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Weatherability of Bio-Based versus Fossil-Based Polyurethane Coatings †

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Abstract: The use of bio-based feedstock for the formulation of protective coatings has been implemented in the increased industrial supply of building blocks synthesized from biomass. The alternation of traditional polyurethane coatings by bio-based polyurethanes has focused on the replacement of the polyisocyanate component in combination with polyester or polyacrylate polyols. In this research, the performance of an aliphatic isocyanate synthesized from crude oil (i.e., HDI, or hexamethylenediisocyanate) has been compared to an alternative hardener synthesized through fermentation of biomass (i.e., PDI, or pentamethylenediisocyante). As the chemical structure of the bio-based PDI is slightly different, with an aliphatic chain of five compared to six carbon atoms, an almost similar or better performance as a protective coating is demonstrated. The application of bio-based PU coatings resulted in lower drying times and higher hardness with similar gloss, chemical resistance and mechanical resistance. In particular, the resistance of bio-based coatings after QUV accelerated weathering testing was improved owing to the better hydrophobicity of the bio-based PDI hardener. There was a gradual trend in evolution of the performance with stepwise replacement of fossil-based with bio-based content.

Keywords: polyurethane; coating; bio-based; testing; durability

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1. Introduction

Polyurethanes (PUs) are versatile polymers of interest for a wide range of applications such as foams, adhesives, coatings, paints, sealants or elastomers. The PU can be synthesized with excellent chemical, physical and mechanical properties for tailored use depending on the selection of isocyanates and polyols. The protective PU coatings are particularly known for a high level of durability, UV resistance, chemical resistance and hydrolytic stability. As the weathering degradation of PU top-coats was assessed more critically [1], the build-up of hydrophilic moieties during coating degradation promoted the absorption of water, thus leading to the formation of blisters on the coating surfaces after alternating dry and wet environments. The failure mechanisms of a polymer coating during weathering are controlled by a complex set of photochemical oxidation processes and creation of reactive sites (e.g., scission of polymer chains, rearrangement and crosslinking [2], promoting final cracking. These reactions can be controlled through the optimization of clearcoat composition and curing conditions [3].

In a transition towards bio-based PU grades, a review on the major biological sources for the development of PU precursors has recently been presented [4]. On the one hand, several bio-based polyols are industrially available, derived from vegetable oils, carbohydrates, lignocellulose or proteins [5]. On the other hand, the grades of commercially available bio-based polyisocyanates remain limited, and these include, e.g., pentamethylene-diisocyanate (PDI) and its oligomers, L-lysine ethyl ester diisocyanate (LDI), and hexamethylene diisocyanate (HDI) allophanate combined with palm oil [6]. The bio-based di-/polyisocyanates can technically be synthesized from amino acids, furan derivatives, carbohydrates (sugars), lignin-based aromatics, cashew nutshell liquid and vegetable oils as precursors [7]. The synthesis of a bio-based PDI polyisocyanate was patented (2015) [8], forming an isocyanurate trimer with at least one allophanate group in addition. The PDI can be obtained by fermentative operation from lysine. Important parameters in comparing the coating formulations with PDI or HDI are the number of OH-group containing binders intended for the crosslinking of polyisocyanates, which include, in particular, their hydroxyl group content. This parameter is reported in terms of mass of hydroxyl groups per 100 g solids content of the binder. Particularly with the increasing requirements regarding the robustness of a coating system in terms of weathering resistance, chemical resistance, high abrasion resistance, gloss retention and lightfastness, the coatings with high OH-group content and crosslinking density are favoured. Alternatively, the increase in OH-group content increases the polarity of the coating with different water sensitivities. An assessment of bio-based PU coatings indicated that they have significant potential to be used as industrial products, with a partial or total replacement of petroleum-based PU providing additional environmental benefit [9]. In parallel, the variations in performance can also bring additional benefits of bio-based grades. It has been claimed that bio-based diisocyanate synthesized from oleic acid and fatty acid diesters, which is a non-phosgene route, give PU with similar physical properties as those derived from petroleum, and even higher tensile strength in some cases [10].

