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Hydroxyurethane modifiers (HUM): an environmentally-friendly route to improve chemical resistance of alkyd coatings

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Graphical abstract



Abstract

This article highlighted the first synthesis of HydroxyUrethane modified alkyd resins by polycondensation reaction. Two new hydroxyurethane modifiers (HUM), with two hydroxyl functions, have been synthetized from renewable resources and have been copolymerized with alcohols and acid derivatives to yield HydroxyUrethane modified alkyd resins. Chemical resistance analysis has showed that HUM increased the alkali resistance of alkyd resins up to 44 %. Film properties such as gloss or drying time remained equivalent with the exception of color. Moreover, the flexibility of the films increased could be interestingly modified according to the structure of the HUM (aromatic or aliphatic). This result highlights a simple, greener and less toxic solution to improve the chemical resistance of alkyd resins.

Keywords

Alkyd resin, hydroxyurethane modifiers, hybrid, coating, chemical resistance

1. Introduction

Alkyd resins (ARs) are defined as polyesters with unsaturated fatty acids. They have been used as coatings or binders in paints since the 1930s.^{1–3} These resins have several properties such as excellent gloss, heat resistance, fast drying time, which can be interestingly adjusted by changing the fatty acid content (oil length).^{4–6} Additionally, the raw materials are mostly biobased, making ARs an "eco-friendly" polymer.^{1,3,7,8} However, ARs suffer from limitations such as poor abrasion, UV and chemical resistance which can be unfavorable for outdoor applications.^{6,9} Hence, industrial and academic research focuses on improving the properties of alkyd resins by functionalizing them with

additives or polymers. Recently, a review on hybrid alkyds was published and highlighted the addition of polyurethanes in alkyd resins to improve the outdoor properties.¹⁰ Indeed, alkyd resins can easily be functionalized with urethane moieties, leading to hybrid alkyd-urethane, named poly(alkyd-urethane) (PAU) or uralkyds, which interestingly combine the properties of both polymers.^{11,12} Polyurethane (PU) are synthetized by a step growth polymerization between a polyol and a diisocyanate.¹³ The presence of hard and soft segments gives them flexibility and hardness.¹⁴ PAU were developed in the late 1970s by reacting isocyanate with the residual hydroxyl groups (-OH) of alkyd resins. These PAU exhibited interesting mechanical properties for coating applications. Athawale et al. used isophorone diisocyanate (IPDI) to obtain crosslinked PAU that exhibited higher chemical resistance than reference alkyd resins.¹⁵ However, this route leads to PAU with a low content of urethane functions. Güner et al. reported the polyaddition of a monoglyceride with an aromatic diisocyanates such as toluene diisocyanate (TDI) or hexamethylene diisocyanate (HMDI) to obtain PAU with higher content of urethane functions.¹⁶ The PAU synthetized with TDI showed good abrasion and chemical resistance whereas the HMDI-based PAU exhibited excellent resistance to ultraviolet (UV) light. Ling et al. have developed a PAU from the synthesis of a new diol by polycondensation of monoglyceride and phtalic anhydride.¹⁷ Then, the diol was cured with methylene diphenyl 4,4'-diisocyanate (MDI) in order to form urethane bonding. The PAU provided better adhesion to the substrate and chemical resistance than conventional alkyd resins. Figure 1 summarized the different PAU structures previously discussed.



