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Polyurethane coatings from formulations with low isocyanate content using a transurethane polycondensation route.

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ABSTRACT

A strategy aiming to decrease the amount of isocyanate in the PU industries without changing their current facilities is proposed. Hydroxyl terminated non-isocyanate polyurethane (NIPU) oligomers (H-OI) with controlled molecular weights and chemical structures have been prepared as precursors. They were prepared by transurethane polycondensation between bis(methylcarbamate) (BMC), hydroxyterminated poly(tetramethyleneoxide) (PTMO) and butanediol at several molar ratios. H-OI were then reacted with a polyisocyanurate as crosslinking agent to afford several partially NIPU coatings. Polyurethanes based on the PTMO polyols and the polyisocyanurate were also prepared as controls to highlight the importance of the urethane function in the H-OI. The influence of the chemical structures on the thermal and mechanical properties of the final coatings has been investigated. The prepared coatings displayed thermal stabilities above 200°C, Young modulus ranging from 3 to 64 MPa, tensile strength values from 0.9 to 17 MPa and elongation at break varying from 25 to 530 %. H-OI with the highest urethane content gave a coating with the best adhesion properties on a metal surface. All the obtained properties were within the characteristic range of two commercial PU reference coatings.

KEYWORDS:

Polyurethane; non-isocyanate; NIPU; transurethanization; coating.

INTRODUCTION

Polyurethanes (PUs) are a range of versatile and essential polymers with applications in many fields (construction, consumer, industry, automotive, aeronautics, medical, transport...). They are mainly marketed in the form of crosslinked materials (foams, coatings...). However, conventional PUs are manufactured from isocyanates which are hazardous chemicals. In accordance with the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), exposure to them may potentially cause severe adverse effects such as respiratory and skin irritations, immune sensitization and have suspected carcinogenicity. In addition, isocyanates are made from phosgene, which is a highly toxic gas.¹ This awareness has led to a tightening of the regulatory context with respect to these substances and has favored the development of isocyanate-free polyurethanes (NIPUs). Indeed, isocyanate agents are intended to be restricted by the REACH regulation. During the last two decades, few alternative methods have been developed.¹⁻¹⁴

The transurethane polycondensation reaction, involving the reaction of dialkyl dicarbamates²⁻⁶ or dihydroxyethyl dicarbamates⁷⁻⁹ with diols, in presence of organic or organo-metallic catalysts, is one of the promising non-isocyanate and non-phosgene routes to polyurethanes. Nevertheless, as far as dihydroxyethyl dicarbamates are used, a back-biting side reaction may take place leading to creation of urea units.⁷⁻⁹ In comparison with the aminolysis of cyclic carbonate method, affording poly(hydroxyurethane) structures (PHUs),¹⁰⁻¹⁴ the transurethanization technique has the advantage of producing conventional PU structures. In addition, it involves a wide choice of dialkyl dicarbamates monomers comparing to the commercially available diisocyanate monomers, which offers a higher versatility in terms of chemical structures and properties of the final polyurethane materials. However, because transurethanization requires high reaction temperatures and vacuum to eliminate the released alcohols such as methanol or ethylene glycol, direct preparation of crosslinked coatings with this technique is quasi-impossible. Therefore, one alternative consists to prepare telechelic NIPU oligomers allowing post-crosslinking via polyaddition mechanisms under smooth conditions (**room or moderate temperature and without vacuum**). Indeed, recently allyl and acryloyl terminated NIPU have been prepared and used to prepare photo-crosslinked coatings.^{4,15-16}

In this work, we propose to address the problem of isocyanate agents by reducing their content in PU coatings without affecting urethane content in the final material by using designed hydroxyl-terminated NIPU oligomers. In short and medium terms, this will allow the concerned industries to keep their facilities and processes by replacing only their polyols by telechelic NIPUs in their formulations. Thus, we describe first the preparation of biosourced or potentially biosourced NIPU oligomers by using the transurethane polycondensation reaction between dialkyl dicarbamates and diols. Then, we will describe their use in the preparation of partially NIPU coatings by reaction with a polyisocyanurate as crosslinking agent. The assessment of the thermal, mechanical and surface properties of the obtained materials is also reported.

EXPERIMENTAL PART

Materials

Poly(tetramethylene oxide) (PTMO) of $M_n = 650, 1000$ and 2000 g/mol, 1,6-diaminohexane (98%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), dimethyl carbonate (DMC, 99%, anhydrous), 1,4-butanediol (BD, 99%) and 4,4'-methylenebis(cyclohexylamine) (H_{12} MDA, >98%) were obtained from Sigma Aldrich. Desmodur N3600 was supplied by Covestro. All the other reagents and solvents were used without further purification.

Synthesis

Preparation of dimethyl dicarbamate monomers

In a round-bottomed flask equipped with a magnetic stirrer, diamine (1 eq.), TBD (0.1 eq.) and DMC (10 eq.) were mixed and stirred for 5 h at 80°C (24 h for BMC- H_{12}). The mixture was then cooled down to room temperature. Crystallized products (BMC- C_6 and BMC- H_{12}) were collected by filtration and washed by distilled water to remove TBD (yield > 85 %). BMC-Pr was liquid and was purified by washing with distilled water in diethyl ether medium. The organic phase was then separated, dried over MgSO_4 , filtrated and the solvent was evaporated.

Dimethylhexane-1,6-dicarbamate (BMC- C_6)

$^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): 4.67 (s, broad, 2H; NH), 3.65 (s, 6H; $\text{NH}(\text{CO})\text{OCH}_3$), 3.15 (m, 4H; NHCH_2); 1.48 (m, 4H; NHCH_2CH_2), 1.32 (m, 4H; $\text{NHCH}_2\text{CH}_2\text{CH}_2$). **$^{13}\text{C NMR}$** (75 MHz, CDCl_3 , δ): 26.2, 29.9, 40.7, 52.0, 157.1 ; IR (ATR): $\nu \sim 3300$ cm^{-1} (m; ν_{NH}), ~ 1700 (s, $\nu_{\text{CO H-bonded}}$) cm^{-1} , ~ 1530 cm^{-1} (s, $\nu_{\text{NH bending}}$). DSC: $T_m = 115^\circ\text{C}$.

4,4'-methylenebis(cyclohexylamine) (BMC- H_{12})

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 3.77 and 3.40 (m, 2H; NHCH); 3.66 (s, 6H; $\text{NH}(\text{CO})\text{OCH}_3$), 2.1 to 0.75 (20H; methylene and cycle CH and CH_2). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3 , δ): 156.4 (C=O), 51.9 (OCH_3), 50.5 (NHCH), 47.1 (NHCH), 44.1 (NHCHCH_2), 42.9 (NHCHCH_2), 33.7 and 33.6 (CH), 33.4 (bridge CH_2), 32.6 (CH), 32.0 (bridge CH_2), 29.7 (CH_2), 28.0 (CH_2). DSC: $T_m = 189^\circ\text{C}$.

Dimethyl Dicarbamate of Priamine 1074 (BMC-Pr)

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 4.68 (s, broad, 2H; NH), 3.65 (s, 6H; $\text{NH}(\text{CO})\text{OCH}_3$), 3.15 (m, 4H; NHCH), 2 to 1 (54H; CH and CH_2), 0.87 (m, 6H, CH_3). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3 , δ): 157.2 (C=O), 52.0 (OCH_3), 41.2 (NHCH_2), 37.2 (CH_2), 33.7 (CH_2), 32.0 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 26.8 (CH_2), 22.8 (CH_2), 19.8 (cycle CH), 14.2 (CH_3). DSC: $T_m < -70^\circ\text{C}$.

Preparation of hydroxy-terminated NIPU oligomers (H-OI)

In a three-neck round-bottomed flask fitted with a mechanical stirrer, Dean Stark condenser and connected to a vacuum pump, bismethylcarbamate (BMC), poly(tetramethylene oxide) (PTMO) and a chain extender were added at an appropriate molar ratio, previously calculated by Carothers theory, to achieve the desired M_n . For 1kg scale, a 5 L-four-necked-jacketed glass reactor equipped with a mechanical stirrer and thermometer was employed. The temperature was gradually raised to 160°C under nitrogen flow and agitation. Then, 10 mol% of catalyst (MeOK) relative to the BMC

monomer was introduced to the medium. After 1 h reaction at 160 °C, the Dean Stark condenser was removed and the medium was placed under vacuum (400 mbar) for 1 h. Finally, the pressure was carefully decreased to 0.5 mbar for 4 h. After cooling to room temperature under nitrogen flow, the resulting oligomers were collected without any purification. When BD was used as chain extender, evaporation was quantified by NMR calculations. To obtain the accurate oligomer's molecular weight, the experiment was renewed by adjusting the BD equivalents.

Preparation of PU with low isocyanate content and reference PU coatings

Formulations were prepared by dissolving H-OI oligomers in an appropriate amount of butyl acetate, leading to homogeneous media and convenient viscosity. Then, the accurate calculated quantity of Desmodur® N3600 was introduced to the medium, with respect to the optimal NCO/OH ratio. Resulting formulations were mixed up to 4 hours in order to obtain homogeneous media and were then applied to stiff matte steel "Q-panel" plates supplied by Labomat. After degreasing the plates with a cloth soaked in ethanol (EtOH), two types of coatings were obtained for each type of formulation used, called "thin" and "thick" films, respectively. In order to obtain thin films, the desired formulation was applied on the top of the plate and wet thickness control was provided using a roll coater. To obtain thick films, slides of an adhesive tape were used to calibrate the thickness. **All the coating were obtained after curing at 60°C in a ventilated oven for 24h. PUs based on hydroxy-terminated PTMOs as polyols and Desmodur® N3600 were also prepared as references in the same conditions. Commercial thin and thick reference PU coatings (references 1 and 2) without additives were also prepared, according to a confidential procedure provided by the research company Mäder.**

Measurements and Instrumentation

¹H and ¹³C NMR analysis were achieved on a Bruker 300 Fourier Transform spectrometer at 300 MHz and 75 MHz, respectively, in CDCl₃ solutions comprising tetramethylsilane (TMS) as internal standard. FTIR spectra were recorded with Perkin-Elmer Spectrum 2000 FTIR, equipped with a diamond ATR device (Attenuated Total Reflection). Spectra were acquired from 10 scans in the 650 to 4000 cm⁻¹ range.

