Abstract: In recent years, many efforts are being devoted to the development of new materials that originate from renewable resources. Polyesters are one of the most important classes of such materials and several bio-based monomers are available for their synthesis. In this work, the development of fully bio-based and solvent-free polyester polyol used for two-component polyurethane coatings on industrial scale is presented. Fossil-based raw materials were substituted with bio-based alternatives that are commercially available on a large scale. Properties of polyols and coatings were determined and measured. Polyols were characterized by the determination of acid number, hydroxyl number, glass transition temperature and refractive index, and measurement of viscosity, color and molecular weight. Coatings were characterized by the determination of mechanical properties, such as hardness, elasticity and impact resistance, and the measurement of optical properties such as gloss, haze, distinctness of image (DOI) and reflected image quality (RIQ) and weathering resistance. Three variations of bio-based polyol were synthesized, then the most suitable version was validated in a clear coat. The results showed that the properties of the bio-based polyol and coating met the requirements and were comparable to the properties of the synthetic counterpart. Results indicate that this newly developed 100% bio-based and solvent-free polyol can be used as a drop-in replacement for synthetic polyol. Furthermore, this work implies that the supply chain is established which allows the green transition in the paint industry.

Keywords: resins; bio-based; solvent-free; polyester polyol; polyurethane coating; industrial scale

1. Introduction

Nowadays, much effort in the paint and coating industry is being invested in the development of bio-based materials since the conversion of biomass and bio-based ingredients into useful products for paints and coatings offers considerable and sustainable growth potential. In recent years, the potential replacement of fossil fuels to produce appropriate monomers using inexpensive and renewable starting materials, such as cellulose, starch, lignin, proteins, vegetable oils and fats, is increasingly being explored [1–7]. These bio-based materials can be used to make bio-based polyester polyols, polyurethane dispersions, modified acrylic dispersions, polyacrylate polyols, polyurethanes, epoxy coatings, powder coatings, UV coatings and printing inks, architectural coatings, wood and plastic coatings, paper coatings, films and others [6,8–21].

Bio-based polyesters are one of the most important classes of polymers for coatings. There are many monomers available for their synthesis, including acids (succinic acid, sebacic acid, adipic acid, levulinic acid, gluconic acid, terephthalic acid, 2,5-furandicarboxylic acid, itaconic acid, lactic acid, 3-hydroxypropionic acid, etc.), and glycols (ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, isosorbide, xylitol, sorbitol, glycerol, etc.) [3–7,9,22–30]. There are two main approaches when introducing bio-based raw materials, (a) the conventional substance is substituted with a bio-based alternative, for example synthetic terephthalic acid can be replaced with 2,5-furandicarboxylic acid (FDCA) derived...
from biomass [21,31], and (b) the so-called drop-in approach where a fossil-fuel derived raw material is substituted with the chemically identical substance which is derived from biomass, e.g., synthetic adipic acid can be replaced with bio-based adipic acid [3,25]. In addition, a biomass balance approach can be used. Since 2021, our company is ISCC (International Sustainability and Carbon Certification) PLUS [32] certified and the mass balance approach is used for raw materials, such as neopentyl glycol, trimethylol propane and pentaerythritol. The ISCC PLUS certification scheme uses the mass balance method to determine the content of bio-based or recycled material. This approach can facilitate a gradual increase of renewable and recycled raw materials by enabling the use of existing infrastructure and equipment instead of constructing separate plants and value chains for renewable and/or recycled raw materials. It also ensures product sustainability, as certification schemes have been developed to meet the requirements of the EU Renewable Energy Directive (RED) [33].

