to 200°C, the  $\tan \delta$  of **A** + Primid

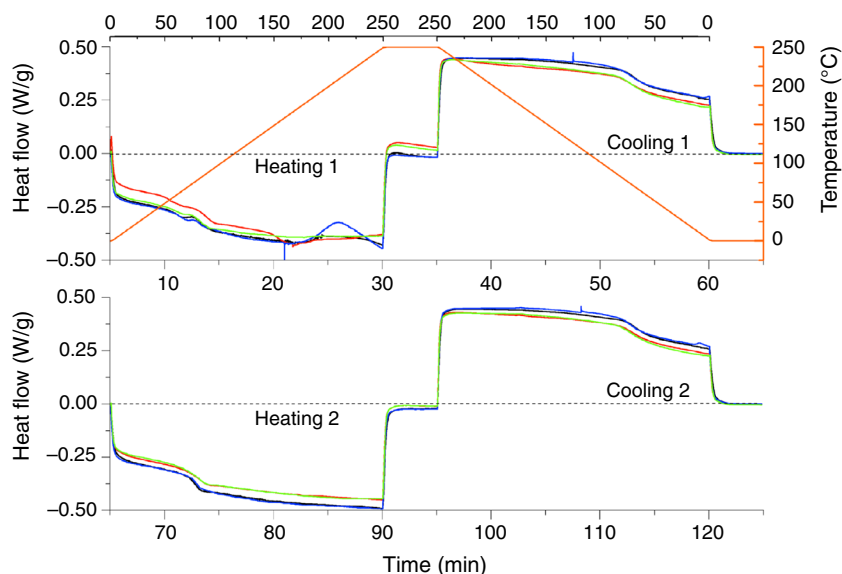
increased again to six. This indicated that the system contained thermally labile physical crosslinks, in addition to the chemical crosslinks. The crosslinker and resin may have formed hydrogen bonds which are dissociated upon further heating. When a temperature of 200°C is reached,  $\tan \delta$  decreases again, indicating that the crosslinking reaction continues. The crossover point is almost achieved at the end of the experiment. **B1** + Primid has  $\tan \delta > 1$  during the entire temperature profile, indicating that either no complete curing is possible, or that the energy input of this temperature profile is insufficient to bring the reaction to completion. The low ratio of acid to amine end groups (1:2.8) is most likely the reason for the lack of gelation. As the  $AV$  is less than half the  $AmV$ , fully amine-terminated polymers will reside in the final coating when Primid is used as a curing agent. The Primid-based compositions could have also performed less due to the necessity to remove the water being formed during the reaction.

The gel contents of the samples were determined after the rheology measurements (Table 2). Part of the samples were soaked in DMAc overnight at 110°C to extract the soluble fraction above  $T_g$ . Afterward, the samples were isolated by filtration and dried at  $p = 4$  Pa until constant weight. The remaining solid content of the samples with TGIC were 97 (**A**) and 66 wt% (**B1**). For samples containing Primid, these were 27 (**A**) and 12 wt% (**B1**). Dry DMAc was used but it cannot be excluded that the presence of water has resulted in the hydrolysis of a small fraction of the ester linkages. Still, TGIC clearly forms a network which is crosslinked to a higher extent than Primid. This observation supports the results obtained from the rheological experiments.

After the rheological measurements, the sample disks were broken and the resulting pieces were analyzed using DSC (see Fig. 3). The first heating run showed two ranges for the  $T_g$  values (49–61 and 72–87°C) for all four samples. The presence of two separate  $T_g$  values in one material indicates that two phases were present. The first transition at lower temperatures was attributed to domains of pure resin with unreacted crosslinker. The crosslinker will act as a plasticizer and hence reduce the  $T_g$  of the unreacted resin (see Table 1).<sup>32</sup> The second transition was 21 to 35°C higher and is attributed to the  $T_g$  value of the formed network. The  $T_g$  of the network is usually higher than that of the resin.

