Bio-Based 2K PU Coating for Durable Textile Applications

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Abstract: Polyurethane (PU) coatings are often applied on high added value technical textiles. To date, most PU textile coatings are solvent based or water based. Recent advances are made in applying high solid and two-component (2K) PU on textiles. Currently, polymers made from renewable raw materials are experiencing a renaissance, owing to the trend to reduce CO₂ emissions and switch to CO₂-neutral renewable products. There is also the tendency towards the “bio, eco, natural” consciousness-awakening of the end consumer and the market-driven question to implement renewable materials. However, the application of bio-based coatings on textiles is limited. In this regard, the present study is conducted to develop bio-based 2K PU coating specifically designed for waterproof textiles. A 2K PU coating formulation, composed of bio-based polyol and bio-based isocyanate Desmodur Eco N7300, was made and directly applied on a polyester fabric prior to thermal curing in an oven. The coating was characterized via Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The coatings were not thermoplastic and had a glass transition temperature of approximately 50 °C. Since a bio-based pentamethylene diisocyanate trimer (PDI-trimer), Desmodur Eco N7300 was used as an isocyanate source and not a diisocyanate derivative, and the resulting bio-based 2K coating was a thermoset instead of a thermoplastic. The effect of the additives and content of isocyanate on the elongation and stress at break was studied by performing tensile tests (ISO 13934-1) on 50 μm 2K PU films and comparing the obtained values. The performance of the coating was studied by evaluating the resistance to hydrostatic pressure initially and after washing, the Q-panel Laboratory UltraViolet (QUV) aging and the hydrolysis test. The developed bio-based 2K PU coating had excellent hydrostatic pressure, QUV aging resistance, hydrolysis resistance and wash fastness at 60 °C.

Keywords: 2K polyurethane; coating; bio-based; textile

1. Introduction

Polyurethane (PU) is widely used in diverse applications, such as coatings, foams, adhesives, sealants and elastomers. A key factor to the success of PU coatings is its versatility and durability. PU outperforms many other coating polymers. Abrasion resistance, flexibility, durability to washing and strength are by far higher in PU compared to other coating polymers. Therefore, PU is used in a lot of coating applications. For textile coating, polyester, polyether and polycarbonate PU are available. Their use is related to the final properties desired in an application. In general, the following properties can be related to the type of chemistry:

- Polyester: good weather stability, poor resistance to hydrolysis;
- Polyether: poor weather stability, good resistance to hydrolysis;
- Polycarbonate: good weather stability + good resistance to hydrolysis.

Companies working with solvent-based PU coatings or diisocyanates, will eventually be forced to change to non-solvent or water-based technologies to comply with all the regulations. REACH regulation wants to guarantee the safe use of chemical substances and preparations throughout the entire industrial production chain. REACH imposes
not only obligations concerning the gathering and distribution of information about the characteristics of the substance on the producers and importers of chemicals, but also on the downstream users, such as the textile coating companies processing PU since they use chemicals (e.g., DMF (dimethylformamide)). DMF is a substance of very high concern (SVHC), an obligation of communication if a coated textile contains more than 0.1% DMF. The next step is the prioritization for authorization followed by the authorization [1]. Based on this information, alternative PU needs to be found to enable companies to continue their activities.

Currently, the biopolymers and synthetic polymers made from renewable raw materials are experiencing a renaissance, related to the trend to switch to CO₂-neutral renewable products. There is also a tendency towards the “bio, eco, natural” consciousness-awakening of the end consumer and the market-driven question to implement renewable materials. These developments are also applicable to polyls used for the synthesis of PU. Years ago, polyls were produced mainly from vegetable oils applied for the synthesis of strongly cross-linked PU, e.g., rigid foams and composite materials [2–5]. Natural oil polyls (NOPs) are used for PU synthesis, e.g., produced from soybean and castor oil, but polysaccharides and lignin are also frequently used raw materials to synthesize bio-based PU [6]. According to the industry estimates, manufacturing polyester and polyether diols from NOPs (compared to similar polyls from oil) produces 36% less global warming emissions, 61% less non-renewable energy use and 23% less total energy demand [7]. Fridrihsone et al. performed a life cycle analysis (LCA) study of rapeseed oil-based polyl for PU synthesis. Compared to petrochemical polyls, bio-based rapeseed oil polyls have a better environmental performance in 8 out of the 18 ReCiPe midpoint impact categories, and lower a cumulative energy demand [8].

