

Article

Design of Debondable PU Coating for Degradation on Demand

David De Smet  and Myriam Vanneste 

Centexbel, Technologiepark 70, 9052 Zwijnaarde, Belgium; mv@centexbel.be

* Correspondence: dds@centexbel.be; Tel.: +32-92418684

Abstract: Polyurethane (PU) coatings are applied on technical textiles for their superior properties. Up to now, PU-coated textiles are not recycled at end of life. Landfilling is still the most occurring way of processing PU waste. Next to looking to sustainable routes for processing PU waste, there is the drive towards bio-based polymers. With this regard, a bio-based trigger degradable PU coating specifically designed for textiles was developed. The PU was characterized via FT-IR, TGA, and DSC. The performance of the coating was assessed by examining the mechanical properties and the resistance to hydrostatic pressure initially and after washing. The developed bio-based PU coatings had a high tensile strength, were waterproof, and had excellent wash fastness at 40 °C. The coating could be easily debonded from the textile by immersion in a tetra-n-butylammoniumfluoride solution. FT-IR and microscopic analysis indicated that the coating was completely removed and that the polyester fabric was not degraded.

Keywords: polyurethane; coating; bio-based; trigger degradable; textile

1. Introduction

Polyurethane (PU) is widely applied in several industries (coatings, foams, adhesives, sealants, and elastomers) due to its versatility. Although PU usage is widespread, PU waste is often landfilled. Indeed, PUs are not sensitive to biological or chemical degradation, and combustion could result in toxic by-products. Research is conducted to process PU at the end of life (EoL), especially in the case of foams and elastomers. Solvation and solvolysis are possible solutions to degrade PU. Most reported solvolysis processes to recycle PU include glycolysis, glycerolysis, and acidolysis. Urethane elastomer was degraded by cleaving C–N and C–O linkages via acid-assisted solvolysis. The process did not degrade polyether bonds, and the original used polyether polyol and the amine derivative of the used isocyanate (2,4-diaminotoluene) were recovered [1]. A similar process was reported to selectively degrade 2 K PU-based textile coatings [2]. Glycerolysis of PU foams and elastomers was studied. In both cases, a relevant part of recovered polyether and polyester polyol could be found in the glycerolysates. In the case of PU foam, replacement of 25% of the original polyol by the recovered polyol resulted in no significant changes in properties [3,4]. Acidolysis of PU, applying adipic acid in a microwave-assisted process, was reported. The recovered polyols could be re-used for producing PU foams [5]. Thermoset polyacrylate-urethane coatings were depolymerized using diethylene glycol catalyzed by KOH [6]. Glycolysis with ethylene glycol followed by hydrolysis of PU is reported. At the end of this multistage process, polyols and amines were recovered [7].

Next to solvolysis, degradation or debonding on demand using specifically designed trigger degradable polymers is examined. Triggers include mainly light (UV), pH, temperature, and chemicals. Polyurea with a photolabile 6-nitroveratroxyloxycarbonyl in the backbone was synthesized to encapsulate dyes. Upon radiation with UV light (365 nm), polyurea started to degrade, and the dye was released [8]. Polyurethane-urea (PUU) hydrogel films were synthesized bearing labile β -aminoacrylate bonds, which cleaved upon UV radiation [9]. Photo-triggered base-generating degradable PU was reported by Xu et al. Upon UV light irradiation (365 nm), a base was generated, which in turn initiated a base



Citation: De Smet, D.; Vanneste, M. Design of Debondable PU Coating for Degradation on Demand. *Coatings* **2024**, *14*, 731. <https://doi.org/10.3390/coatings14060731>

Academic Editors: Simona Căprărescu and Cristina Modrojan

Received: 6 May 2024

Revised: 27 May 2024

Accepted: 5 June 2024

Published: 7 June 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

propagated degradation process. This resulted in complete PU degradation without the need for continuous UV irradiation. The PU consisted of labile *o*-nitrobenzene diol and Fmoc-based diol [10]. A thermoset PU bearing cleavable acetal moieties for composite applications was synthesized. The PU could be degraded within 1 h in acid solution [11]. Acid-degradable PU particles with acetal groups for protein-based vaccines were synthesized. The acetal groups in the PU degraded at a pH of 5 [12]. Acid-degradable PU with boron-urethanes links and high mechanical strength was described. Because of the labile nature of the boron-urethane bonds, the PU could be degraded under mild acid conditions (0.1 M HCl/THF solution) at room temperature [13]. Vanillin based PU thermosets were completely degraded in alkaline solution, based on the degradation of the ester bonds of the vanillin-based diol [14]. Base-triggered self-amplifying degradable PU, incorporating base-sensitive Fmoc groups, was synthesized. A small amount of base initiated the self-propagating degradation [15]. Degradable, healable non-isocyanate polyurethane vitrimers were hydrolyzed and decarbonated in acid solution (1 M HCl), resulting in a 75% pure monomer [16]. Next to Fmoc-groups, silyl ethers are also used as protection groups in organic synthesis. By incorporating silyl ethers in a polymer backbone, triggered depolymerization could be obtained [17]. Thermally debondable PU adhesives, based on Diels–Alder segments, were reported [18]. A fluoride-degradable and thermally debondable PU adhesive based on *tert*-butyl dimethylsilyl protected cresol was synthesized. Upon exposure to tetra-butylammonium fluoride (TBAF) the polymer started to degrade, resulting in reduced adhesion. An analogue *tert*-butyl dimethylsilyl protected tri-benzyl alcohol was incorporated as a crosslinker in PU. Upon exposure to TBAF, loss in adhesion strength was observed [19,20]. However, upon degradation, the PU did not dissolve and therefore cannot be removed from the substrate.

Many reports of EoL solutions of PU focus on adhesives, foams, or elastomers and not on (textile) coatings. However, the majority of textile waste is burned or ends up in landfills, contributing to 2%–8% of greenhouse gas emissions, although many producers claim environmental benefits of their products [21]. This report describes the design of debond on demand bio-based PU for textile coatings to ease recycling of fabrics. Therefore, fluoride-sensitive moieties were incorporated in the PU backbone, which allow degradation at room temperature in the presence of tetra-*n*-butylammoniumfluoride (TBAF). This selective degradation of PU-coated textile allows to recycle the textile afterwards and to study the PU degradation products as building blocks for chemicals. Contrary to the use of a fluoride degradable crosslinker for PU, the incorporation of a silyl ether group in the PU backbone results in cleavage of the PU backbone upon exposure to TBAF solution, which in turn results in dissolving of the degraded products, even if the PU is crosslinked with conventional isocyanates. Next to the debond on demand potential, the PU was chemically characterized, and the properties were evaluated. Bio-based polyol Priplast 3172 was used to synthesize the PU. The bio-based content of the polyol is 39%, according to the supplier.

2. Materials and Methods

2.1. Materials

Bismuth neodecanoate, propanediol, tetra-*n*-butylammoniumfluoride (TBAF), dimethylol propionic acid (DMPA), and isophorone diisocyanate (IPDI) were bought from Merck. 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane (HBTMS) was purchased from Gelest. Tetrahydrofuran (THF) and methylethyl ketone (MEK) were bought from ChemLab, Zedelgem, Belgium. Respumit NF01, Edolan XCI, and Edolan XTP were supplied by Tanatex Chemicals, Ede, The Netherlands. Priplast 3172 was sampled by Cargill, Düsseldorf, Germany. Polyester woven fabric (105 g/m²) was acquired from Concordia Textiles, Waregem, Belgium.

