

# Polydimethylsiloxane containing waterborne hydrophobic polyurethane coatings with good adhesion to metals: synthesis and characterization

Aarón Pérez Das Dores<sup>a,b</sup>, Oihane Llorente<sup>a</sup>, Loli Martín<sup>c</sup>, Alba González<sup>a</sup>, Lourdes Irusta<sup>a</sup>

<sup>a</sup>POLYMAT, Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, University of the Basque Country UPV/EHU, Avda. Tolosa 72, 2018, Donostia-San Sebastián, Spain

<sup>b</sup>Universitat Rovira i Virgili, Departament de Química Analítica i Química Orgànica, Campus Sescelades Marcel·lí Domingo 1, 43007, Tarragona, Spain

<sup>c</sup>Macrobehaviour-Mesostructure-Nanotechnology SGiker Service, Faculty of Engineering, University of the Basque Country UPV/EHU, Plaza Europa 1, 20018 Donostia-San Sebastián, Spain.

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### **Abstract**

Waterborne polyurethanes (WPU) are of great importance in the industrial field as adhesives and coatings due to reduced use of organic solvents in their formulations. One of the main drawbacks of these formulations is their high hydrophilic character. In order to this problem to be solved, in this work siloxane groups were introduced in the soft segment. Thus, the synthesis of polyurethane dispersions varying the proportions of the polyols (poly- $\epsilon$ -caprolactone (PCL) and polydimethylsiloxane (PDMS)) was carried out following the acetone process in three stages: the polyurethane synthesis, water dispersion of the polymer and acetone removal. The reactions were monitored by Infrared Spectroscopy (FTIR) and the particle size was determined by Dynamic Light Scattering (DLS). Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Size Exclusion Chromatography-Gel Permeation Chromatography (SEC-GPC), and Proton Nuclear Magnetic Resonance ( $^1\text{H-NMR}$ ) were used to characterize the polyurethanes. Finally, after coating the dispersions onto metal substrates, adhesion strength, contact angle and phase morphology were studied. The introduction of siloxane as soft segment increased the surface roughness and hydrophobicity but did not change the adhesion values.

## Graphical Abstract



### 1. Introduction

Owing to the changes in legislation on organic solvents, industries have been forced to develop new environmentally friendly products such as waterborne polyurethanes (WPU), that are widely used as coatings and adhesives [1]. In order a polyurethane to be synthesized in water media, different strategies must be designed due to the reactivity of the water with the isocyanate [2]. Among them, the acetone process is one of the most employed [3–5]. This methodology implies 3 reaction steps: in the first step, the polyurethane is synthesized with isocyanate, polyols and dispersant agent in acetone, in the second, water

is added to perform “phase inversion” process. In this step, dispersant agents play a fundamental role to give rise to stable dispersions [6,7]. Lastly, the VOCs free dispersion is obtained after acetone removal.

One of the most important applications of WPU is in the field of coatings. However, the main problem that WPU dispersions present is related to the presence of the internal emulsifier employed to stabilize the dispersions. This component makes the obtained films hydrophilic which limits their applications in some extent. In order this problem to be solved, it is very interesting to increase the hydrophobicity of the dispersion but it should be borne in mind that the changes in the composition can decrease the coating adhesion to the substrate.

The use of fluorinated structures in the material is a general strategy to decrease the surface tension of the material and accordingly to increase its hydrophobicity [8–12]. Other methodologies studied for preparation of hydrophobic surfaces are based on the phase separation generated during the sol-gel method [13], or in using different solvents and no-solvents with common polymers [14]. These materials offer hydrophobic properties without adding surface tension modifiers to the polymer chain, just controlling surface roughness.

The introduction of Poly(dimethyl siloxane) (PDMS) segments to polyurethanes is described in literature as a way to increase the surface hydrophobicity. Thus, according to different authors, the introduction of moderate amounts of PDMS increase the water contact angle but do not produce significant changes in another polyurethane properties [15–17]. The hydrophobicity of these materials is not only related to a decrease of the surface tension but also to the morphology of the coating. It is worth mentioning that the presence of PDMS in polyurethane formulations can lead to a microphase separated structure altering surface roughness [16], which is considered an important factor in order to establish the surface hydrophobicity.

This strategy has been used to obtain hydrophobic waterborne polyurethanes. Thus, PDMS segments have been introduced to UV-curable polyurethanes for improving mechanical properties and water resistance [9,10,18–20]. According to literature results, it is clear that the introduction of siloxane segments increases the hydrophobicity of the coatings and can modify their mechanical properties. In addition, adhesion to different substrates is an important factor, but it can be argued that introduction of siloxane segments will reduce the adhesion strength to the surface. So, in order a coating or adhesive with good characteristics to be obtained a balance must be found between hydrophobicity and adhesion.