Figure 1: Scheme of different PAU structures in the literature

However, some isocyanates are classified as carcinogenic, mutagenic and reprotoxic (CMR) substances and European regulation tend to replace them. Hence, new methods have been studied to obtain Non-Isocyanate PolyUrethane (NIPU). Nowadays, three main pathways have been studied: Curtius rearrangement from azide, transurethanization and carbonate aminolysis reaction.¹⁸ Some of these routes have also been studied for the synthesis of PAU. The azides are not used because they are toxic and explosive. Silbert et al. have investigated the synthesis of PAU through transurethanization reaction.¹⁹ Alkyd resins were reacted with a carbamate and then, dialdehyde was added to the reaction mixture to form urethane bonds. However, this reaction requires higher temperatures (150 °C) than the third route, the carbonate aminolysis reaction. Indeed, the polyaddition between diamines and cyclic carbonates seems one of the most promising routes for access to NIPU and leads to polyhydroxyurethanes (PHUs). PHUs exhibit higher adhesion properties than conventional PUs with similar structure thanks to their additional hydroxyl functions which can strengthen hydrogen bonds.²⁰ Hence, Haniffa et al. epoxidized double bonds of fatty acids present in alkyd resins prior carbonation with carbon dioxide (CO₂).²¹ PAU was obtained by reacting carbonated alkyd resin with diamines. The authors demonstrated that obtained PAU exhibited better chemical resistance than conventional alkyd resins. Nevertheless, the cyclic carbonates present on the fatty chains has a low reactivity.^{22,23} Moreover, this approach prevents oxidative cross-linking of alkyd resins since double bonds are no longer present, which is generally expected for industrial coatings. To our knowledge, the introduction of monomers containing hydroxyurethane (HU) functions during the synthesis of alkyd resins has never been reported in the literature and could improve the alkali resistance without using toxic compounds such as TDI or MDI. This approach relies on the interest of

HydroxyUrethane Modifiers (HUM) proposed by Figovsky *et al.*^{22,24} This term emerged in the literature during the past decade to describe hydroxyl urethane monomers.²² In this study, we have synthesized novel HU diols to replace polyols in the alkyd resins synthesis in order to lead to the formation of the first alkyd resin containing hydroxyurethane modifiers (HUM-AR) (Scheme 1). Then, HUM-ARs were studied by different characterization techniques such as nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR), size exclusion chromatography (SEC). The properties of the coatings were also studied.



Scheme 1: General scheme of HU diols, HUM-AR and reference alkyd (without the use of HU-diol in the composition) syntheses

2. Material and methods

1) Materials

Tall oil fatty acid (TOFA), pentaerythritol, phthalic anhydride, White Spirit and mixture of through/auxiliary driers (mixture of cobalt octoate, calcium octoate and zirconium octoate) and a commercial poly(alkyd urethane) resin were supplied by Lixol (Groupe Berkem, Blanquefort, France). Glycerol carbonate was purchased from TCI. Xylene, p-toluenesulfonic acid (pTSA), chlorhydric acid (HCl), sodium chloride (NaCl), sodium hydroxide (NaOH), benzylamine and hexylamine were purchased from Sigma Aldrich. Tetrahydrofuran (THF), methanol were purchased from VWR International S.A.S (Fontenay-sous-Bois, France). The NMR solvents used was DMSO-d6 from Eurisotop. All reagents were used as received.

2) Characterizations

Nuclear Magnetic Resonance

NMR samples were solubilized in DMSO-d6. The analyses were executed using a Bruker Avance 400 MHz spectrometer at 25 °C. The ¹H NMR spectra were recorded at 8 kHz spectral width, 3 kHz transmitter frequency offset. The acquisition time was 4 seconds and 8 scans were performed.

Quantitative conditions were obtained with a 30° pulse (3 μ s) and a relaxation delay at 1 second. Trimethylsilane (TMS) was used as external reference for ¹H NMR. Shifts were given in ppm.

Acid values (AV)

Acid value was determined according to ISO 2114:2000 standard. AV corresponds to the mass of potassium hydroxide (KOH) in milligrams required to neutralize one gram of alkyd resin. Hence, approximatively, 1 g of the reaction mixture was sampled and solubilized in a 80/20 xylene/ethanol. The solution was then titrated with a KOH solution at 0.1 mol.mL⁻¹. The acid value was calculated from the equation (1).

$$AV = \frac{V_{KOH} \times M_{KOH} \times C_{KOH}}{m \times N.V.C.}$$
(1)

AV: Acid value; V_{KOH} : volume of KOH solution introduced to neutralize the alkyd resin (mL); M_{KOH} : molar mass of KOH (g.mol⁻¹); C_{KOH} : concentration of KOH (mol.mL⁻¹); m: mass of alkyd resin sampled (g); N.V.C.: Non Volatile Content.

Rheological analyses

Rheological analyses have been performed on a ThermoScientific Haake Mars 60 rheometer equipped with a 35-mm-cone-plate geometry. The analyses have been performed at 20 °C with a shear rate of 10 s⁻¹. The comparison of the resins was done at the non-volatile content of 55 wt%.