2.2. Synthesis of Bio-Based Trigger Degradable PU Dispersion

The trigger-degradable PU was made in a flask equipped with a thermometer, mechanical stirrer, water condenser, and nitrogen inlet. Twenty grams of Priplast 3172 and

2.36 g of internal emulgator (DMPA) were weighed in the flask, and 60 mL of solvent (MEK) was added afterwards. The solution was heated at 50 °C for 20 min before the temperature was increased to 80 °C. Next, 0.06 g of bismuth neodecanoate was added, followed by the addition of 12.26 g of IPDI (OH:NCO ratio of 1) using a dropping funnel. Three hours later, 2 g of HBTMS was added. Finally, the reaction was cooled before adding 1.78 g of TEA. After dispersing the PU in deionized water, the solvent was evaporated under reduced pressure at 40 °C. The solid content of the dispersion was 40 wt%. A control bio-based PU dispersion was produced using propanediol as a chain extender. The composition of the different bio-based PUDs is given in Table 1.

Table 1. Composition of bio-based trigger-degradable PUD and control PUD.

	Priplast 3172 (g)	IPDI (g)	DMPA (g)	HBTMS (g)	Propanediol (g)
Control PUD	20	24.34	2.36	-	2
Trigger degradable PUD	20	12.26	2.36	2	-

2.3. Fabric Coating

Fifty grams of PU dispersion and 2.5 g of Edolan XCI (polyisocyanate-based crosslinker) were mixed. Then, 0.5 g of Respumit NF01 was subsequently added to avoid foaming of the formulation, and the viscosity of the formulation was adjusted by adding Edolan XTP. A polyester fabric was coated with the formulation. 3 layers of 100 µm were coated. In between coating the different layers, the coating was dried 1 min at 110 °C and 2 min at 155 °C. To examine the film properties (mechanical and thermal properties) of the PUD, the corresponding formulations were made but without the addition of a crosslinker and coated (1 layer of 100 µm) on a release paper.

2.4. Characterisation

FT-IR analysis was performed using a Nicolet 6700 spectrometer from ThermoFisher Scientific, Waltham, MA, USA to characterize the synthesized PUD and the degradation PU. The morphology of the coated textile before and after exposure to fluoride ions was visualized using field emission gun scanning electron microscopy (FEG-SEM) (JSM 7600 F from JEOL, Tokyo, Japan). The samples were coated with palladium to avoid charging.

Thermogravimetric analysis of the PU and (coated) PET fabric was performed in air in the range of 30 to 600 °C via a Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA). The ramp rate was set at 10 °C/min. The thermograms were analyzed using Universal Analysis Software v5.5.24.

Differential scanning calorimetry (DSC) analysis of the PU and (coated) PET fabric was performed to determine the glass transition temperature (T_g) and melting point (T_m) in the range of −50 °C to 200 °C using TA Instruments Discovery DSC2500. The samples were conditioned at 23 °C and 50% relative humidity. The heating and cooling rate was set at 10 °C/min.

Elongation at break and tensile strength were determined according to ISO 13934-1 [22] using an Instron electronic fabric tension tester. The tension loading speed was set at 100 mm/min. The water barrier properties were measured following the ISO 811 standard [23] with a Textest FX 800 apparatus. The same test was also performed after 10 domestic washing cycles at 30 °C and 40 °C followed by drying at ambient temperature (ISO 6330) [24] to assess wash fastness.

The degradation of the PU coating on coated fabric was studied by cutting the coated fabric into small pieces and stirring these for 2 h in 200 mL of a 2% TBAF solution in THF at room temperature (Figure 1). Afterwards, the recovered fabric pieces were washed in MEK and water and dried overnight at 40 °C.

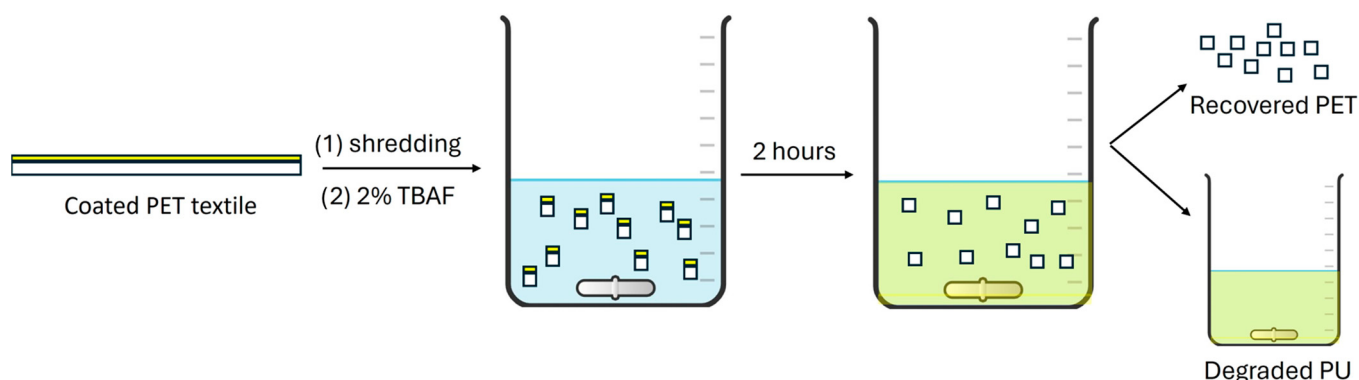


Figure 1. Scheme of debonding process of PU coating from textile.

3. Results

3.1. Structural Characterisation of PU Coating

The trigger-degradable PU coatings were characterized with FT-IR (Figure 2). The absence of the $\text{N}=\text{C}=\text{O}$ stretch revealed that the PU synthesis was successful. The presence of urethane bands is confirmed by the appearance of NH bands and the absence of peaks corresponding to OH and isocyanate moieties.

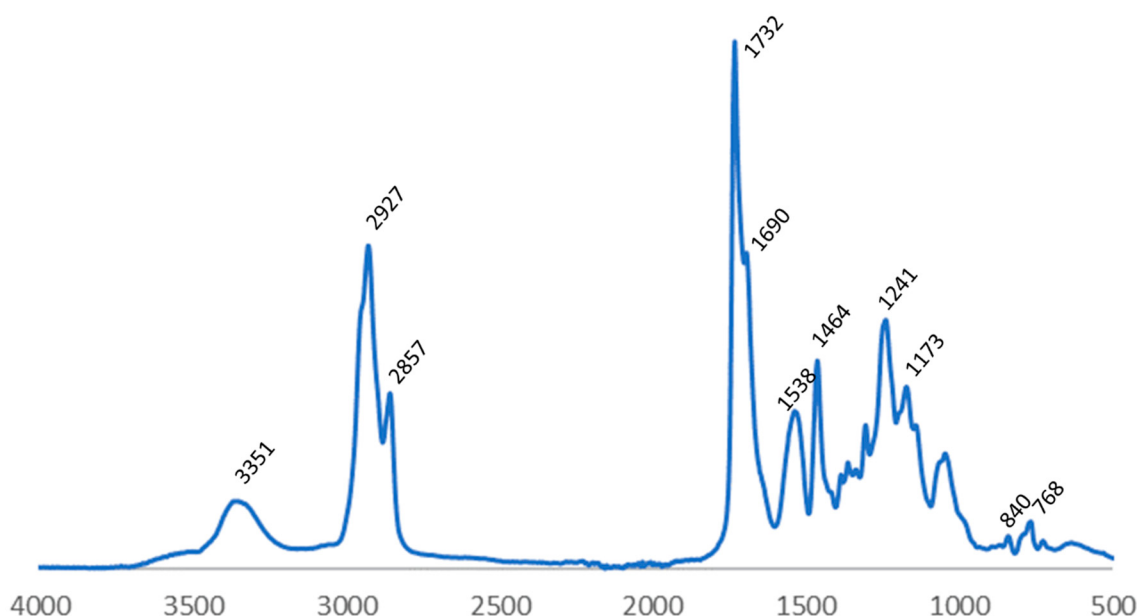


Figure 2. FT-IR spectrum of trigger-degradable PU.