Two-component (2K) bio-based PU coatings were made based on rapeseed oil and applied via spray. The coatings showed good physical and mechanical properties and have the potential to be used as the inner coating for potable water tanks [9]. Soybean oil phosphate ester polyls with a varying hydroxyl content were synthesized as polyls for 2K PU coating. These polyls can be used as the sole polyl or as the reactive diluent in 2K PU coating [10]. The bio-based polyester polyls from eugenol were solvent free prepared and then applied to transparent and anticorrosive PU coatings. The developed coatings revealed excellent physico-mechanical properties, such as transparency, gloss, flexibility and cross-cut adhesion [11]. Water-based polyls from epoxy cardanol modified with tartaric, citric and adipic acid were prepared [12]. The effects of the different hardeners on the properties of castor oil-based 2K waterborne PU wood coatings were examined. Castor oil was modified using glycerol. The coating with hexamethylene diisocyanate had the best hardness, highest tensile strength and superior water resistance among all the tested coatings, and is suitable for wood coatings [13]. The 2K PU adhesives, also based on castor oil, were synthesized for wood [14]. Different bio-based PUs with a variable amount of cashew nutshell liquid were synthesized. The synthesized PU showed self-healing behavior, corrosion resistance and degraded when exposed to microbes [15]. Isosorbide is one of the most applied sugar-based polyls in PU synthesis, owing to the fused ether rings providing rigidity [16–18]. A series of polyester polyls was also prepared based on succinic acid, adipic acid, suberic acid and sebacic acid. All of them were bio-based except for the adipic acid. The polyester polyls were further reacted with 4,4′-methylenebis(phenylisocyanate) to prepare the 2K PU coatings. The sebacic acid-based formulation was considered to be the most suitable among all, for the coating performance (anticorrosive property, gloss and pencil hardness) [19].

In some cases, particles were added to the 2K coating to improve the desired properties. Bio-based 2K PU coatings based on the sebacic acid and polyethylene glycol were made. Hydroxyapatite nanoparticles, synthesized from waste eggshells, were added in amounts of 1%, 3% and 5% to improve the physical properties of the coating [20]. The 2K PU coating based on sorbitol was made, to which nano ZnO was added to improve the
scratch resistance and anticorrosive properties. The addition of nano ZnO resulted in matt finishes [21].

Since PU is the result of a reaction between hydroxyl compounds and isocyanates, bio-based PU can also be obtained by implementing bio-based isocyanates. PU dispersions were made from dimer fatty acid diisocyanates and castor oil. The addition of alkoxysilane modified castor oil increased the tensile strength and corrosion resistance [22]. The use of ethyl ester L-lysine diisocyanate and ethyl ester L-lysine trisocyanate in the PU films were reported. Compared to the isophorone disocyanate-based PU, the bio-based PU tended to swell in the organic solvents [23]. The bio-based PU adhesives for wood applications were synthesized by first reacting the cellulose acetate with 1,6-hexamethylene diisocyanate, followed by mixing with a variable amount of castor oil [24]. Bio-based pentamethylene diisocyanate (PDI) has a significant bio-based content of 68% and is the first example of bio-based diisocyanate, which has been commercialized. The trimeric PDI is commercialized under the trade name DESMODUR® eco N 7300 by Covestro [25].

However, the majority of the reported applications of (bio-based) 2K PU coatings were on hard substrates, such as wood or metal and not on flexible substrates. This report describes the solvent-free synthesis and application of bio-based 2K PU on textiles for waterproof fabrics. A 2K PU coating formulation was made and directly applied to a polyester fabric prior to thermal curing in an oven. Bio-based polyol, bio-based isocyanate and non-toxic catalyst were used as the raw materials. The resulting PU was characterized via FT-IR, TGA and DSC, and the water barrier properties were assessed.

2. Materials and Methods

2.1. Materials

Bismuth neodecanoate (catalyst) was purchased from Sigma-Aldrich (Darmstadt, Germany). Desmodur Eco N7300 (bio-based polyisocyanate) was sampled by Covestro (Leverkusen, Germany). The Tego Airex 900 (organo modified polysiloxane) and Dynasylan 1189 (N-(n-butyl)-3-aminopropyltrimethoxysilane) were supplied by Evonik (Essen, Germany). Dynasylan 1189 was used as the adhesion promoter and Tego Airex 900 as the deaerator to remove air bubbles in the coating formulation. Tanacoat AWP (fluorocarbon emulsion) was sampled by Tanatex Chemicals (Ede, The Netherlands). The woven polyester fabric (105 g/m²) was purchased from Concordia Textiles (Waregem, Belgium). A cardanol-based polyester polyol (Polyol 1, Mw: 2000 g/mol; OH value: 291 mg/g KOH) and vegetable oil-based polyester polyol (Polyol 2, Mw: 3000 g/mol; OH value: 39 mg/g KOH) were used as the polyols.

2.2. Pre-Treatment of the Fabric

The fabric was pre-treated with Tanacoat AWP to prevent the penetration of the 2K coating into the fabric. Therefore, the fabric was immersed in a solution of 20% Tanacoat AWP in water. The fabrics were padded using a padding mangle pressure of 2 bar. After the padding process, the samples were dried for 1 min at 100 °C and 1 min at 155 °C, according the technical data sheet of the product.