In the present paper waterborne polyurethane dispersions containing different amounts of Poly(caprolactone) (PCL) and Poly(dimethyl siloxane) (PDMS) were obtained and the dispersions were coated on metal substrates. Afterwards, hydrophobicity and adhesion properties of the coatings were

studied with the aim to define the appropriate polyol combination that could give rise to hydrophobic surfaces with good adhesion.

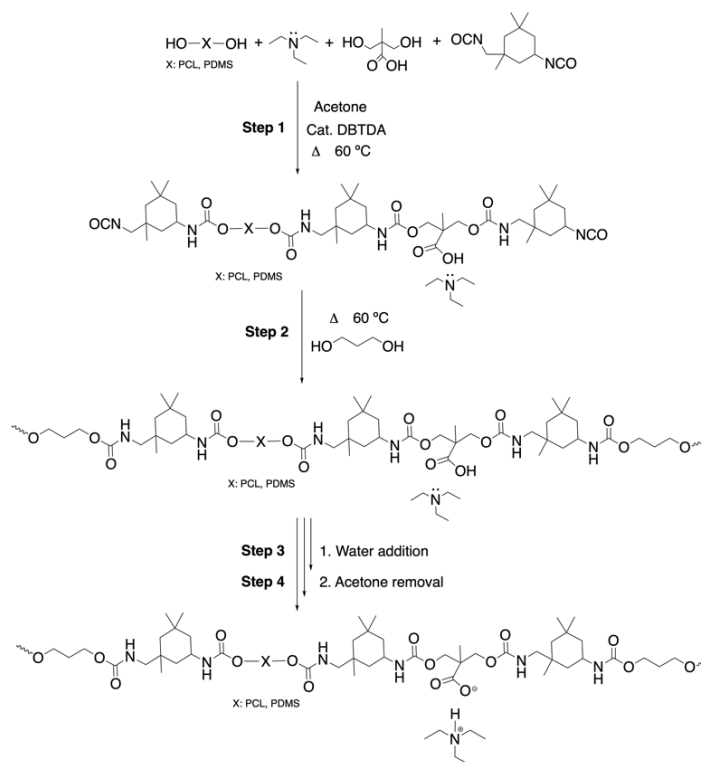
## **2. Experimental part**

### **2.1. Materials**

1,4-butanediol (BD), 2,2-bis(hydroxymethyl)propionic acid (DMPA), Isophorone diisocyanate (IPDI), triethylamine (TEA) and dibutyltin diacetate (DBTDA) were supplied by Sigma Aldrich S.L. Poly- $\epsilon$ -caprolactone (PCL,  $M_w \approx 1250 \text{ g mol}^{-1}$ ) terminated in hydroxyl group was supplied by Polyscience Inc. Poly(dimethylsiloxane) hydroxyethoxypropyl terminated (PDMS,  $M_w \approx 1250 \text{ g mol}^{-1}$ ) was supplied by Fluorochem Ltd. Acetone was supplied by Scharlab S.L. Bi-distilled water was supplied by Bifa Kit, S.L. All materials were used as received. Chemical structures,  $^1\text{H-NMR}$  spectra, GPC-SEC data and thermal properties of the employed polyols are shown in the Supporting Information (Section S1).

### **2.2. Synthesis of polyurethane dispersion**

Waterborne polyurethanes (WPU) were synthesized in three steps by acetone process (Scheme 1). In all the reactions, the PCL and PDMS amount was varied but maintaining the isocyanate/alcohol ratio  $[\text{NCO}/\text{OH}] = 1$ . In order to calculate the polyol amounts, the molecular weight reported by the suppliers were used. In the first step, the polyols (PCL and PDMS) (total amount PCL+PDMS 9 mmol, 11.25 g), IPDI (22.6 mmol, 5.02 g), DMPA (9 mmol, 1.21 g), TEA (12 mmol, 1.21 g), acetone (10 mL) and DBTDA (800 ppm) were fed into a 50 mL Schlenk flask at 60 °C. The reaction proceeded until the absorbance of the NCO infrared absorption was constant with time (see SI S.2.1.). In the second step, 1,4-butanediol (4.6 mmol, 0.41 g) was added and the reaction was kept until NCO band disappeared in the FTIR. The solid content for the polymer solution was 70 wt%. In the third one, polymer was dispersed adding water (45 mL) at 1 mL min $^{-1}$  by phase inversion. In the last step, acetone was removed at room temperature and reduced pressure (300 mbar). The final solid content of dispersion was 30 wt%. Each formulation was carried out three times. Formulations of the synthesized polyurethanes are summarized in Table 1 [21].