Average molecular weights of polymers (M_n and M_w) and dispersity ($\mathcal{D} = M_w/M_n$) were determined by Size Exclusion Chromatography (SEC). Polymers were dissolved in dichloromethane (the mobile phase), filtered (0.45 μm) and analyzed by a Varian PL-GPC50 system equipped with two mixed packed columns (PL gel mixed type C), thermostatically controlled at 25°C. Calibration was performed with PMMA standards (from 875 to 62000 g mol⁻¹).

Thermo-Gravimetric Analysis (TGA) was carried out with a TGA Q500 device (TA Instruments), using a heating rate of 10°C/min under a nitrogen flow. The temperature at 5% of weight loss ($T_{5\%}$) was employed as reference to evaluate the degradation of polymers.

Differential Scanning Calorimetry (DSC) analysis was carried out with a DSC Q2000 device (TA Instruments), using a heating rate of 10°C/min under a nitrogen flow. The midpoint method was employed to assess the glass transition temperature (T_g). Melting temperature (T_m) was measured at the maximum of the endothermic signal. DSC curves were recorded in a temperature range of -70 to 250°C.

The thickness of crosslinked thin films (less than $50.0 \pm 1.0 \mu\text{m}$) was assessed by magnetic determination using the PosiTector 6000, in accordance with ISO 2808: 2007. The device possesses a probe, which is applied on the surface of the sample, placed on a flat surface. The thickness of the thick crosslinked films (between $100 \mu\text{m}$ and 1 mm , with an accuracy of ± 1.0 micron) was assessed with a Digimatic micrometer. The film was fixed by a micrometer screw between the two circular measuring surfaces of the device.

The tensile tests were carried out on a Zwick/Roell device equipped with a 500 N load cell, two jaws (pneumatically or manually clamped, depending on the type of sample characterized) and a movable crosshead. The tests were conducted in accordance with ISO 527_3 "Test conditions for films and sheets". For each coating, 5 to 15 rectangular specimens were cut with a scalpel. Specimens with irregularities or nicks were systematically removed. Manually clamped jaws limited the width of the specimens to 6 mm, the specimens had the following dimensions: total length l_3 of 50 mm; width b of exactly 4 mm; thickness h less than 1 mm. The values of b and h were accurately measured at three points and the average values were used for calculations. The distance between the jaws l_0 was set to 35 mm. The test speed u was set to 20 mm/min, and the preload value was kept at 0.05 MPa. After each specimen broke, the following values were determined based on the cross-sectional area A ($A = b \times h$, expressed in mm^2) of the specimen: The strength at break of the material σ_r (MPa), which corresponds to the stress experienced when the specimen breaks, equal to the maximum stress; the elongation at break ϵ_r (%), which represents the elongation of the material before it breaks; Young's modulus or elasticity E (MPa), which refers to the slope of the stress-strain curve in the range between $\epsilon_1 = 0.05\%$ and $\epsilon_2 = 0.25\%$ of the elongation of the material considered reversible.

Swelling tests were performed in THF at the equilibrium state. Mass (m_i) of samples, of about 15 mg for thin films and 50 mg for thick films, were placed in a pill dispenser of 4 mL of capacity, containing 3.5 mL of THF. Then, the system was placed under magnetic agitation at room temperature for 24 hrs. Afterward, samples were removed from the solvent, dried on the surface with absorbent paper and weighed (m_h). These samples were then dried in a vacuum oven at 40°C for 24 h and weighed (m_f).

- The extractables percentage (τ_{EX}) of the materials is expressed as follows:

$$\tau_{EX} = \frac{m_i - m_f}{m_i} \times 100 \quad \text{Eq.1}$$

- The swelling percentage (Q) of the materials is expressed as follows:

$$Q = \frac{m_h - m_f}{m_f} \times 100 \quad \text{Eq.2}$$

The surface energies of the coatings were assessed using a Digidrop Goniometer (GBX, France), through static contact angle (θ_i) measurements with 3 liquids, i.e. water, diiodomethane and glycerol. At least five measurements, at the equilibrium time, on different surfaces were performed to calculate the mean contact angle and its standard deviation. According to the Owens-Wendt relationship (1) the dispersive γ_s^d and polar γ_s^p components of the surface energies ($\gamma_s = \gamma_s^d + \gamma_s^p$) of the samples as well as the according surface polarities ($P = (\gamma_s^p / \gamma_s) \times 100$) were determined.

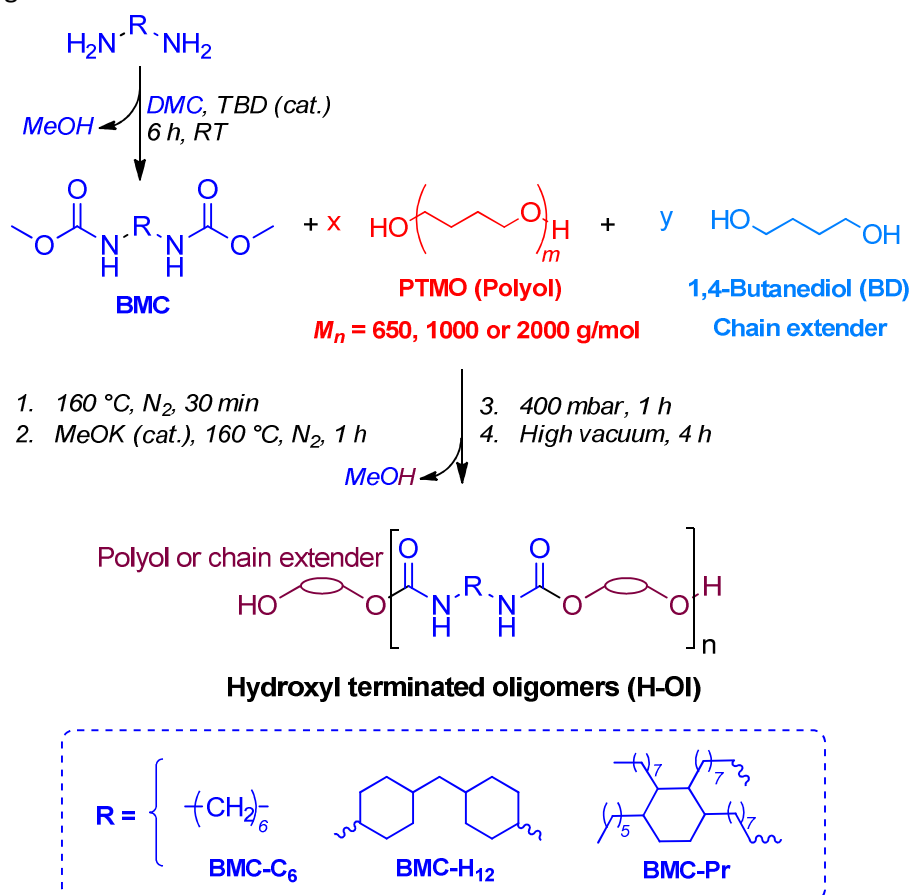
The adhesion properties of the prepared thin coatings were tested using a grid test comb, equipped with 6 slides spaced at 1 mm. The blades conform to ISO 2409. The gridded coating was

brushed 5 times in the direction of each diagonal, and then the excess polymer that was pulled off was removed with standard tape. The grid was then examined under a magnifying glass and graded according to the standard for adhesion to the metal substrate (Iso 0: the best to Iso 5: the worst).

RESULTS AND DISCUSSION

Synthesis and characterizations of hydroxyl terminated NIPUs oligomers

Aliphatic and cycloaliphatic bis(methyl carbamate) monomers (BMC, Scheme 1) were synthesized by reacting a large excess of dimethylcarbonate (DMC) (preventing cyclization and chain extension) with several diamines, using TBD as catalyst, as previously described.^{3-5,17-18} The monomer mixture was allowed to react at 80°C for 6 h. Hexamethylene diamine (C₆), which is potentially biobased,¹⁹⁻²⁰ petroleum-based 4,4'-methylenebis(cyclohexylamine) (H₁₂), and the commercially available Priamine (Pr) based on vegetable oil derivatives (from Croda), were used as diamine monomers. DMC can also be considered as a potentially renewable reactant.²¹⁻²² Solid BMCs (C₆ and H₁₂) were collected by crystallization, while liquid BMC-Pr was purified by extraction in diethyl ether after washing with water.



Scheme 1. Synthesis approach of the hydroxyl terminated NIPU oligomers (H-OI).

Then, the prepared BMCs were reacted with an excess of poly(tetramethylene oxide) (PTMO) through a transurethane polycondensation affording NIPU oligomers with hydroxyl chain-ends (H-OI). PTMO with different molecular weights ($M_n = 650, 1000 \text{ or } 2000 \text{ g/mol}$) were used. Both TBD and MeOK were tested as catalysts (Scheme 1). The kinetics of the reaction was followed by NMR and SEC (Figure 2 and supporting data), which allowed the assessment of the optimal reaction conditions.

