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UV-mediated Thiol-ene Polyol Functionalization for Synthesis of Biobased Waterborne Polyurethanes

Jevgenij Lazko[1*], Loïc Poussard[1], Jérôme Mariage[1], Fouad Laoutid[1], Jean Marie Raquez[1,2], Philippe Dubois[1,2]

[1]Materia Nova Research Center, Laboratory of Polymeric and Composite Materials (SMPC), Mons 7000, Belgium.
[2]Center of Innovation and Research in Materials & Polymers (CIRMAP), University of Mons (UMons), Mons 7000, Belgium.

Correspondence to: Jevgenij Lazko, Materia Nova Research Center, Laboratory of Polymeric and Composite Materials (SMPC), Avenue Copernic 3, Mons 7000, Belgium. E-mail: jevgenij.lazko@materianova.be

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Abstract

Developing waterborne polyurethane coatings from biobased polyols represents an interesting alternative, allowing at the same time to increase the use of sustainable renewable raw materials and to reduce volatile organic compounds emissions. In this work, biobased Veopur polyol was first functionalized with mercaptopropionic acid using solvent-free UV-mediated thiol-ene reaction performed in bulk. Grafted carboxylic moieties were then neutralized by triethylamine in order to obtain the required amphiphilic behavior. In the final step, functionalized water dispersible polyol was polymerized with water soluble polyisocyanate to form waterborne polyurethane (WPU). The influence of key-process parameters on grafting efficiency was investigated by iodometric titration, Fourier-transform infrared spectroscopy and proton nuclear magnetic resonance. Particle size measurements and stress-strain tests were carried out to characterize WPU water dispersions and corresponding materials, respectively.

Keywords

Waterborne polyurethane; biobased polyol; thiol-ene grafting; soft segment; functionalization; UV; dispersion

1. INTRODUCTION

The evolution of the regulatory requirements relevant to health, safety and environment is currently driving research into finding new alternatives for polyurethane-based coatings. Developing waterborne polyurethanes (WPU) was undoubtedly a major technological advance that significantly reduced volatile organic compounds emissions[1,2]. Further sustainability improvements can be achieved replacing petro-based chemistry by renewable bio-based alternatives, using for instance polyols issued from abundant and low cost agro-industrial oils, and particularly of unsaturated ones[3-11](Desroches et al., 2012). Such biobased and water dispersable polyurethanes (bio-WPU) for coating applications were already synthetized, inter alia, from castorbean (*Ricinus communis*)[12-14], rapeseed (*Brassica napus*)[15,16], jatropha (*Jatropha curcas*)[17] soybean (*Glycine max*)[18,19] and linseed (*Linum usitatissimum*)[20] functionalized oils.

Due to the intrinsic hydrophobicity of all previously cited plant oil-based polyols, the predominant strategy to obtain WPU consisted in *hard segment* functionalization by the incorporation of ionic hydrophilic segments directly into polymer backbone during the synthesis. Dimethylolpropionic acid (DMPA) neutralized with triethylamine (TEA) seems to be the most commonly used pair of charges improving biobased PU amphiphilic properties[21]. Hard segment functionalization strategy with DMPA/TEA has been also the subject of our recent works relevant to biobased WPU for coating applications and the influence of process parameters on their physicochemical, mechanical and thermal properties[22].

An alternative strategy, involving *soft segment* functionalization, consists to graft charges directly on the biobased polyols. This functionalization is expected to bring new amphiphilic properties to the polyols, enhancing their hydrophilic character and eventually their dispersability in water. Such modified polyols may finally react with diisocyanates to form WPUs. In this respect, solvent-free UV-mediated thiol-ene grafting of mercapto-carboxylic acids on polyol double bonds might represent a sustainable environmentally friendly approach fully considering intrinsic chemical assets of unsaturated vegetal oils.

UV-mediated thiol-ene chemistry has been the subject of increased interest in polymer synthesis, crosslinking and functionalization[23-30]. Crosslinked hydrogels for biomedical applications were formed via photopolymerization of functionalized PEG and bis-cysteine peptides[31]. Crosslinked networks could be also obtained upon UV exposure of polyfunctional thiols and waterborne polyurethane pre-polymers containing pendant unsaturations[32].