All samples showed an exothermic reaction in the first heating run. For **A** + TGIC (11 J g<sup>-1</sup>, 178 to 250°C) and **B1** + TGIC (27 J g<sup>-1</sup>, 164 to 250°C), these were rather clear, while for **A** + Primid and **B1** + Primid the curing was observed mostly while the samples were kept isothermal at 250°C ( $t = 30$ –35 min). This indicated that for both polyamides, the reaction with TGIC proceeded more readily than with Primid.

During the cooling run, none of the samples showed crystallization, indicating that the networks were amorphous. A neat glass transition was observed. The second heating run showed only one  $T_g$  value in the range of 78 to 81°C for all samples, indicating that the distinction between the domains in the samples had disappeared. This verifies that the  $T_g$  value at 49–61°C was caused by unreacted species. Furthermore, no additional curing is observed in this heating run. The second cooling run is a copy of the first cooling run. The DSC thermograms of the samples after rheology



**Fig. 3:** DSC thermograms as functions of time for samples experiments **A** + TGIC (black), **A** + Primid (red), **B1** + TGIC (blue), and **B1** + Primid (green) after the rheology experiment. The temperature profile is depicted in orange and as *top X*-axis to help the reader. The exotherm is directed upwards (Color figure online)

indicated that none of these formulations were fully cured. However, all samples had very similar  $T_g$  values after curing in the first DSC heating run and all the formed networks appeared to be amorphous.

### Performance of solventborne poly(ester amide) coatings

The resins described here have been tested on standard chromated aluminum Q-panels for their coating performance upon curing. It was decided not to add other additives like flow agents, degassing agents, and pigments to make a fair comparison between the resins. The resins were cured with TGIC and Primid, both with 5 mol% excess relative to the amount of reactive resin end groups. To properly assess a powder coating, at least 100 gram of the formulation should be prepared, of which about 50 wt% consists of the resin. Unfortunately, this amount of resin could not be prepared due to limited availability of monomer (i.e., **IIA**) and, consequently, the resins were cured from solution in smaller scale experiments. *N,N*-dimethylacetamide (DMAc) was selected as the most suitable solvent in terms of dissolving power and final coating appearance. It was observed that, at room temperature, a solution of polyamide resin ( $C_{\text{solids}} = 17$  wt%) in DMAc formed a physical gel. To prevent this gelation, the coatings were applied onto a heated Q-panel. Based on test panels and the results of the rheology experiments, the wet paints were cured at 180°C for 1 h in an inert atmosphere.

Comparing the resulting coatings, almost all panels showed dewetting despite the fact that the surface energy of the aluminum surface was increased by roughening with Scotch-Brite (see Fig. SI4). Especially for resin **B2**, a very irregular coating was obtained. For **A**, many craters were observed with both curing agents. A rim was observed around the craters indicating that they were not pinholes originating from released water of the reaction of the resin with Primid. Resin **B1** produced the best looking coatings: with TGIC a fairly smooth surface with some craters was formed. These results indicate that the surface tension of the resin solution is rather high. The surface tension is a measure of the force that strives to decrease the

surface area. A surface with a low surface energy will not be wetted properly, and contamination with hydrophobic particles (e.g., dust particles) can cause cratering. With Primid, the coating was smooth but a large amount of material flowed to the edges. The large difference between **B1** and **B2** is due to removal of low molecular weight chains during the precipitation step to isolate **B2**. These low molecular weight chains have a higher mobility than higher molecular weight polymers.

The thickness of the coatings was found to be around 10  $\mu\text{m}$  which was roughly half of the calculated value. This can partly be explained by the application of the paint at 80°C. This decreased the viscosity and it was observed that all solutions flowed between the edge of the doctor blade and the panels. This produced a wider coating than intended, reducing its thickness. The color of the coatings is subject to thickness and substrate, but the color is reasonably light.