MeOK has been found to be a better catalyst than TBD for the urethane polycondensation but was not efficient to catalyze the synthesis of BMCs. Reaction with PTMO650 and PTMO1000 led to a total conversion of the methylcarbamate groups of BMCs under atmospheric pressure. In contrast, reaction with PTMO2000 needed high vacuum.

PTMO brings interesting properties to polymer materials such as good resistance to hydrolysis and good mechanical properties.²³ The NIPU oligomers were named "H-BMC- M_n PTMO". For instance, the H-OI based on BMC-Pr and PTMO of $M_n = 2000$ g/mol was denoted "H-Pr-2000". NIPU materials bearing butane diol (BD) as chain extender were also prepared (Table 1, supporting data). The PTMO/BD ratio was varied from 1/0.5 to 1/2, but only three oligomers based on BD were retained for preparation of coatings. Thus, more than ten hydroxy terminated NIPU oligomers have been prepared at laboratory and kilogram scales (Table 1).

The targeted M_n values for NIPU materials based on PTMO650, PTMO1000 and PTMO2000, were of 2000, 2500 and 5500 g/mol, respectively. The targeted degree of polymerization (X_n) was calculated using the following method:

$$M_n = (X_n - 1) \times M_0 + M_{diol} \quad \text{Eq.3}$$

With:

- M_0 = Molecular weight of the monomer unit = $(M_{diol} + M_{BMC} - 2M_{MeOH})/2$
- M_{diol} = Average molecular weight of "PTMO + chain extender" mixture, with respect to their equivalent ratio.
- M_{BMC} = Molecular weight of BMC.
- M_{MeOH} = Molecular weight of methanol.

Using Carothers' theory,²⁴ " X_n " as well as the number of repeating unit "n", can be expressed as follows:²⁵

$$X_n = \frac{1 + r}{1 + r - 2rp} = 2n + 1 \quad \text{Eq.4}$$

With:

- r = stoichiometric ratio of reagents, with $r < 1$
- p = conversion of the limiting reagent monomer.

Assuming that $p \rightarrow 1$, the stoichiometric excess of diols to be used « $1/r$ » can be deduced as follows:

$$\frac{1}{r} = \frac{X_n + 1}{X_n - 1} \quad \text{Eq.5}$$

The FTIR spectra of the obtained H-OI (Figure 1 and supporting data) showed the C=O stretching vibration bands of the free and H-bonded urethane groups at around 1720 cm^{-1} and 1686 cm^{-1} , respectively. The bending and stretching vibrations of the N-H bonds of the urethane groups were observed at around 1526 cm^{-1} and 3300 cm^{-1} , respectively.

¹H NMR spectra of H-OI (Figure 2 and supporting data) showed the signal of protons of the terminal methylene groups at $\delta = 3.61$ ppm ($\text{CH}_2\text{-OH}$). Signals of protons in alpha position to the nitrogen and the oxygen atoms of the urethane functions appeared at about 3.15 and 4.05 ppm,

respectively. The signal of protons of the methylcarbamate chain-ends at 3.65 ppm disappeared totally at the end of the reaction. Derivatization of the hydroxyl groups of H-OI with trifluoroacetic anhydride (TFAA) led to the formation of ester groups and the shift of the triplet at 3.62 ppm to 4.37 ppm in the ^1H NMR spectra, which also showed the absence of a residual signal from the starting methylcarbamate groups (supporting data). ^{13}C NMR analysis (supporting data) revealed the signal of carbon of the terminal methylene groups at around 62.6 ppm ($\text{CH}_2\text{-OH}$). Signals of carbons in alpha position to the nitrogen and the oxygen atoms of the urethane functions appeared at about 41.0 and 64.5 ppm, respectively. The quaternary carbon of the urethane function was observed at around 156.8 ppm. The peak at 52.0 ppm of the methyl group of the starting methylcarbamate function disappeared completely.

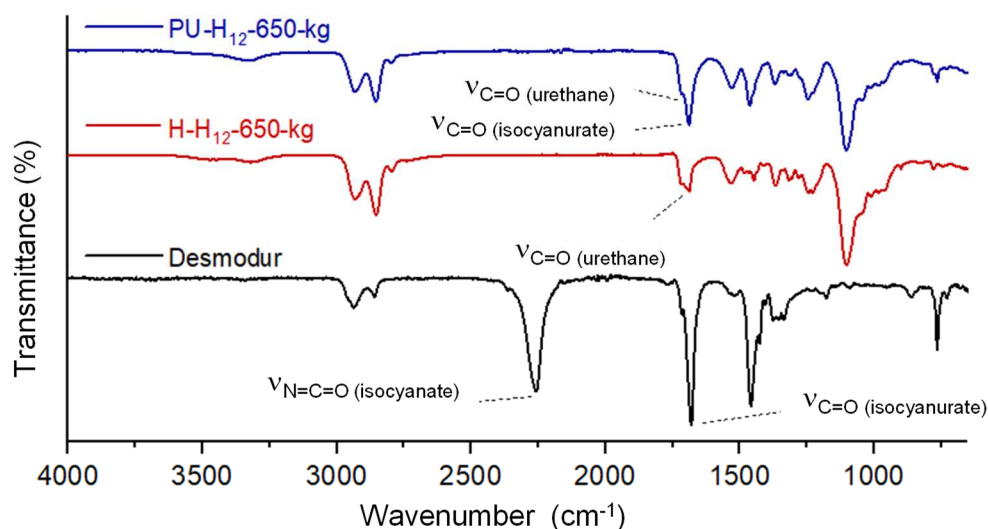


Figure 1: FTIR spectra of H- H_{12} -650-kg, PU- H_{12} -650-kg and Desmodur.

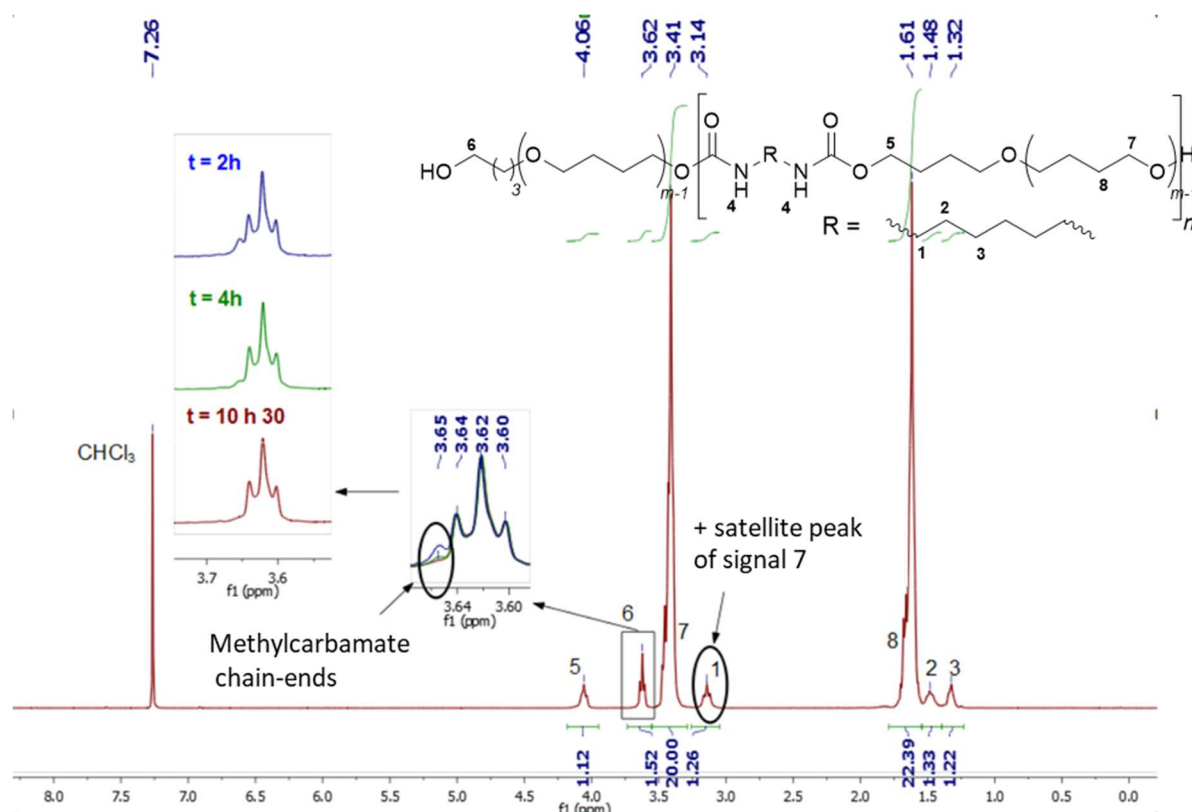


Figure 2: ^1H NMR spectrum of H-C6-650.

The experimental M_n can be deduced by knowing the number of repeating unit "n" of the oligomer formed:

$$M_n = 2n \times M_0 + M_{PTMO} \quad \text{Eq. 5}$$

The estimation of the value of "n" by ^1H NMR is obtained by the ratio of the integrals of the signal of the α -protons of the oxygen of the - OCONH group within the repeat unit (triplet "5", 4nH, I_5) and the signal of the α -protons of the terminal hydroxyl functions (triplet "6", 4H, I_6). We then obtain by replacing in Eq. 5:

$$M_n = 2 \frac{I_5}{I_6} \times M_0 + M_{PTMO} \quad \text{Eq. 6}$$

The physico-chemical characteristics of H-OI are listed in Table 1. They have a yellowish appearance and were obtained in good yields (>87%). One can observe that H-OI based on PTMO650 and PTMO100 series exhibited similar NMR and SEC M_n values. H-OI based on PTMO2000 exhibited a **ratio** M_n (SEC)/ M_n (NMR) close to 2.