The band at 3351 cm^{-1} corresponds to NH stretching, while the band at 1690 cm^{-1} corresponds to $\text{C}=\text{O}$ stretching of the urethane groups. The signals at 2857 cm^{-1} and 2927 cm^{-1} are assigned to $-\text{CH}_2$ stretching, while other modes of $-\text{CH}_2$ vibrations are allocated to the band at 1464 cm^{-1} . The peak at 1538 cm^{-1} is characteristic for PU and is attributed to N-H bending and C-N stretching in polyurethanes. The peak at 1241 cm^{-1} corresponds to C-O-C urethane vibrations, while the peak at 1173 cm^{-1} is allocated to C-O-C vibrations of esters. The small peak at 768 cm^{-1} is assigned to COO urethane vibrations [25–28]. The small peak at 840 cm^{-1} is allocated to $\text{CH}_3\text{-Si-CH}_3$ asymmetric deformation vibrations.

3.2. Properties of the Coating

Elongation and tensile strength of the coating were measured according to ISO 13934-1 (Figure 3). The elongation and tensile strength of trigger-degradable (crosslinked) bio-based

PU coating are given in Table 2. The addition of a crosslinker resulted in a more dense and rigid network, which in turn results in lower elongation at break. The control PU coating had a much lower elongation and tensile strength of 3.2% and 3 MPa, respectively. Indeed, the control PUD had a higher level of hard segments in the backbone due to the higher isocyanate content, resulting in lower mechanical properties.

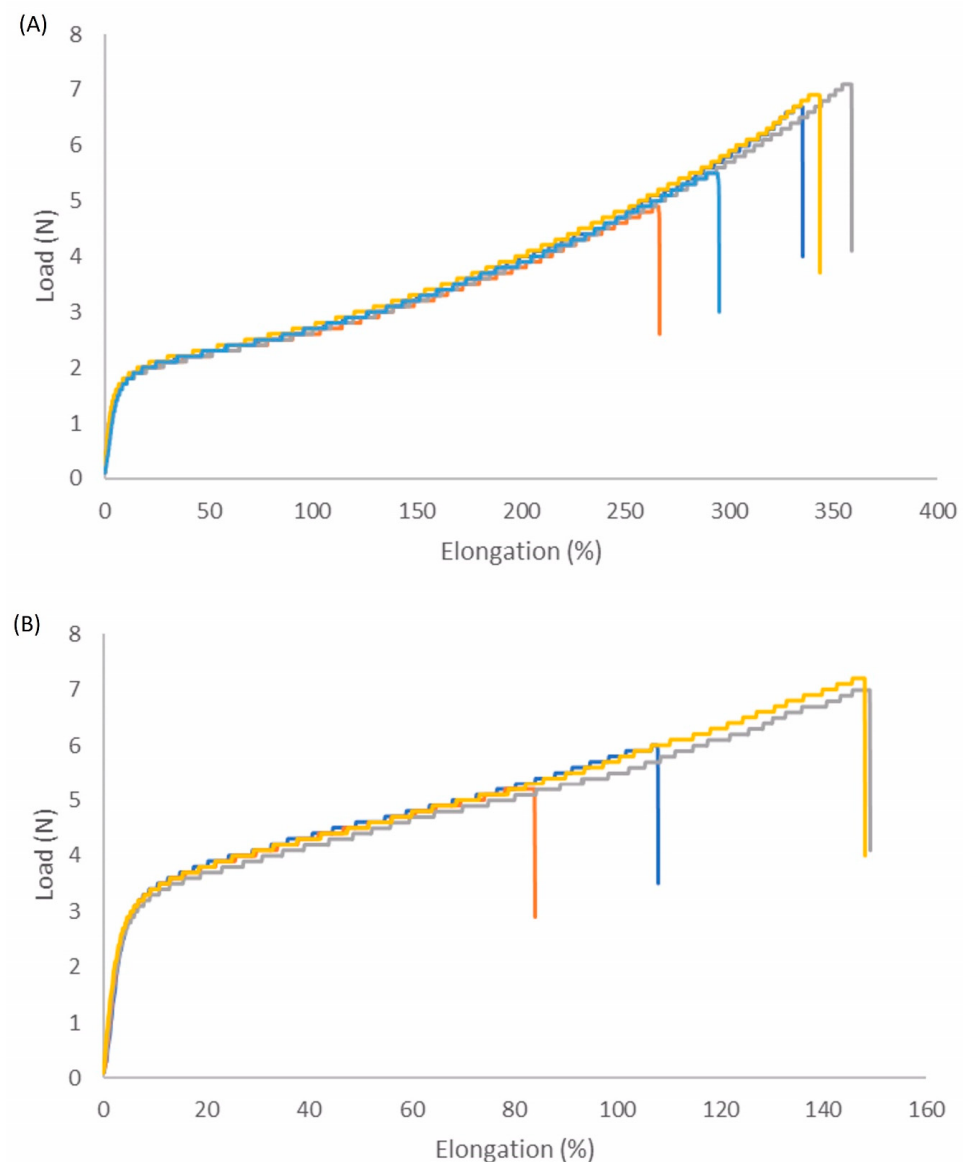


Figure 3. Tensile curves of trigger-degradable PU films without crosslinker (A) and with crosslinker (B). The different colors represent each a tensile measurement.

Table 2. Mechanical properties data of bio-based trigger degradable PU.

	Tensile Strength (MPa)	Elongation (%)
Trigger degradable PU	15	319
Crosslinked trigger degradable PU	16	122

The water barrier properties of bio-based PUD-coated polyester fabric initially and after 10 domestic laundry cycles were evaluated. The resistance to hydrostatic pressure was 1000 mbar, which is the maximum value that could be measured. After 10 domestic laundry cycles at 30 and 40 °C, the water barrier properties were not altered, indicating

that the developed coating can be applied for waterproof textiles with good wash fastness such as rain wear.

The thermal degradation of the trigger degradable PU was characterized by TGA in air up to 600 °C (Figure 4). The PU started to degrade above 200 °C, but at the end of the analysis, almost no residue was found. Degradation of PU occurred in three steps: Initial degradation is attributed to dissociation of the urethane segments, while second thermal degradation is associated with degradation of linear hydrocarbon chains and ester groups. Finally, C=C bonds were cleaved in the last degradation step [29–31].

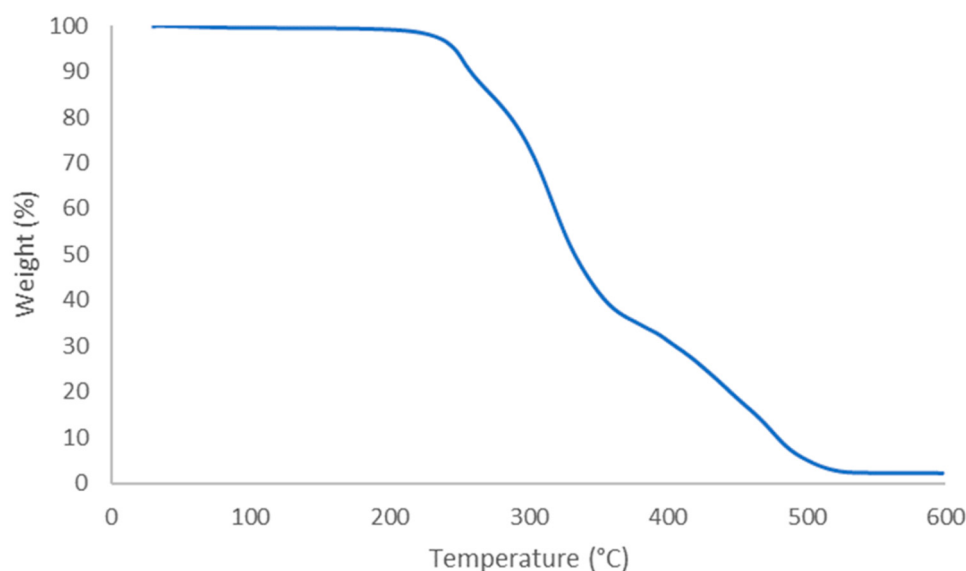


Figure 4. TGA of trigger-degradable PU.