Several tests have been performed on the coated panels. The results are collected in Table 3. As mentioned, the thicknesses of the coatings were low. Despite that, all the coatings passed the solvent resistance double-rub test with acetone without showing damage. To further examine the solvent resistance of these films, ethanol was applied during the double-rub test. Ethanol is a better solvent for amorphous polyamides than acetone. The use of ethanol revealed large differences between the coatings. Except for **B1** cured with TGIC, all coatings failed well before reaching 100 double rubs. **B1** cured with TGIC did lose its gloss during the rubbing, probably due to swelling of the coating, but it remained undamaged and regained gloss upon evaporation of the ethanol. The failure of the other formulations indicates that network formation was insufficient. For the combinations of **B1** and **B2** cured with Primid this was expected as the curing chemistry should yield unreacted chains in the final coatings. These results are in agreement with the observations from the rheological and DSC experiments described in the previous two sections. These experiments showed insufficient crosslinking of the resins, especially when Primid was used as the curing agent. The network formation can be improved by introducing monomers with higher functionality into the polymers. This will give a higher crosslink density in the coating.

**Table 3: Ratio between reactive groups  $r$ , gel point  $p_c$ , and test results of the coatings from A, B1, and B2**

Polymer	Curing agent	$r$	$p_c$	$D$ ( $\mu\text{m}$ )	Pencil hardness	Reverse impact	Double rub	
							Acetone	Ethanol
<b>A</b>	TGIC	0.94	0.73	9–15	2H	No fractures	100+	45
<b>A</b>	Primid XL-552	0.95	0.59	8–15	2H	No fractures	100+	10
<b>B1</b>	TGIC	0.95	0.44	11–16	4H	No fractures	100+	100+
<b>B1</b>	Primid XL-552	0.89	0.61	4–12	F	No fractures	100+	10
<b>B2</b>	TGIC	0.94	0.44	3–13	n.d.	No fractures	100+	24
<b>B2</b>	Primid XL-552	0.96	0.59	0–60	n.d.	No fractures	100+	8



Pencil hardness values of the coatings were between F and 4H. This is similar to the literature, and the value for **B1** with TGIC is even higher than common values.<sup>1</sup> The pencil hardness test could not be performed on the coatings made from **B2** as the highly irregular surface is unsuitable. The reverse impact test, in which a 1 kg weight is dropped from 1.00 m on the back of the panels, was passed for all compositions. The thinness of the coatings may have helped prevent cracks upon impact, although even the thicker areas, especially in **B2-Primid**, were free of fractures.

## Conclusions

In this paper, the synthesis, characterization, and testing of polyamides based on pimelic acid, butane-1,4-diamine, and isoidide diamine have been described. These resins have been developed for powder coating applications. The  $M_n$  values of these polyamides were between 3000 and 3800 g mol<sup>-1</sup> and they had both amines as carboxylic acid end groups. The total values of the  $AV$  and  $AmV$  combined were 0.54 to 0.64 mmol g<sup>-1</sup>. The  $T_g$  values exceeded 60°C and the crystallinity was low with  $\Delta H_m \leq 20$  J g<sup>-1</sup> in the first heating run. Controlled heating and curing during the DSC experiment produced amorphous polyamides.

The curing of the polyamide resins with TGIC or Primid XL-552 (see Fig. 2) was investigated using a rheometer and subsequent DSC analysis of the same samples. The data indicated that a curing temperature of 150°C is insufficient to produce a completely cross-linked product. Furthermore, TGIC performs significantly better than Primid for both carboxylic acid and amine-terminated resins. After the experiment, the gel content of systems with Primid was less than 25%. However, for TGIC it was over 66% (up to 97%). The results of DSC analysis of the cured disks demonstrated that additional curing occurred at higher temperatures. Therefore, a higher temperature than 150°C is necessary for curing the resins. Furthermore, all the cured samples were amorphous.

Curing at 180°C on standard aluminum Q-panels was done with a solution of resin and curing agent in DMAc. Dewetting of the coatings on the aluminum panels was observed. Network formation was shown to be inadequate as ethanol double rubs damaged most of the coatings. Only **B1** + TGIC showed excellent resistance against ethanol. Pencil hardness values were between F and 4H which is similar to literature values. The reverse impact tests showed the coatings to be flexible as no fractures were observed. A remark has to be made that the thickness of all the coating layers was rather low, i.e., around 10 µm.