Table 1: Physico-chemical characteristics of some prepared H-OI oligomers.

H-OI ¹	Yield n^2 (%)	M_n^3 (g/mol)	M_n^4 (g/mol)	\bar{D}^4	$\%U_{H-OI}$ (%HSO) ⁵	Aspect
H-C ₆ -650	96	1850	2240	2.7	9.4 (13.4)	Waxy and
H-C ₆ -650-kg	92	1650	1560	3.6	8.7 (12.5)	crumbly

H-OI ¹	Yield η^2 (%)	M_n^3 (g/mol)	M_n^4 (g/mol)	\bar{D}^4	$\%U_{H-OI}$ (%HS ₀) ⁵	Aspect
H-C ₆ -650-/BD-1/0.5	>90	1930	PS*	PS*	14.2 (23.9)	solids
H-H ₁₂ -650-kg	87	2000	2960	2.6	8.7 (19.4)	Soft solid
H-Pr-650-kg	97	1750	1725	4.0	6.0 (29.8)	Oily
H-Pr-650/BD-1/0.5	>90	1900	1610	6.4	11.7 (64.0)	Viscous oil
H-C ₆ -1000	>90	2480	2980	2.5	6.0 (8.6)	Waxy solid
H-C ₆ -2000	95	5410	10400	2.2	3.4 (4.9)	
H-C ₆ -2000/BD-1/2	93	3320	PS*	PS*	10.3 (20.0)	Soft solid
H-H ₁₂ -2000	89	5600	10730	2.0	3.4 (7.5)	Viscous oil
H-Pr-2000	96	5710	9560	2.4	3.0 (14.7)	Viscous oil

¹ Kg means kilogram scale; the ratio PTMO/BD was 1/2 or 1/0.5.

² Yield η : overall mass yield of the 2 synthesis steps (Scheme 1).

³ Calculated from ¹H NMR.

⁴ Obtained from SEC.

⁵ Percentage of urethane: $\%U_{H-OI} = [(2 \times n \times M_{Urethane}) / M_n] \times 100$

Percentage of hard segments:

$$\%HS_0 = [(a \times (M_{BMC} - 2 \times M_{MeOH}) + b \times (M_{BMC} + M_{Extender} - 2 \times M_{MeOH})) \times n] / M_n \text{ exp} \times 100$$

a = PTMO molar fraction; b = chain extender molar fraction, with " $a + b = 1$ ".

* Partially soluble in DCM.

It is noteworthy that oligomers from laboratory and industrial scales exhibited similar properties. However, at the kg scale, it is necessary to control the stirring and heating of the medium to avoid the formation of side products. Indeed, in few cases, the formation of carbonate (peak at 4.13 ppm in the ¹H NMR spectrum) and urea functions (evidenced by FTIR) in low proportion was observed (supporting data), suggesting a metathesis reaction between two urethane functions, as described by Kebir *et al.*¹⁷

Preparation and characterizations of partially NIPU coatings

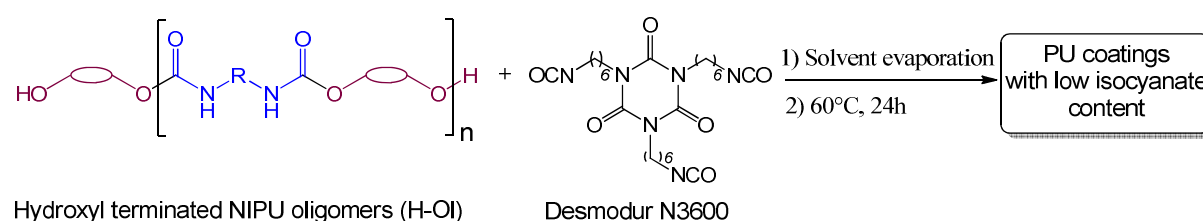
The Hydroxyl terminated NIPU oligomers H-OI were formulated with Desmodur N3600 (Scheme 2) in butyl acetate (AcOBu). The mixtures were then roll-coated on metallic plates in two series of thicknesses. After solvent evaporation, the films were cured at 60°C during 24h.

Dusek *et al.* have used ESI-TOF mass spectrometry to calculate the percentages of the different species contained in Desmodur N3600®, which is essentially composed of the HDI trimer but also oligomers of higher functionality, as well as traces of HDI.²⁹ From this study, they calculated its average functionality f_D and reported a value between 3.1 and 3.2. The weight percentage of isocyanate (%NCO) was of 23% (5.47 mmol/g) (given by the supplier), and can be mathematically expressed as follows:

$$\%NCO = \frac{f_D \times M_{NCO}}{M_D} \times 100 \quad \text{Eq.7}$$

The average molar mass of Desmodur N3600®, i.e. $M_D = 575.2 \text{ g/mol}$, can then be easily deduced from Eq.7 by using an intermediate value of $f_D = 3.15$.

Because of the approximative value of the functionality (and the %NCO) of Desmodur N3600, combined to the systematic error on the hydroxyl equivalent weight of the prepared H-OI (coming from M_n and dispersity) and also isocyanate consuming by moisture, the actual and optimal ratio NCO/OH (>1) was determined experimentally, as reported in the literature,²⁶⁻²⁸ by choosing the minimum value leading to non-sticky materials and a complete conversion of the NCO groups. Actually, FTIR measurements in the ATR mode showed that the characteristic NCO elongation vibration band at 2260 cm^{-1} disappeared completely at the end of the thermal process. In general, the optimal NCO/OH value was of 1.2, except for materials based on PTMO2000 without BD, for which the value was of 1.6. The obtained coatings and references exhibited thicknesses ranging from 19 to $65 \mu\text{m}$ for thin films and from 92 to $295 \mu\text{m}$ for thick films.



Scheme 2. Crosslinking of the H-OI oligomers affording PUs with low isocyanate content.

Overall, coatings based on Priamine were yellowish and those based on BD were opaque. The other materials were colorless and transparent. Materials based on BMC-C6 and BD were semi-rigid unlike the other materials, which were soft. All the prepared coatings exhibited smooth and regular surfaces. Images of some of them are given in the supporting data.

Table 2: Characteristics of the prepared partially NIPU coatings and PU references.

Coating	DE ¹ (%)	Wt% OH ² (<i>mmol/g</i>)	NCO/ OH	Aspect ³	Thickness (μm)	%HS _D ⁴ (%)	%HS _r ⁴ (%)
PU-650	84	5.23 (3.07)	1.2	C, S, T	19 ± 4 281 ± 42	44	0
PU-1000	76	3.40 (2.00)	1.2	C, S, T	40 ± 4 263 ± 89	33	0
PU-2000	69	1.70 (1.00)	1.2	C, S, T	48 ± 7 295 ± 14	20	0
PU-C ₆ -650-kg	48 45	2.06 (1.21)	1.2	C, S, O	43 ± 8 114 ± 6	21	10
PU-C ₆ -650/BD-1/0.5	16 25	1.66 (0.98)	1.2	W, SR, O	13 ± 2 169 ± 26	20	18
PU-H ₁₂ -650-kg	60 60	1.70 (1.00)	1.2	C, S, T	59 ± 3 182 ± 3	18	16
PU-Pr-650-kg	80 85	1.94 (1.14)	1.2	Y, S, T	65 ± 4 158 ± 3	20	23
PU-Pr-650/BD-1/0.5	61 57	1.79 (1.05)	1.2	Y, S, O	41 ± 8 199 ± 90	19	52

Coating	DE ¹ (%)	Wt% OH ² (<i>mmol/g</i>)	NCO/ OH	Aspect ³	Thickness (μm)	%HS _D ⁴ (%)	%HS _r ⁴ (%)
PU-C ₆ -1000	58 58	1.37 <i>(0.81)</i>	1.2	C, S, T	26 \pm 3 178 \pm 12	15	7.3
PU-C ₆ -2000	55 55	0.63 <i>(0.37)</i>	1.6	C, S, T	18 \pm 3 159 \pm 8	10	4.4
PU-C ₆ -2000/BD-1/2	25 25	0.99 <i>(0.58)</i>	1.2	W, SR, O	19 \pm 1 162 \pm 22	11	18
PU-H ₁₂ -2000	56 56	0.61 <i>(0.36)</i>	1.6	C, S, T	22 \pm 4 198 \pm 22	9.4	6.8
PU-Pr-2000	69 69	0.60 <i>(0.35)</i>	1.6	Y, S, T	35 \pm 6 213 \pm 5	9.4	13
Reference 1	/	/	/	W, S, T	32 \pm 3 92 \pm 2	/	/
Reference 2	/	/	/	C, S, T	20 \pm 4 151 \pm 3	/	/

¹ Dry extract: wt% of non-volatile matter after solvent evaporation.

² Weight percentage of hydroxyl groups, calculated from molecular weights.

³ C = Colorless, W = White, Y = Yellow, S = Soft, R = Rigid, SR = Semi-rigid, T = Transparent, O = Opaque.

⁴ Eq. 11 and Eq. 12.

In order to discuss their impact on the final coating properties, the molar percentage of hard segments arising from Desmodur N3600® (%HS_D) and H-OI resins (%HS_r) were calculated. Thus, from the optimal NCO/OH ratio, the molar ratio between Desmodur and H-OI molecules can be formulated as follows:

$$\frac{n_D}{n_{H-OI}} = \frac{NCO}{OH} \times \frac{f_D}{f_{H-OI}} \quad \text{Eq. 8}$$

Thus, for 1 equivalent of H-OI resin ($n_{H-OI}=1$), the molar quantity of Desmodur (n_D) can be deduced and used for the calculation of the mass contributions of each kind of hard segments as follows:

$$m_{HSD} = n_D \times M_D \quad \text{Eq. 9}$$

$$m_{HSr} = \%HS_o \times m_{H-OI} \quad \text{Eq. 10}$$

With: m_{HSD} : the weight of Desmodur; m_{HSr} and $\%HS_o$: the weight and the percentage of intrinsic hard segment in H-OI, respectively.