2.3. Bio-Based 2K PU Coating

Figure 1 represents the flow chart of the coating process. The PU coatings were prepared by reacting renewable polyols with the Desmodur Eco N7300 in a molar equivalent ratio 1:1 (NCO:OH) using bismuth neodecanoate as a catalyst. A total of 9 g of cardanol-based polyester polyol (Mw: 2000 g/mol; OH value: 291 mg/g KOH) and 18 g of vegetable oil-based polyester polyol (Mw: 3000 g/mol; OH value: 39 mg/g KOH) were molten at 50 °C and mixed with 0.02 g of catalyst (bismuth neodecanoate). A total of 0.3 g of Dynasylan 1189 and 0.3 g of Tego Airex 900 were added. Tego Airex 900 was added to remove the air inclusion from the formulation, which would result in coating defects and a loss of water barrier properties. Subsequently, 11.68 g of Desmodur Eco N7300 (bio-based polyisocyanate) was added to the polyol mixture, which was kept at 40 °C. The 2K
formulation was applied to a polyester fabric via the knife-over-roll coating method. The applied coating thickness was 50 µm. A total of 2 layers was applied and, after applying each layer, the coating formulation was cured for 2 min at 155 °C. Other bio-based 2K PU coatings were similarly produced (Table 1).

![Schematic flow of the 2K PU coating on polyester fabric involving the preparation of coating formulation, application of the formulation via the knife-over-roll method and curing in an oven for 2 min at 155 °C to obtain the coated fabric.]

**Figure 1.**

| Table 1. Composition of the bio-based 2K PU coatings and molar equivalent NCO:OH ratio. |
|---|---|---|---|---|---|---|
| Polyol 1 (g) | Polyol 2 (g) | Catalyst (g) | Desmodur Eco N7300 (g) | Dynasylan 1189 (g) | Tego Airex 900 (g) | NCO:OH Ratio |
| Bio 2K PU-1 | 9 | 18 | 0.02 | 11.68 | 0.3 | 0.3 | 1 |
| Bio 2K PU-2 | - | 28 | 0.02 | 3.95 | - | 0.3 | 1 |
| Bio 2K PU-3 | - | 28 | 0.02 | 3.95 | 0.3 | 0.3 | 1 |
| Bio 2K PU-4 | - | 28 | 0.02 | 4.35 | 0.3 | 0.3 | 1.10 |
| Bio 2K PU-5 | - | 28 | 0.02 | 3.55 | 0.3 | 0.3 | 0.9 |
| Bio 2K PU-6 | - | 28 | 0.02 | 3.16 | 0.3 | 0.3 | 0.8 |

2.4. Characterization

Fourier transform infrared spectra (in µ-ATR mode) were recorded using a Nicolet 6700 spectrometer from Thermofisher Scientific (Waltham, MA, USA). A spectral range from 500 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) was used. The infrared analysis was used to characterize the 2K PU. The surface morphology and the penetration of the coating into the fabric was visualized using field emission gun scanning electron microscopy (FEG-SEM) (JSM 7600 F from Jeol Europe, Zaventem, Belgium). To prevent charging, the specimens were sputtered with a palladium coating.

The thermogravimetric analysis (TGA) of the PU was performed to examine the thermal decomposition and char formation using a Q500 thermogravimetric analyzer (TA Instruments, Asse, Belgium). All the samples were conditioned at 23 °C and 50% relative humidity. Analyses were performed in air with a ramp rate of 10 °C/min from 30 to 600 °C. The thermograms were analyzed using Universal Analysis Software.

Differential scanning calorimetry (DSC) analysis of the PU was performed to measure the glass transition temperature (Tg) using TA Instruments Discovery DSC2500 (TA Instruments, Asse, Belgium). All the samples were conditioned at 23 °C and 50% relative humidity. All the samples were heated from 0 to 250 °C, cooled down from 250 to 0 °C and heated back from 0 to 250 °C. The analyses were performed with a heating and cooling rate of 10 °C/min.

The air permeability was assessed according to ISO 9237 using Textest FX 3300 apparatus (Textest AG, Schwerzenbach, Switzerland). The rate of air flow passing perpendicularly through the coated fabric was measured at a pressure drop of 100 Pa across the fabric test area (20 cm\(^2\)). A total of 10 measurements were performed.

The flexibility was assessed according to EN ISO 7854-C using a crumple flex tester (VVC, Linselles, France). The crumple flex tester simulates the flexing of the textile during
use by twisting the coated fabric. Subsequently, an evaluation of the coating was conducted by assessing the presence of cracks or aspect loss.