The thermal properties of the developed PU were further characterized by DSC (Figure 5). Glass transition temperature was situated approximately at 1 °C, while melting point during the second heating was at 44 °C. Crystallization was observed at −13 °C.

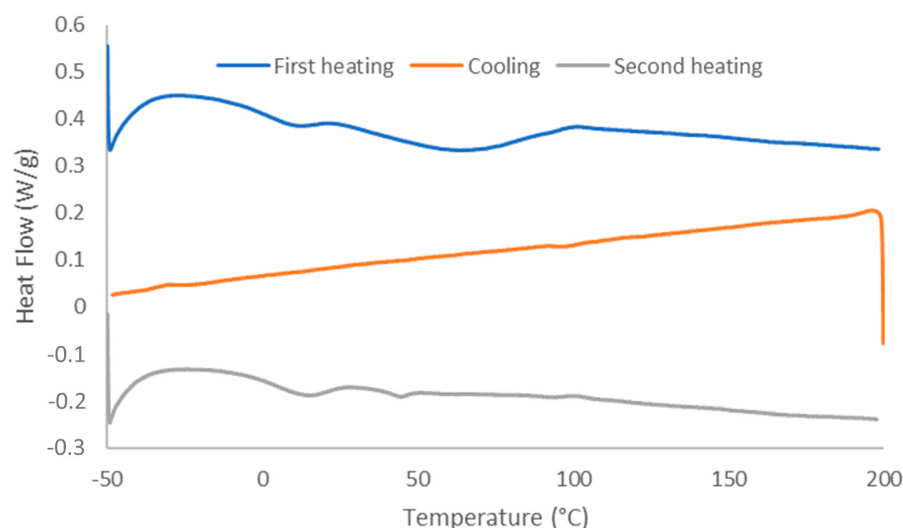


Figure 5. DSC of trigger-degradable PU.

3.3. Degradation Study

PU films and PU coated PET pieces were immersed in a solution of 2% TBAF in THF. After 2 h, the pieces were rinsed in MEK and water and dried at room temperature. Films of both control PU and the developed trigger degradable PU were tested. The trigger

degradable PU dissolved completely, while the control PU did not dissolve or disintegrate (Figure 6). Indeed, the control PU did not have silyl ether moieties in the polymer backbone, which are sensitive to fluoride ions.

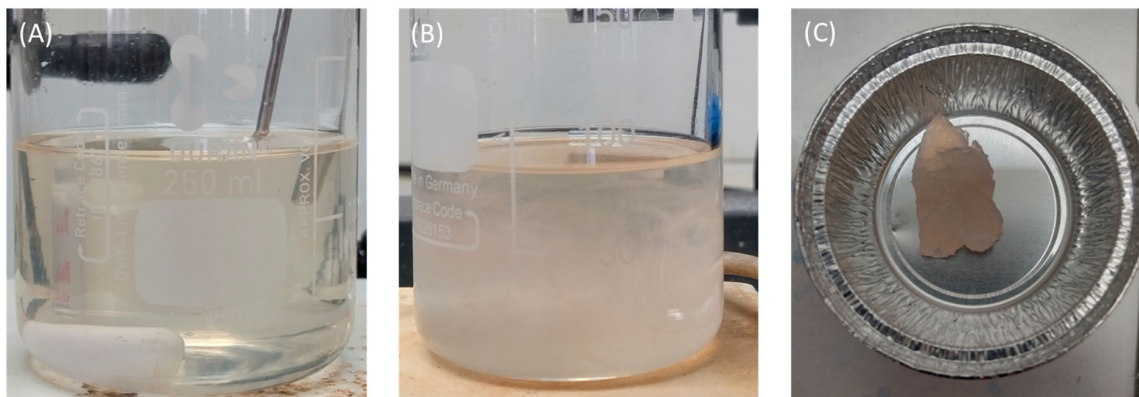


Figure 6. (A) Transparent solution of trigger degradable PU in 2% TBAF in THF after 2 h, (B) turbid solution of control PU in 2% TBAF after 2 h, and (C) control PU recovered after 2 h in 2% TBAF in THF.

Figure 7 shows the IR spectra of the trigger degradable (debondable) PU before and after immersion in TBAF solution. In the spectrum of both PU, characteristic PU peaks are observed: C=O stretching of the urethane groups (1690 cm^{-1}), N-H bending and C-N stretching (1538 cm^{-1}), C-O-C urethane vibrations (1241 cm^{-1}), and COO urethane vibrations (768 cm^{-1}). The signals at 2857 cm^{-1} , 2927 cm^{-1} and 1464 cm^{-1} are assigned to $-\text{CH}_2$ stretching and $-\text{CH}_2$ vibrations. The signal at 1173 cm^{-1} is allocated to C-O-C vibrations of esters. The band at 840 cm^{-1} is allocated to $\text{CH}_3\text{-Si-CH}_3$ asymmetric deformation vibrations [32]. Contrary to the IR spectrum of the degradable PU before immersion in TBAF, a new peak appeared in the IR spectrum of the degraded PU (after immersion in TBAF). This small signal at 886 cm^{-1} is originating from Si-F stretching. The degraded PU also showed a more intense and broadened peak above 3000 cm^{-1} due to OH stretching. These findings support the hypothesis that degradation of PU and consequently the solvation is caused by the fluoride ion, which readily attacks the silicon and cleaves the Si-O bond in the PU backbone, while the urethane groups are less prone to degradation.

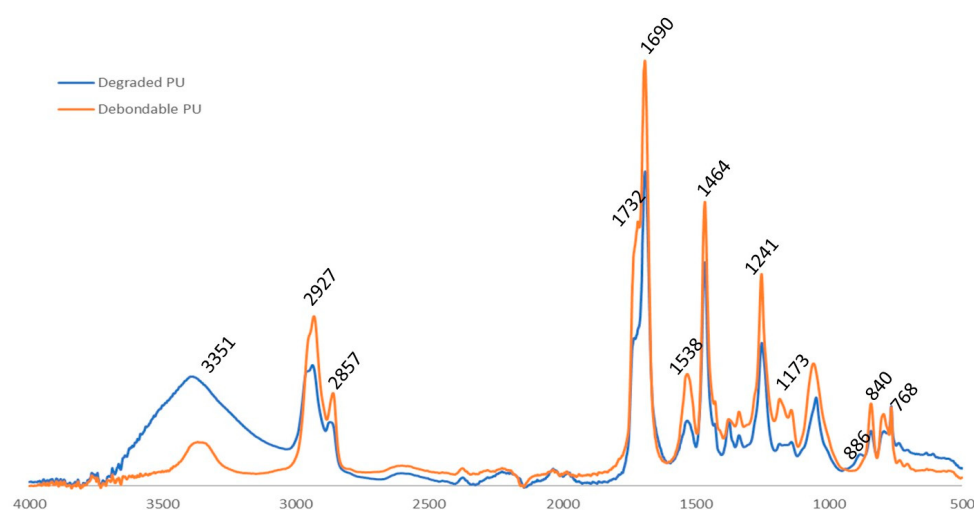


Figure 7. IR spectra of trigger-degradable PU before (debondable PU) and after (degraded PU) immersion in TBAF solution.