**Scheme 1.** Process of polymer synthesis

Formulation	PCL:PDMS mol Ratio	PCL (mmol)	PDMS (mmol)	IPDI (mmol)	DMPA (mmol)	TEA (mmol)	BD (mmol)	DBTDA (ppm)
<b>WPU1</b>	100:0	9	0	22.6	9	12	4.6	800
<b>WPU2</b>	90:10	8.1	0.9	22.6	9	12	4.6	800
<b>WPU3</b>	80:20	7.2	1.8	22.6	9	12	4.6	800

**Table 1.** Summary of the synthesized polyurethanes.

### 2.3. Coating preparation

7 mL of the aqueous dispersion were placed on a stainless-steel substrate (7x7 cm) and after water evaporation, 2 mm thickness film was obtained. For that, the dispersion was kept under 20 °C and 55 wt% relative humidity (RH) for 24 h.

### 2.4. Measurements and Instrumentation

### **Polymer characterization**

Infrared spectra were collected every 30 minutes in a Nicolet 6700 (Thermo Scientific) spectrometer. 10 scans were signal averaged at a resolution of  $4\text{ cm}^{-1}$ . Samples were prepared from solution casting onto KBr windows.

Proton Nuclear Magnetic Resonance ( $^1\text{H-NMR}$ ) spectra were carried out in Bruker Fourier Transform 300 MHz spectrometer using deuterated chloroform ( $\text{CDCl}_3$ ) as solvent. Molecular weight ( $M_n$ ) and polydispersity index (PDI) were determined by Size Exclusion Chromatography-Gel Permeation Chromatography (SEC-GPC). Experiments were performed dissolving the samples in Tetrahydrofuran (THF) in a Thermo Scientific Ultimate 3000 model with refractive index detector and four columns of Phenogel as stationary phase at room temperature and was used as mobile phase. Molecular weight was referred to Polystyrene standards. In order to establish the thermal stability of the polymer, Thermogravimetric Analysis (TGA) was carried out. Samples were heated in nitrogen from  $40\text{ }^\circ\text{C}$  to  $800\text{ }^\circ\text{C}$  at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  in a TA Instruments Q500. Thermal properties were determined in a TA instruments Q2000 Differential Scanning Calorimeter (DSC). Three heating/cooling/heating consecutive scans were performed from  $-80\text{ }^\circ\text{C}$  to  $120\text{ }^\circ\text{C}$  using heating and cooling rates of  $10\text{ }^\circ\text{C min}^{-1}$ . The second heating scan was employed to determine the thermal properties.

### **Dispersion Characterization**

After diluting the WPU in deionized water, the diameter of the particles was measured in a Brookhaven Instruments 90 Plus Particle Size Analyzer Dynamic Light Scattering (DLS). Each sample was measured three times in order to obtain an average value.

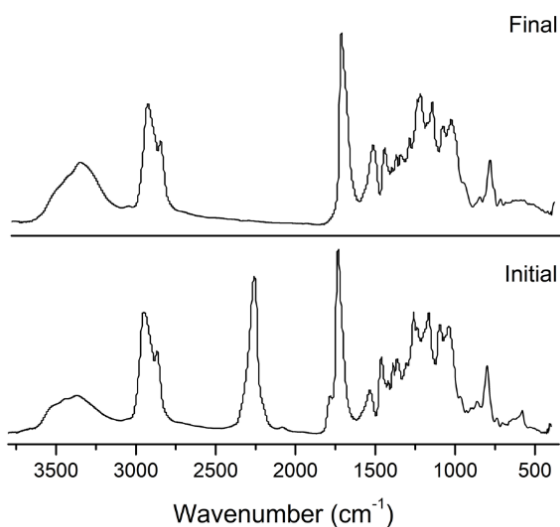
### **Coating Characterization**

Adhesion test was used to determine adhesion force between stainless steel surface and coating. This test was performed following ASTM D4541 standard using Positest AT-A Automatic Adhesion Tester (Pull-off adhesion testing) with a dolly size of 20 mm. Static contact angle measurements to determine coating hydrophobicity were performed on a Dataphysics OCA 20 goniometer in controlled temperature and relative humidity conditions ( $25\text{ }^\circ\text{C}$ ; 55 %). Atomic Force Microscopy (AFM) height images of  $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$  were obtained in air under tapping mode in a Dimension Icon Bruker. AFM samples were prepared in a SCE-150 spin coater attached to a LABOPORT Mini Series Vacuum Pump. 12 mm diameter stainless steel disks were spin coated with  $5\text{ }\mu\text{l}$  of the dispersion at room temperature at 2000 rpm for 2 minutes. Samples were dried at room temperature for at least 48 hours before AFM experiments.