Finally, $\%HS_D$ and $\%HS_r$ were deduced as follows:

$$\%HS_D = \frac{m_{HSD}}{m_{HSD} + m_{H-OI}} \quad \text{Eq. 11}$$

$$\%HS_r = \frac{m_{HSr}}{m_{HSD} + m_{H-OI}} \quad \text{Eq. 12}$$

The outstanding trials are described in Table 2. We can notice that H-OI resins with high urethane content (with BD) exhibited lower solubility in AcOBu. Indeed, the crystalline zones, promoted by the more numerous H-bonds between the urethane hard segments (higher % U_{H-OI}), limit the solubility of these oligomers (lowest DE, Table 2). As mentioned above, these kinds of films were opaque, suggesting a microphase segregation.

The swelling test in THF was used to determine the extractable percentage (τ_{Ex}) as well as the swelling percentage (Q) of the studied materials (Table 3). The extractable content gives an indication of the quality of the polymer network. Values around 10% or less are generally indicative of good conversion and good network quality.³⁰ The swelling percentages (Q), also give information on the crosslinking density of the studied PUs, as Q is related to the average molar mass between **crosslinks** (M_c) by the Flory-Rehner formula, taking into account the interaction parameter χ polymer/solvent of Flory.³¹ The presented results are the average of three measurements. We will equate the molar mass between theoretical **crosslinks** (M_c) with the molar mass of the difunctional H-OI, because crosslinking takes place in majority at their chain-ends.

The films of the PU-Polyol and PU-H-OI series globally keep their initial aspect after contact with THF (Table 3); only the thin "PU-C6-650/BD-1/0.5" and thick "PU-H12-650-kg" films show severe degradation after 24 h in THF, suggesting weak conversions and crosslinking densities. The τ_{Ex} of the "PU-H-OI" coatings (3-25%, Table 3) are higher than those of the "PU-Polyol" range (<7%). The thick films generally show lower τ_{Ex} than the thin films. Overall, for same chemical structure, swelling percentages were in good agreement with crosslinking density, which increases with decreasing of M_c . Indeed, for PU based on BMC-C₆, the swelling percentage increased from around 35%(thin)/75%(thick) to 154%(thin)/247%(thick) to 443%(thin)/269%(thick) when M_c varied from 1650 to 2480 to 5410 g/mol. For PU based on BMC-H₁₂, the swelling percentage increased from around 49%(thin)/344%(thick) to 126%(thin)/392%(thick) when M_c varied from 2000 to 5600 g/mol. For PU based on BMC-Pr, the swelling percentage increased from around 46%(thin)/187%(thick) to 597%(thin)/468%(thick) when M_c varied from 1750 to 5710 g/mol. Nevertheless, thick films, except PU-C₆-2000 and PU-Pr-2000 films, swell more in THF than their thin analogues, even at same amount of extractables, which could be correlated to samples geometric reasons. Finally, the introduction of BD in the composition of PU led to competition between the effect of increase of M_c and the effect of decrease of solubility in THF, leading to unpredictable values of swelling percentages. PU reference coatings exhibited extractable values ranging from 9 to 39% and swelling percentages ranging from 181 to 483 %. Reference 2 exhibited the highest extractable values.

Table 3: Extractables and swelling percentages of partially NIPU coatings and PU references.

Coating code	NCO /OH	M_c (g/mol) ¹	Thin films		Thick films		Observation ²
			τ_{Ex} (%)	Q (%)	τ_{Ex} (%)	Q (%)	
PU-650	1.2	650	-	-	6.8 ± 3.9	134 ± 30	ND
PU-1000	1.2	1000	-	-	6.5 ± 4.8	116 ± 20	ND
PU-2000	1.2	2000	-	-	6.9 ± 2.4	256 ± 66	ND

Coating code	NCO /OH	M_c (g/mol) ¹	Thin films		Thick films		Observation ²
			τ_{Ex} (%)	Q (%)	τ_{Ex} (%)	Q (%)	
PU-C ₆ -650-kg	1.2	1650	12 ± 4	35 ± 4	7.1 ± 0.6	75 ± 8	ND
PU-C ₆ -650/BD-1/0.5	1.2	2050	-	-	14 ± 1	144 ± 5	D+ (Thin)
PU-H ₁₂ -650-kg	1.2	2000	21 ± 2	49 ± 6	-	-	D+ (Thick)
PU-Pr-650-kg	1.2	1750	16 ± 1	46 ± 4	16 ± 1	187 ± 16	ND
PU-Pr-650/BD-1/0.5	1.2	1900	19 ± 0	34 ± 3	5.5 ± 0.5	172 ± 6	D
PU-C ₆ -1000	1.2	2480	16 ± 1	154 ± 16	8.8 ± 0.6	247 ± 15	ND
PU-C ₆ -2000	1.6	5410	18 ± 2	443 ± 39	11 ± 1	269 ± 18	D
PU-C ₆ -2000/BD-1/2	1.2	3430	3.3 ± 1.0	60 ± 2	2.8 ± 0.5	121 ± 10	ND
PU-H ₁₂ -2000	1.6	5600	3 ± 1.5	126 ± 22	12 ± 1	392 ± 11	ND
PU-Pr-2000	1.6	5710	25 ± 2	597 ± 17	16 ± 1	468 ± 18	D
Reference 1	-	-	19 ± 1	313 ± 80	9.2 ± 2.0	431 ± 13	ND
Reference 2	-	-	39 ± 2	-	25 ± 2	181 ± 3	ND

¹ Theoretical average molecular weight between crosslinks (Desmodur N3600), $M_c = M_{n(H-OI)}$.

² ND = No or little degradation, D = degradation, D+ = high degradation.

Thermal properties

The thermal stability of the prepared PU materials was assessed by TGA under nitrogen atmosphere. The temperature values at 5% of weight loss ($T_{5\%}$) are reported in Table 4. Typical TGA curves are presented in Figures 3 and 4. As with conventional polyurethanes,²⁶⁻²⁸ thermal degradation of the prepared partially NIPU materials occurs in two steps, i.e. degradation of the hard segments (HS, $T_{max} \approx 300$ °C) followed by the degradation of the PTMO soft segment, through the scission of the ether groups³² (SS, $T_{max} \approx 400$ °C). $T_{5\%}$ values varied from 249 to 318 °C, suggesting very good thermal stabilities. The H-OI oligomers showed similar two-step degradation curves comparing to their corresponding PU. This suggests that the crosslinking reaction and the presence of isocyanurate groups, reported as much more stable than the urethanes (degradation temperature > 300 °C),³³ has no significant influence on thermal stability of the prepared PUs. One can observe also that PU-650 series are less thermally stable in terms of weight loss ($T_{max} \approx 249-276$ °C) than their PU-1000 and PU-2000 analogues ($T_{max} \approx 256-318$ °C), which is ascribed to a higher concentration of

urethane groups within the PU-650 series. For the same reason, PU based on BD exhibited the lowest thermal stabilities ($T_{\max} \approx 249\text{-}256^\circ\text{C}$). Finally, the prepared PU-Polyol materials exhibited intermediate thermal stabilities ($T_{\max} \approx 280^\circ\text{C}$). Finally, PU references coatings exhibited similar thermal stabilities than the PU-650 series ($T_{5\%} \approx 269\text{-}277^\circ\text{C}$).

Table 4: Thermal properties of the partially NIPU coatings and PU references.

Coating code	%U _{H-OI} ¹	T _{5%} ² (°C)	T _g ³ (°C)	ΔCp ³ (J/g. °C)	T _c ³ (°C)	ΔH _c ³ (J/g)	T _m ³ (°C)	ΔH _m ³ (J/g)
PU-650	0	280	-47	0.28	-	-	-	-
PU-1000	0	283	NV	NV	-	-	-	-
PU-2000	0	280	NV	NV	-35	36	8	35
PU-C ₆ -650-kg	8.7	262	-41	0.14	-	-	-	-
PU-C ₆ -650/BD-1/0.5	14.2	249	-58	0.32	-	-	-	-
PU-H ₁₂ -650-kg	8.7	274	NV	NV	-	-	-	-
PU-Pr-650-kg	6.0	276	NV	NV	-	-	-	-
PU-Pr-650/BD-1/0.5	11.7	256	-40	0.38	-	-	-	-
PU-C ₆ -1000	6.0	281	NV	NV	-	-	-	-
PU-C ₆ -2000	3.4	290	NV	NV	-23	42	15	47
PU-C ₆ -2000/BD-1/2	10.4	256	NV	NV	-34 140*	22 3.4*	23 166*	29 2.7*
PU-H ₁₂ -2000	3.4	311	NV	NV	-34	28	8	29
PU-Pr-2000	3.0	318	NV	NV	-25	42	17	45
Reference 1	-	277	-46	0.39	-	-	-	-
Reference 2	-	269	-40	0.18	-	-	-	-

¹ Percentage of urethane functions within H-OI.

² Determined by TGA.

³ Determined by DSC. T_c: crystallization temperature (1st cooling cycle); T_m: melting temperature (1st heating cycle).

NV = Non-visible in the scanned temperature range (-70 °C to 200 °C).

* Crystallization/melting temperatures of the hard segments.