Size-exclusion chromatography (SEC)

Molar masses of alkyd resins were determined by size-exclusion chromatography (SEC) using a tripledetection GPC from Agilent Technologies with a corresponding Agilent software, for multidetector GPC calculation. The system used THF with two PL1113-6300 ResiPore 300×7.5 mm columns. The elution flow rate was 1 mL min⁻¹. The GPC is equipped with a 390-LC PL0390-0601 refractive index detector. The entire SEC system was thermostated at 35 °C. Polymethylmethacrylate (PMMA) standards were used for calibration between 540 and 2 210 000 g.mol⁻¹. The typical sample concentration was 15 mg.mL⁻¹.

Fourier Transform Infrared Spectroscopy

The Fourier transform infrared spectroscopy (FTIR) spectra were carried out on a Thermo Scientific Nicolet iS50 FT-IR equipped with an attenuated total reflectance cell (ATR). The data were analyzed using the software OMNIC Series 8.2 from Thermo Scientific.

Gel content

The resins were mixed with 5 wt% mixture of through/auxiliary driers (cobalt octoate, calcium octoate and zirconium octoate) in order to accelerate the autoxidative process. A film applicator was used to cast films (thickness of 55 μ m for dried films). Around 20 mg of three samples from same alkyd resin were separately immersed in THF during 24 h. The three samples were then dried in a ventilated oven at 80 °C for 24h. The gel content (GC) was calculated using equation (3), where m₂ is the mass of the dried material and m₁ is the initial mass. Reported gel content are average values of the three samples.

$$GC = \frac{m_2}{m_1} \times 100 \tag{3}$$

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analyses were performed using a NETZSCH DSC200F3 calorimeter. The calibration was carried out using adamantane, biphenyl, indium, tin, bismuth and

zinc standards. Nitrogen was the purge gas. The thermal properties were analyzed at 20 °C.min⁻¹ between -100 and 100 °C to observe the glass transition temperature.

Thermogravimetric analyses

Thermogravimetric analyses (TGA) of the cured alkyd resins were performed to determine the thermal stability and were acquired on a Netzsch TG 209F1 apparatus under 40 mL.min⁻¹ nitrogen flow. Nitrogen (20 mL.min⁻¹ flow) was used as protective gas. Approximately 10-12 mg of sample was placed in an alumina crucible and heated from room temperature to 850 °C with a 20 °C.min⁻¹ heating rate.

Film properties

The resins were mixed with 5 wt% mixture of through/auxiliary driers (cobalt octoate, calcium octoate and zirconium octoate) in order to accelerate the autoxidative process. Then, 100 µm wet films were casted with a film applicator and dried at 25 °C under relative humidity of 30 % to reach 55 µm thickness for all films. Adhesion was determined with a cross-cut tester 1 mm BYK on a glass plate according to ISO 2409:2020 standard (see supporting information (SI)). The Persoz hardness was measured according to ISO 1522:2006 standard with a TQC SP0500 pendulum hardness tester (see supporting information (SI)). Gloss was measured following ISO 2813:2014 standard and on substrates at 60° and 20° using a TQC Polygloss (see supporting information (SI)). The color of the alkyd resins was measured with the Gardner color scale (SI). The hardness and the gloss were measured at day +10 (D+10) after the application of the film. The time required to obtain a tack-free film was defined as the drying time of the resins. The chemical resistance of the alkyd resins was studied with water (H₂O), hydrochloric acid (HCl), sodium hydroxide (NaOH) and sodium chloride $(NaCl)^{25}$. Approximatively 10 ± 1 mg of the cured alkyd resins were immersed inside each solvent during six hours at room temperature and stirred at 200 rpm. Then, resins were dried in an oven at 80 °C for 12 hours. The residual mass percentage (wt% residue) was determined with equation (4). The analyses were made in triplicate for each sample and the reported residual mass percentages are average values of the three samples.

$$vt\% residue = \frac{m_2}{m_1} \times 100$$
⁽⁴⁾

 m_1 : mass of the alkyd resin sample before being immersed in solvent; m_2 : mass of the alkyd resin sample after being immersed in a solvent and dried in oven.

Complementary information was available in supplementary material.