The potential of UV-initiated solvent-free thiol-ene reactions, carried out without deoxygenation, at room temperature and without the use of any metal catalyst, was highlighted for the synthesis of dendrimers and well-defined functional macromolecules[33]. Photoinduced thiol-ene couplings were successfully carried out for preparation of thermoset polymers using multifunctional alkyl ester mercaptopropionates and biobased unsaturated fatty acids[34], macrolactones[35] and limonene[36]. Photochemically initiated thiol-ene click couplings were compared to thermally induced reactions on a series of alkene-functional polymers such as polystyrene (PS), polycaprolactone (PCL), poly(methyl methacrylate) (PMMA) and polyethylene glycol (PEG), UV treatments systematically leading to higher yields and shorted reaction times[37]. In this study, the grafting of mercaptoacetic acid was precisely selected for its ability to add carboxylic groups in place of carbon-carbon double bounds and, consequently, to bring significant change in the solubility of functionalized polymers.

UV-mediated thiol-ene coupling strategy was also applied for the synthesis of fully-biobased waterborne polyurethanes[13]. Fatty dicarboxylic acid (precursor which would be later transformed into diisocyanate by Curtius rearrangement) as well as hydrophilic chain extender were successfully synthetized by coupling of 3-mercaptopropionic acid with undecylenic acid and castor oil, respectively. In both cases, UV-induced thiol-ene couplings were carried out in solution (dichloroethane and ethanol), under stirring for 4.5 and 6 h, resulting in yields as high as 92%. Finally, after the completion of the polymerization reaction, dispersability in water of such synthesized PU was ensured by neutralization of carboxylic acid moieties by addition of triethylamine. Such a strategy to obtain the both reactants by thiol-ene reaction is of strong interest but although presents the drawback of the use of organic solvent.

Due to the low viscosity of fatty acid dimers at ambient temperature, the soft segment functionalization strategy investigated in the present study consists to graft mercaptopropionic acid (MPA) on the biobased polyol Veopur from esterified soybean oil fatty acids, using solvent-free UV-mediated thiol-ene reaction performed in bulk. Grafted carboxylic moieties were then neutralized by TEA and thus water dispersable functionalized polyol was finally polymerized with commercial water soluble polyisocyanate to form waterborne polyurethanes (WPU). The emphasis was placed on the influence of key-process parameters on grafting efficiency, modifications being followed by iodometric titration, fourier-transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (^{1}H NMR). The study also concerned the influence of grafting rate on water dispersability of functionalized polyols and properties of corresponding WPUs, characterized respectively by particle size measurements in the dispersion state and by stress-strain measurements in the solid state after water evaporation.

2. MATERIALS AND METHODS

2.1. Materials

Biobased polyol Veopur 721075 from esterified soybean oil fatty acids was supplied by Vandeputte Oleochemicals (Belgium) and used without any further purification. According to the provided analyses, hydroxyl value I_{OH} (70 mg KOH/g) and Wijs titration iodine value (102 g I_2/100 g) revealed the following characteristics: a molecular weight around 1600 g/mol and 5.2 double bonds in mean per molecule. Irgacure 2022 photoinitiator, composed of phosphine oxide phenyl bis (2,4,6-trimethyl benzoyl) 20 wt% and 2-hydroxy-2-methyl-1- phenyl-1-propanone 80 wt%, was kindly provided by Ciba Specialty Chemicals (Germany). Mercaptopropionic acid (MPA, 99% purity) and triethylamine (TEA, 99% purity) were purchased from Sigma-Aldrich. Bayhydur 401-70, a self-emulsifiable polyisocyanate for 2K WPUs coatings based on polyethylene glycol functionalized isophorone diisocyanate (IPDI) (NCO 2.34 mmol/g) was supplied by Bayer (Germany). Methylethyl ketone (MEK), methanol (MeOH) and isopropanol were purchased from Merck and deuterated chloroform ($CDCl_3$, 99.8% d) from Euriso-Top.

2.2. UV Grafting Procedure

Photochemical thiol-ene grafting was carried out in a DYMAX UV Lamp chamber (Torrington, USA), under 50-80 mW/cm^2 irradiation at 365 nm, during 90-200 min in order to graft carboxylic moieties on fatty acid dimers [Figure 1]. Components were mixed manually before introduction in the UV chamber. The reaction was done in bulk, without any additional solvent, in glass-covered rectangular 160 mm × 150 mm × 10 mm Teflon moulds. Different MPA/Veopur ratios were investigated from 0.5 to 2 (mol/mol) thiol/ene ratio. Another parameter was the weight ratio of photoinitiator Irgacure/Veopur varying from 1/10 to 1/3 g/g (10 to 33 wt%). In order to remove unreacted thiol and the residues of photoinitiator after UV treatment, modified polyol was purified by 5 consecutive liquid-liquid extractions with 2 equivalent volumes of methanol. Finally, the product was dried under vacuum at 60 °C to a constant weight.