In conclusion, the developed resins can be used with standard crosslinkers of which the epoxy-based crosslinker showed better results than the  $\beta$ -hydroxyalkylamide-based curing agent. To obtain well-performing coatings, a higher crosslink density of the network is

necessary and therefore the functionality of the resins needs to be increased, for example, by introducing branching in the resins with tri- or tetrafunctional monomers. Furthermore, the wetting of the substrates is poor. Therefore, either the resins have to be modified to reduce their surface energy, or additives have to be added to reduce the surface tension of the paint.

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## References

- Misev, T, van der Linde, R, “Powder Coatings Technology: New Developments at the Turn of the Century.” *Prog. Org. Coat.*, **34** (1–4) 160–168 (1997)
- Minesso, A, Moens, L, Amor, AH, “Powder Compositions.” PCT application WO2009106454, 2008
- Wicks, ZWJ, Jones, FN, Pappas, SPJ, “Powder Coatings: IV.” *J. Coat. Technol.*, **71** (895) 67–73 (1999)
- Wicks, ZWJ, Jones, FN, Pappas, SPJ, “Powder Coatings: I.” *J. Coat. Technol.*, **71** (892) 41–46 (1999)
- Weiss, KD, “Paint and Coatings: A Mature Industry in Transition.” *Prog. Polym. Sci.*, **22** (2) 203–245 (1997)
- Wicks, ZWJ, Jones, FN, Pappas, SPJ, “Powder Coatings: II.” *J. Coat. Technol.*, **71** (893) 47–51 (1999)
- Loutz, JM, Demarteau, W, Vandervorst, D, “Characterization and Control of Odours and VOC in the Process Industries.” *Proceedings of the Second International Symposium on Characterization and Control of Odours and VOC in the Process Industries*, pp. 205–228. In: Vigneron, S, Hermia, J, Chaouki, J (ed.) *Studies in Environmental Science*. Elsevier, New York, 1994
- Belder, EG, Linde, R, van der, Schippers, J, Polyester and its Use in Powder Coating. US Patent 4,528,341, 1985
- Misev, TA, *Powder Coatings: Chemistry and Technology*. Wiley, Chichester, (1991)
- Awasthi, S, Agarwal, D, “Influence of Cycloaliphatic Compounds on the Properties of Polyurethane Coatings.” *J. Coat. Technol. Res.*, **4** (1) 67–73 (2007)
- Noordover, BAJ, Duchateau, R, van Benthem, RATM, Ming, W, Koning, CE, “Enhancing the Functionality of Biobased Polyester Coating Resins Through Modification with Citric Acid.” *Biomacromolecules*, **8** (12) 3860–3870 (2007)
- Noordover, BAJ, van Stalduinen, VG, Duchateau, R, Koning, CE, van Benthem, RATM, Mak, M, Heise, A,