3) Synthesis

Synthesis of HU-benzyl

In a round bottom flask, 55 g of glycerol carbonate (1.1 eq., 0.466 mol) and 45 g of benzylamine (1 eq., 0.424 mol) were dissolved in 250 mL of methanol. The solution was heated at 65 °C under stirring for 5 h. Once the solution was cooled down, the final product was precipitated in 750 mL of ethyl acetate at -18 °C to remove the excess of glycerol carbonate. The white powder was then washed several times with cold ethyl acetate and dried under vacuum. The pure product HU-benzyl diol was obtained as a white powder with a yield of 98 % (Figure 2).

¹H NMR (400 MHz, DMSO-d6, ppm): δ = 7.7 (1H, t, NH), 7.4-7.2 (5H, m, H_a), 4.8 (0.65H, s, H_i), 4.7 (0.35 H, s, H_e), 4.6 (0.8H, m, OH_e and H_c), 4.2 (2H, m, H_f), 4.0 (1H, m, H_b), 3.9 (1H, m, H_b), 3.6 (0.65H, s, H_g), 3.5 (0.7H, m, H_d), 3.4 (1.3H, m, H_h).



Figure 2: Structure of HU-benzyl diols

Synthesis of HU-hexyl diol

In a round bottom flask, 55 g of glycerol carbonate (1.1 eq., 0.466 mol) and 43 g of hexylamine (1 eq., 0.424 mol) were dissolved in 250 mL of methanol. The solution was heated at 65 °C under stirring for 5 h. Once the solution was cooled down, the solvent was removed under reduced pressure (10 mbar) at 40 °C. Then, the crude mixture was dissolved in diethyl ether and washed with water to remove the excess of glycerol carbonate. The organic layer was then dried with magnesium sulfate and under vacuum. The pure product HU-hexyl diol was obtained as a viscous transparent liquid with a yield of 92 % (Figure 3).

¹H NMR (400 MHz, DMSO-d6, ppm): δ = 7.0 (1H, t, NH), 4.9 (0.65H, s, H_j), 4.7 (0.35H, s, H_f), 4.6 (0.35H, m, OH_k), 3.8-4.0 (2H, m, H_g), 3.7 (2H, m, H_i), 3.6 (0.35H, m, H_e), 3.5 (0.65H, s, H_l), 3.3 (0.7H, m, H_h), 2.9 (2H, m, H_d), 1.3 (2H, m, H_c), 1.2 (6H, m, H_b), 0.8 (3H, m, H_a).



Figure 3: Structure of HU-hexyl diols

Synthesis of tall oil fatty acid (TOFA) alkyd resin with HU-benzyl diol or HU-hexyl diol

A TOFA alkyd resin was synthesized in solvent using TOFA, pentaerythritol, phthalic anhydride, and HUM-diol. The reaction was carried out in a five necked reactor flask, equipped with a mechanical stirrer, a dean stark, a thermometer and a nitrogen inlet. The quantity of TOFA (Table 1), was firstly added. Then, when the reactor was heated at 160 °C, HU-benzyl diol or HU-hexyl diol and pentaerythritol were introduced. Different amounts of HU-benzyl diol were added, between 5 wt% and 20 wt% (for HU-hexyl diol, between 10 and 20 wt%). At 200 °C, phthalic anhydride and 2 mol% of pTSA were added. The compositions of alkyd resins are summarized in Table 1. Reaction mixture reached 210 °C. The water was removed using xylene as azeotropic solvent. The reaction was continued until reaching an acid value of 5 mg of KOH/g of resin. Then, xylene was removed by vacuum prior addition of White Spirit to reach a solid content of 55 wt%. The resins have been designed to obtain the same medium oil length, which is defined as the mass percentage of fatty chains to the total mass of the alkyd resin. The resins had 55 wt% of fatty acids in their composition. Therefore the resins can be classified as medium oil length. The stoichiometry of f_{OH}/f_{COOH} for all the alkyd resins was keep between 1.15 and 1.20.