Alternatively, the waterborne PU dispersions (PUDs) are mostly environmentally compatible products because they do not contain or at least have low amounts of volatile organic compounds (VOC) [11]. The waterborne hardeners employ stabilizing agents in their structure in order to create good compatibility with PU dispersions in aqueous environments. The hydrophilization routes of polyisocyanates can either be performed by the addition of emulsifiers through a physical mixing or through the chemical modification and insertion of hydrophilizing groups into the molecular structure of the polyisocyanate. The first route of emulsification may cause migration of the emulsifiers towards the coating surface, with consequent loss in hardness and chemical resistance. Therefore, the anionically hydrophilized polyisocyanates are preferred and can be synthesized in combination with an ionic salt [12].

The recent developments in the synthesis of di- and polyisocyanates from renewable resources as summarized before mention that the final utility and value of these bio-based monomers can only be assessed by carrying out the detailed validation of specific end-user applications. For that, collaboration between industry and research institutes is imperative in order to identify benefits in terms of a unique and better set of properties and performance of bio-based coatings compared to existing commercial petroleum-based traditional coatings.

2. Materials and Methods

2.1. Materials

The formulations of bio- and fossil-based PU coatings were based on commercially available products (Covestro, Leverkusen, Germany), including a resin-based PU coating system and a waterborne PUD dispersion coating system. For the two-component resin-based system (solvent-free), the performance of PU coatings with a HDI hardener (trimer) and a PDI hardener (trimer) were compared in different ratios in combination with a fatty-acid-modified branched polyester-polyol. Both types of isocyanate hardener are illustrated in Figure 1. For the two-component waterborne system of PUD, the hydrophilic aliphatic polyisocyanates were used based on anionically-stabilized PDI isocyanurate or HDI isocyanurate. The bio-based type of anionically stabilized PDI polyisocyanurate for formulation of bio-based water-borne PU dispersions is shown in Figure 2. The waterborne hardeners were used for crosslinking with a polyacrylate polyol.