2.3. Iodometric Titration

Decrease in the amount of free thiols remaining in the reaction medium was directly followed during the UV-treatment by iodometric titration[38]. 500 mg samples were dissolved in 15 g MEK/Isopropanol 1/2 g/g and titrated with 0.025 N iodine solution. The quantity of the free thiol was calculated using the formula $n_{thiol} = N_{I_2} \times V_{I_2}$, with N_{I_2} and V_{I_2} representing the molarity and the volume of iodine solution, respectively. Grafting rate was then defined as SH consumed per CC double bond equivalent.

2.4. FTIR Spectroscopy

FTIR spectra were recorded in absorbance (3800-600 cm^{-1}) at a nominal resolution of 1 cm^{-1} using Bruker TENSOR 27 spectrometer (Ettlingen, Germany).

2.5. NMR Spectroscopy

^{1}H NMR spectroscopy was performed using Bruker Avance 500 Spectrometer (Billerica, USA) at a frequency of 500 MHz to confirm each step of polyol functionalization on samples dissolved in $CDCl_3$ (20 mg/600 µL).

2.6. Particle Size Distribution

WPU dispersions were characterized by dynamic light scattering measurements using Malvern Instruments Zetasizer Nano-S (Malvern, UK). Samples were systematically diluted by 100 to reach 0.2 wt% solid content and analyzed at 20 °C. All measurements were performed in triplicate.

2.7. Mechanical Properties

Tensile properties [Young modulus (E), the stress at break (σ_b) and the strain at break (ε_b)] were evaluated