The use of polyols in industrial organic coatings is regulated by Directive 2010/75/EU of the European Parliament and the Council of 24 November 2010 on industrial emissions [34], which limits the emissions of volatile organic compounds (VOCs) due to the use of organic solvents in certain activities and installations. One of the practically useful technologies for meeting the requirements of this directive are high-solid coatings. The directive does not prescribe a maximum content of VOCs in the coating, nevertheless, in large industrial paint shops the coating should have at least 72.7% of non-volatile matter. This also applies to polyurethane topcoats and single-layer coatings. Such coatings are usually prepared based on acrylic polyols, but formulators often decide to include polyester polyol as a binder in the formulation as well to increase solid content. For this purpose, low-viscosity solvent-free polyester polyols with a viscosity between 750 and 1000 mPa-s, a glass transition temperature between $-70$ and $-50^\circ$C and a hydroxyl number between 240 and 290 mg KOH/g are especially suitable.

The performance of bio-based materials needs to match the performance of fossil fuel-based materials, therefore the balance of bio-based content against performance and costs needs to be achieved. Polyester polyol that was 100% bio-based and solvent-free polyol was developed to be used as a replacement for synthetic polyester polyol in combination with an acrylic polyol in high-solid two-component polyurethane protective coatings for metal surfaces. The bio-based raw materials used in this work are already being produced on a large scale and were obtained from commercially available sources. Bio-based succinic acid and sebacic acid were used to replace adipic acid, bio-based 1,3-propanediol was used to replace 1,6-hexanediol and propylene glycol, and bio-based neopentyl glycol was used according to ISCC Plus mass balance approach to replace fossil-based neopentyl glycol. The biobased polyester polyol can thus be produced on an industrial scale using the equipment depicted in Figure 1. The properties of this newly developed bio-based polyester polyol and model coatings are comparable to the properties of its synthetic counterpart and comply with the requirements.
2. Materials and Methods

2.1. Materials

For the synthesis of synthetic polyol, the following standard industrial monomers from the market which were obtained from BASF were used: adipic acid (99.8%), neopentyl glycol (99.0%), 1,6-hexanediol (96.0%) and propylene glycol (99.5%). For the synthesis of bio-based polyols neopentyl glycol (99.0%) was obtained from Perstorp (Perstorp, Sweden), bio-based succinic acid (99.5%) from Roquette (Lestrem, France), sebacic acid (99.5%) from Arkema (Colombes, France) and 1,3-propanediol (99.9%) from Covation Biomaterials (Newark, DE, USA).

The materials used for the preparation of the coatings were our commercially available acrylic polyol, which is a 75% solution of hydroxy acrylic resin with the acid number of maximum of 12 mg KOH/g, hydroxyl number between 135 and 155 mg KOH/g and viscosity (at 23 °C) of 8000–12,000 mPa·s from Helios Resins, and the solvent-free aliphatic polyisocyanate based on the hexamethylene diisocyanate (HDI) trimer with a NCO content between 22 and 24% and a viscosity (at 25 °C) of 450–750 mPa·s obtained from Vencorex (Saint-Priest, France). All chemicals were used without any further purification.

2.2. Polyol Synthesis

The synthesis of the polyol was carried out in a 6 L three-neck glass reactor, equipped with a mechanical stirrer, thermometer, condenser and external heating. The reactor was charged with raw materials and purged with nitrogen. The mixture was heated with constant stirring up to 210 °C. During the reaction, acid value and viscosity were checked and when the required values were reached, the reaction was finished. Afterward the resin was cooled down to room temperature and filtered through 190 µm filter.

Four polyester polyols were synthesized. Synthetic polyol (PE-SYN), which is already commercially produced, was used as a reference and compared to the three bio-based polyols where synthetic raw materials were replaced with bio-based alternatives. Neopentyl glycol was substituted with bio-based neopentyl glycol using ISCC Plus mass balance approach, 1,6-hexanediol and propylene glycol were substituted with bio-based
1,3-propanediol and adipic acid was replaced with bio-based succinic acid and sebacic acid. The following three variations of adipic acid replacement were used in the formulation: (a) 100% replacement with bio-based succinic acid (PE-BIO-Succ), (b) 100% replacement with sebacic acid (PE-BIO-Seb) and (c) a replacement with a combination of bio-based succinic and sebacic acid at the molar ratio of 1:1 (PE-BIO-Succ+Seb).