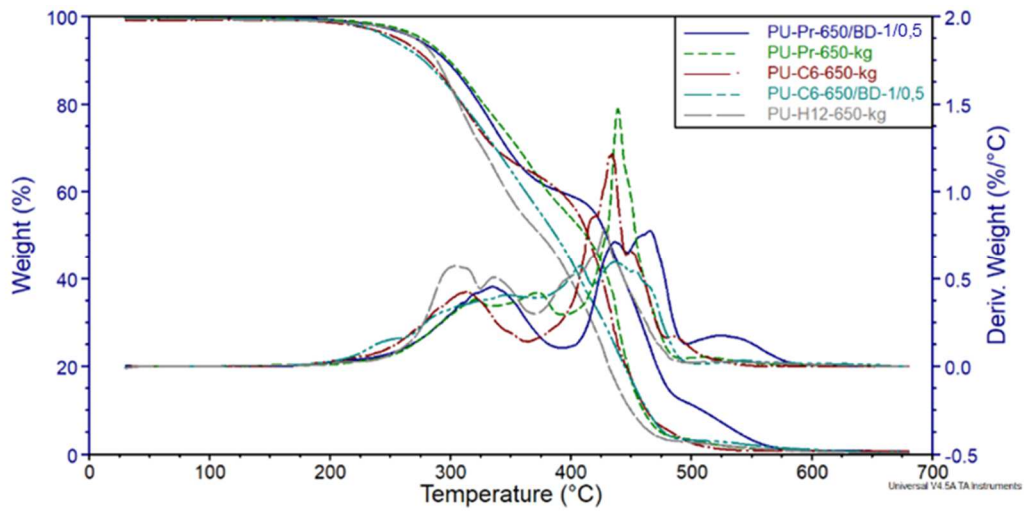


Figure 3: TGA thermograms of PU-BMC-650 based coatings.

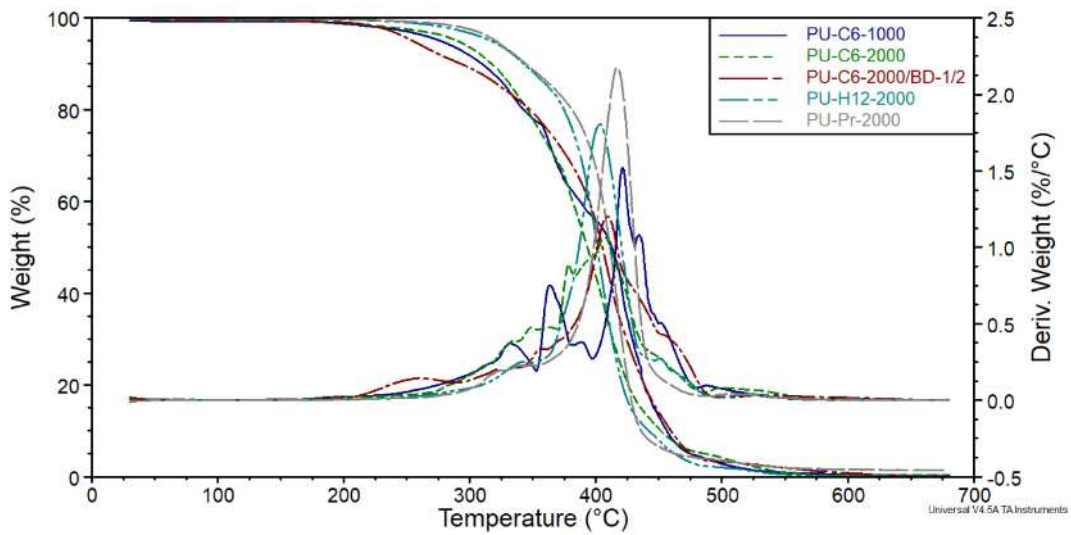


Figure 4: TGA thermograms of PU-BMC-1000 and PU-BMC-2000 based coatings.

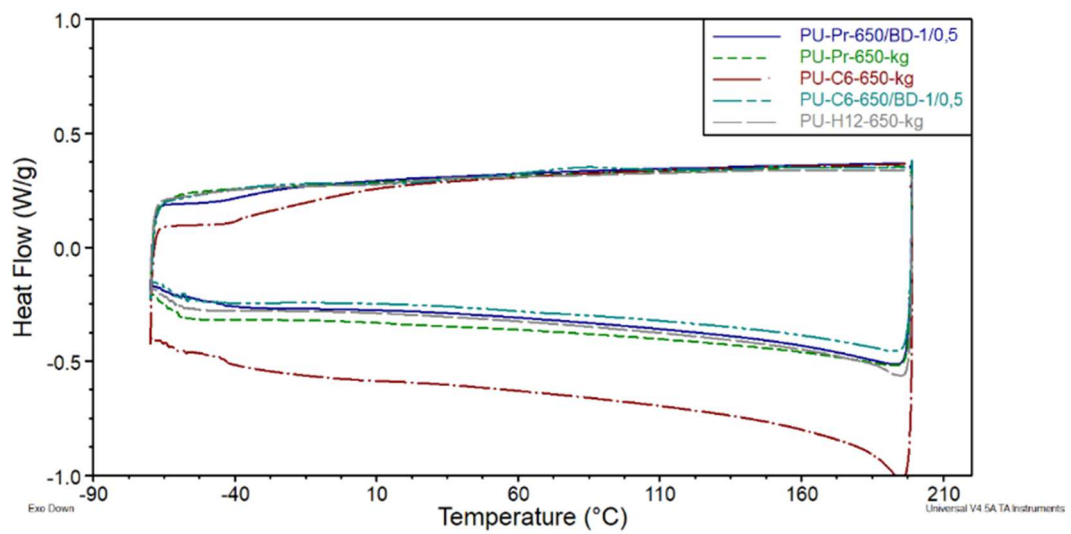


Figure 5: DSC thermograms of PU-BMC-650 based coatings.

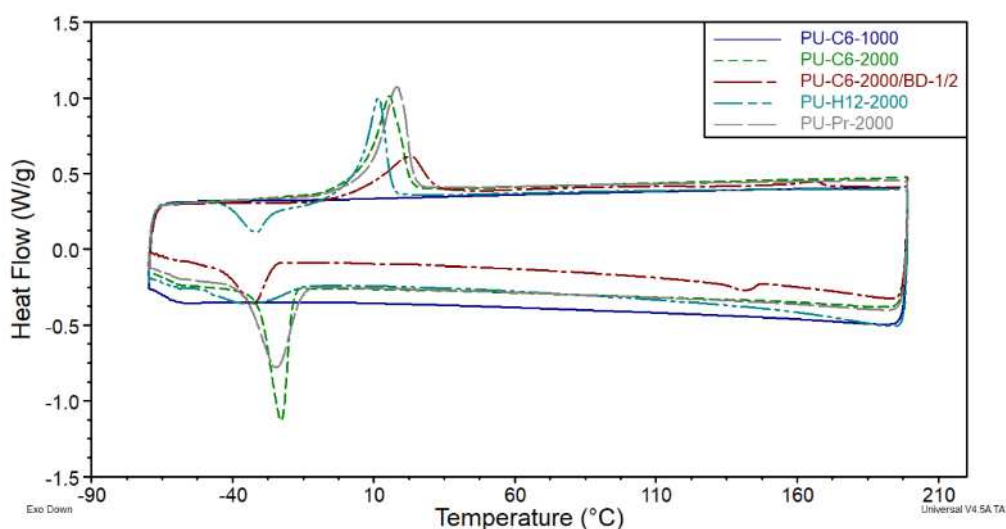


Figure 6: DSC thermograms of PU-BMC-1000 and PU-BMC-2000 based coatings.

The thermal properties of the partially NIPU materials were assessed by DSC. The thermal parameters are depicted in Table 4. Typical DSC curves are displayed in Figures 5 and 6.

The glass transition temperature of the soft segments (T_g (SS)) was observed for only some materials based on PTMO650, i.e. PU-650, PU-C₆-650-kg, PU-C₆-650/BD-1/0.5 and PU-Pr-650/BD-1/0.5, with values ranging from -58 to -40°C, associated to calorific capacity values ranging from 0.14 to 0.38 J/g.°C. However, probably due to a low calorific capacity, T_g (SS) of PU based on BMC-H₁₂, which should be higher than T_g of PU-C₆-650-kg, was not observed. PU based on branched BMC-Pr without BD led to polymer chain softening, which likely induced decrease of the T_g (SS) under the lower temperature detected by the DSC system used, which is between -70 and -60°C. T_g (SS) of materials based on PTMO1000 and PTMO2000 were also not observed, which is likely due to the higher molecular weight of their soft segments and their lower urethane content, leading to lowering of T_g under the detection limit.³⁴ One can also observe that PU based on PTMO2000 exhibited semi-crystalline behavior. The melting (T_m) and crystallization temperatures (T_c) ranged from 8 to 23°C and from -34 to -23°C, with associated enthalpy values of 29 to 47 J.g⁻¹, and of 22 to 42 J.g⁻¹, respectively. These values correspond to the organized parts of the PTMO soft segments. This phenomenon is widely reported in the literature.³⁵ The melting and crystallization temperatures of the hard segments (T_m = 166°C, T_c = 140°C) was observed only in the case of PU-C₆-2000/BD-1/2, i.e. based on BD as chain extender, with low melting and crystallization enthalpies (2.7 and 3.4 J.g⁻¹). This result is often obtained with conventional polyurethanes and is ascribed to the low content of hard segments within these materials.

The reference coatings 1 and 2 showed similar thermal behavior to the PU-650 series, with T_g values of -46 and -40°C, respectively, and no crystallinity.

Mechanical properties

The mechanical properties were studied by the uniaxial tensile test **on the thick film series**, by approximating the ISO 527_3 standard "Test conditions for films and sheets". For each tested material, 5 to 15 rectangular "type 2" specimens were cut. The specimens with unevenness or

notches were systematically discarded. The results are presented in Table 5. Typical stress/strain curves are displayed in Figures 7 to 10.