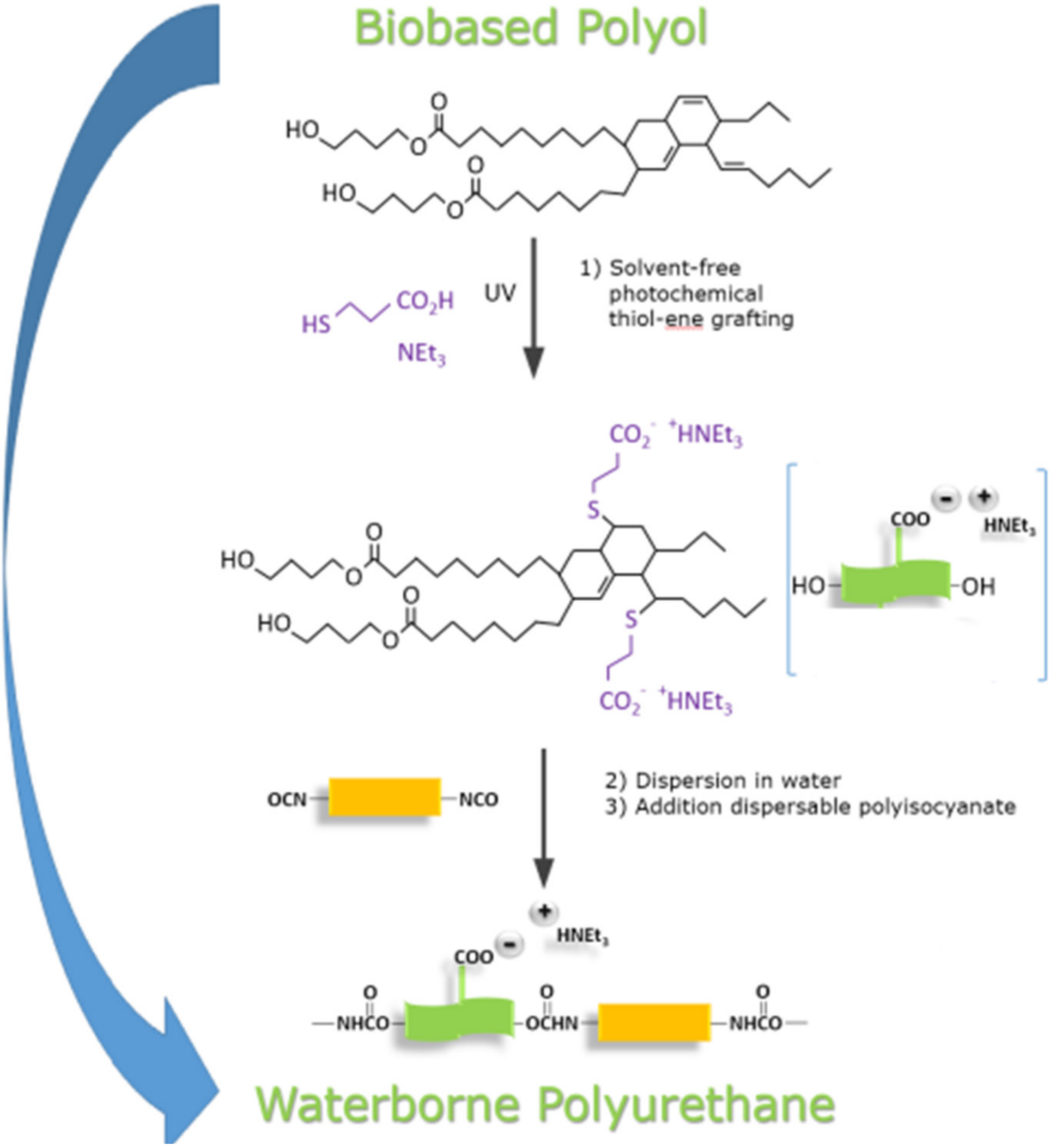

Figure 1. Reaction scheme for synthesis of waterborne polyurethane through UV-mediated functionalization of biobased Veopur polyol.

according to the ASTM D638 standard on dumbbell-shaped samples cut from the WPU sheets at 10 mm·min^{-1} using a Benelux Scientific Hounsfield H10KT apparatus (Nazareth, Belgium) equipped with 100 N load cell.

3. RESULTS AND DISCUSSION

3.1. Main UV Treatment Parameters

Concentration of the photoinitiator, initial thiol/ene ratio and UV intensity are three key-parameters influencing grafting kinetics that have been studied in this work. First, the influence of UV intensity was evidenced comparing 50 mW/cm^2 and 80 mW/cm^2 treatments [Table 1]. Grafting kinetics and final grafting rates were increased from 43% to 51% with the increase of the UV intensity from 50 to 8 mW/cm^2, for the set of trials at low Irgacure concentration (10%). The overall increase in grafting efficiency was also noticed at high Irgacure

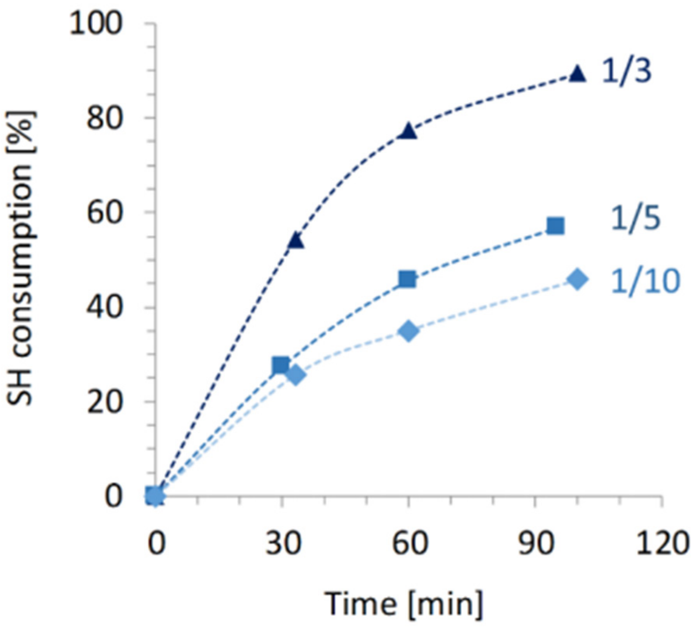

Figure 2. Influence of the initial photoinitiator concentration on MPA consumption kinetics. (1/10, 1/5 and 1/3 Irgacure 2022/Veopur g/g, 4 g samples, 1/1 thiol/ene mol/mol, 50 mW/cm^2).

concentration (33%), reaching 95%. However, in the context of this study, UV intensity of 50 mW/cm^2 has been found to be more suitable for further investigation and up-scaling trials, primarily due to UV device specificities and also to avoid heat generation phenomena leading to undesirable secondary decompositions reactions.

The influence of the photoinitiator concentration on UV-mediated grafting kinetics was clearly shown using 1/10, 1/5 and 1/3 g/g initial Igracure 2022/Veopur ratios for low-amount (4 g) Veopur samples prepared in small circular 40 mm moulds [Figure 2]. When treated at 50 mW/cm^2 with 1/1 thiol/ene, higher conversion rates around 90% could be reached in 100 min using 33% Irgacure media. For the scale-up of the polyol production (up to 60 g, *vide infra,* section 3.2), the initial photoinitiator content was consequently chosen at 33 wt% of the introduced polyol.