Samples		Reference	5	10	15	20
Wt% HU-benzy	/l or -hexyl diol	0	5	10	15	20
HU-benzyl or hexyl diol	mol	0.00	0.03	0.07	0.11	0.15
	f _{он} (mol)	0.00	0.06	0.14	0.22	0.30

Table 1: Composition of poly(alkyd hydroxyurethane) resins with HU-benzyl or -hexyl diol

28.						
TOFA	mol	0.22	0.25	0.27	0.30	0.32
	f _{соон} (mol)	0.22	0.25	0.27	0.30	0.32
Doutoon theited	mol	0.21	0.20	0.18	0.18	0.15
Penderythmoi	f _{он} (mol)	0.84	0.80	0.72	0.72	0.60
Phthalic	mol	0.24	0.24	0.24	0.24	0.20
anhydride	f _{соон} (mol)	0.48	0.48	0.48	0.48	0.44
f _{oн} (mol)		0.84	0.86	0.86	0.94	0.90
f _{соон} (mol)		0.70	0.73	0.75	0.78	0.76
Ratio f _{OH} / f _{соон}		1.20	1.18	1.15	1.20	1.18

3. Results and discussion

1) Synthesis of HydroxyUrethane Modified alkyd resins

The synthesis of new di-hydroxyurethane modifiers (HUM) was performed in methanol at 65 °C without catalyst during 5 h under stirring.²⁶ Two different amines, an aromatic (benzylamine) and an aliphatic (hexylamine) amines were reacted with glycerol carbonate to yield respectively HU-benzyl diol and HU-hexyl diol (Figures 2 and 3). An excess of glycerol carbonate was reacted with amines to ensure a complete functionalization. These two monomers were obtained with a yield greater than 92 %. The success of the reaction was confirmed by ¹H NMR analysis. The protons b at 4.0 and 3.9 ppm (J_{H-H}^1 = 40 Hz) for HU-benzyl diol and d at 2.9 ppm for HU-hexyl diol, confirmed the formation of the urethane bonding (Figure 4 a) and b)). Moreover, the integration of proton peaks confirmed that the ring opening aminolysis of cyclic carbonate led mostly to the formation of secondary hydroxyl groups (~ 65 % of the proton of CH-OH at 3.6 ppm, labeled g for HU-benzyl diol in Figure 4a) and I for HU-hexyl diol in Figure 4b)) which was expected as, secondary hydroxyl groups are thermodynamically more stable than primary ones.²⁷ Thus, protons of CH_2 -OH labeled d at 3.5 ppm for HU-benzyl diol and q at 3.8-4.0 ppm for HU-hexyl diol correspond to the primary alcohols and are estimated at \sim 35 %. The ratio between secondary and primary alcohols was determined to be 65/35 for both HU-benzyl and HU-hexyl diols. Nevertheless, considering the primary hydroxyl groups initially present in the glycerol carbonate, at 3.33 ppm, the overall ratio of primary and secondary hydroxyl groups was determined to be around 70 and 30 %, respectively. This ratio is an important parameter for the synthesis of alkyd resins using these HU diols, pentaerythritol (four primary hydroxyl functions) and phthalic anhydride. Indeed, primary alcohols are more reactive than secondary alcohol in the polycondensation step.

b) HU-hexyl diol



Figure 4: ¹H NMR spectra of a) HUM-benzyl diol and b) HUM-hexyl diol (DMSO-d6)

Moreover, on the FTIR spectra (Figure 5), the band around 3330 cm^{-1} is characteristic of the NH groups of the urethane bonds. The band at 1680 cm^{-1} is attributed to the C=O bond of the urethane function. The region around 1550 cm^{-1} shows characteristic bands for the CN and NH bonds of the urethane functions.



Figure 5: FTIR spectra of HU-benzyl and -hexyl diols

All alkyd resins have been synthetized in xylene as azeotropic solvent. The synthesis of hydroxyurethane modifiers-based alkyd resin (HUM-AR) is presented in Scheme 2. The composition of resins has been designed to reach the same medium-oil length so as not to modify film properties.²⁸ The stoichiometry of f_{OH} / f_{COOH} was maintained between 1.15 and 1.2 for all alkyd resins. Hence, an excess of hydroxyl functions is needed to avoid the gelation of the network. The final acid value (AV) was also maintained in the same range, around 5 mg KOH.g⁻¹ for all the alkyd resins. It is defined as the mass of potassium hydroxide (KOH) in milligrams required to neutralize one gram of alkyd resin. This corresponds to the free acid functions in the resins. The advancement of the

reaction was monitored by the measure of AV. Indeed, the decrease of AV indicates the advancement of step growth polymerization.