### 3. Results and discussion

#### Polymer Characterization

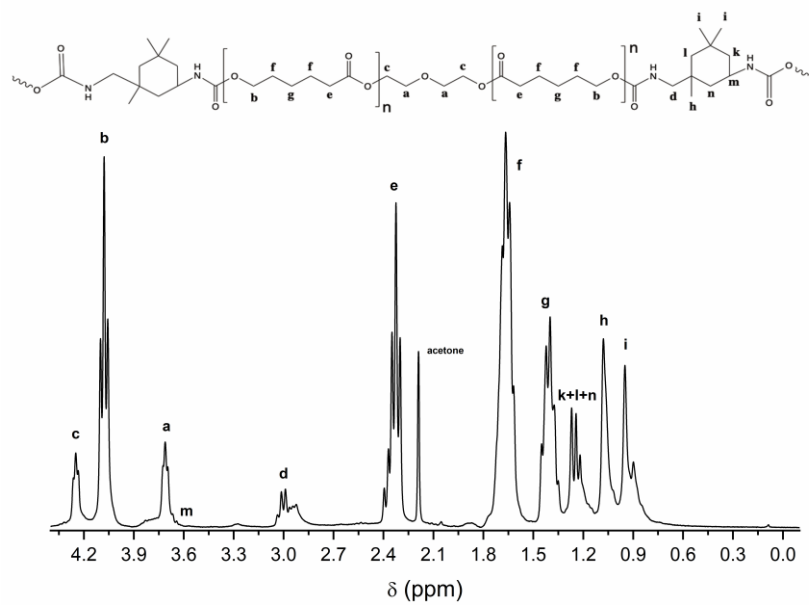
The reactions were characterized by FTIR,  $^1\text{H-NMR}$ , SEC-GPC and TGA. As an example, infrared spectra of the formulation WPU3 are shown in figure 1 (data for WPU1 and WPU2 can be found in SI S.2.1.1 and S.2.1.2). As observed, the band centered at  $2270\text{ cm}^{-1}$  which corresponds to isocyanate stretching, disappeared in the final spectrum as the NCO group reacted with the polyols and dispersant agent. Furthermore, the absorption of the OH stretching of alcohols at  $3500\text{ cm}^{-1}$  was narrowed since this group was consumed and another band at  $3300\text{ cm}^{-1}$ , related to NH stretching, appeared owing to the formation of urethane group [6]. Moreover, carbonyl band stretching ( $\text{C=O}$ ) of urethane group (Amide I) at  $1714\text{ cm}^{-1}$  was overlapped with carbonyl band of PCL at  $1740\text{ cm}^{-1}$ . The increase of the absorbance at  $1550\text{ cm}^{-1}$ , related to the N-H bending (amide II) confirmed the formation of the urethane group [12]. This band was already present in the first spectrum because the reaction was very fast. Finally, symmetric C-Si stretching at  $805\text{ cm}^{-1}$  confirmed the presence of methylsilyl ( $\text{Si-CH}_3$ ) groups [13]. It is to remark that WPU1 did not contain siloxane groups and accordingly the spectrum of WPU1 (Figure S.2.1.1) did not present this absorption.



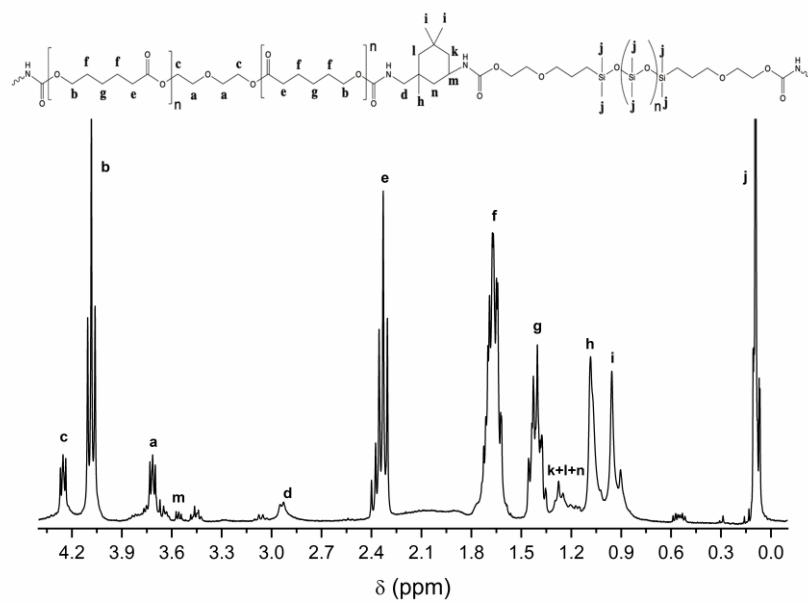
**Figure 1.** FTIR spectra of WPU3 at the first and last reaction steps.

Therefore, the infrared spectra showed that the reaction proceeded in a proper way. However, with the aim to complete the polymer characterization, NMR spectrum were recorded.