Swelling experiments in ethyl acetate were performed to calculate the crosslinking density. The PU films were placed for 48 h in solvent. After removal, the residual amount of solvent on the PU films was wiped off, before being weighed. From the weight of the swollen polymer \( (w_s) \), the volume fraction of swollen polymer \( (V_p) \) can be calculated as follows:

\[
V_p = \frac{w_d/d_p}{[(w_s/d_s) + (w_d/d_p)]}
\]

where \( w_d \) is the dry weight of the polymer, and \( d_p \) and \( d_s \) are the densities of the polymer and solvent, respectively. The crosslink density \( (n) \) values were obtained from \( V_p \) with the Flory–Rehner equation:

\[
-[\ln(1 - V_p) + V_p + \chi V_p^2] = \text{vs.} \ n \ [V_p^{1/3} - (V_p/2)]
\]

where \( \text{vs.} \) is the molar volume of the solvent and \( \chi \) is the polymer–solvent interaction parameter, which can be found from equation:

\[
\chi = (\delta_1 - \delta_2)^2 V_s/RT
\]

where \( R \) is a gas constant and \( T \) is the temperature (expressed in Kelvin), whereas \( \delta_1 \) and \( \delta_2 \) are the solubility parameters of the solvent and polymer.

The abrasion resistance was evaluated according to EN 530-2 using a Martindale wear and abrasion tester. The instrument was used in an inverted mode, i.e., the specimen was placed on the abradant table instead of in the test piece holder, and the abradant was mounted on the test piece holder. This provides an abraded area, which allows a measurement of resistance to hydrostatic pressure afterwards. The test was carried out for 500 cycles with an F2 abradant (sandpaper), and an applied pressure of 9 kPa on the sample. Besides determining the resistance to hydrostatic pressure, the mass loss was determined after 500 abrasion cycles.

Elongation at break and the break at stress were determined using an Instron electronic fabric tension tester (Instron, Norwood, MA, USA) according to ISO 13934-1 on 50 \( \mu m \) of 2K PU films. The tension loading speed was 100 mm/min. The resistance to the hydrostatic pressure was measured according to ISO 811 using a Textest FX 800 apparatus (Textest AG, Schwerzenbach, Switzerland). The coated fabric was subjected to a steadily increasing pressure of water on one face, under standard conditions, until penetration occurred in three places. The same test was repeated after washing and the exposure to UV or a high temperature and humidity to examine, respectively, the wash fastness, Q-panel Laboratory UltraViolet (QUV) and hydrolysis resistance. The wash fastness was evaluated according to ISO 6330. A total of 20 washing cycles at 60 \(^\circ\) C were performed in a Wascator FOM 71 type A (James Heal, Halifax, UK). The detergent was the ECE detergent type 3 (Christeyns, Ghent, Belgium). The samples were dried at room temperature after washing. The hydrolysis resistance was measured according to ISO 1419-C (tropical test), by exposing the coated fabric for 3 weeks to a temperature of 70 \(^\circ\) C and a relative humidity of 95%, and examining the resistance to hydrostatic pressure afterwards. The resistance towards aging by means of heat, light and humidity (QUV test) was evaluated according to ISO 4892. The details are presented in Table 2. Generally, the total duration of the test was set at 500 h.
Table 2. Experimental details of the QUV test.

| QUV Parameters               | UVA 340                      |
|------------------------------|-----------------------------|
| Light source                 | UVA 340                     |
| Mode of exposure             | Alternate light/condensation|
| Temperature                  | 60 °C                       |
| Duration of aging            | 4 h                         |
| Condensation                 | 50 °C                       |
| Duration of aging            | 4 h                         |

3. Results

3.1. Characterization of 2K PU

The 2K bio-based PU coatings were characterized with FT-IR. Figure 2 demonstrates the FT-IR spectrum of Bio 2K PU-1. The absence of the asymmetrical N=C=O stretch between 2250 and 2285 indicates that the 2K PU coating is completely cured. Some bands, characteristic for PU, appeared in the FT-IR spectrum. Table 3 presents an overview of the different bands and the corresponding groups for Bio 2K PU-1. The formation of the urethane bands is mainly identified by the absence of OH and isocyanate groups, and the appearance of NH bands in the FT-IR spectrum.

![FT-IR spectrum of Bio 2K PU-1.](image)

Table 3. Overview of the functional groups in Bio 2K PU-1 detected by FT-IR.

| Wavenumber (cm⁻¹) | Corresponding Group                          |
|-------------------|----------------------------------------------|
| 765               | COO urethane (deformation vibration)        |
| 1171              | C–O–C ester (elongation vibration)          |
| 1244              | C–O–C urethane (elongation vibration)       |
| 1465              | CH (deformation vibration)                  |
| 1527              | N–H and C–N amide                           |
| 1689              | C=O ester (elongation vibration)            |
| 1733              | C=O urethane (elongation vibration)         |
| 2856              | CH (elongation vibration)                   |
| 2929              | CH (elongation vibration)                   |
| 3389              | NH (elongation vibration)                   |