3.4. Characterisation of Recovered PET Fabric

FT-IR spectra of recovered polyester fabric and virgin polyester are shown in Figure 8. The spectra were very similar, demonstrating that the fabric, recovered upon immersion in TBAF solution, was not degraded. The signal at 2966 cm^{-1} is originating from C–H stretching, while the band at 1714 cm^{-1} can be attributed to C=O stretching. The peaks at 1578 , and 1505 cm^{-1} are corresponding to aromatic C=C stretching. The signals at 1471 , 1409 , and 1339 cm^{-1} are allocated to C–O stretching of the OH group and bending and wagging of the ethylene glycol part. The peak at 1244 cm^{-1} is corresponding to C–O stretching of esters. Bands at 1098 and 1017 cm^{-1} can be allocated to methylene group and ester C–O bond vibrations. Peaks at 970 , 872 and 847 cm^{-1} are attributed to the aromatic moieties. The band at 724 cm^{-1} is originating from the interaction of ester groups with benzene rings [33,34]. The mechanical properties of the recovered PET fabric and the virgin PET were measured and compared (Table 3). A small decrease in the tensile strength was observed, while the elongation remained unchanged after immersion in 2% TBAF in THAF and rinsing in MEK and water.

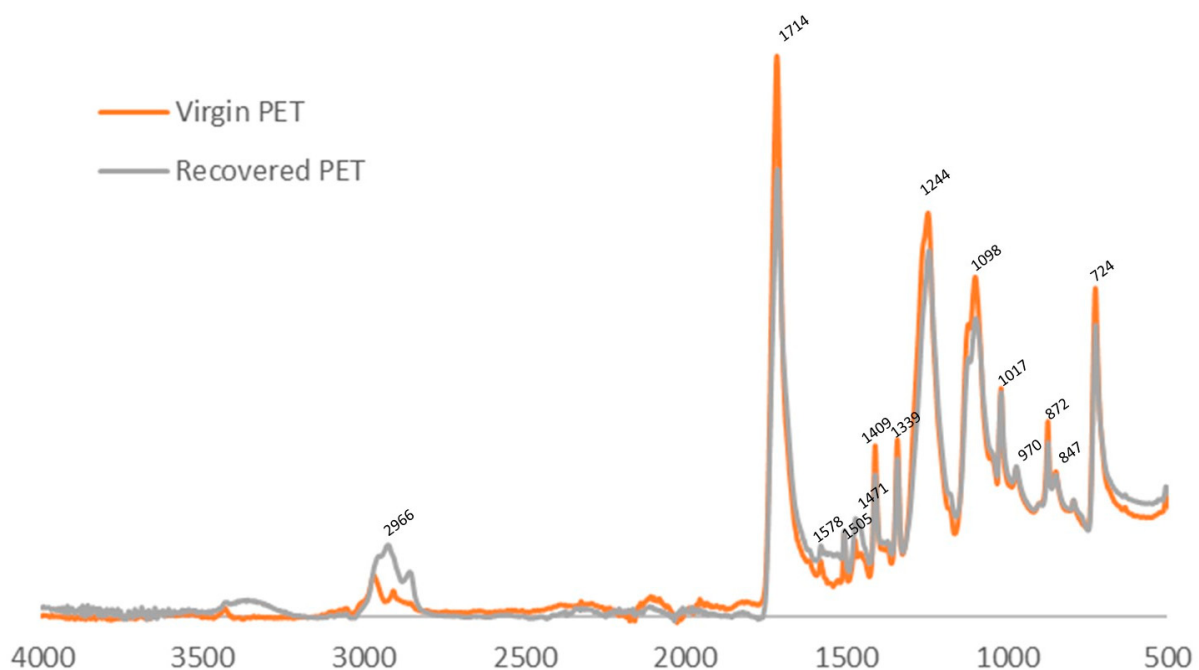


Figure 8. IR spectrum of virgin and recovered PET fabric.

Table 3. Mechanical properties of virgin and recovered PET.

	Tensile Strength (MPa)	Elongation (%)
Virgin PET	120	37
Recovered PET	110	37

After immersion in TBAF of debondable PU-coated PET fabric, the surfaces of virgin and recovered PET fabric were analyzed with SEM, and the pictures are exhibited in Figure 9. SEM analysis indicated that the PU coating was removed after immersion in TBAF, and no degradation of the PET fibers was observed.

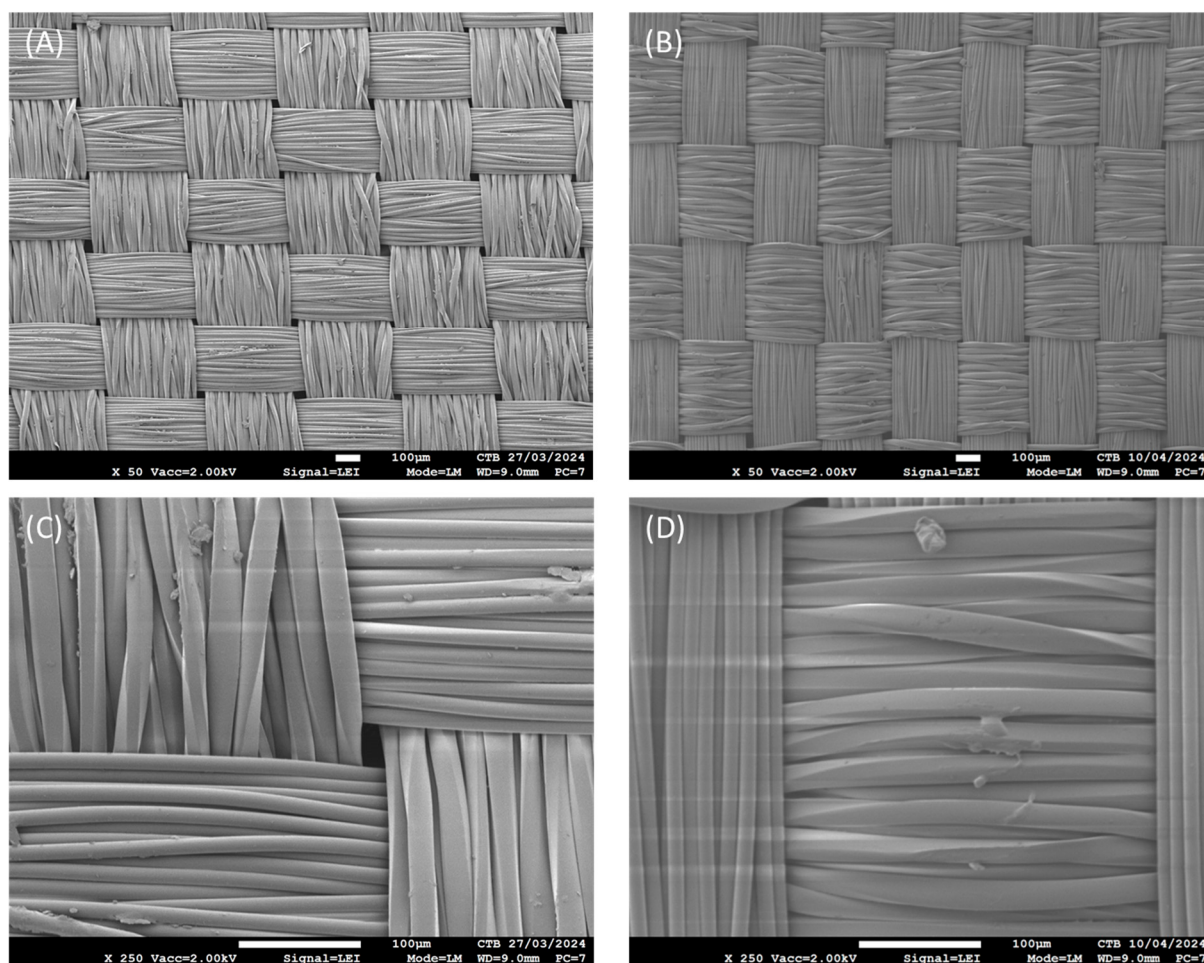


Figure 9. SEM images of virgin PET ((A): magnification of 50 and (C): magnification of 250) and recovered PET fabric ((B): magnification of 50 and (D): magnification of 250).