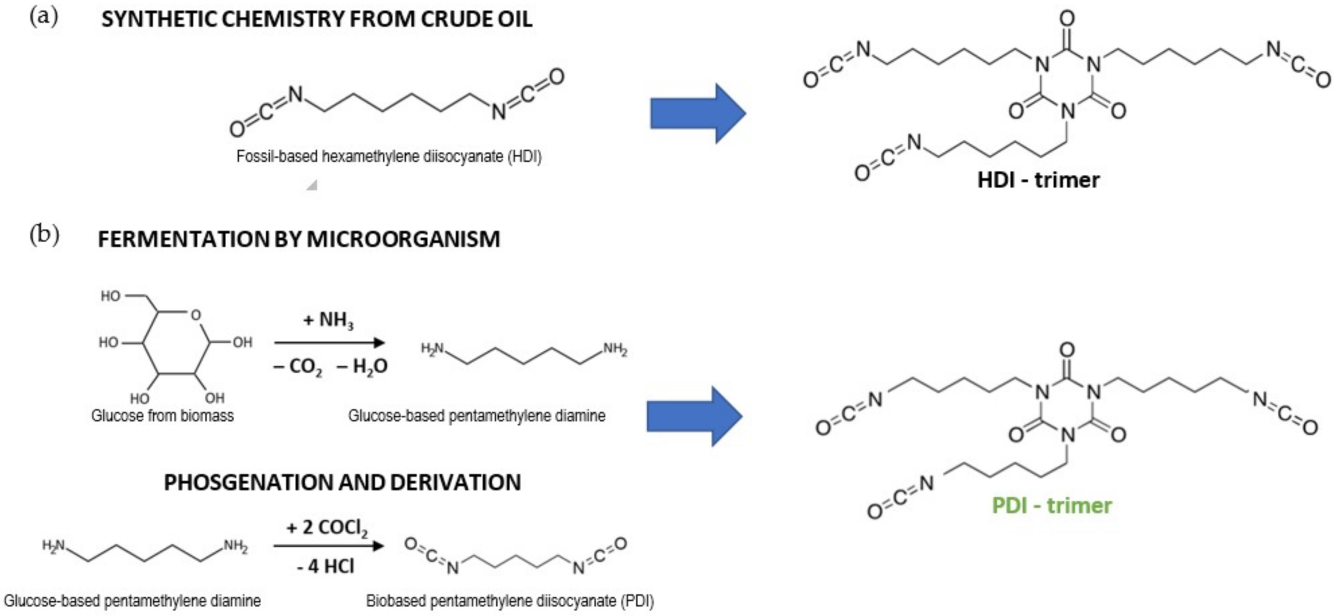

Figure 1. Chemical structure of polyisocyanates with trimer structure to be used as building blocks in PU coatings: (**a**) HDI isocyanate (fossil-based Desmodur® ultra), or (**b**) PDI isocyanate (bio-based Desmodur® eco).

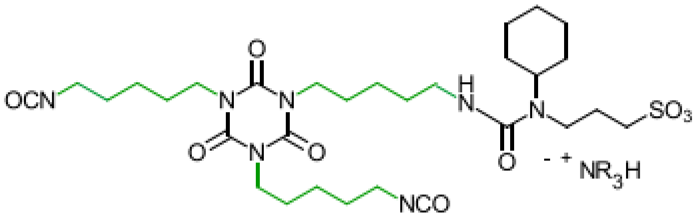

Figure 2. Example of anionically stabilized PDI isocyanate for formulation of aqueous bio-based PU dispersion (PUD) coatings.

An overview of the different coating formulations included in present screening tests is given in Table 1. The coatings were formulated with progressive variation in amounts of PDI- and HDI-trimers, therefore illustrating the influence of composition on testing properties with a gradual transition from fossil-based into bio-based coating grades. The series 1 (sample 1 to 5) include the resin-based PU coating types and the series 2 (sample 6 to 14) include the waterborne PUD dispersion coatings. The resin-based PU coatings include bio-based PDI-1 (PDI trimer, Desmodur® eco) and fossil-based HDI-1 (HDI trimer, Desmodur® ultra) as hardeners and a reference polyester polyol binder (Desmophen 1300 BA, i.e., fatty acid-modified branched polyester polyol) as recommended for fast-drying 2K coatings. The waterborne PUD coatings are formulated with bio-based PDI-2 (hydrophilic aliphatic PDI polyisocyanate, Bayhydur eco®), fossil-based HDI-2 (hydrophilic aliphatic HDI polyisocyanate, Bayhydur ultra 305®) or alternative HDI-3 (hydrophilic aliphatic HDI polyisocyanate, Bayhydur XP2655®). The materials are equivalent to commercially available grades gratefully donated by Covestro Co. (Leverkusen, Germany).

Table 1. Overview of different coating formulations (numbers given as parts, weight ratios further calculated according to NCO content and equivalent weight) and identification of sample numbers.

Sample n°	Resin-Based PU Coating			Waterborne PUD Coating			
	PDI-1	**HDI-1**	**Polyester Polyol**	**PDI-2**	**HDI-2**	**HDI-3**	**Polyacrylate Polyol**
1	1	-	1				
2	0.75	0.25	1				
3	0.50	0.50	1				
4	0.25	0.75	1				
5	-	1	1				
6				1	-	-	1
7				0.75	0.25	-	1
8				0.50	0.50	-	1
9				0.25	0.75	-	1
10				-	1	-	1
11				0.75	-	0.25	1
12				0.50	-	0.50	1
13				0.25	-	0.75	1
14				-	-	1	1

2.2. Testing Procedures

The viscosity of coating formulations was determined with a low shear viscosity meter and appropriately selected spindle according to ASTM D2196 (DV-III Ultra, Brookfield Engineering, Hadamar-Steinbach, Germany).