Initial thiol/ene ratio is also an essential parameter influencing grafting kinetics and grafting rates [Table 2]. As reported in literature, most researches on thiol-ene reactions were performed with a high excess of thiol, with two or more thiol functions per carbon-carbon double bond[39]. In this work, we used a derivative method[40] and investigated a reduced range of thiol/ene ratio, to limit the thiol excess to be removed afterwards. Different sets of modified polyols, covering a wide range of grafting rates from 47% to 98%, were obtained at 50 W/cm^2, by varying thiol/ene initial ratio from 0.5 to 2. Clear relationship can be observed between initial thiol/ene ratio, absolute thiol consumption and grafting rate (thiol consumption relative to the theoretical amount of carbon-carbon double bonds). Lower 0.5 thiol/ene ratios trigger higher thiol consumptions, MPA preferentially reacting with the most accessible carbon-carbon double bonds, i.e., conversion rate being close to the theoretical value of 50%. For stoichiometric thiol/ene ratio, an average conversion rate of 67% was obtained. Finally, high grafting rates superior to 95% could be reached in presence of a large excess of thiol.

Accordingly, the optimized conditions to reach high conversion rates with 4 g Veopur samples were found at 50 mW/cm^2 irradiation using 33% Irgacure/Veopur media and 1/1 thiol/ene mol/mol ratio. In the next section, similar operational conditions were used for upscaling the process, in order to obtain functionalized polyols in quantities allowing further polymerization and characterization tests from being performed.

3.2. MPA Grafting Upscale

MPA grafting UV treatments were performed in larger 160 mm × 150 mm × 10 mm rectangular moulds

Table 1. Impact of UV intensity and photoinitiator concentration on grafting rates, determined by iodometric titration. 4 g Veopur samples, 1/1 thiol/ene mol/mol ratio, 90 min

UV intensity (mW/cm^2)	Photoinitiator/Polyol (g/g)	Grafting rate (%)
50	1/10	43
80	1/10	51
50	1/3	86
80	1/3	95

Table 2. Influence of the initial thiol/ene ratio on thiol consumption and grafting rate, determined by iodometric titration. 30 g Veopur samples, 1/3 Irgacure 2022/Veopur g/g, 50 mW/cm^2, 180 min

Thiol/ene (mol/mol)	Absolute thiol consumption (%)	Grafting rate (%)
0.5	94	47
0.67	79	53
1.0	67	67
1.2	71	86
2.0	49	98

Table 3. Upscaling of the UV treatment. Grafting rates determined by iodometric titration and obtained with 30 and 60 g Veopur samples (1/1 thiol/ene mol/mol ratio, 50 mW/cm^2)

Polyol (g)	Photoinitiator/Polyol (g/g)	Time (min)	Grafting rate (%)
30	1/10	180	64
30	1/5	180	72
30	1/3	180	81
60	1/10	200	46
60	1/5	200	58
60	1/3	200	74

containing up to 60 g of Veopur [Table 3]. Major upscaling bottlenecks, such as heterogeneous UV intensity in the UV chamber, heat accumulation and mass loss, have been overcome by improving the experimental device, homogenizing the reaction medium and extending the treatment time up to 200 min. For instance, due to the experimental device geometry inducing a heterogeneous UV exposure, grafting rates measured at the end of the treatment could locally vary by a factor of two, only depending on the sample position in the center or the periphery of the mould. Hence, it was possible to increase up to 7% the overall grafting rate by several homogenizations of the reaction medium during the treatment, spaced out by 45 min.

As previously observed, the grafting rates considerably increased with the Irgacure content. Depending on photoinitiator concentration, different ranges of grafting rates between 64%-81% and between 46%-74% were obtained with 30 and 60 g production scale, respectively. More interestingly, the lower grafting rates for up-scale modified polyol, whatever the photoinitiator content, would be assumed to the higher thickness of the mixture limiting the UV beam penetration.

The impact of UV grafting treatments on structural modifications was first investigated by FTIR [Figure 3]. The grafting rate could be recorded by following the increase of the MPA characteristic absorption bands at 1440 cm^{-1}, 1340 cm^{-1} and in the 1250-1150 cm^{-1} region, corresponding to -CH$_2$-S-R and -COO- bonds[40-44].