The absorption band at 3389 cm⁻¹ corresponds to the NH stretching, while the bands at 1733 and 1689 cm⁻¹ are assigned to the C=O stretching of the urethane and ester moieties. The peaks at 2856 and 2929 cm⁻¹ are attributed to −CH2 stretching, while other modes of −CH2 vibrations correspond with the band at 1465 cm⁻¹. The band at 1527 cm⁻¹ is characteristic of the polyurethanes and is due to the N–H bending and C–N stretching.
in the polyurethanes. The sharp peak at 1244 cm\(^{-1}\) can be attributed to C–O–C urethane vibrations, while the peak at 1171 cm\(^{-1}\) corresponds to the C–O–C vibrations of the ester groups. The small peak at 765 cm\(^{-1}\) is assigned to COO urethane vibrations \[26–29\]. All other developed bio-based 2K PU coatings show an analog FT-IR spectra (Figure 3). They all show characteristics PU bands at 3389, 1733 and 1526 cm\(^{-1}\). Contrary to all the other recorded spectra, the FT-IR spectrum of Bio 2K PU-4 shows a band at 2273 cm\(^{-1}\), which is attributed to N=C=O stretching. Indeed, an excess of Desmodur Eco N7300 was used for Bio 2K PU-4 (NCO:OH ratio of 1.10) resulting in unreacted isocyanate groups.

The coating penetration of the 2K system was evaluated on a neat polyester fabric and a Tanacoat AWP pre-treated fabric using SEM. No difference in the surface morphology of the 2K bio-based PU coating was observed between the coatings on neat polyester fabric or pre-treated fabric; however, the fabrics pre-treated with Tanacoat AWP showed significantly less penetration of the 2K coating compared to the non-pre-treated, fabric resulting in an increase in the flexibility (Figure 4). The bio-based 2K PU coating penetrated the non-pre-treated polyester fabric half-way. The low penetration of the coating in the pre-treated polyester fabric had a positive effect on the flexibility of the coated fabric (better drapability and less cracking or white stripes due to the bending on the surface of the coated textile during the crumple flex test), and, as a consequence, also on the wash fastness. Indeed, a greater penetration depth of the coating reduces the mobility of the yarns, prevents the yarns from rotating and stiffens the fabric \[30\].

Figure 5 presents an SEM picture of the surface of Bio 2K PU-1. The surface is relatively smooth and uniform. No defects, such as craters or air inclusion, were noticed.

The elongation of the coating was assessed according to ISO 13934-1 on 50 \(\mu\)m of 2K PU films (Figure 6). The developed bio-based 2K PU coating composed of a polyol mixture (Bio 2K PU-1) had an elongation of 28%. The low elongation made the Bio 2K PU-1 coating less suitable for coating on knitted fabrics (transfer coating). Although difunctional polyols were used, the elongation was expected to be lower compared to the PU dispersions, since polyisocyanate was used (PDI-trimer) instead of disocyanate, and an adhesion promoter was added in the formulation, which resulted in a more crosslinked and denser PU network. Furthermore, the cardanol-based polyol had a high OH value and a low molecular weight (compared to the vegetable oil-based polyol), promoting the formation of a dense network, which in turn resulted in a lower elongation at break. Bakhshi et al. reported similar observations. They observed that using polyols with a higher OH value increased the crosslinking density, which resulted in a lower elongation at break \[31\].
Different 2K PU coatings were made with different levels of isocyanate, using vegetable oil-based polyol as the sole polyol source, and both with and without adhesion promotor to assess the hypothesis of the effect of isocyanate and adhesion promotor on elongation. The developed bio-based 2K PU (Bio 2K PU-3) coating with adhesion promotor had an elongation of 44%. Skipping the adhesion promotor in the coating formulation (Bio 2K PU-2) increased the elongation to 134% due to the formation of a less dense network. Indeed, the adhesion promotor contains amino groups that react rapidly with isocyanate groups. The effect of the amount of isocyanate on elongation was also studied. Adding 10% extra isocyanate (Bio 2K PU-4) led to a small decrease in the elongation from 44 to 42%. Decreasing the level of isocyanate with 10 (Bio 2K PU-5) and 20% (Bio 2K PU-6), resulted in a significant increase in the elongation, respectively, 103 and 140%. Higher amounts of isocyanate (PDI-trimer) result in a more rigid network, causing a decrease
in the elongation and flexibility (Table 4). The elongation of the bio-based 2K coating is rather limited (<300%), making it less suitable for coating on knitted fabrics. Indeed, knitted fabrics are elastic and, when stretched, the coating breaks. Since woven fabrics have a low stretchability, the developed coating is more suited for coating on woven fabrics. However, it is known that elongations of the coatings are affected by several factors and that the elongation can be increased by adding a compatible plasticizer, increasing the polyol content (increase in the soft segments) or by using a linear diisocyanate instead of a PDI-trimer as the isocyanate source. The stress at break varied between 0.7 and 1.1 MPa (Table 4). The addition of adhesion promoter resulted in a decrease in the stress at break, while the lowering of the isocyanate levels increased the stress at break due to a higher mobility of the chains. Swelling experiments were performed to study the crosslink density and support our hypothesis that a denser network results in a lower elongation (Table 4). Generally, the elongation increased when the crosslinking density decreased. Bio 2K PU-1 exhibited the highest crosslinking density due to the high hydroxy value of polyol 1. The other coatings that were not made from polyol 1, showed a much lower crosslinking density. The increase in isocyanate (Bio 2K PU-4) increased the crosslinking density, while the increase in polyol (Bio 2K PU-5 and Bio 2K PU-6) decreased the crosslinking density.