3.5. Thermal Properties of Recovered PET Fabric

TGA analysis of the PET fabric after removing the coating was performed to evaluate possible alternation of the thermal stability of the PET fabric during the degradation test due to degradation of PET or remaining residue. The TGA curves of virgin PET and recovered PET are shown in Figure 10. Both recovered and virgin PET exhibited a similar two-step thermal degradation. The biggest weight decrease appeared in the temperature range of 300 to 450 °C. During the first degradation step, ester links are broken. The thermal degradation leads to cyclic oligomers due to intramolecular backbiting and hydrogen transfer. Terephthalic acid, benzoic acid, and vinyl benzoate are produced amongst other compounds. Further degradation of aromatic cyclic compounds occurred during the second degradation [35,36]. Recycled PET tends to decompose at higher temperatures in comparison to virgin material. Indeed, the onset temperature, at 5% mass loss, changed from 348 to 362 °C.

Table 4 displays the glass transition temperature (T_g), melting temperature (T_m), and crystallinity degree (X_c), obtained via DSC, of virgin and recovered PET fabric. The virgin and recovered polyester had a slightly different T_g and T_m (Figures 11 and 12). A small decrease in X_c , T_g , and T_m was noticed for the recovered fabric. However, the increased crystallinity had no significant influence on the mechanical properties since elongation and tensile strength of recovered and original PET were similar.

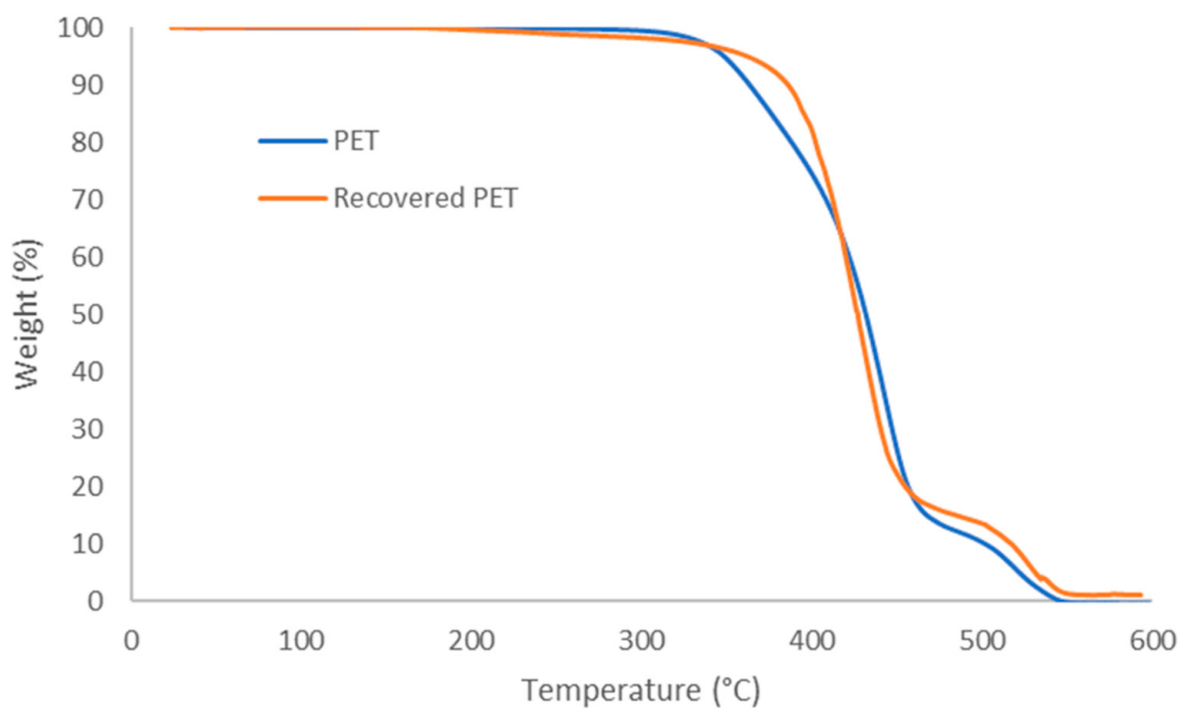


Figure 10. TGA of virgin and recovered PET fabric.

Table 4. T_g , T_m , and X_c of virgin and recycled PET obtained by DSC.

	T_g (°C)	T_m (°C)	X_c (%)
Virgin PET	83	252	39
Recycled PET	73	244	35

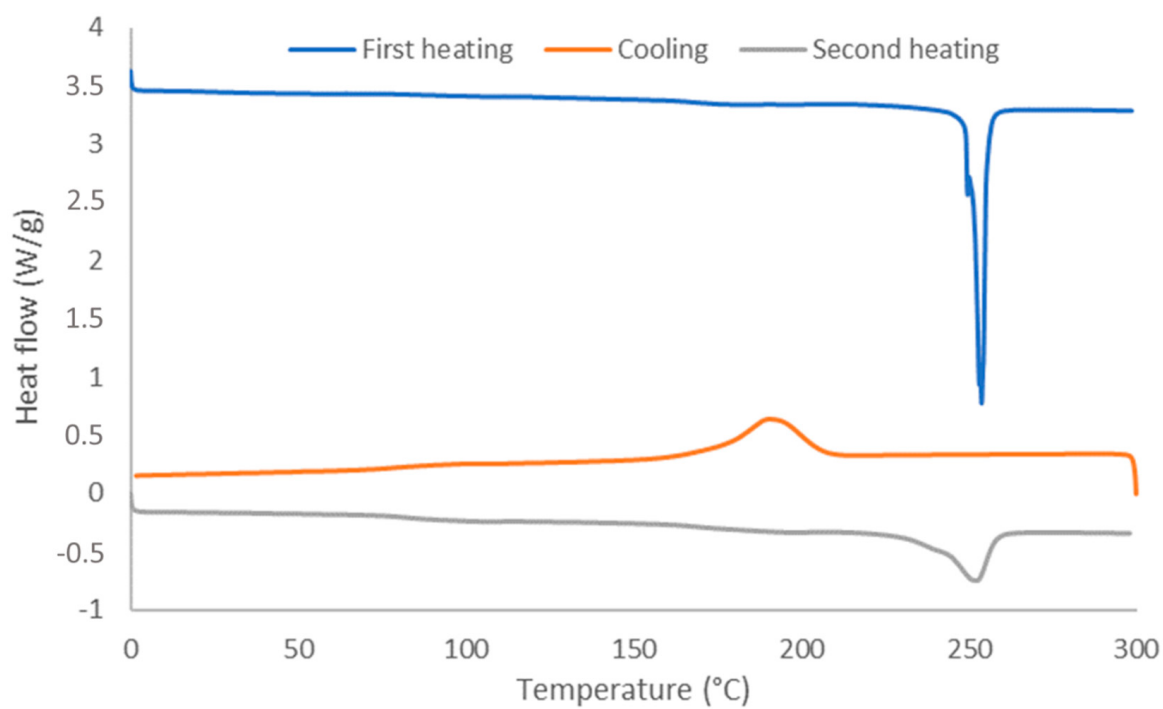


Figure 11. DSC curve of virgin PET fabric.