**Figure 2.** <sup>1</sup>H-NMR spectrum of the polyurethane with 0% PDMS (WPU1)



**Figure 3.** <sup>1</sup>H-NMR spectrum of the polyurethane with 20% PDMS (WPU3)

Figure 2 and 3 show <sup>1</sup>H-NMR spectra of two formulations, WPU1 and WPU 3, containing 0 % and 20 % PDMS respectively. (spectrum of sample WPU2 can be found in supplementary material, Figure S.2.2.2.). Signals at 2.3 [ e , -CH<sub>2</sub>COO- ], 4.1 [ b , -CH<sub>2</sub>OCO- ], 1.65 [ f , -CH<sub>2</sub>CH<sub>2</sub>CO- ], 1.4 [ g , -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- ], 3.7 [ a , -CH<sub>2</sub>O- ] and 4.25 [ c , -CH<sub>2</sub>OCO- ] ppm correspond to PCL unit (SI Figure S.1.1.1). Moreover signals at 2.9 [ d , -CH<sub>2</sub>NHCO-], 1.0 [ i , -CH<sub>3</sub> ], 1.3[ h , -CH<sub>3</sub> ] ppm correspond to IPDI [22]. Finally, the signal at 0.2 [ j , -OSiCH<sub>3</sub> ] ppm [23,24], corresponds to methyl siloxane group (SI Figure S.1.2.1.). As expected, the relative area of this signal increased with the siloxane content confirming the chemical structure of the different polymers.

The molecular weight of the samples was calculated by SEC-GPC (table 2). As can be seen, regardless of the employed polyol, the obtained values remained similar. This means that the reactivity of both polyols was in the same range. The polydispersity values were close to 2.2 in all the synthesized polymers which was in accordance with the anticipated value in a step-growth polymerization reaction.[25]

Sample	(M <sub>n</sub> )	(M <sub>w</sub> )	PDI
	[g/mol]	[g/mol]	
WPU1	12300 ± 1530	29000 ± 4600	2.3 ± 0.1
WPU2	12400 ± 5047	25900 ± 9500	2.1 ± 0.1
WPU3	11700±1600	25400±3000	2.2±0.1

**Table 2.** Molecular weight and polydispersity of the synthesized polymers

### Dispersion Characterization

The particle size of the dispersion is a key factor to establish the application and stability of the WPU. According to literature [26], the particle size could increase or conversely decrease with the introduction of siloxane units, depending on the characteristics and composition of the dispersion. The data obtained in the present work by DLS are summarized in table 3. The results showed that siloxane units provoked a considerable increase in the particle size that raised from 55 to 325 nm for samples with 0 and 20 wt% of PDMS respectively. The increase of the interfacial tension produced by the PDMS units was considered responsible for this behavior [22,27,28]. The diameter rise was visually valued when transparent dispersion changed to milky white.

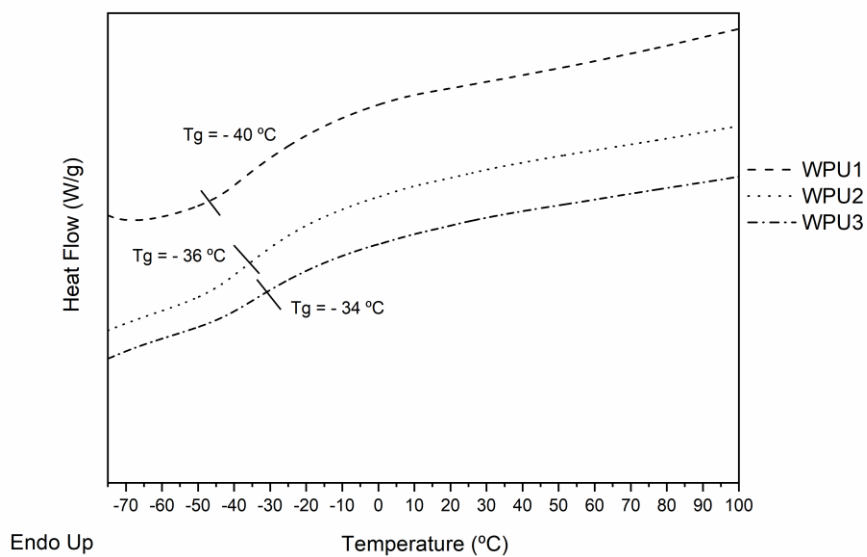
<b>Sample</b>	<b>Initial (nm)</b>	<b>Week 1 (nm)</b>	<b>Week 2 (nm)</b>	<b>Appearance</b>	<b>Stability</b>
<b>WPU1</b>	55±7	46±14	47±12	Transparent	Stable
<b>WPU2</b>	114±27	111±28	122±37	Milky White	Stable
<b>WPU3</b>	325±44	331±46	327±47	Milky White	Stable

**Table 3.** Particle size, appearance and stability of WPU

In order the stability of the dispersions to be established, samples were stored without stirring and the particle size was measured after 1 and 2 weeks. The results of this experiments are shown in table 3. Particle size generally increases with time due to water swelling. However, because of the standard deviation of the measurement our data did not show a clear tendency and the evolution of the particle size with time was between the standard deviation range. In light of the above, the particle size remained constant with time and consequently it was assumed that the dispersions were stable.