Quantitative structural studies of the modified polyols were carried out by ^{1}H NMR. Specific resonance signals were identified for each reagent, i.e.,Veopur, MPA and Irgacure 2022, and were normalized with respect to Veopur methylene proton signal at 0.85 ppm (which always remained unchanged, before or after grafting). Purification efficiency (5 washing steps with MeOH) was verified for all samples: integration of Irgacure 2022 specific signals in 8.0-7.9 ppm domain, corresponding to aromatic protons, proved systematically close to the detection limits and the baseline noise. For MPA, emphasis was placed onto 3.0-2.4 ppm specific domain corresponding to -CH$_2$- in α and β positions of S atom of the grafted MPA [Figure 4]. Due to the overlap of

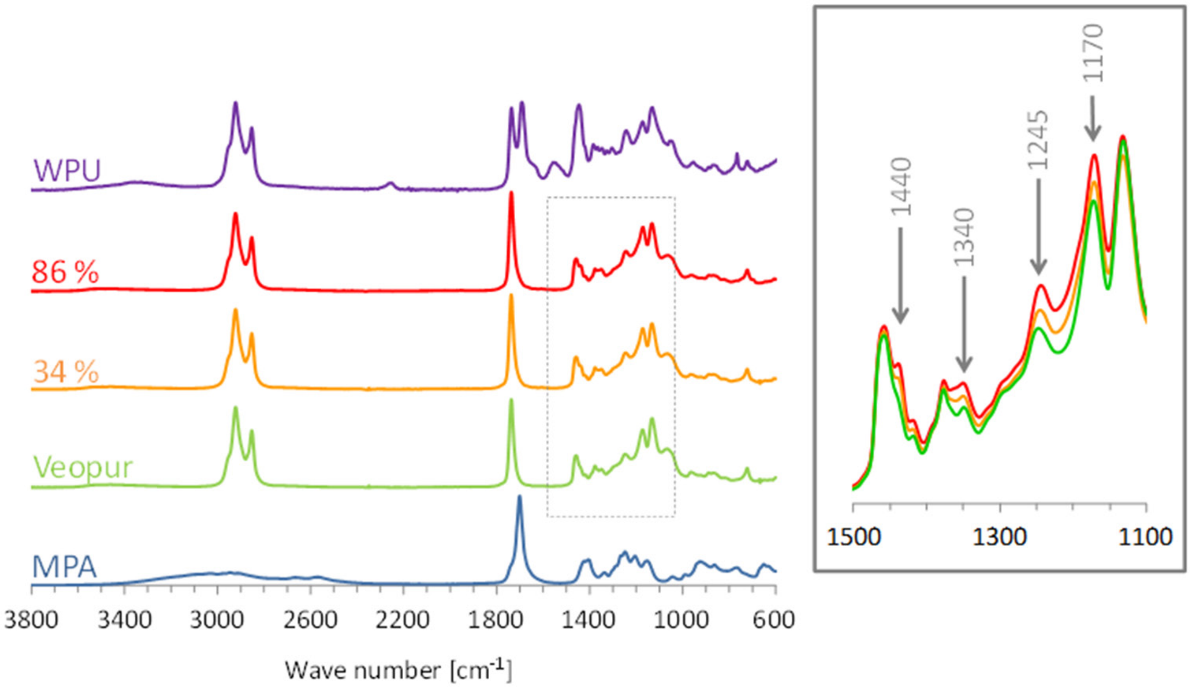

Figure 3. FTIR spectra of MPA, Veopur, functionalized Veopur after UV thiol-ene grafting and final waterborne polyurethane.