The coatings were applied by bar coating on standard steel panels (type QD-36, cold rolled steel, low carbon, SAE 1008/1010, thickness 0.5 mm, Ra < 0.5 µm, Q-lab, Saarbrucken, Germany) with a dry film thickness of 50 µm. The coatings were cured for at least 10 days under controlled atmospheric lab conditions (23 °C, 50% RH) before testing. The drying times T1 (sand-dry) and T4 (total dry) at room temperature were determined according to ASTM D1640. The QUV weatherability testing was performed according to ASTM G154 under UVA-340 nm conditions with alternating light cycles (8 h UV at 60 °C) and condensation exposure cycles (4 h condensation at 50 °C) under light intensity of 0.76 W/m^2. The periodic evaluations were made after testing intervals of 500, 1000 and 2000 h.

The coating's microhardness was measured with a handheld digital Shore D durometer following the ASTM D2240 method, using a hardened steel tip with a 30 ± 0.5° conical point and 0.100 ± 0.012 mm tip radius. The specular gloss was measured with a micro-tri-glossmeter (BYK-Gardner Instruments, Geretsried, Germany) under 60° following ASTM D523. Static water contact angles were measured (Dataphysics Instruments GmbH, Filderstadt, Germany), using water droplets of 3 µL and fitted with a Laplace–Young geometry. All measurements were averaged from ten independent locations over the surface. The optical microscopy of coated surfaces was made on a stereomicroscope at magnifications 50× (Leica, Wetzlar, Germany).

3. Results and Discussion

3.1. Processability of Bio-Based and Fossil-Based Coatings

The coating processing conditions for bio-based and fossil-based coatings may rely on the selection of the monomers, mainly including variations in viscosity and drying properties. The processing properties of some reference coating compositions are compared in Figure 3.

The results of drying times for PU and PUD coatings with either PDI or HDI hardener are plotted in Figure 3a, indicating the lower drying times for the PDI-based hardeners used in both resin and waterborne coatings. The improved drying conditions of PDI-based coatings are favourable for the further processing of the coating layer. The drying times for waterborne compositions, however, are obviously higher compared to resin-based composition, which is an inherent property of aqueous solutions and is commonly noticed as a drawback. The reduction of drying times or aqueous 2K PUD coatings has been intensively researched and further optimized by using more reactive polyisocyanates containing the aromatic isocyanate groups, in line with studies on fast hardeners such as fast-drying polyols [13].

The viscosity of the PU coatings with PID and HDI hardeners is compared in Figure 3b as a function of different dilutions in butyl acetate. The PDI hardener has originally much higher viscosity (9200 mPa.s at 23 °C) than the HDI hardener (3000 mPa.s at 23 °C); however, this drops strongly towards comparable values after dilution in solvent, as the bio-based monomer can be used as a near drop-in for the HDI-based hardener. The viscosity of the hardener strongly relates to the chain length (number of CH_2 groups), as the shorter chains of PDI imply more rigidity and higher viscosity. A comparable pot-life for application of the PDI- and HDI-based coatings was obtained with sufficient timing for homogeneous coating application.