### **Thermal properties**

Coatings were obtained by casting from the dispersion. All the samples showed good film forming abilities. The thermal properties of the coatings were studied by DSC (Figure 4).

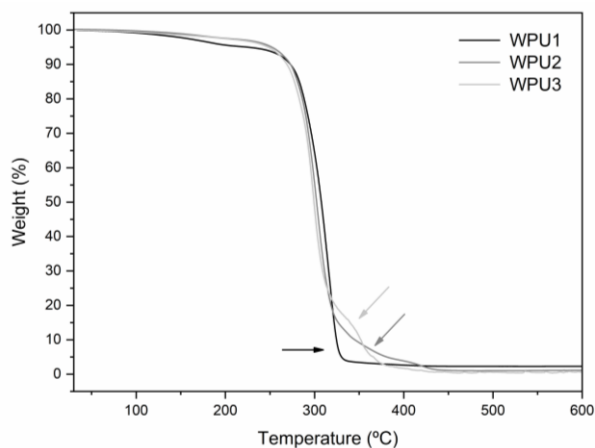


**Figure 4.** DSC thermograms of the prepared coatings.

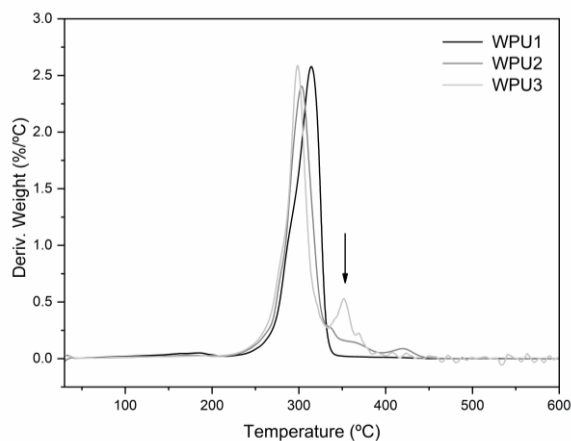
It is well known that segmented polyurethanes present phase separated morphology and that each phase maintains its thermal properties. Pure PCL segments, presented the glass transition temperature at  $-66\text{ }^{\circ}\text{C}$  and melting temperature in the range  $30\text{--}40\text{ }^{\circ}\text{C}$  (SI Table S.1.1.2.) while pure PDMS, presented a glass transition temperature at  $-31\text{ }^{\circ}\text{C}$  (SI Table S.1.2.2.). This transition was related to the final groups of PDMS since according to literature the glass transition of PDMS was out of the measurement range of the equipment used in this work ( $-120\text{ }^{\circ}\text{C}$ ) [29]. Regarding the thermal behavior of the polyurethane samples (Figure 4), it is worth mentioning that no melting peak was observed. This result evidenced the restriction to the crystallization of the PCL segments provoked probably by the partial mixing with the polyurethane hard segment. In addition, the data of figure 4 showed a single glass transition around  $-35\text{ }^{\circ}\text{C}$  (SI Table S.2.3.) that was assigned to PCL glass transition. As observed, the Tg values showed a slight increase with the PDMS concentration, which confirmed the incompatibility between both soft segments. Thus, when the PDMS concentration increased, the relation between the PCL/hard segment decreased and a slight increase in the Tg was observed because of the effect of the partial mixing between the hard urethane segments and the PCL. Therefore, the internal repulsion between both soft segments was a key factor that favored the mixing of urethane/PCL segments increasing the Tg of the PCL.

The thermogravimetric behavior of the samples was analyzed by TGA and the results are summarized in Figure 5a and 5b. For sample WPU1 (0 % PDMS) two decomposition steps were observed. The first one, located at temperatures lower than  $200\text{ }^{\circ}\text{C}$ , was related to evolved water. However, as stated in literature for IPDI based polyurethanes, the main weight loss started at  $250\text{ }^{\circ}\text{C}$  [30]. The percentage of this step was 83 % and therefore it was related to both, urethane hard segment and polycaprolactone soft segment decomposition [31]. Finally, at  $600\text{ }^{\circ}\text{C}$  the sample did not leave significant residue. For samples WPU2 and 3, containing siloxane, and additional degradation step was observed at temperature near  $350\text{ }^{\circ}\text{C}$ . This step,