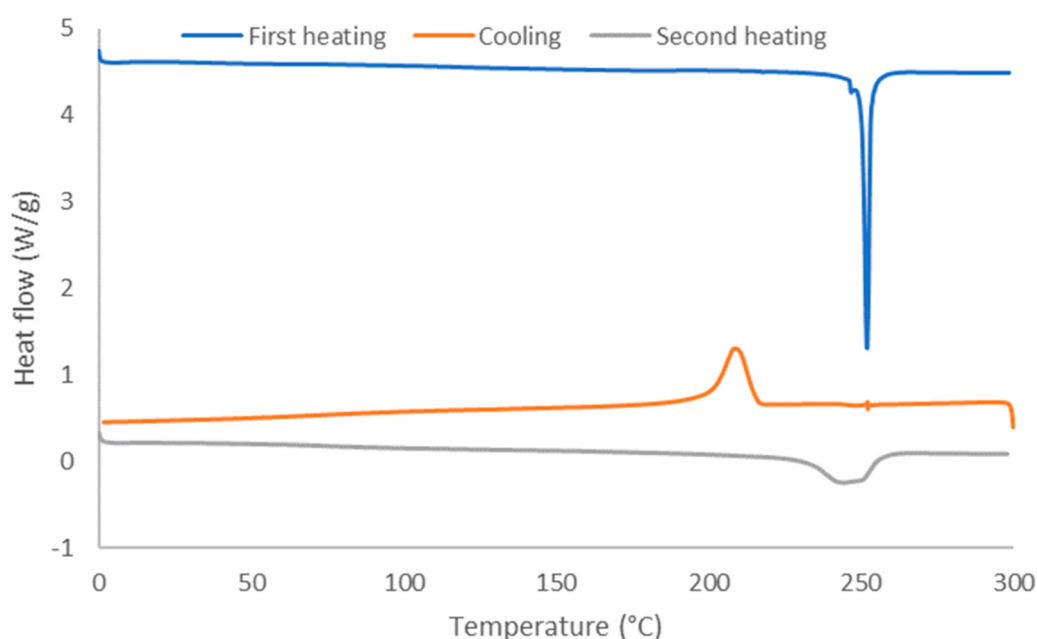


Figure 12. DSC curve of recovered PET fabric.

4. Discussion

A trigger-degradable PU was developed that is suited for waterproof textile applications since the coating is waterproof and survives at least 10 domestic washing cycles. The coating could easily be removed at room temperature in the presence of TBAF, but still requires organic solvent. In future research, the conversion of the recovered PET into new PET-based textiles needs to be assessed, as well as (chemical) recycling of the degraded PU. There is a variety of reports about debondable adhesives to facilitate disassembly of materials, but limited reports for coatings. Although removal of coatings is often necessary to recycle materials. This is the first report describing the design of debond on demand bio-based PU for textile coatings. Next to textile coatings, other applications of the developed PU could include other types of coatings (e.g., automotive), sealants, and foams, but might require adaptation of the PU synthesis, such as the selection of other types of polyol depending on the final requirements of the PU.

UV radiation and temperatures are the most applied debonding triggers. However, a major limitation with respect to these triggers, is unintended exposure and thus degradation of materials before EoL [37]. Since the degradation of the developed PU is triggered by fluoride ions and not by UV light or temperature, like described in many other manuscripts, the PU is possibly suited for outdoor or automotive applications [8–10]. Indeed, Thomas et al. discussed the application of PU coatings on polycarbonate and thermoplastic olefin substrates in automotive [38]. However, the main issue for industrial implementation could be the cost of HBTMS, which is much higher compared to the cost of isocyanates and polyols. Although it is used in small quantities, it results in a significantly higher price of the developed PU compared to conventional PU used for coatings. The synthesis of a silyl ether-based diol at high yield and purity and at an affordable price would be a leap forward. Within that regard, Barbra et al. described the synthesis and implementation of silyl ether-based diol. However, the yield of the synthesis was low, and the process involved the use of toxic products (imidazole and DMF) and expensive products as well [20].

5. Conclusions

Bio-based PU textile coatings, developed for triggerable degradation, were synthesized and coated on polyester fabric. The PU exhibited a high tensile strength, moderate elongation, excellent water barrier properties, and good wash fastness. The developed bio-based and trigger-degradable PU coating is suitable for waterproof and wash-resistant

textile applications. The coating could be easily debonded from the textile by immersion in a tetra-n-butylammoniumfluoride solution. The polyester fabric was, before and after removing the coating, characterized via FT-IR, TGA, and DSC. The polyester showed no degradation during the debonding of the PU coating, and no coating impurities were found on the surface of the recovered fabric.

Author Contributions: Conceptualization, D.D.S.; methodology, D.D.S.; validation, D.D.S.; formal analysis, D.D.S.; investigation, D.D.S.; resources, D.D.S.; data curation, D.D.S.; writing—original draft preparation, D.D.S.; writing—review and editing, 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 Debond, funded by Flanders Innovation & Entrepreneurship (HBC.2022.0245).

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: Authors David De Smet and Myriam Vanneste were employed by the company Centexbel. The authors declare no conflict of interest.

References

- Wang, Y.; Song, H.; Wang, J.; Wang, Y.; Jia, S.; Deng, T.; Hou, X. Controllable degradation of polyurethane elastomer via selective cleavage of C-O and C-N bonds. *J. Clean. Prod.* **2018**, *176*, 873–879. [\[CrossRef\]](#)
- De Smet, D.; Verjans, J.; Vanneste, M. Selective Solvolysis of Bio-Based PU-Coated Fabric. *Polymers* **2022**, *14*, 5452. [\[CrossRef\]](#) [\[PubMed\]](#)
- Datta, J.; Kopczyńska, P.; Simón, D.; Rodríguez, J. Thermo-Chemical Decomposition Study of Polyurethane Elastomer through Glycerolysis Route with Using Crude and Refined Glycerine as a Transesterification Agent. *J. Polym. Environ.* **2018**, *26*, 166–174. [\[CrossRef\]](#)
- Jutrzenka Trzebiatowska, P.; Beneš, H.; Datta, J. Evaluation of the glycerolysis process and valorisation of recovered polyol in polyurethane synthesis. *React. Funct. Polym.* **2019**, *139*, 25–33. [\[CrossRef\]](#)
- Grdadolnik, M.; Drinčić, A.; Oreški, A.; Onder, O.; Utróša, P.; Pahovnik, D.; Žagar, E. Insight into Chemical Recycling of Flexible Polyurethane Foams by Acidolysis. *ACS Sustain. Chem. Eng.* **2022**, *10*, 1323–1332. [\[CrossRef\]](#) [\[PubMed\]](#)
- Sánchez-Cadena, L.; Tersac, G.; Coqueret, X.; Gamiño-Arroyo, Z. Solvolysis of acrylate-urethane coatings cured by electron-beam and UV radiation. *Prog. Org. Coat.* **2021**, *136*, 105268–105633. [\[CrossRef\]](#)
- Zahedifar, P.; Pazdur, L.; Vande Velde, C.; Billen, P. Multistage chemical recycling of polyurethanes and dicarbamates: A glycolysis–hydrolysis demonstration. *Sustainability* **2021**, *13*, 3583. [\[CrossRef\]](#)
- Dispinar, T.; Colard, C.; Du Prez, F. Polyurea microcapsules with a photocleavable shell: UV-triggered release. *Polym. Chem.* **2013**, *4*, 763. [\[CrossRef\]](#)
- Paula, C.; Pereira, P.; Coelho, J.; Fonseca, A.; Serra, A. Development of light-degradable poly(urethane-urea) hydrogel films. *Mater. Sci. Eng. C* **2021**, *131*, 112520. [\[CrossRef\]](#)
- Xu, Y.; Morado, E.; Zimmerman, S. Construction from destruction using a photo-triggered self-propagating degradable polyurethane as a one-pot epoxy. *Polym. Chem.* **2020**, *11*, 6215. [\[CrossRef\]](#)
- Wang, B.; Ma, S.; Xu, X.; Li, Q.; Yu, T.; Wang, S.; Yan, S.; Liu, Y.; Zhu, J. High-Performance, Biobased, Degradable Polyurethane Thermoset and Its Application in Readily Recyclable Carbon Fiber Composites. *ACS Sustain. Chem. Eng.* **2020**, *8*, 11162–11170. [\[CrossRef\]](#)
- Bachelder, E.; Beaudette, T.; Broaders, K.; Paramonov, S.; Dashe, J.; Fréchet, J. Acid-degradable polyurethane particles for protein-based vaccines: Biological evaluation and in vitro analysis of particle degradation products. *Mol. Pharm.* **2008**, *5*, 876. [\[CrossRef\]](#) [\[PubMed\]](#)
- Bao, C.; Zhang, X.; Yu, P.; Li, Q.; Qin, Y.; Xin, Z. Facile fabrication of degradable polyurethane thermosets with high mechanical strength and toughness via the cross-linking of triple boron–urethane bonds. *J. Mater. Chem. A* **2021**, *9*, 22410. [\[CrossRef\]](#)
- Zhao, D.; Liang, X.; Wang, J.; Du, J.; Zhu, Y. Vanillin-Based Degradable Polyurethane Thermosets Demonstrating High Bio-Content and Mechanical Properties. *ACS Appl. Polym. Mater.* **2023**, *5*, 4536. [\[CrossRef\]](#)
- Xu, Y.; Sen, S.; Wu, O.; Zhong, X.; Ewoldt, R.; Zimmerman, S. Base-triggered self-amplifying degradable polyurethanes with the ability to translate local stimulation to continuous long-range degradation. *Chem. Sci.* **2020**, *11*, 3326. [\[CrossRef\]](#) [\[PubMed\]](#)
- Wu, H.; Jin, B.; Wang, H.; Wu, W.; Cao, Z.; Wu, J.; Huang, G. A Degradable and Self-Healable Vitriimer Based on Non-isocyanate Polyurethane. *Front. Chem.* **2020**, *8*, 585569. [\[CrossRef\]](#) [\[PubMed\]](#)