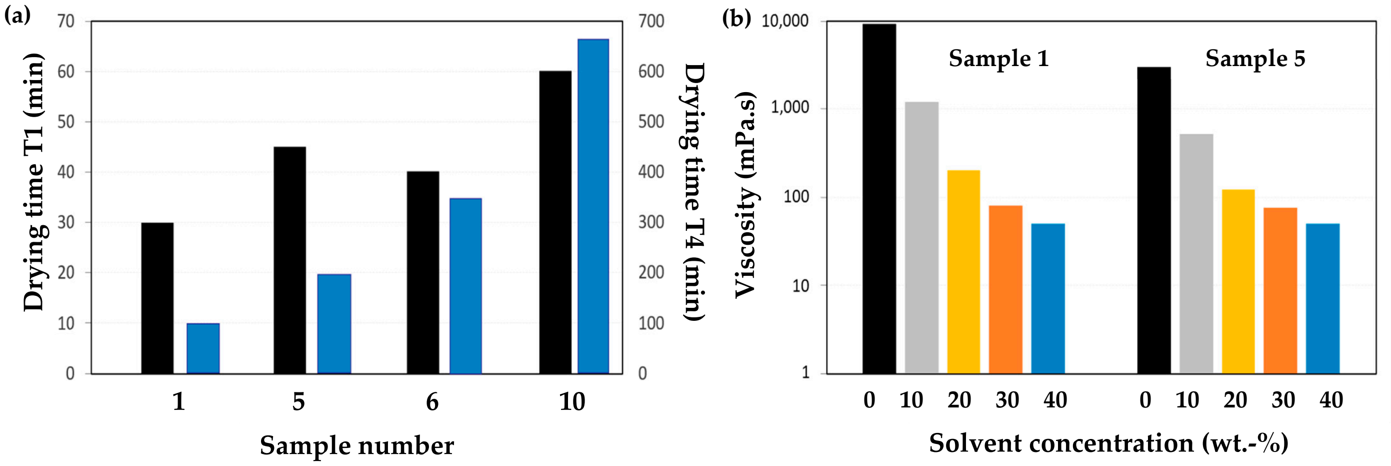

Figure 3. Processing properties of selected reference PU and PUD coatings with bio-based PDI versus fossil-based HDI hardener: (**a**) drying time T1(black) and T4 (blue) for PU and PUD samples, (**b**) viscosity for PU samples after dilution with different concentrations in butyl acetate solvent. Sample numbers and compositions according to Table 1.

3.2. Coating Performance

The hardness measurements for coatings after full drying were measured, illustrating the systematic evolutions with progressive replacement of bio-based PDI towards fossil-based HDI in both the PU and PUD coatings (Figure 4a). The resin-based PU coatings form more homogeneous covering layers with higher hardness compared to the PUD coatings, while the use of PDI hardener is more favourable than the HDI hardener in obtaining high hardness. Indeed, the reduced flexibility of the short-chain PDI at the molecular level may be expressed in improved mechanical properties. Both the PDI and HDI hardeners can be used in good compatibility and mixed in different ratios in order to adopt the mechanical properties towards the required level, with an almost linear decrease in hardness with higher concentrations of the more flexible HDI hardener. The waterborne PUD coatings have different drying mechanisms and consequently different coating structures compared to PU coatings, resulting in relatively lower hardness and mechanical properties.

The evaluation of QUV resistance was made in parallel with the static water contact angle measurements on the native and exposed coatings, indicating progressive degradation after different testing intervals as a decrease in water contact angle (Figure 4b). For original non-exposed coatings, the hydrophobicity was highest for the resin-based PU coatings with PDI hardener and decreased for the coatings with HDI hardener. In parallel, the hydrophobic protection in combination with high mechanical hardness seems favourable for the better weathering protection of the PDI-based coatings with a higher retention value of the water contact angle after QUV exposure over the full exposure time. Although the hydrophobicity for original PUD coatings is comparable to that of the resin-based PU coatings, the lower hardness and reduced mechanical integrity causes reduced resistance in weathering testing. Overall, however, the coatings with aqueous PDI hardeners perform better than the HDI hardeners in weathering resistance.