![Figure 5. SEM picture of the surface of Bio 2K PU-1.](image)

| Elongation (%) | Stress at Break (MPa) | Crosslinking Density (m³/mol) |
|---------------|-----------------------|-----------------------------|
| Bio 2K PU-1   | 28 ± 1                | 0.9 ± 0.1                   | 1134 ± 182                  |
| Bio 2K PU-2   | 134 ± 60              | 1.1 ± 0.3                   | 444 ± 134                  |
| Bio 2K PU-3   | 44 ± 7                | 0.7 ± 0.1                   | 516 ± 90                   |
| Bio 2K PU-4   | 42 ± 10               | 0.8 ± 0.2                   | 572 ± 175                  |
| Bio 2K PU-5   | 103 ± 36              | 0.9 ± 0.3                   | 421 ± 111                  |
| Bio 2K PU-6   | 140 ± 25              | 1.1 ± 0.1                   | 296 ± 2                    |

Table 4. Elongation, stress at break and crosslinking density of the different bio-based 2K PU coatings. The reported elongation and stress at break values are the averages of four measurements. The crosslinking densities are the average of 3 measurements.
The air permeability was also assessed for polyester fabric coated with the different developed bio-based 2K-PU. The resistance to wind penetration was assessed by measuring the air permeability. The air permeability of the coated fabrics was very low. The air permeability of all the polyester fabrics coated with the bio-based 2K PU was lower than 1.00 1/(m²·s), which was the minimum value that could be measured with the current test set-up. This corresponds to other air permeability values for the PU coatings reported in the literature, and suggests that there are no defects (e.g., air bubbles) in the coating [32,33].

There was no difference among the several bio-based 2K PU coatings, but it was expected that if lower values could be measured, different air permeabilities for the different coatings might be observed due to the differences in the crosslinking density. The hand-touch of the coatings was medium–soft and the coating was not tacky.

3.2. Performance of the Bio-Based 2K PU Coating

The resistance to hydrostatic pressure of the bio-based 2K PU coated polyester fabric was measured initially and after the QUV aging, hydrolysis or washing. The maximum resistance to the hydrostatic pressure that could be measured with the equipment was 1000 mbar. The results are listed in Table 5. Initially, the coated fabrics show an excellent resistance to the hydrostatic pressure. This indicates no defects, such as air bubbles, in the coating. Indeed, deaerator was added to the formulation to prevent undesired air voids. Deaerators are active in the air/2K interface and cause the stabilized structure of air voids to rupture in the liquid medium, thus allowing air to escape. After exposing to 70 °C and 95% relative humidity for 3 weeks (hydrolysis test), no degradation of the
bio-based 2K coatings was observed and the same level of performance was obtained. The excellent hydrolysis performance was due to the use of hydrophobic polyol (low water uptake) and the adhesion promoter, resulting in a dense hydrophobic PU network. Indeed, Dynasylan 1189 acts as a bifunctional binding agent. The silane methoxy group hydrolyzes (due to humidity or surface moisture), resulting in reactive silanol groups. Both the amino and silanol groups of the adhesion promoter can react with the substrate as well with the isocyanate groups in the 2K coating. Bio 2K PU-2, which was the only tested coating without adhesion promoter, showed a minor resistance to the hydrostatic pressure after the hydrolysis test. After 500 h of aging (QUV test), a light yellow discoloration of the bio 2K PU-1 coating was observed; however, there was no decrease in the resistance to the hydrostatic pressure. All the other bio-based 2K PU coatings were degraded and became sticky and yellow, indicating that the addition of cardanol-based polyol with a higher OH value improved the aging resistance of the bio-based 2K PU coatings due to the formation of a denser network. After 20 washing cycles at 60 °C, all the bio-based 2K PU coatings still exhibited excellent resistance to the hydrostatic pressure.