2.3. Resin Characterization

2.3.1. Acid Number Determination

The acid number was determined according to the SIST EN ISO 2114 standard [35], as follows: a 0.4 g of sample was weighed in a 250 mL Erlenmeyer flask and dissolved in 50 mL of solvent mixture. The solvent mixture consisted of xylene and ethanol (2:1 v/v). Then, 0.5 mL of phenolphthalein indicator solution (1% in ethanol) was added and titrated with 0.1 N KOH solution in methanol, to the equivalent point. The acid number (mg KOH/g of the sample) was calculated using Equation (1), as follows:

\[
\text{Acid number} = \frac{V \times M \times 56.1}{m} \quad (1)
\]

here, \(V\) is the volume of the potassium hydroxide solution required for the titration of the sample (mL), \(M\) is the molarity of the potassium hydroxide solution and \(m\) is the amount of the sample (g) being analyzed.

2.3.2. Viscosity Measurement

The reaction viscosity of the sample was measured using a Brookfield CAP 2000+ viscometer (50 °C, spindle 2, 500 rpm) because a smaller sample is needed and it takes considerably less time to get the result, while the final viscosity of the polyol was measured using a Haake Viscotester (Rheolab QC Anton Paar, Graz, Austria) 550 at 23 °C according to standard SIST EN ISO 3219 [36].

2.3.3. Hydroxyl Number Determination

The hydroxyl number of the resin was determined according to the SIST EN ISO 4629 standard [37] as follows: 1.0 g of sample was weighed in a 250 mL Erlenmeyer flask and dissolved in 5 mL of ethyl acetate. Then, 5 mL of acetylating reagent was added. The mixture was heated in a water bath at 50 °C for 45 min and then cooled down to room temperature. After cooling the 10 mL mixture of pyridine and water (3:1 v/v) was added and left at room temperature for 5 min. Then, 60 mL of a neutralized mixture of toluene and n-butanol (1:2 v/v) and 0.5 mL of phenolphthalein indicator solution (1% in ethanol) was added and titrated with 0.5 N KOH solution in methanol to the equivalent point. The hydroxyl number (mg KOH/g of the sample) was calculated using Equation (2).

\[
\text{Hydroxyl number} = \frac{(B - A) \times M \times 56.1}{m} + \text{acid number} \quad (2)
\]

Here, \(A\) is the volume of the potassium hydroxide solution required for the titration of sample (mL), \(B\) is the volume of the potassium hydroxide solution for the titration of blank solution (mL), \(M\) is the molarity of the potassium hydroxide solution and \(w\) is the amount of the sample (g) being analyzed.

2.3.4. Color Measurement

The color of the polyls was measured according to the SIST EN ISO 6271 standard [38] using the spectrophotometric method. All measurements were performed on Hach Lico 690 spectral colorimeter (Loveland, CO, USA). A sample of the polyol was placed in a glass cuvette and inserted into the measuring instrument. The color value according to the platinum-cobalt (Hazen) scale was read from the screen of the instrument.
2.3.5. Gel Permeation Chromatography (GPC)

Gel permeation chromatographic (GPC) measurements were performed on a GPC Waters system, consisting of an isocratic pump Waters 2690 Separation Modul and a refractive index detector Waters 410 Differential Refractometer. Three Waters Styragel columns (HR 5E, 5 \( \mu \)m, 4.6 mm \( \times \) 300 mm, HR 4E, 5 \( \mu \)m, 4.6 mm \( \times \) 300 mm and HR 0.5, 5 \( \mu \)m, 4.6 mm \( \times \) 300 mm) connected in-series were used. The column temperature was 40 °C. Polystyrene standards were used for the calibration curve. The mobile phase was tetrahydrofuran with a flow rate of 0.2 mL/min.

2.3.6. Glass Transition Temperature (Tg)

Glass transition temperature (Tg) was determined using the differential scanning calorimetry method. All samples were scanned by a differential scanning calorimeter DSC 1 Mettler Toledo at a heating rate of 10 °C/min on temperature range from −80 °C to 100 °C. The mass of the sample was 5.0 mg. All scans were conducted in a nitrogen atmosphere with a 40 mL/min flow rate.