was related to the siloxane decomposition as reported previously in literature [32,33]. The percentage of the different steps as well as the obtained residue for all the samples can be found in table (SI S.2.4.). From these data it is worth mentioning that the percentage of the first step decreased with the siloxane content of the sample, which was related to the hydrophobicity of the siloxane segments. Thus, samples containing more siloxane retained less water and consequently showed a reduced percentage of the first step. In addition, the percentage of the second and third steps, related to the polycaprolactone and polysiloxane diols, changed according to the sample composition. Thus, as expected, the percentage of the third step was the highest in the sample WPU3. The value of the residue did not show significant changes with the composition of the sample. However, and on the contrary to the data obtained by other authors [26,29], the introduction of the siloxane did not increase the thermal stability of the samples. Thus, the temperature of the highest degradation rate of the second step decreased with the introduction of siloxane groups. In our opinion this behavior was related to the composition of the samples. Therefore, as the siloxane content increased, the PCL content decreased meanwhile the urethane concentration remained constant. So, the urethane/PCL ratio increased with the siloxane content. As the second step was related to urethane and PCL decomposition and bearing in mind that the urethane linkage is the more labile, the lower thermal stability of the siloxane containing samples can be explained considering their composition. Thus, even if the siloxane groups decompose at higher temperature, the introduction of these groups in the polyurethane structure was not able to stabilize the polymer, probably because of the phase separation between the siloxane and the rest of the components of the polyurethane.



**Figure 5a.** TGA curves of the polyurethanes

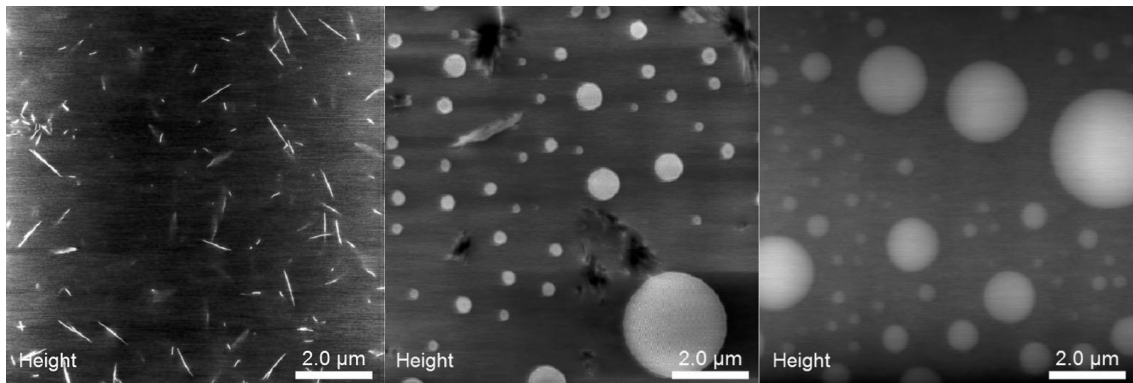


**Figure 5b.** DTG curves of the polyurethanes

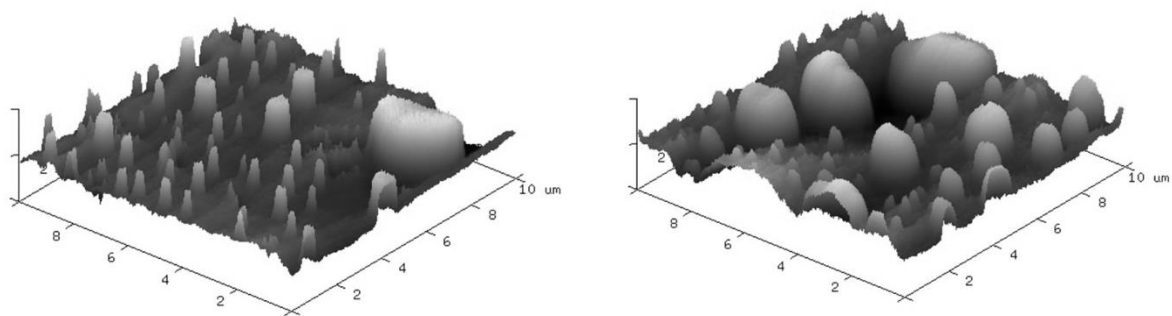
### Surface characterization

DSC and TGA results demonstrated that the siloxane containing samples presented phase separated morphology that could generate surface roughness. Therefore, surface morphology was studied by AFM (Figures 6 and 7).

On the first image, (WPU1) small crystals were observed. Even if no melting point was observed in DSC runs, the crystals were related to PCL, as the DSC and AFM samples were not prepared in the same way. These crystals were not observed in samples WPU2 and WPU3 containing PDMS owing to the disturb in the crystallization originated by the use of polyol mixtures. In addition, samples WPU2 and WPU3 showed a two-phase morphology, where spherical domains related to PDMS domains could be observed. The size of these domains increased with the PDMS content. According to literature, the origin of the phase separation is the incompatibility of the PDMS segments with the polyurethane [27,34,35]. In dispersion, the PDMS domains remained inside the particle due to their hydrophobicity. However, when cast, they migrated to the surface due to the lower surface energy. Large PDMS domains were generated because of the immiscibility driven coalescence of small domains[36]. Considering that in the present work lineal polysiloxane structures were used, it can be argued that they presented enough flexibility for producing microdomains formation. Surface roughness of the samples is shown in table 4.