Table 5. Performance of the bio-based 2K PU coated polyester fabric. n.d.: The resistance to hydrostatic pressure could not be determined since the coatings were sticky and degraded.

|          | Initial | QUV Aging | 20 Washing Cycles (60 °C) | Hydrolysis |
|----------|---------|-----------|---------------------------|------------|
| Bio 2K PU-1 | ≥1000   | ≥1000     | ≥1000                     | ≥1000      |
| Bio 2K PU-2 | ≥1000   | n.d.      | ≥1000                     | 254        |
| Bio 2K PU-3 | ≥1000   | n.d.      | ≥1000                     | ≥1000      |
| Bio 2K PU-4 | ≥1000   | n.d.      | ≥1000                     | ≥1000      |
| Bio 2K PU-5 | ≥1000   | n.d.      | ≥1000                     | ≥1000      |
| Bio 2K PU-6 | ≥1000   | n.d.      | ≥1000                     | ≥1000      |

The resistance to abrasion was assessed via the Martindale test (500 cycles with sandpaper). After the test, the mass loss was measured to determine the wear (Table 6). The developed 2K PU coatings based on polyester polyols showed minor mass losses. It is known that polyester-based PU have better wear resistance, compared to polycarbonate or polyether PU, and that an increase in the soft segments improves the abrasion resistance [34]. Bio 2K PU-1 showed the lowest mass loss, which reveals that adding the cardanol-based polyol in the bio-based 2K PU improves its abrasion resistance. A possible reason could be that the incorporation of the cardanol-based polyol in the PU increased the hardness of the surface due to the higher hydroxy number, and thereby increased the abrasion resistance [35]. Other coatings exhibited mass losses, which were, at a minimum, double of the mass loss of Bio 2K PU-1. The coatings with adhesion promoter showed a lower mass loss compared to the coatings without adhesion promoter (Bio 2K PU-3 vs. Bio 2K PU-2), which could be attributed to better adhesion resulting in better abrasion resistance. By comparing the mass loss of sample Bio 2K PU-3 until 6, it can be concluded that the abrasion resistance decreased if NCO:OH ratios were higher or lower than 1. The resistance to hydrostatic pressure was also determined after the abrasion (Table 6). As expected, based on the results of the mass loss, Bio 2K PU-1 shows the highest resistance to the hydrostatic pressure after abrasion. However, there is no correlation between the mass loss and the resistance to hydrostatic pressure after abrasion.
Table 6. Mass loss and the resistance to hydrostatic pressure after abrasion.

| Mass Loss (g) | Mass Loss (%) | Resistance to Hydrostatic Pressure (mbar) |
|---------------|---------------|------------------------------------------|
| Bio 2K PU-1   | 0.027         | 0.7                                      | 768 |
| Bio 2K PU-2   | 0.112         | 3.6                                      | 114 |
| Bio 2K PU-3   | 0.059         | 1.8                                      | 150 |
| Bio 2K PU-4   | 0.074         | 2.2                                      | 266 |
| Bio 2K PU-5   | 0.074         | 2.2                                      | 224 |
| Bio 2K PU-6   | 0.111         | 3.2                                      | 176 |

3.3. Thermal Properties

TGA analysis was performed to assess the thermal stability of the bio-based 2K PU coatings. The temperature at weight loss of 5% ($T_{5\%}$), the maximum decomposition temperature of the different degradation steps and the weight residue at 600 °C are presented in Table 7. The TGA curves are shown in Figure 7. All bio-based 2K PU coatings show similar thermal degradation. Generally, the degradation started above 250 °C, taking into account that the temperature at weight loss of 5% ($T_{5\%}$) was for all 2K PU higher than 250 °C. Bio 2K PU-1 showed the highest weight residue at 600 °C and a degradation at higher temperatures (less weight loss compared to the other 2K PU samples, especially above 350 °C), compared to the other 2K PU, due to the incorporation of the cardanol-based polyol. The use of cardanol-based polyol results in a denser and more stable urethane network, since it has a much higher hydroxyl value compared to the vegetable oil polyol.

Table 7. Overview of $T_{5\%}$, maximum decomposition temperatures ($T_{\text{max}1}$) for the different degradation steps and the weight residue at 600 °C for the bio-based 2K PU coatings.

|             | $T_{5\%}$ (°C) | $T_{\text{max}1}$ (°C) | $T_{\text{max}2}$ (°C) | $T_{\text{max}3}$ (°C) | Weight Residue (%) |
|-------------|----------------|------------------------|------------------------|------------------------|--------------------|
| Bio 2K PU-1 | 291            | 364                    | 420                    | 450                    | 1.814              |
| Bio 2K PU-2 | 290            | 365                    | 401                    | 432                    | 0.476              |
| Bio 2K PU-3 | 278            | 366                    | 411                    | 438                    | 1.332              |
| Bio 2K PU-4 | 278            | 362                    | 401                    | 438                    | 0.903              |
| Bio 2K PU-5 | 274            | 365                    | 400                    | 435                    | 1.243              |
| Bio 2K PU-6 | 278            | 367                    | 406                    | 439                    | 1.299              |

Figure 7. TGA curves of the bio-based 2K PU coatings in air.