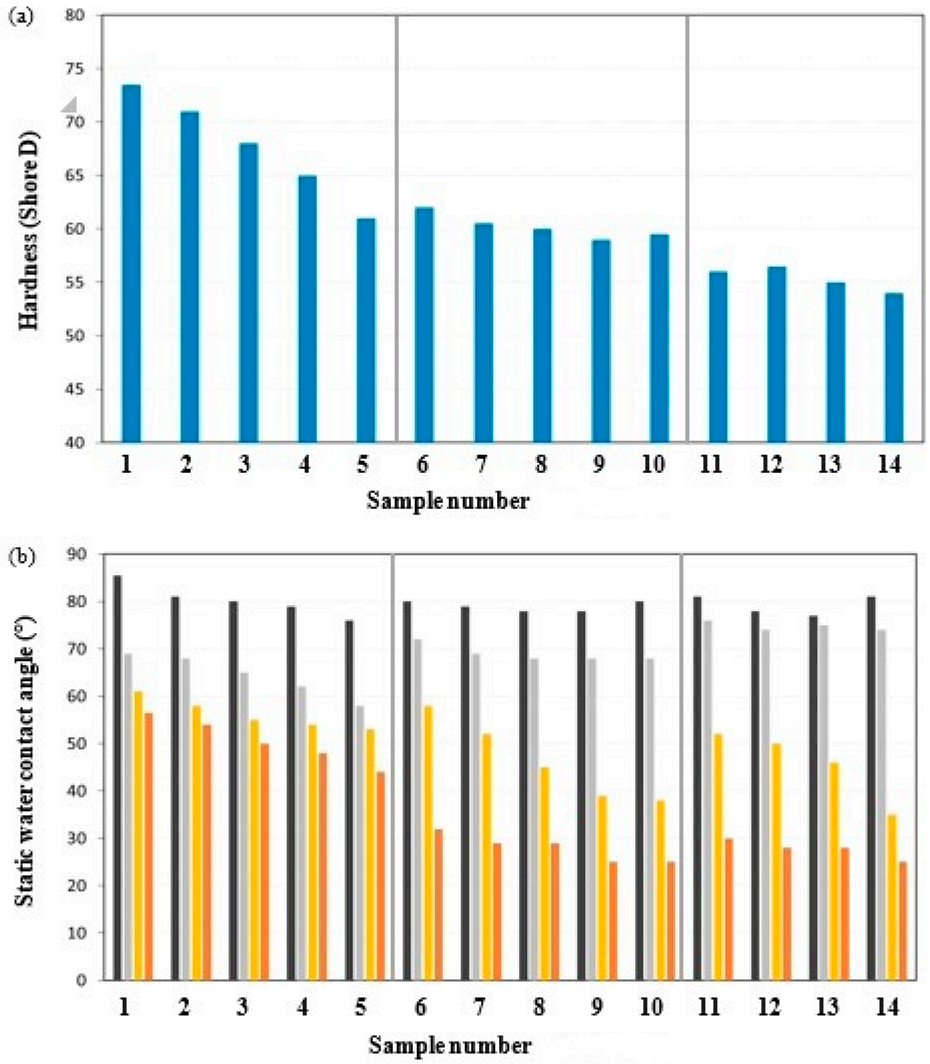

Figure 4. Coating performance of PU and PUD coatings with variable ratios of bio-based PDI hardener versus fossil-based HDI hardener: (**a**) hardness measurements, (**b**) contact angle measurements taken after different time intervals of QUV testing, i.e., 0 h (black), 500 h (grey), 1000 h (yellow) and 2000 h (orange). Sample numbers and compositions according to Table 1.

3.3. Coating Visualization

The results of gloss measurements for two reference PU coatings with bio-based PDI hardener (sample 1) and HDI-based hardeners (sample 5) are evaluated in Figure 5, indicating the higher gloss of the bio-based coatings with PDI hardener compared to the coatings with fossil-based HDI hardener. After weathering exposure tests, better retention of the coating gloss is maintained for the coatings with PDI hardener.

The previous evaluations are in agreement with optical inspection of the coating surfaces in Figure 6, showing optical micrographs of some coating compositions taken after final QUV exposure with 2000 h. The PU coatings with PDI hardener remain completely covered and smooth, without indications of local degradation, while the PU coatings with increasing amount of HDI hardener become a little sensitive to some local corrosion spots. The discoloration of the aqueous PUD coatings is more intense compared to the resin-based PU coatings, pointing to more intensive corrosive degradation. However, the PDI-based aqueous coatings have less discoloration compared to the HDI-based aqueous coatings. In parallel with previous observations for the resin-based PU coatings, the PUD coatings with PDI hardener are less sensitive to corrosive degradation compared to the PUD coatings with HDI hardener.