2.3.7. Refractive Index

Refractive index was determined using Atago RX-5000a refractometer (Tokyo, Japan) for measurement of refractive index of liquid samples. Measurements were performed at 20 °C according to ASTM D1218 standards [39].

2.4. Validation of Polyols in Coatings

Synthetic polyol (PE-SYN) and its bio-based version (PE-BIO-Succ+Seb) were mixed with our acrylic polyol (1:5 \( m/m \)) and crosslinked with solvent free low viscosity polyisocyanate based on HDI trimer. The amount of polyisocyanate needed was calculated based on the hydroxyl number of the resin mixture as determined and calculated in Section 2.3.3.

The mixture of polyols and polyisocyanate was applied to the CRS panel of 0.8 mm thickness (Q-Panel R-36, Q-Lab Deutschland GmbH, Saarbrücken, Germany) with a manual film applicator for determination of mechanical properties. For the determination of optical properties, the mixture thinned with a commercial polyurethane grade thinner was applied using SATA jet 5000 B RP spray gun and 1.2 mm nozzle on precoated 10 \( \times \) 15 cm CRS panels (Ernst Sauter AG, Meßstetten, Germany). All films were cured at 60 °C for 48 h.

2.4.1. Thickness of the Film

The coatings’ thickness was determined according to SIST EN ISO 2178 standard [40]. The method is based on non-destructive measurements of the thickness of non-magnetizable coatings on magnetizable base metals. In this study, 12 measurements were taken on a 7.5 \( \times \) 15 cm panel with an Elcometer 456 thickness gauge calibrated to the substrate of the same type as used in sample preparation. The results were expressed as an average value and uncertainty values were calculated.

2.4.2. Hardness of the Film

The hardness of the crosslinked films was determined as pendulum hardness according to standard SIST EN ISO 1522 [41] using König pendulum using BYK Gardiner Pendulum Hardness tester 5854 (Geretsried, Germany). The results were expressed as an average of three measurements rounded to the nearest second.

2.4.3. Elasticity of the Film

The elasticity of the crosslinked films was determined by a cupping test according to SIST EN ISO 1520 standards [42] using an Erichsen model 202C Lacquer and Paint Testing Machine (Geretsried, Germany). The results were expressed as an average of two measurements rounded to the nearest 0.1 mm.
2.4.4. Impact Resistance

Resistance of the crosslinked films against rapid deformation was determined according to SIST EN ISO 6272-2 standards [43] using a BYK 5512 Impact tester (Geretsried, Germany). As no defects in the impacted area were detected within the instrument limits, a resistance of more than the maximal load available with the instrument are reported.

2.4.5. Optical Properties

Gloss, haze, distinctness of image (DOI) and reflected image quality (RIQ) of the crosslinked films were measured using Elcometer 408 gloss meter (Manchester, UK). Gloss values were measured at 20° and 60° angles according to SIST EN ISO 2813 standards [44]. Haze values were measured according to ASTM E430 standards [45]. DOI and RIQ values were measured according to the instrument proprietary method and can be used for comparison between the samples only. All reported values are an average of 6 measurements.

2.4.6. Weathering

A UV-B test, according to ISO 16474-3 [46], Method C, cycle no. 4, was performed using a QUV UV tester (Q-Lab Deutschland GmbH). Film degradation was monitored by changes in the coatings’ IR spectra. The spectra were recorded using a Thermo Nicotet Nexus 6700 FT-IR spectrometer (Waltham, MA, USA). Photo oxidation values (POV) were calculated using methodology devised by Gerlock et al. [47] as a ratio between combined -NH and -OH absorbances and -CH absorbance. -NH and -OH absorbances were integrated in the entire 4000–2000 cm⁻¹ region with subtracted -CH absorbance. Initial -NH and -OH absorbances were subtracted for subsequent measurements for POV calculations.