Scheme 2: Synthesis of HydroxyUrethane Modified-based alkyd resin (HUM-AR)



Size exclusion chromatography (SEC) permitted to determine the weight average molar mass Mw, the number average molar mass Mn, and the dispersity Đ of the seven alkyd resins, as well as a commercial PAU resin obtained with IPDA (Scheme 3). The last one has an isocyanate ratio around 20wt%. For the reference alkyd resin, the values of weight (M_w) and number (M_n) average molar masses were respectively 26,000 g.mol⁻¹ and 3,500 g.mol⁻¹ with a high dispersity, which is characteristic of alkyd resins. During the polycondensation, a same small chain of oligomers with a hydroxyl function on the one hand and with an acid function on the other hand, could react on itself and then lead to the formation of cycles.²⁹ Those cycles have a low molar mass and they can no longer react which explains the high dispersity of alkyd resins.³⁰ This phenomenon is not controlled and appears at any time during the polycondensation. That is why some alkyd resins contain various quantities of cyclic oligomers. All the alkyd resins exhibited similar M_w values to the reference alkyd resin (Table 2). Indeed, all the M_w values were between 21,000 and 26,000 g.mol⁻¹, acceptable values

for obtaining films. All M_n are also very similar with values between 2,500 and 4,000 g.mol⁻¹. The slight decrease in M_w could be attributed to the increasing amount of HU-diol (functionality of 2) in the synthesis of alkyd resins and the reduced amount of pentaerythritol (functionality of 4).

Samples	HU-diol (wt %)	Acid value (AV)	Мп (g.moГ¹)*	Mw (g.mol⁻¹)*	Ð
Commercial PAU	20*	5	4,000	25,000	6.6
Reference***	0	5	3,500	26,000	7.8
HU-benzyl diol AR	5	5	3,000	25,000	9.1
	10	4	3,500	22,500	6.9
	15	4	3,000	22,500	7.5
	20	5	2,500	21,000	8.3
HU-hexyl diol AR	10	4	3,500	24,000	6.9
	20	5	3,000	22,000	7.3

Table 3: Acid value and molar masses of poly(alkyd hydroxyurethane) resins

*Molar masses given in PMMA equivalents, **toluenediisocyanate ratio, ***urethane-free alkyd resin

2) Rheological and thermal properties

Thermal and rheological properties analyses were studied in order to determine the impact of HUM on the rheological properties of the alkyd resins and the final properties of the films.

Viscometry analyses of the resins were carried out at 20 °C with a shear rate of 10 s⁻¹ with the same non-volatile content of 55 wt % (Table 4). The viscosity of all the alkyd resins were in the same range, between 11.5 and 13.9 Pa.s, which is suitable for film application. Those results were expected as the M_w and the M_n obtained by SEC analysis were similar. Indeed, viscosity results are in agreement with SEC results previously discussed. Nevertheless, the hydrogen bonds classically provided by the urethane bonds could have increased the viscosity.³¹

The gel content (GC) was determined to confirm the crosslinking of the cured resins. For all the AR films, the GC were higher than 90 %, which confirmed crosslinking (Table 4).

Differential scanning calorimetry (DSC) analyses allowed to determine the glass transition temperature (T_g) values (Table 4). The reference resin has a T_g value of 21 °C and the commercial poly(alkyd urethane) resin a T_g value of 25 °C. All the T_g of HU-benzyl diol containing alkyd resins showed values between 21 and 22 °C, which is close to the room temperature. As expected, the T_g values of HU-hexyl diol containing alkyd resins slightly decreased and shown values between 16 and 18 °C, which could be due to the aliphatic chain. Indeed, aliphatic chains are more flexible than aromatic rings which exhibit rigidity structure. Nevertheless, those results remained closed to the values of HU-benzyl diol containing alkyd resins. Thus, the performance of the HUM-AR could be maintained as well as the intended application.