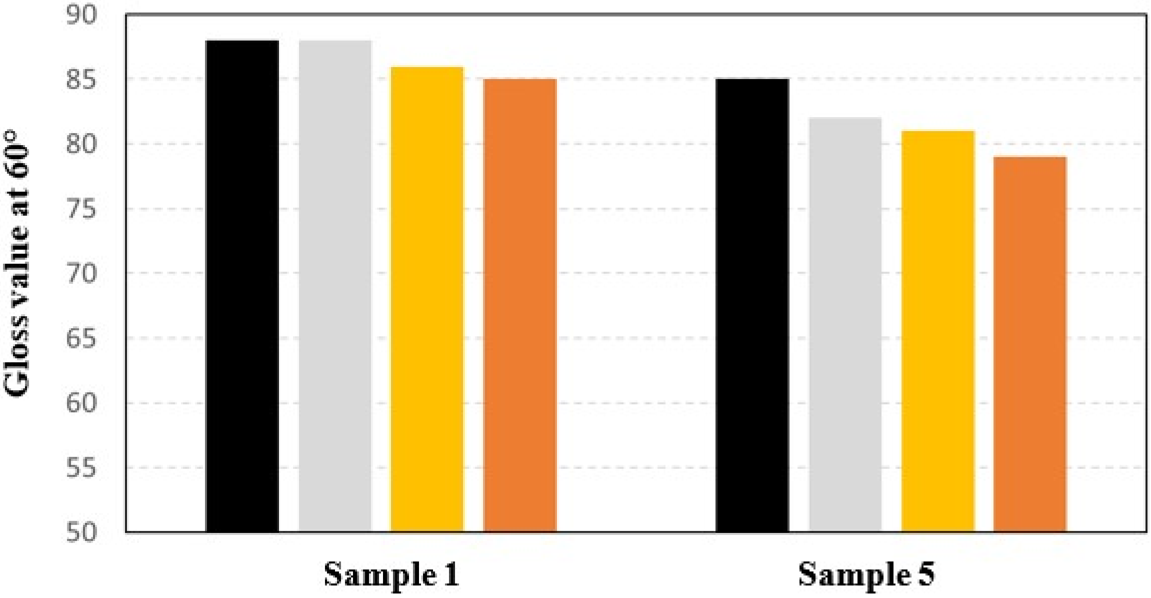

Figure 5. Gloss evaluation of PU coatings with bio-based PDI hardener versus fossil-based HDI hardener, after different time intervals of QUV exposure, i.e., 0 h (black), 500 h (grey), 1000 h (yellow) and 2000 h (orange). Sample numbers and compositions according to Table 1.

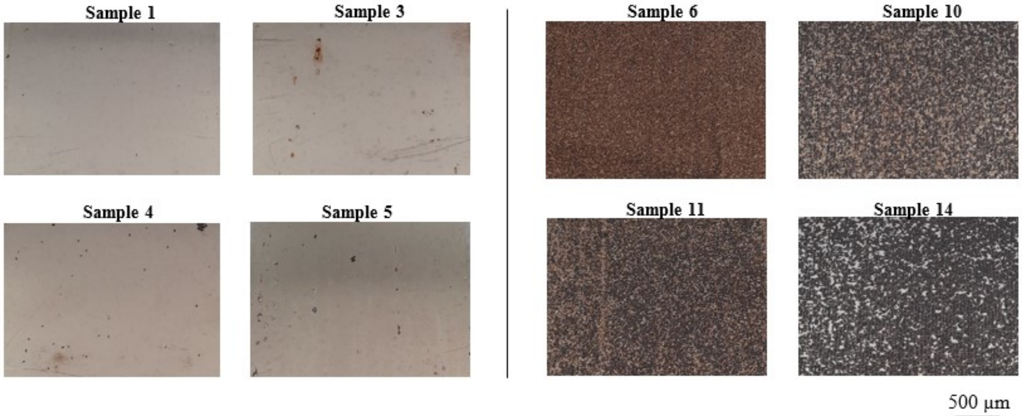

Figure 6. Optical microscopy of QUV-exposed coatings after 2000 h of testing (same length scale applies to all pictures). Sample numbers and compositions according to Table 1.

4. Conclusions

The comparative study on PU and PUD coatings with progressive conversion of the fossil-based HDI hardener into the bio-based PDI hardener indicates good mechanical properties and weathering resistance of the bio-based coating types.

The processing conditions of the bio-based hardener is almost similar to the fossil-based hardener as it can serve for a drop-in solution of traditional PU coatings. The reduction in chain length for the PDI hardener is expressed as an elevation in coating hardness and coating hydrophobicity. Both physical characteristics enhance the weathering resistance of bio-based coatings with PDI hardener.

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