17. Bols, M.; Pedersen, C. Silyl-protective groups influencing the reactivity and selectivity in glycosylations. *Beilstein J. Org. Chem.* **2017**, *13*, 93. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Carbonell-Blasco, M.; Moyano, M.; Hernández-Fernández, C.; Sierra-Molero, F.; Pastor, I.; Alonso, D.; Arán-Aís, F.; Orgilés-Calpena, E. Polyurethane Adhesives with Chemically Debondable Properties via Diels–Alder Bonds. *Polymers* **2024**, *16*, 21. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Babra, T.; Trivedi, A.; Warriner, C.; Bazin, N.; Castiglione, D.; Sivoir, C.; Hayes, W.; Greenland, B. Fluoride degradable and thermally debondable polyurethane based adhesive. *Polym. Chem.* **2017**, *8*, 7207. [\[CrossRef\]](#)
20. Babra, T.; Warriner, C.; Bazin, N.; Hayes, W.; Greenland, W. A fluoride degradable crosslinker for debond-on-demand polyurethane based crosslinked adhesives. *Mater. Today Commun.* **2021**, *26*, 101777. [\[CrossRef\]](#)
21. Thomas, J.; Patil, R.S.; Patil, M.; John, J. Addressing the Sustainability Conundrums and Challenges within the Polymer Value Chain. *Sustainability* **2023**, *15*, 15758. [\[CrossRef\]](#)
22. ISO 13934-1:2013; Textiles—Tensile Properties of Fabrics. Part 1: Determination of Maximum Force and Elongation at Maximum Force Using the Strip Method. ISO: Geneva, Switzerland, 2013.
23. ISO 811:2018; Textiles—Determination of Resistance to Water Penetration—Hydrostatic Pressure Test. ISO: Geneva, Switzerland, 2018.
24. ISO 6330:2021; Textiles—Domestic Washing and Drying Procedures for Textile Testing. ISO: Geneva, Switzerland, 2021.
25. Wilhelm, C.; Gardette, J.-L. Infrared analysis of the photochemical behaviour of segmented polyurethanes: 1. Aliphatic poly(ester-urethane). *Polymer* **1997**, *38*, 4019. [\[CrossRef\]](#)
26. Irusta, L.; Fernandez-Berridi, J. Aromatic poly(ester-urethanes): Effect of the polyol molecular weight on the photochemical behavior. *Polymer* **2000**, *41*, 3297. [\[CrossRef\]](#)
27. Coates, J. *Interpretation of Infrared Spectra: A Practical Approach in Encyclopedia of Analytical Chemistry*; Meyers, R., Ed.; Wiley: Hoboken, NJ, USA, 2000; p. 10815.
28. Kaushiva, B.; McCartney, S.; Rossmly, G.; Wilkes, G. Surfactant level influences on structure and properties of flexible slabstock polyurethane foams. *Polymer* **2000**, *41*, 285. [\[CrossRef\]](#)
29. Ahmad, S.; Zafar, F.; Sharmin, E.; Garg, N.; Kashif, M. Synthesis and characterization of corrosion protective polyurethane-fattyamide/silica hybrid coating material. *Prog. Org. Coat.* **2012**, *73*, 112. [\[CrossRef\]](#)
30. Anand, A.; Kulkarni, R.; Gite, V. Preparation and properties of eco-friendly two pack PU coatings based on renewable source (sorbitol) and its property improvement by nano ZnO. *Prog. Org. Coat.* **2012**, *74*, 764. [\[CrossRef\]](#)
31. Marathe, R.; Tatiya, P.; Chaudhari, A.; Lee, J.; Mahuliker, P.; Sohn, D.; Gite, V. Neem acetylated polyester polyol—Renewable source based smart PU coatings containing quinoline (corrosion inhibitor) encapsulated polyurea microcapsules for enhance anticorrosive property. *Ind. Crop. Prod.* **2015**, *77*, 239–250. [\[CrossRef\]](#)
32. Yu, L.; Zhang, C.-C. Synthesis of 1,3-Bis(4-Hydroxybutyl)tetramethyldisiloxane and α,ω -Bis(4-Hydroxybutyl)-polydimethylsiloxane. *Iran. Polym. J.* **2007**, *16*, 153.
33. Holland, B.; Hay, J. The thermal degradation of PET and analogous polyesters measured by thermal analysis—Fourier Transform infrared spectroscopy. *Polymer* **2002**, *43*, 1835–1847. [\[CrossRef\]](#)
34. dos Santos Pereira, A.; da Silva, M.; Lima Júnior, E.; dos Santos Paula, A.; Tommasini, F. Processing and characterization of PET composites reinforced with geopolymer concrete waste. *Mater. Res.* **2017**, *20*, 411–420. [\[CrossRef\]](#)
35. Miandad, R.; Rehan, M.; Barakat, M.; Aburizaiza, A.; Khan, H.; Ismail, I.; Dhavamani, J.; Gardy, J.; Hassanpour, A.; Nizami, A.-S. Catalytic pyrolysis of plastic waste: Moving toward pyrolysis based biorefineries. *Front. Energy Res.* **2019**, *7*, 27. [\[CrossRef\]](#)
36. Sustaita-Rodríguez, J.; Medellín-Rodríguez, F.; Olvera-Mendez, D.; Gimenez, A.; Luna-Barcenas, G. Thermal Stability and Early Degradation Mechanisms of High-Density Polyethylene, Polyamide 6 (Nylon 6), and Polyethylene Terephthalate. *Polym. Eng. Sci.* **2019**, *59*, 2016–2023. [\[CrossRef\]](#)
37. Mulcahy, K.; Kilpatrick AHarper, G.; Walton, A.; Abbott, A. Debondable adhesives and their use in recycling. *Green Chem.* **2022**, *24*, 36–61. [\[CrossRef\]](#)
38. Thomas, J.; Patil, R.S.; John, J.; Patil, M. A Comprehensive Outlook of Scope within Exterior Automotive Plastic Substrates and Its Coatings. *Coatings* **2023**, *13*, 1569. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.