Table 4: Viscosity, gel content and	Tg of poly(alkyd	hydroxyurethane)	resins
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Samples	HU-diol (wt %)	η (Pa.s)	Gel content (GC)	Т _д (°С)
Commercial PAU	20*	13.2	95 ± 3	25
Reference	0	13.9	92 ± 1	21
HU-benzyl diol AR	5	13.2	94 ± 1	22

	10	12.6	90 ± 1	22
	15	12.4	91 ± 2	21
	20	11.9	90 ± 1	21
HU-hexyl diol AR	10	11.5	93 ± 1	18
	20	11.7	93 ± 2	16

*toluenediisocyanate ratio

The thermal stability of alkyd resins was studied by thermogravimetric analyses (TGA) under nitrogen flow. Figure 6 shows the thermograms of the commercial PAU, the reference alkyd resin and HUM-AR. The temperatures at 5 % and 50 % weight loss, and the residue yield at 750 °C, are reported in Table 5. First, temperature at 5 % weight loss ($T_{d,Swt\%}$) is in the same range for all the alkyd resins, between 150 and 180 °C. This could be due to the evaporation of residual solvent trapped in the polymer matrix during crosslinking reaction. Indeed, the solvent used is White Spirit which exhibits a boiling point above 130 °C.

The temperature at 50 % weight loss ($T_{d,50wt\%}$) is between 372 and 388 °C for the HU-benzyl-diol containing alkyd resins, the reference alkyd resin and the commercial PAU. Then, for the HU-hexyl-diol containing alkyd resins, the $T_{d,50wt\%}$ was slightly reduced around 350 °C. Those results were expected as aliphatic chains exhibit a lower thermal stability than aromatic rings. Moreover, the residue yields at 850 °C was 11.5 wt% for the reference alkyd resin, while they were halved for the commercial PAU and the HU-benzyl-diol containing alkyd resins. The alkyd resin with 20% HU-hexyl-diol had the lowest residue yield which could be due to the higher content of aliphatic chains which provided less char formation than the aromatic rings. The thermal stability of alkyd resins with HU-hexyl-diol decreased which could be due to the lower thermal stability of alkyd resins with HU-hexyl-diol decreased which could be due to the lower thermal stability of aliphatic chains compared to aromatic rings.



Figure 6: TGA curves of reference alkyd resin, commercial PAU resin and HU-benzyl-diol and HU-hexyl-diol containing alkyd resins

Table 5: Results of TA analyses of HUM-AR.

Samples	HU-diol (wt %)	Т _{d,5wt%} (°С)	T _{d,50wt%} (°C)	Residue at 850°C (%)
Commercial PAU	20*	168	377	6.5
Reference	0	157	370	11.5
	5	173	376	7.0
HII bonzul dial AP	10	185	384	6.0
HO-belizyi ulul An	15	171	388	8.0
	20	180	372	7.5
HIL-beryl diol AP	10	155	350	6.0
HU-REXYI DIDI AR	20	150	350	4.0

* toluenediisocyanate ratio

3) Films properties

Dry films with a thickness of 55 μ m were casted from the different resins. The adhesion, the flexibility, the gloss, the drying time and the chemical resistance have been determined for all resins. The results are summarized in Tables 6 and 7.

Samples	HU-diol	Adhesion ^a	Hardness ^b	Gloss ^c	Drying time	Gardner
	(wt %)		(s)	20°/60°	(min)	color
				(G.U)		
Commercial PAU	20*	0	155	75/97	210	5
Reference	0	0	161	73/96	270	4
	5	0	105	73/98	250	11
	10	0	95	76/97	230	12
HO-benzyi uloi	15	0	85	79/100	240	15
	20	0	79	82/100	250	12
HU-hexyl diol	10	0	35	73/94	240	18
	20	0	25	71/96	250	17

Table 6: Adhesion, hardness, gloss and drying time of HUM alkyd resins

*toluenediisocyanate ratio

^a: ISO 2409:2020 standard

^b: ISO 1522:2006 standard

^c: ISO 2813:2014 standard

All the alkyd resins have similar drying times between 3 h 30 min and 4 h 30 min, as expected. Indeed, all the resins exhibited M_w around 25,000 g.mol⁻¹.

The adhesion was determined by using the crosscut test. All the alkyd resins showed very good adhesion properties on aluminum substrate. The edges of the cuts were completely smooth and none of the squares of the grid were torn off, that is why they were evaluated at class 0 according to ISO2409:2020. The introduction of HU-diols had no impact on the adhesion properties of the resins.