The properties of the PU-polyol and PU-H-OI coating series were investigated in relation to their chemical structures. The influence of the length and chemical nature of the soft segment, the molar mass between **crosslinks**, as well as the percentage and chemical nature of the hard segment has been studied.

With the same molar mass between **crosslinks** ($M_{c\ th.}$) and Desmodur content (%HS_D), the stiffness properties of the materials are increased by a factor of 2 when using H-OI oligomer as polyol (PU-C6-650-kg, E = 8.04 MPa), compared to using PTMO (PU-2000, E = 3.43 MPa). The urethane hard segments imparted by the H-C6-650-kg oligomer (%HS_r ≠ 0) allow the formation of additional intermolecular -H bonds and stiffen the system.

In the PU-BMC-650-kg series, the lowest Young's modulus (E) values were obtained with BMC-Pr (E = 5.75 MPa for PU-Pr-650-kg versus 8.04 MPa for PU-C6-650-kg and 14.5 MPa for PU-H12-650-kg, Table 5, Figure 8). Its long and branched aliphatic chains make it very flexible ($\epsilon_r = 120\%$ for PU-Pr-650-kg versus $\epsilon_r = 73 - 96\%$ for PU-C6-650-kg and PU-H12-650-kg, Table 5, Figure 8), which accounts for this decrease in stiffness and strength. The stiffest materials were obtained from BMC-H₁₂. This is due to its rigid cycloaliphatic structure, which restricts the degrees of freedom of the chemical bonds, and thus the freedoms of motion of the polymer chains.³⁵ The strength properties are also improved. BMC-C6 gives coatings with intermediate properties. The breaking stress σ_r in this series ranged from 1.15 to 1.70 MPa.

These effects were less pronounced on the PU-BMC-2000 series, because the BMC contents were lower (%HS_r, Table 5 and Figure 9). Indeed, these materials exhibited Young's modulus (E) values around 3 MPa and elongation at break (ϵ_r) around 500%. However, the breaking stress (σ_r) was higher for PU based on BMC-H₁₂ (16.7 MPa versus around 6 MPa for the others). Furthermore, the shape of the tensile curves of the materials of this series suggests strain-induced crystallization leading to self-strengthen.

Table 5: Mechanical properties of the main prepared partially NIPU coatings and PU references. NCO/OH = 1.2 for PU-BMC-650-kg, and NCO/OH = 1.6 for PU-BMC-2000.

Coating code	M_c^1 (g/mol)	E^2 (MPa)	σ_r^2 (MPa)	ϵ_r^2 (%)	%HS _D ³ (%)	<u>%HS_r</u> ³ (%)
PU-650	650	4.74 ± 0.30	0.90 ± 0.28	25 ± 10	40	0
PU-1000	1000	3.82 ± 0.52	1.21 ± 0.20	46 ± 9	31	0
PU-2000	2000	3.43 ± 0.27	2.93 ± 1.33	220 ± 98	18	0
PU-C ₆ -650-kg	1650	8.04 ± 0.67	1.59 ± 0.15	73 ± 10	21	10
PU-C ₆ -650/BD-1/0.5	1930	64.0 ± 7.6	4.45 ± 0.90	50 ± 17	18	20
PU-H ₁₂ -650-kg	2000	14.5 ± 2.11	1.70 ± 0.15	96 ± 8	18	16

Coating code	M_c^1 (g/mol)	E^2 (MPa)	σ_r^2 (MPa)	ϵ_r^2 (%)	%HS _D ³ (%)	$\frac{\%HS_r^3}{(\%)}$
PU-Pr-650-kg	1750	5.75 ± 1.05	1.15 ± 0.09	120 ± 13	20	24
PU-C ₆ -2000	5410	3.04 ± 0.65	6.18 ± 1.36	440 ± 21	9.8	4.4
PU-C ₆ -2000/BD-1/2	3430	29.1 ± 1.4	13.3 ± 2.4	280 ± 45	11	18
PU-H ₁₂ -2000	5600	3.81 ± 0.67	16.7 ± 2.9	530 ± 30	9.4	6.8
PU-Pr-2000	5710	3.43 ± 0.48	5.43 ± 1.34	500 ± 47	9.4	13
Reference 1	-	5,72 ± 0,67	9,05 ± 0,99	460 ± 32	-	-
Reference 2	-	2,43 ± 0,60	2,05 ± 0,54	250 ± 21	-	-

¹ Average molecular weight between two hydroxyl functions.

² E = Young modulus; σ_r = breaking stress; ϵ_r = elongation at break.

³ %HS = Hard segment percentage.

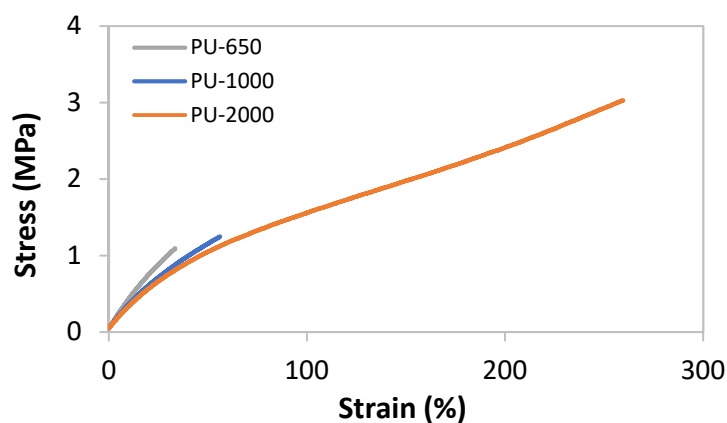


Figure 7 : Average stress/strain curves of the PU-PTMO series.

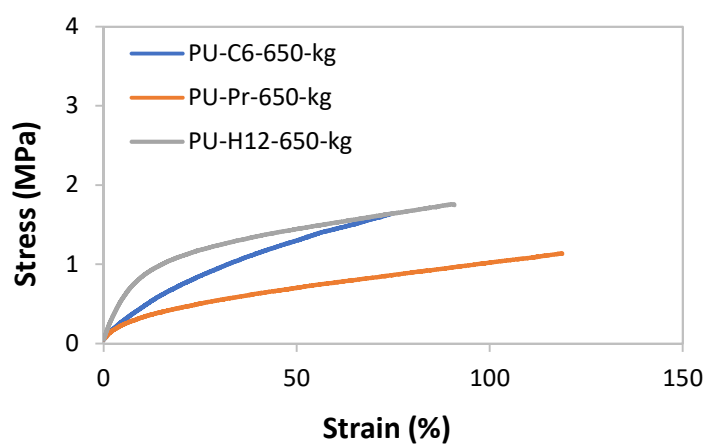


Figure 8: Average stress/strain curves of the PU-BMC-650-kg series.

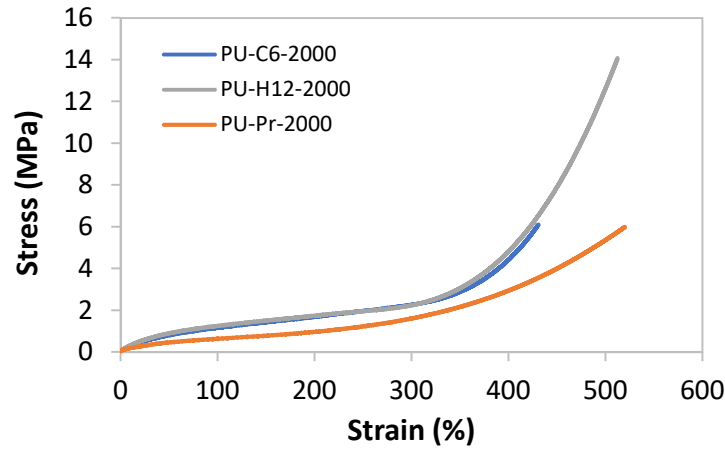


Figure 9: Average stress/strain curves of the PU-BMC-2000 series.

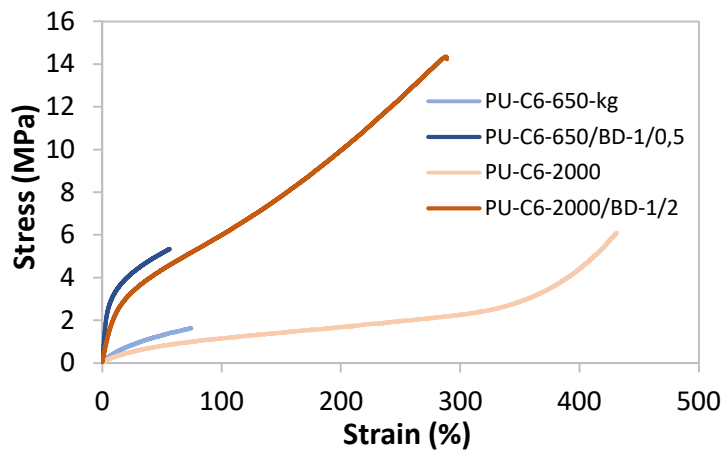


Figure 10: Typical stress/strain curves of PU-C6-PTMO/BD-1/y series.