3. Results and Discussion

3.1. Properties of the Polyols

The properties and the appearance of synthesized polyols are presented in Table 1 and Figure 2. Acid number, hydroxyl number, viscosity, color and glass transition temperature (Tg) are highly important parameters and requirements for the formulators of the coatings. In the table, requirements for polyester polyol used in combination with acrylic polyol for high-solid two-component polyurethane coatings for metal are stated.

Table 1. Properties of synthetic and bio-based polyols.

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirements</th>
<th>PE-SYN</th>
<th>PE-BIO-Succ</th>
<th>PE-BIO-Ste</th>
<th>PE-BIO-Succ+Ste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-volatile matter (%)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Acid number (mg KOH/g)</td>
<td>7–12</td>
<td>8.1</td>
<td>9.7</td>
<td>10.3</td>
<td>10.2</td>
</tr>
<tr>
<td>Hydroxyl number (mg KOH/g)</td>
<td>240–290</td>
<td>267</td>
<td>248</td>
<td>250</td>
<td>280</td>
</tr>
<tr>
<td>Viscosity Brokfield (mPa·s)</td>
<td>160–200</td>
<td>164</td>
<td>306</td>
<td>161</td>
<td>179</td>
</tr>
<tr>
<td>Viscosity 23 °C (mPa·s)</td>
<td>750–1000</td>
<td>890</td>
<td>2340</td>
<td>2700</td>
<td>960</td>
</tr>
<tr>
<td>Color (Hazen)</td>
<td>≤500</td>
<td>43</td>
<td>19</td>
<td>81</td>
<td>36</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>–70–50</td>
<td>–64.9</td>
<td>–49.7</td>
<td>–66.2</td>
<td>–64.7</td>
</tr>
<tr>
<td>Tg of crosslinked polyol (°C)</td>
<td></td>
<td>53.5</td>
<td></td>
<td></td>
<td>51.6</td>
</tr>
<tr>
<td>Refractive index (20 °C)</td>
<td>-</td>
<td>1.4656</td>
<td>-</td>
<td>-</td>
<td>1.4648</td>
</tr>
<tr>
<td>Mn (g/mol)</td>
<td>500–1000</td>
<td>646</td>
<td>611</td>
<td>4762</td>
<td>552</td>
</tr>
<tr>
<td>Mw (g/mol)</td>
<td>1000–2000</td>
<td>1231</td>
<td>1153</td>
<td>50,619</td>
<td>1046</td>
</tr>
</tbody>
</table>
All synthesized polyols had an acid number, hydroxyl number and color in the range as required, whereas viscosity was much higher for polyols where 100% bio-based succinic acid and 100% sebacic acid were used as a replacement for adipic acid. The requirement for the viscosity of the polyol is 750–1000 mPa·s, while the viscosity of the polyol with 100% bio-based succinic acid reached the value of 2340 mPa·s and the viscosity of the polyol with 100% sebacic acid increased up to 2700 mPa·s. The combination of bio-based succinic acid and sebacic acid at a molar ratio of 1:1 as a replacement for adipic acid resulted in the viscosity of 960 mPa·s, which complies with the requirement and is comparable to synthetic polyol.

As can be seen from the results for the polyol with 100% bio-based succinic acid, the Tg of the crosslinked polyol increased, along with the viscosity, and was approximately 15 °C higher compared to other polyols, while molecular weight was comparable to standard polyol and is in agreement with the requirements. Compared to 1,6-hexanediol in PE-SYN and sebacic acid in PE-BIO-Seb succinic acid in PE-BIO-Succ has a shorter chain which has lower mobility and therefore gives more stiff products. Consequently, the viscosity and Tg of the polyol are higher when 100% succinic acid is used to replace adipic acid.