The Persoz hardness of the coatings was measured. The more flexible is the film, the more it is able to absorb the energy of the pendulum, the faster the pendulum is damped and therefore the less oscillations are required. Hence, the number of oscillations decreased with the increased amount of di-HU. Indeed, the reference alkyd resin had a hardness value of 161 whereas with 5 wt% HU-benzyl

diol the hardness values was 105. Then, the more the amount of HU-benzyl diol increased, the more the hardness decreased, until reaching a value of 79 with 20% by weight of HU-benzyl diol. This result is expected because HU-benzyl diol replaces pentaerythritol by reducing cross-linking, which has a direct effect of lowering hardness. Nevertheless, the films remained quite flexible, allowing the resins to retain their film-forming properties on wood or metal substrates. The hardness of alkyd resins containing 10 wt% HU-benzyl diol was lower than that of resins with 10 wt% HU-benzyl diol . This results was expected because aromatic group exhibits more rigidity than aliphatic chain. Thus, alkyd resins containing HU-hexyl diol exhibited the greatest flexibility, allowing the resins to be used on wood substrates.

The gloss of the coatings was first measured at 60° to determine the gloss level. All the alkyd resins showed a high gloss level with values higher than 94 (between 94 and 100). Then the measurements were done at 20°. The reference resin showed a value of 73 and all the alkyd resins containing HU-benzyl or -hexyl diols exhibited values between 72 and 82. The addition of di-HU in alkyd resins had no impact on the gloss of the resins. Moreover, all the alkyd resins were classified with a high gloss level.

The color of all the alkyd resins was determined with the Gardner color scale. The values are between 1 and 18. The darker is the color, the higher is the value. The addition of di-HUM darkened the resins with values between 11 and 18.

Table 7 summarizes the results of the chemical resistance of alkyd resins. The higher is the weight loss, the lower is the residual mass percentage and the less resistant is the resin to the solvent. All the alkyd resins containing di-HU- had similar chemical resistances compare to the reference and the commercial PAU resin for water, HCl and NaCl solutions. However, the synthesis of HUM-ARs improved the chemical resistance of the resins to alkali solution (NaOH 0.1 M) up to 44 % with a di-HU ratio of 20 wt%. These results were similar to the NaOH resistance of commercial PAU resin and were expected as the urethane bonds are well known to improve the chemical resistance of hybrid alkyd resins.^{10,15} The –NH groups of urethane linkages form hydrogen bonds with the substrate leading to enhanced chemical resistance.³² Moreover, there is no difference in chemical resistance between aromatic and aliphatic HUM. This improvement in alkali solution resistance could allow the use of alkyd resins containing di-HU for marine paints or varnishes in near-sea environments.

Samples	HU-diol	Water	HCI (0.1 M)	NaOH (0.1 M)	NaCl (5 %)
	(wt %)	(%)	(%)	(%)	(%)
Commercial PAU	20*	95 ± 2	83 ± 2	95 ± 2	99 ± 2
Reference	0	94 ± 3	80 ± 2	52 ± 3	97 ± 4
HU-benzyl diol	5	96 ± 1	80 ± 3	83 ± 2	95 ± 2
	10	96 ± 1	82 ± 3	88 ± 4	96 ± 1
	15	95 ± 2	81 ± 1	92 ± 2	95 ± 3
	20	94 ± 1	82 ± 2	96 ± 2	98 ± 2
HU-hexyl diol	10	94 ± 2	80 ± 1	87 ± 3	98 ± 3
	20	95 ± 2	81 ± 3	96 ± 2	97 ± 1

 Table 7: Chemical resistances of HU-diol modified alkyd resins

* toluenediisocyanate ratio

4 Conclusion

New hydroxyurethane modifiers diols have been successfully synthesized from renewable resources and then used for the synthesis of alkyd resins by polycondensation. All the obtained alkyd resins exhibited similar M_w values compared to the reference alkyd resin. The modification of the chemical structures of polyols did not interfere with the mass evolution of AR. Then, the impact of di-HUM on the film properties was studied. The introduction of di-HU had no impact on resin gloss or adhesion. However, adding di-HUM darkened the color of alkyd resins. However it is still possible to formulate primers from darker resins. Indeed, these formulations are the first coating applied to the substrate before other coatings, hence the color does not matter much. Hardness was also decreased with increasing content of di-HUM in modified alkyd resins. Furthermore, the introduction of di-HUM increased the alkali resistance of alkyd resins by up to 44 % similar to a commercial PAU but without the use of toxic isocyanates. Thus, these resins could be used to formulate paints intended to be applied in environments close to the sea. Moreover, these new di-HUM could be used for the synthesis of others materials.

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