At constant %HS_D and $M_{c\ th.}$, one can observe that increasing %HS_r, through the use of BD as chain extender, has a very significant positive impact on all mechanical properties of the coatings (Figure 10). This influence derives from the HS - HS and HS - SS bonds that the urethane functions are capable of establishing in the PU material.^{36,37} Thus, by doubling %HS_r values from 10 to 20% at $M_{c\ th.} \approx 2000$ g/mol, the stiffness increased with Young's modulus values multiplied by 8 (E from 8.04 to 64.0 MPa), and stress at break values multiplied by 3 (σ_r from 1.59 to 4.45), for a loss of elongation of less than 33% (ϵ_r from 73 to 50%) (Table 5, PU-C6-650-kg and PU-C6-650/BD-1/0.5). The increase of %HS_r values from 4.4 to 18% at $M_{c\ th.} \approx 4000$ g/mol led to increase of stiffness with increasing in E and σ_r values (from 3.04 and 6.18 MPa to 29.1 MPa and 13.3 MPa, respectively), while elongation at break dropped from 440 to 280% (Table 5, PU-C6-2000 and PU-C6-2000-1/2).

In summary, increasing the urethane functions, by incorporating a chain extender (BD), have improved the mechanical properties of the partially NIPUs coatings. However, the average molecular weight between the **crosslinks** must be sufficient to allow obtaining of elastic properties.

Reference 1 coating showed mechanical properties in the range of PU-BMC-2000 series without BD, while reference 2 was close to PU-2000 coating.

Surface properties

An ideal coating must have high surface energy to adhere firmly to other surfaces, and low hydrophilicity to avoid hydrolysis and/or swelling by water from moisture or weathering. It is often very difficult to find a good balance between these two parameters, so adhesion promoters are added to compensate for the lack of surface energy and increase the adhesion between the coating and the surface.

The hydrophilic or hydrophobic character of the films were evaluated by measurement of the surface contact angle with water (θ_{water}). The surface energy was determined by the Owens - Wendt model, which distinguishes polar γ_s^p and dispersive γ_s^d components of the total surface energy (γ_s). The obtained values are displayed in Table 6.

Overall, one can observe that the prepared PUs have an average surface energy compared to PTFE (19 mN/m²) and glass (89 mN/m²). Their values ranged from 30 to 44 mN/m² and were close to the commercial PU references 1 and 2 (43 and 40 mN/m², respectively). They also exhibited low hydrophilicities, with water contact angle ranging from 62 to 92°C. One can also observe that the reference coatings showed hydrophilicities in the range of the prepared PU coatings ($\theta_{\text{water}} = 69$ and 84°, respectively).

Furthermore, the polarity was calculated from the surface energy components to study the structure/properties relationships. The influence of the hardener was studied on the coatings based on PTMO as polyol (PU-Polyol series). For the three PTMO coatings, the polarity values increased in an expected way with the introduced percentage of isocyanurate hardener (from 1.9% for PU-2000 to 8.6% for PU-650). This results in a very slight increase in surface energies from 37 to 40 mN/m, which were higher than the surface energy of a pure PTMO with $M_n = 43$ kg/mol ($\gamma_s = 31.9$ mN/m).³⁸ The PU-2000 coating containing the least hardener was rather hydrophobic ($\theta_{\text{water}} = 92^\circ$) when the two others were slightly hydrophilic ($\theta_{\text{water}} = 84^\circ$ and 80°).

Table 6: surface properties of the prepared partially NIPU coatings and PU references.

Coating code	θ_{water} (°) ¹	γ_s (mN/m) ²	γ_s^d (mN/m) ²	γ_s^p (mN/m) ²	Polarity (%) ³	Grid test ⁴
PU-650	79.2 ± 1.3	39.5	36.0	3.4	8.6	Iso 5
PU-1000	84.3 ± 1.2	39.3	37.3	2.0	5.1	Iso 5
PU-2000	91.8 ± 1.5	36.7	36.0	0.7	1.9	Iso 5
PU-C ₆ -650-kg	62.2 ± 0.4	44.0	30.6	13.4	30.5	Iso 5
PU-C ₆ -650/BD-1/0.5	62.7 ± 1.7	40.5	27.4	13.0	32.1	Iso 4
PU-H ₁₂ -650-kg	73.2 ± 0.7	43.7	39.3	4.4	10.1	Iso 5
PU-Pr-650-kg	77.6 ± 1.2	33.2	26.7	6.5	19.6	Iso 5
PU-C ₆ -2000	79.6 ± 1.7	32.9	26.9	5.3	16.1	Iso 5
PU-C ₆ -2000/BD-1/2	77.2 ± 1.5	40.5	36.6	4.0	9.9	Iso 5

Coating code	$\Theta_{\text{Water}} (^{\circ})^1$	γ_s (mN/m) ²	γ_s^d (mN/m) ²	γ_s^p (mN/m) ²	Polarity (%) ³	Grid test ⁴
PU-H ₁₂ -2000	88.1 ± 0.5	35.6	33.9	1.7	4.8	Iso 5
PU-Pr-2000	72.6 ± 0.7	31.1	20.0	11.1	35.7	Iso 5
Reference 1	69.0 ± 1.2	42.9	35.9	6.9	16.1	Iso 5
Reference 2	83.9 ± 1.9	40.0	38.0	2.0	5.0	Iso 4

¹ Contact angle values.

² γ_s = total surface energy, γ_s^d : dispersive component and γ_s^p : polar component.

³ Polarity = γ_s^p / γ_s .

⁴ Iso 0: the best; Iso 5: the worst.

When using oligomers of $M_n \approx 2000$ g/mol (PU-BMC-650), the surface energy values remain, as for the PU-PTMO series, around 40 mN/m. By raising the molar mass of the oligomers to $M_n \approx 6000$ g/mol (PU-BMC-2000), a clear decrease was observed (γ_s between 31 and 36 mN/m). This is due to the influence of the hardener, but also to the higher percentages of urethane functions ($\%U_{H-OI}$) of the PU-BMC-650 coating precursors ($\%U_{H-OI} = 6 - 10$ %) compared to the PU-BMC-2000 precursors ($\%U_{H-OI} = 3 - 4$ %).

For the PU-BMC-650 series, the use of the BMC-Pr monomer drops the surface energy value compared to BMC-H12 and BMC-C6 ($\gamma_s = 33$ mN/m versus $\gamma_s > 40$ mN/m). Its long and branched C36 hydrocarbon chain, which is highly non-polar, was likely responsible for this decrease. This effect was lower on the PU-BMC-2000 series, owing to a lower mass concentration of BMC.

However, it is important to note that the PU-Pr-2000 and PU-C6-2000 coatings show abnormally high polarity values with respect to the morphology of their crosslinked H-OI oligomers (high M_n , low $\%U_{H-OI}$). Actually, these two films exhibited one of the highest values of extractible ($\tau_{Ex} = 18\%$ for PU-C6-2000 for and 25% for PU-Pr-2000), suggesting that the crosslinking of these films was incomplete, which could result in higher concentrations of non-reacted hydroxyl endings within the coatings. The presence of amine groups deriving from hydrolysis of isocyanates is also possible. These functions, potentially present at the interface, could increase the polarities, which would justify such values.

The adhesion properties of the prepared PU coatings were determined by the grid test method, according to the conditions specified in ISO 2409. The results are classified in 6 levels, after cutting and brushing, from "ISO 0" characterizing a perfect solidarity between substrate and substrate, to "ISO 5", where at least 65% of the coating disengages. In general, adhesion between two materials is improved if the maximum number of interactions, ranging from Van der Waals forces to ionic or covalent bonds, can develop at the interface.³⁹ Urethane functions provide good adhesion properties for coatings on their substrates, in particular through their hydrogen acceptor/donor character.^{40,41} However, because these functions are in weak amount within coatings made from NIPU oligomers (PU-H-OI) and polyols (PU-Polyol), they all have poor adhesion characteristics classified as ISO 5, with the exception of the single PU-C6-650/BD-1/0.5 coating that has the highest mass content of urethane functions and polarity (ISO 4, Figure 11, $\%U_{H-OI} = 14,5$ %, polarity: 32.1%).

These results are not prohibitive, as they are similar to reference PU coatings, for which adhesion promoters are added in their formulations to improve their interaction with the coated surface.

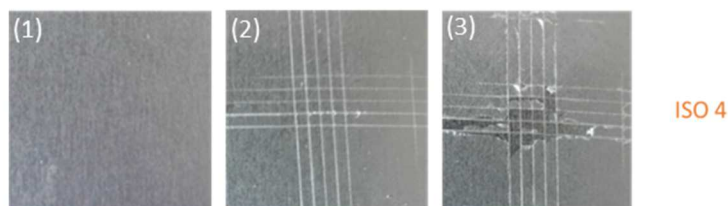


Figure 11: Photographs of the PU-C6-650/BD-1/0.5 coating during the grid test. (1) before cutting, (2) after cutting, (3) after cutting and brushing.

CONCLUSIONS

In this research work, we prepared good quality coatings by crosslinking synthesized hydroxy-functional NIPU oligomers (H-OI) with a commercial polyisocyanate, namely Desmodur N3600®. The importance of the urethane hard segments contained in the H-OI on the properties of the coatings was demonstrated. The study of the surface properties showed their important role in the polar component of the measured energies. Due to their ability to make H-bonds, they are able to confer better adhesion properties. Despite their lower thermal stability, the coatings containing more hard segments showed the best mechanical properties, both in stiffness and strength, while limiting elongation losses with the use of longer soft segments. On the other hand, insertion of urethane linkages in the polyol structure through transurethanization could reduce isocyanate consumption without altering the final material properties in the PU industry (coating, foam, adhesive...) in 2K formulations. Moreover, this amount could be further reduced by using longer and BD-rich H-OI in an aqueous dispersion process, where H-OI solubility is not an issue. Finally, the obtained coatings exhibited thermal and mechanical properties similar to those of the flexible PUs currently developed on the market ($T_{5\%} > 248^{\circ}\text{C}$, $E = 3.04 - 64.0 \text{ MPa}$, σ_r from 0.9 to 16,7 MPa, $\epsilon_r = 25 - 530 \%$), and some of them were partially biobased.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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