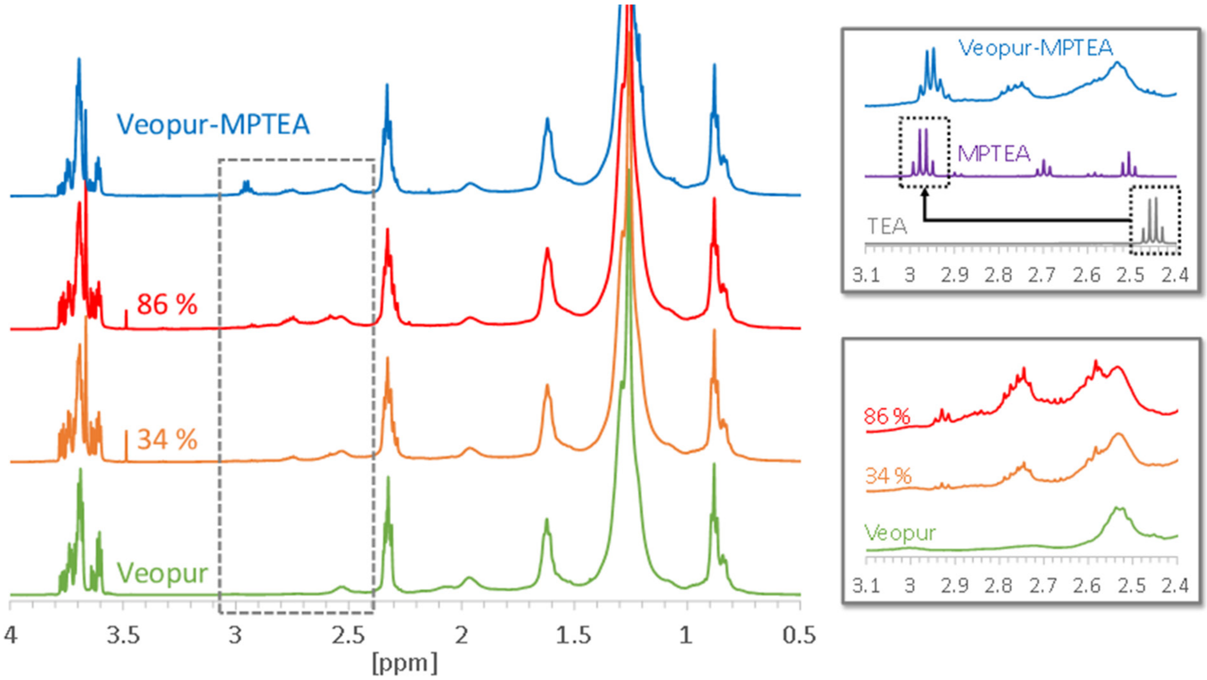

Figure 4. ^{1}H NMR spectra of the reference Veopur, MPA-grafted Veopur and MPA-grafted Veopur neutralized with TEA (coded as Veopur-MPTEA).

Veopur aliphatic signal at 2.6-2.5 ppm, the final integration of the grafted MPA was obtained after subtraction of the respective integration of (MPA + Veopur) minus integration of (Veopur). ^{1}H NMR was also considered as a suitable analytical technique to confirm TEA neutralization of MPA-grafted Veopur, as the major resonance

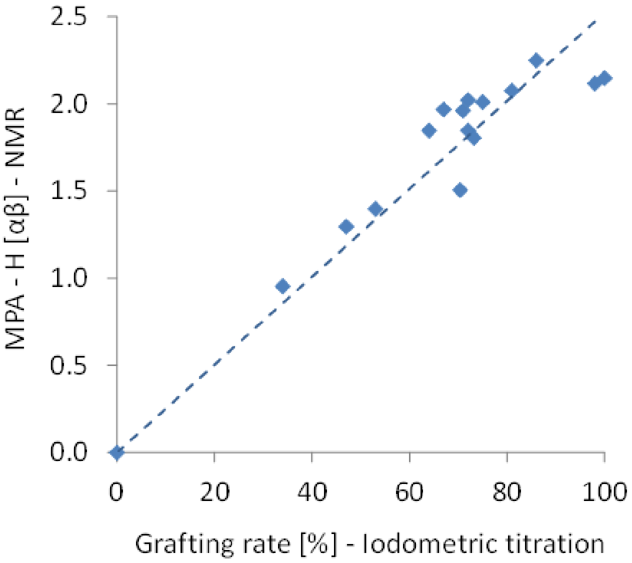

Figure 5. Relationship between 1H NMR integrations and iodometric titration results obtained for the set of MPA grafting experiments.

signals corresponding to grafted MPTEA were perfectly identifiable in the final product: $-S-CH_2-CH_2-COO^-$ protons at 2.75 ppm (in α position of S atom) specific to the grafted MPA and $-CH_2-$ protons at 2.95 ppm specific to neutralized TEA.

Finally, results obtained by iodometric titration have been compared to ^{1}H NMR data [Figure 5]. Complementarity between these two approaches, indicating respectively thiol consumption and grafting efficiency, seemed to be verified for all MPA/Veopur/Irgacure trials described in this study. A linear relation between titration results and ^{1}H NMR integration of $-CH_2-$ of the grafted MPA in the 3.0-2.4 ppm region may be established for the whole set of grafting rates between 35% and 100%.