On the other hand, the viscosity of the polyol with 100% sebacic acid also increased while the Tg of crosslinked polyol remained in the range of requirements and standard polyol. In addition, the molecular weight greatly increased to a Mn of 4762 g/mol and Mw of 50,619 g/mol, which is also evident in Figure 3. Other polyols have an average Mn of 600 g/mol and Mw of 1140 g/mol. Such an increase in viscosity and molecular weight is attributed to the crystallization of the polymer which occurs when polyol is cooled down to room temperature. This is also seen in the appearance of the polyol in Figure 1. Due to the crystallization, the color of the polyol could not be measured appropriately. To gain reliable results, the polyol had to be heated. When the polyol was heated above the temperature of 35 °C, melting took place and the polyol seemingly became clear and transparent.

According to all results, polyol PE-BIO-Succ+Seb (where the combination of bio-based succinic acid and sebacic acid was used as a replacement for adipic acid) was selected as the most suitable bio-based version to replace synthetic polyol (PE-SYN) for further validation in coatings. The reflective index was determined for both polyols, synthetic and bio-based, and the results showed comparable values. The Tg of the crosslinked polyol was also determined for both samples and it was found that there was only a slight difference in Tg between them. Namely, the Tg of crosslinked polyol was 53.5 °C for synthetic polyol and 51.6 °C for bio-based polyol.
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reliable results, the polyol had to be heated. When the polyol was heated above the tem-
perature of 35 °C, melting took place and the polyol seemingly became clear and trans-
parent.

Figure 3. GPC profiles of synthetic and bio-based polyols.

3.2. Properties of the Coatings

As the synthesized polyester polyols are primarily meant as a modifier of acrylic 
polyols, we tested their basic mechanical and optical properties in model two-component 
polyurethane clear coats both as sole polyol binders (CC1-1 and CC1-2) and in a mixture 
with one of our commercially available acrylic polyols (CC2-1 and CC2-2). We decided to 
keep the formulations of all the model coatings simple and to avoid the use of additives. 
Such formulations may lead to lower performance in comparison to complexly formulated 
commercial 2-component polyurethane clear coats. At the same time, they allow for the 
potential differences between both polyester polyols to show more clearly. Use of levelling 
additives or HALS and UV absorbers may mask the difference in optical properties 
and weathering, respectively.

The basic mechanical properties of crosslinked clear films are presented in Table 2 and 
the optical properties of crosslinked clear films are presented in Table 3. The results point 
to a high level of equivalence in all tested properties. The difference between the pairs of 
materials (CC1-1, CC1-2 and CC2-1, CC2-2) usually lies within the repeatability limit of the 
test method used or is very close to it. As polyester polyol often acts as an elastifier when 
applied together with acrylic polyols, we find it significant that there was no difference in 
elasticity and impact resistance between CC2-1 and CC2-2.

Table 2. Basic mechanical properties of the crosslinked films.

<table>
<thead>
<tr>
<th>Property</th>
<th>CC2-1</th>
<th>CC2-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry film thickness</td>
<td>39.7 ± 2.8 µm</td>
<td>40.2 ± 2.4 µm</td>
</tr>
<tr>
<td>Hardness</td>
<td>219 s</td>
<td>212 s</td>
</tr>
<tr>
<td>Elasticity</td>
<td>&gt;11.0 mm *</td>
<td>&gt;11.0 mm *</td>
</tr>
<tr>
<td>Impact resistance</td>
<td>&gt;100 kg/cm</td>
<td>&gt;100 kg/cm</td>
</tr>
</tbody>
</table>

* Substrate failure.
Table 3. Optical properties of the crosslinked films.