**Figure 6.** Topography images in 2D by AFM. Left to right WPU1/WPU2/WPU3.



**Figure 7.** Topography images in 3D by AFM (Height). Left to right WPU2/WPU3

Formulation	R <sub>a</sub> (nm)	R <sub>q</sub> (nm)	Contact angle (°)
WPU1	0.47	0.79	71±5
WPU2	2.26	3.34	80±2
WPU3	1.75	2.42	83±7

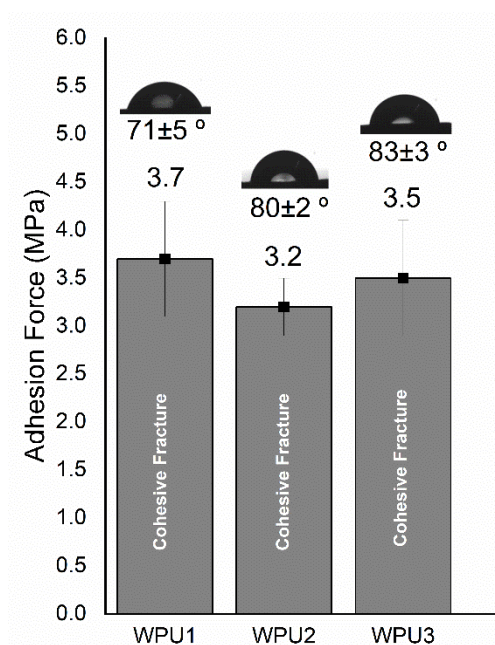
**Table 4.** Roughness R<sub>a</sub> and R<sub>q</sub> in WPU products by AFM and contact angle.

As observed, with the introduction of siloxane groups the roughness of the sample experienced a huge increase, which did not depend on the siloxane concentration. This result emphasized that total siloxane concentration was not controlling the surface wettability as will be concluded for the contact angle and adhesion measurements.

As a way to determine the hydrophobicity of the surface, water static contact angle was measured (Table 4). As observed, the formulation without PDMS (WPU1) was hydrophilic and a value of 71° was obtained. This contact angle values were expected since during dispersion step, hydrophilic segments i.e., DMPA and urethane groups are likely to come to the surface [37,38]. As observed, the introduction of siloxane increased the contact angle 15 % regardless the siloxane content [22,39]. This result evidences that, as described in literature [27], the introduction of the PDMS increased the hydrophobicity of the coating. However, comparing to literature data, the coatings continued being hydrophilic which was probably related to the molecular weight of the siloxane diol. Nevertheless, the TGA data presented in previous paragraphs, showed that the water remaining in the films experienced a considerable decrease with the introduction of the siloxane. This fact evidences that even if the contact angle of the coatings was not very high, it had significant effect in the sample hydrophobicity.

## Adhesion properties

Finally, coating adhesion to metal substrates was studied by Pull-off adhesion testing. This property as well as the contact angle values are related to the surface morphology of the samples, that were described by the AFM experiments. The results obtained for samples containing different PDMS amounts are shown in figure 8. The adhesion force of pure polyurethane (WPU1) was 3.7 MPa. This result was in the range of those reported in literature for similar polyurethanes [40]. Samples containing PDMS (WPU2 and WPU3) showed similar values. As the principal agent of adhesion of the samples was the PCL, the presence of PDMS in the formulation did not significantly affect adhesion properties.



**Figure 8.** Adhesion force and contact angle in WPU coatings in metal substrate

## 4. Conclusions

Siloxane containing waterborne polyurethane dispersions with good adhesion force to metal substrates were successfully obtained by the acetone process. Coatings with superior hydrophobicity were obtained introducing siloxane groups in the polyurethane dispersion. Thus, when increasing the siloxane amount, the dispersion particle diameter and surface contact angle were increased but the films showed lower water uptake ability. The phase separated structure of the hydrophobic polyurethane was established by DSC and AFM measurements. The introduction of the siloxane groups gave rise to a slight decrease of the initial decomposition temperature of the samples. Finally, it is interesting to remark that adhesion properties were not affected with the PDMS content and these samples showed a good balance between hydrophobicity and adhesion. These results could help, after optimization of the WPU formulation, to develop hydrophobic polyurethane coatings with good adhesion.



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## Supporting Information Available

Additional information about reagents characterization, FTIR analysis, GPC-SEC, NMR, DSC and TGA used in this study.

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