Derivative thermogravimetric (DTG) analysis revealed three degradation steps (Figure 8). The first degradation is associated with the dissociation of the hard urethane segments resulting in isocyanate, alcohol, $CO_2$, primary and secondary amines and olefins. The
second and third degradation steps (between 400 and 500 °C) are attributed to the dissociation of ester groups and linear hydrocarbon chains (scission and depolymerization of soft segment), while the degradations in the fourth step (above 500 °C) are due to C–C cleavage [21,36,37]. The DTG curves showed that the second and third, and to a less extent fourth, degradation steps of Bio 2K PU-1 occurred at higher temperatures, compared to the other 2K coatings. This can also be concluded from the maximum decomposition temperatures for the different coatings.

The DSC results of the bio 2K PU are shown in Table 8. The Tg values of the different bio-based 2K PU vary in the range from 49 to 54 °C. The transition does not occur suddenly at one unique temperature, but rather over a small range of temperatures. The temperature in the middle of the sloped region during the second heating step was taken as the Tg. The Tg was not determined during the first heating step since this step was performed to remove any volatile impurities and erase the thermal history of the polymer. The results indicate that the Tg values did not change much with varying the isocyanate content in the studied range or changing the polyol composition. The bio-based 2K PU without adhesion promotor showed the lowest Tg, which could be expected since the addition of adhesion promotor decreases the chain mobility. Most bio-based 2K PU coatings showed no melting point, except for Bio 2K PU-6. Indeed, since a PDI-trimer was used, the resulting PU coatings did not show a thermoplastic behavior, and instead showed a thermoset behavior because of the dense crosslinked polymer network. In case of Bio 2K PU-6, the DSC exhibited a melting peak at 19 °C. This could be attributed to the melting of the unreacted vegetable oil polyol, since a significant excess of polyol was used (NCO:OH ratio of 0.8). Figure 9 demonstrates the DSC curves of all the Bio 2K PU coatings.

**Table 8.** Tg of the different bio-based 2K PU.

| Bio 2K PU      | Tg (°C) |
|----------------|---------|
| Bio 2K PU-1    | 52      |
| Bio 2K PU-2    | 49      |
| Bio 2K PU-3    | 52      |
| Bio 2K PU-4    | 54      |
| Bio 2K PU-5    | 54      |
| Bio 2K PU-6    | 53      |
Bio-based 2K PU coatings, specifically designed for textile coatings, were synthesized and applied via knife-over-roll coating onto polyester fabric. FT-IR analysis was performed to characterize the bio-based 2K PU coating, revealing that the coating was completely cured. The DSC analysis showed that the bio-based 2K PU coatings were not thermoplastic and that the Tg varied form 49 to 54 °C, depending on the composition of the coating. The developed bio-based 2K PU coating was a thermoset coating owing to the use of a PDI-trimer. The fabrics were pre-treated to decrease the penetration of the 2K coating in the fabric, which would result in a lower flexibility. The elongation of the bio-based 2K PU coatings varied according to the composition in the range of 28% to 154%. The decrease in the isocyanate and adhesion promoter content increased the elongation of the coatings. The developed bio-based 2K PU coating had an excellent hydrostatic pressure, QUV aging resistance and hydrolysis resistance, and a wash fastness at 60 °C. Compared to most commercial water-based aliphatic polyester PU coatings, the developed bio-based 2K PU coatings showed a better hydrolysis resistance and wash fastness (due to the use of hydrophobic vegetable oil polyol); however, the elongation at break was much smaller. Adding a cardanol-based polyol to the vegetable polyol resulted in better QUV aging and abrasion properties. This can be attributed to the high hydroxyl number of the cardanol-based polyol. However, the use of only cardanol-based polyol as the sole polyol source in the coating formulation resulted in a too brittle PU coating with a low wash fastness, because of the formation of a too dense and rigid network due to its high hydroxyl number. The developed bio-based 2K PU-1 coating is suitable for high demanding technical textile applications and can be easily applied via knife-over-roll coating, but it is only suitable for coatings on woven fabrics and less suitable for coatings on knitted fabrics, due to the low elongation of the coating and the high elasticity of the knitted fabrics.

**Author Contributions:** Conceptualization, D.D.S. and W.U.; methodology, D.D.S. and W.U.; validation, D.D.S. and W.U.; formal analysis, D.D.S. and W.U.; investigation, D.D.S. and W.U.; resources, D.D.S. and W.U.; data curation, D.D.S. and W.U.; writing—original draft preparation, D.D.S.; writing—review and editing, W.U. and M.V.; visualization, D.D.S.; supervision, M.V.; project administration, D.D.S. and M.V.; funding acquisition, D.D.S. and M.V. All authors have read and agreed to the published version of the manuscript.

**Funding:** The research was performed in the framework of the Cornet Project BioPU (HBC.2017.0246), funded by the Flanders Innovation and Entrepreneurship.
Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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