<table>
<thead>
<tr>
<th>Property</th>
<th>CC2-1</th>
<th>CC2-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gloss at 60°</td>
<td>95.3</td>
<td>95.2</td>
</tr>
<tr>
<td>Gloss at 20°</td>
<td>90.7</td>
<td>90.8</td>
</tr>
<tr>
<td>logHaze</td>
<td>121.5</td>
<td>120.1</td>
</tr>
<tr>
<td>DOI</td>
<td>99.2</td>
<td>99.2</td>
</tr>
<tr>
<td>RIQ</td>
<td>95.4</td>
<td>96.0</td>
</tr>
</tbody>
</table>

Probably the most important property of a practical clear coat is weathering resistance. As both the PE-SYN and the acrylic polyol are well known for their excellent weathering resistance, it was decided to test the weathering resistance in CC1-1 and CC1-2 as the large amount of acrylic polyol in CC2-1 and CC2-2 may well hide the potential difference between the polyester polyols. Previous work by Ogorevc [48] showed the high resilience of PE-SYN to UV-A and daylight filtered xenon irradiation. The UV-B test, according to ISO 16474-3, method C, cycle no. 4, on the other hand, produced measurable degradation. Subsequently, we used the same method of exposure in durations of 250, 500 and 1000 h. The POV derived from IR spectra, as seen in Figure 4, was used for the assessment of the results. They are presented in Table 4 and Figure 5.

Figure 4. IR spectra of crosslinked polyester films before and after 250, 500 and 1000 h of UV B exposure profiles of synthetic and bio-based polyols.

Table 4. Photooxidation values (POV) of crosslinked polyester films in UV-B exposure.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>CC1-1</th>
<th>CC1-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>250</td>
<td>0.53</td>
<td>1.2</td>
</tr>
<tr>
<td>500</td>
<td>2.87</td>
<td>2.83</td>
</tr>
<tr>
<td>1000</td>
<td>8.64</td>
<td>8.21</td>
</tr>
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<th>CC1-1</th>
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<tr>
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</tr>
<tr>
<td>1000</td>
<td>8.64</td>
<td>8.21</td>
</tr>
</tbody>
</table>

Figure 5. POV as a function of UV-B exposure time.

The results show high level of equivalence between PE-SYN and PE-BIO-Succ+Seb in clear coats formed from blends with commercial polyacrylate polyol and warrant a more complex study, preferably in a pigmented coating.

4. Conclusions

In this research, a fully bio-based version of synthetic polyester polyol was successfully synthesized to be used in combination with acrylic polyol for high-solid two-component polyurethane protective coatings for metal surfaces. Synthetic raw materials were substituted with their bio-based alternatives. Neopentyl glycol was replaced with bio-based neopentyl glycol using ISCC Plus mass balance approach, 1,6-hexanediol and propylene glycol were substituted with bio-based 1,3-propanediol and adipic acid was replaced with the bio-based succinic acid and sebacic acid. Three variations of bio-based polyol were synthesized, and then the most suitable version was validated in a clear coat. Bio-based polyol and coating exhibited properties that were comparable to the properties of synthetic counterparts. Further comparative studies on the properties of synthetic and bio-based polyols are needed. The bio-based polyol has been industrialized, and thus represents a step forward to the green transition of the coating industry.

Author Contributions: Conceptualization, N.Č., M.S. and M.O.; methodology, N.Č. and M.S.; validation, M.O. and P.V.; formal analysis, N.Č., M.S. and N.V.; investigation, N.Č., M.S., N.V., M.O. and P.V.; data curation, N.Č., M.S. and N.V.; writing—original draft preparation, N.Č. and M.S.; writing—review and editing, N.Č., M.S., N.V., M.O. and P.V.; visualization, N.Č., M.S. and M.O.; supervision, M.O. and P.V. All authors have read and agreed to the published version of the manuscript.

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References

6. Nakajima, H.; Dijkstra, P.; Loos, K. The recent developments in biobased polymers toward general and engineering applications: Polymers that are upgraded from biodegradable polymers, analogous to petroleum-derived polymers and newly developed. Polymers 2017, 9, 523–548. [CrossRef]
9. Lomeli-Rodriguez, M.; Corpas-Martinez, J.R.; Willis, S.; Mulholland, R.; Lopez-Sanchez, J.A. Synthesis and characterization of renewable polyester coil coatings from biomass-derived isosorbide, FDCA, 1,5-pentanediol, succinic acid, and 1,3-propanediol. Polymers 2018, 10, 600–618. [CrossRef]


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