- Frissen, AE, van Haveren, J, “Co- and Terpolyesters Based on Isosorbide and Succinic Acid for Coating Applications: Synthesis and Characterization.” *Biomacromolecules*, **7** (12) 3406–3416 (2006)
13. Haveren, J, Oostveen, EA, Micciché, F, Noordover, BAJ, Koning, CE, Benthem, RATM, Frissen, AE, Weijnen, JGJ, “Resins and Additives for Powder Coatings and Alkyd Paints, Based on Renewable Resources.” *J. Coat. Technol. Res.*, **4** (2) 177–186 (2007)
  14. Raquez, J-M, Deléglise, M, Lacrampe, M-F, Krawczak, P, “Thermosetting (Bio)Materials Derived from Renewable Resources: A Critical Review.” *Prog. Polym. Sci.*, **35** (4) 487–509 (2010)
  15. Gioia, C, Vannini, M, Marchese, P, Minesso, A, Cavalieri, R, Colonna, M, Celli, A, “Sustainable Polyesters for Powder Coating Applications from Recycled PET, Isosorbide and Succinic Acid.” *Green Chem.*, **16** (4) 1807–1815 (2014)
  16. Gubbels, E, Drijfhout, JP, Posthuma-van Tent, C, Jasinska-Walc, L, Noordover, BAJ, Koning, CE, “Bio-Based Semi-Aromatic Polyesters for Coating Applications.” *Prog. Org. Coat.*, **77** (1) 277–284 (2014)
  17. Belder, EG, Rutten, HJJ, Perera, DY, “Cure Characterization of Powder Coatings.” *Prog. Org. Coat.*, **42** (3–4) 142–149 (2001)
  18. Salla, JM, Ramis, X, Morancho, JM, Cadenato, A, “Isoconversional Kinetic Analysis of a Carboxyl Terminated Polyester Resin Crosslinked with Triglycidyl Isocyanurate (TGIC) Used in Powder Coatings from Experimental Results Obtained by DSC and TMDSC.” *Thermochim. Acta.*, **388** (1–2) 355–370 (2002)
  19. Ramis, X, Cadenato, A, Morancho, J, Salla, J, “Curing of a Thermosetting Powder Coating by Means of DMTA, TMA and DSC.” *Polymer*, **44** (7) 2067–2079 (2003)
  20. Kronberger, K, Hammerton, DA, Wood, KA, Stödeman, M, “Exterior Durability of Polyester/Hydroxyalkyl Amide Powder Coatings: Accelerated Weathering Studies.” *JOCCA-Surf. Coat. Int.*, **74** (11) 405–410 (1991)
  21. Franiau, RP, “Advances in  $\beta$ -Hydroxyalkylamide Cross-Linking Chemistry.” *Eur. Coat. J.*, **10** 24–27 (2002)
  22. Mitchell, MA, Eckert, D, Tomlin, AS, Crosslinking; Surface Treatment. US Patent 6,376,618, 2002
  23. Roller, M, “Rheology of Curing Thermosets: A Review.” *Polym. Eng. Sci.*, **26** (6) 432–440 (1986)
  24. Winter, HH, “Analysis of Linear Viscoelasticity of a Crosslinking Polymer at the Gel Point.” *J. Rheol.*, **30** (2) 367 (1986)
  25. Osterhold, M, “Rheological Methods for Characterizing Modern Paint Systems.” *Prog. Org. Coat.*, **40** (1–4) 131–137 (2000)
  26. Osterhold, M, Niggemann, F, “Viscosity–Temperature Behaviour of Powder Coatings.” *Prog. Org. Coat.*, **33** (1) 55–60 (1998)
  27. Vorster, OC, Halasz, L, “Die gebruik van ’n reologiese tegniek in die bepaling van die verhardingsreaksiekinetika van ’n reaktiewe poliësterpoeldeklaag.” *Suid-Afrikaanse Tydsk. vir Natuurwetenskap en Tegnol.*, **23** (1/2) 13–21 (2004)
  28. Thiyagarajan, S, Gootjes, L, Vogelzang, W, Wu, J, van Haveren, J, van Es, DS, “Chiral Building Blocks from Biomass: 2,5-Diamino-2,5-Dideoxy-1,4-3,6-Dianhydroiditol.” *Tetrahedron.*, **67** (2) 383–389 (2011)
  29. Thiyagarajan, S, Gootjes, L, Vogelzang, W, van Haveren, J, Lutz, M, van Es, DS, “Renewable Rigid Diamines: Efficient, Stereospecific Synthesis of High Purity Isohexide Diamines.” *ChemSusChem.*, **4** (12) 1823–1829 (2011)
  30. Van Velthoven, JIJ, Gootjes, L, Noordover, BAJ, Meuldijk, J, “Bio-Based, Amorphous Polyamides with Tunable Thermal Properties.” *Eur. Polym. J.*, **66** 57–66 (2015)
  31. Mezger, TG, *The Rheology Handbook: For Users of Rotational and Oscillatory Rheometers*. Vincentz Network GmbH & Co KG, Hannover, 2006
  32. “Resins and Curatives: The Binder System for Thermosetting Powder Coatings.” *Paint Coat. Ind.*, **2** (1) (2000)