3.3. WPU Synthesis

The main objective of this last part of the work was to confirm that functionalized polyols could be dispersed in water and finally polymerized. The previous modified polyols were neutralized by the stoichiometric addition of TEA relative to the grafted carboxylic acid groups. MEK was added to reduce viscosity (50 wt%) and then it was possible to disperse them in water after phase-inversion and to obtain 20 wt% waterborne polyol dispersions [Figure 1]. Water self-emulsifiable Bayhydur polyisocyanate was then added in excess, isocyanate index I_{NCO} varying from 110 to 130, and the reaction medium kept under magnetic stirring for 18 h at 20 °C. Final WPU dispersions were poured into Teflon moulds and the dry materials, i.e., WPU coatings, were finally recovered after 2 days evaporation at room temperature, followed by 1 day drying under reduced pressure in a vacuum oven at 40 °C. Polymerization advancement was confirmed by FTIR by the presence of characteristic $-NHCO^-$ stretching band of urethane at 1550 cm^{-1} [Figure 3].

For Veopur-MPA samples, preliminary tests showed that grafting of -COOH functions alone was not sufficient to endow the expected amphiphilic properties to the initially highly hydrophobic polyol. On the other hand, under the form of carboxylate $-COO^-$, stable over two months Veopur-MPTEA suspensions were obtained, with mean particle size in the range of 150-200 nm [Table 4]. After the polymerization step, particle mean diameter remained broadly of the same order, around 180 ± 40 nm. Concerning particle size distribution, at this stage of the study it was not possible to clearly conclude about an eventual impact of the grafting rate, neither for the polyol dispersions, nor for the WPU dispersions. However, the grafting rate seemed to have a significant impact on dispersion stability. The influence was evaluated for samples in the range from 35% to 98%, and it was observed that a minimum grafting rate of 60% was required to obtain homogeneous and stable over time WPU dispersions without any sludge or phase separation. Moreover, WPU dispersions with lower grafting

Table 4. Particle size of waterborne Veopur-MPTEA polyols and corresponding polyurethanes (0.2 wt% dispersions in water)

	Mean particle size (nm)	
Grafting rate (%)	**Veopur-MPTEA**	**WPU**
46	202 ± 6	160 ± 11
72	165 ± 2	151 ± 3
82	159 ± 2	220 ± 10

Table 5. Mechanical characterization of WPU materials. Strain-stress tests performed at 10 mm/min

Grafting rate (%)	I_{NCO}	E (Mpa)	σ_b (Mpa)	ε_b (%)
70	130	0.292 ± 0.031	0.336 ± 0.031	141 ± 18
72	110	0.383 ± 0.052	0.341 ± 0.005	126 ± 23
72	130	0.447 ± 0.060	0.232 ± 0.159	137 ± 8

rates exhibited poor coalescence during drying and led to heterogeneous materials, unsuitable for example for coating applications.

Finally, the mechanical properties of dried WPU were evaluated by stain-stress experiments. Table 5 summarizes values of Young modulus (E), stress at break (σ_b) and strain at break (ε_b) obtained for several representative homogeneous and continuous WPU samples with grafting rates around 70%. According to these results, all tested materials showed ductile behavior with elongation at break higher than 100%. Therefore, our general strategy to functionalize biobased polyols and then synthetize polyurethanes in the aqueous medium, seemed to be validated since it enabled formation of ductile materials, opening perspectives for further coating developments.

4. CONCLUSION

Functionalization of biobased Veopur polyol by grafting mercaptopropionic acid was described in this study. Thiol-ene reaction was successfully performed in bulk using solvent-free UV-mediated process with Irgacure 2022 photoinitiator, reaching an average conversation rate of 70% for stochiometric thiol/ene ratio, and values higher than 95% with thiol excess. Neutralization of grafted carboxylic functions with triethylamine created enough charges to bring amphiphilic behavior to the initially highly hydrophobic substrate, accordingly offering functionalized polyol dispersable in water.

Polymerization of such functionalized biobased polyol with self-dispersable Bayhydur 401-70 polyisocyanate eventually led to waterborne polyurethanes. Suitable grafting rates, above 60% were however necessary to obtain fine stable waterborne polyurethane dispersions, with an average particle size around 180 nm. Finally, homogeneous and continuous materials were obtained after drying, with particularly interesting ductile mechanical behavior, i.e., elongations at break being systematically superior to 100%, setting a path toward further coating development studies.

Further polyol functionalization studies might concern improvement of grafting kinetics via development of continuous UV processes. Selection of biobased polyols, self-emulsifiable polyisocyanates and urethane catalysts might be investigated to synthetize waterborne polyurethanes with tunable mechanical properties for specific applications. For further studies concerning coating applications, the emphasis should also be placed on other specific requirements such as adhesive strength, surface properties, water swelling and thermal stability.

5. ACKNOWLEDGEMENTS

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