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Polyurethane Thermosets Using Lipidic Poly(α -hydroxyketone)

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Abstract

Lipidic polyols based on α -hydroxyketone reactive groups were investigated for polyurethane thermosets. The reactivity of this peculiar secondary alcohol group in triglyceride structure was compared, without use of catalyst, to that of poly(1,2-diol)triglyceride and castor oil to demonstrate the influence of ketone in α position of alcohol group in presence of HDMI for urethanisation rate. The kinetic effect of ketone group was also studied on various lipidic architectures: mono(α -hydroxyketone) ester, di(α -hydroxyketone) diester and tri(α -hydroxyketone) triglyceride. The presence of hydrogen bonds in the network coming from urethane, residual alcohol and ketone in hard segments of PU was discussed and correlated to the thermal stability and the soft mechanical properties of the resulting polyurethane thermosets.

Introduction

Since their discovery in 1930 by Otto Bayer[1], polyurethanes (PU)s production and use keep growing interest. Various physical aspects of PU materials have been investigated including coatings[2, 3], adhesives[4, 5], rigid or soft foams[6-8] and thermosets[9]. Based on the alcohol-isocyanate reaction, a well-understanding relationship between the structure of the precursors (mainly polyether polyol or polyester polyol[10-12]) and the properties of the resulting materials has already been established[13, 14]. Nowadays, for economic and ecological reasons, some of the petro-based polyols are being substituted by polyols coming from natural and renewable resources[15]. The triglyceride structure of the vegetable oils (VO)s is a typical example of the agro-crosslinker structure. VOs have the advantage to be non-toxic, biodegradable, non-volatile, cheap and available in high quantity[16]. The fatty chains of VOs include, in most of the cases, between 18 and 20 atoms of carbon and are saturated or unsaturated with 1 to 3 unsaturations[17]. The VOs could be functionalized into polyols by epoxidation of the double bonds followed by the ring-opening of the oxirane groups with an alcohol [18, 19], a carboxylic acid (acetic, glycolic[20] and lactic acid[19]), an amine[21] or by hydrogenation[22, 23]. Fatty polyols can also be synthesized by ozonolysis of the unsaturations[24] or thiol-ene coupling reaction[25, 26]. The only natural VO used as polyol is the castor oil (CO)[27]. Nevertheless, a lot of lipidic polyols have already been described in the literature from rapeseed oil[28], linseed oil[18] and soybean oil[29] and have been used in the polyurethane field. However, to the best of our knowledge, lipidic compounds bearing α -hydroxyketone moiety have never been used as polyols for the preparation of polyurethanes. These compounds were previously produced by oxidation of oleic acid with neutral KMnO_4 [30], ring-opening with DMSO as oxidant of epoxidized fatty acids in presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ [31] or by oxidation of the diol obtained after hydroxylation of the lipidic acid[32]. These routes are of great interest to access the fatty α -hydroxyketone derivatives even if stoichiometric (toxic) reagents were usually implied. In this context, Vu *et al.*[33] have recently developed two complementary catalytic methods for the preparation of α -hydroxyketones derived from fatty acids. The fatty α -hydroxyketones were obtained from the corresponding fatty 1,2-diols, either by mono-oxidation using a homogeneous $\text{Pd}(\text{OAc})_2$ /neocuproine complex under oxygen atmosphere, or by dehydrogenation using heterogeneous ruthenium-based catalysts under solvent-free conditions (**Figure 1**). These two methods provided original α -hydroxyketone lipidic derivatives on the multi-gram scale.

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3 Herein, we investigated this peculiar α -hydroxyketone group based on fatty ester (MAK),
4 fatty diester (DAK) and triacylglycerol (TAK) (**Figure 2**) in order to determine the influence
5 of functional group in α -position of alcohol (ketone, another alcohol (1,2-diol)) related to the
6 commercial CO which has a non-functional group in α -position of the alcohol group along the
7 fatty chain. The alcohol-isocyanate reaction often occurred using catalysts such as
8 amines[34], iron oxide[35] or tin alkoxide[36] while in this work, the reaction was considered
9 without catalyst to limit the toxic residual by-products. Firstly, we will focus on the
10 comparative urethanisation kinetic using α -hydroxyketone ester (MAK) compare to a
11 commercial reference, methyl ricinoleate (MR) before extending the kinetic to triglyceride
12 (TAK and CO). Secondly, the structure-property relationship will be investigated to evaluate
13 the influence of the ketone moiety of polyol on the mechanical and thermal properties of the
14 resulting PU thermosets.
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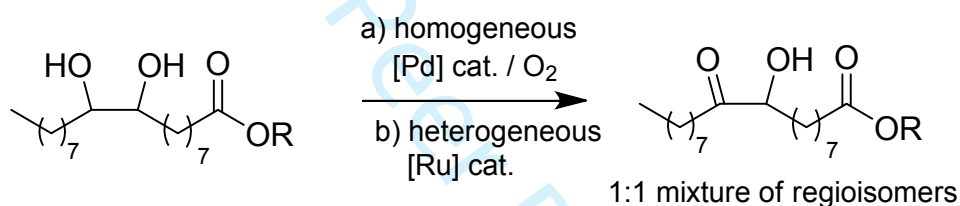


Figure 1. Catalytic synthesis of α -hydroxyketones from fatty acid derivatives.

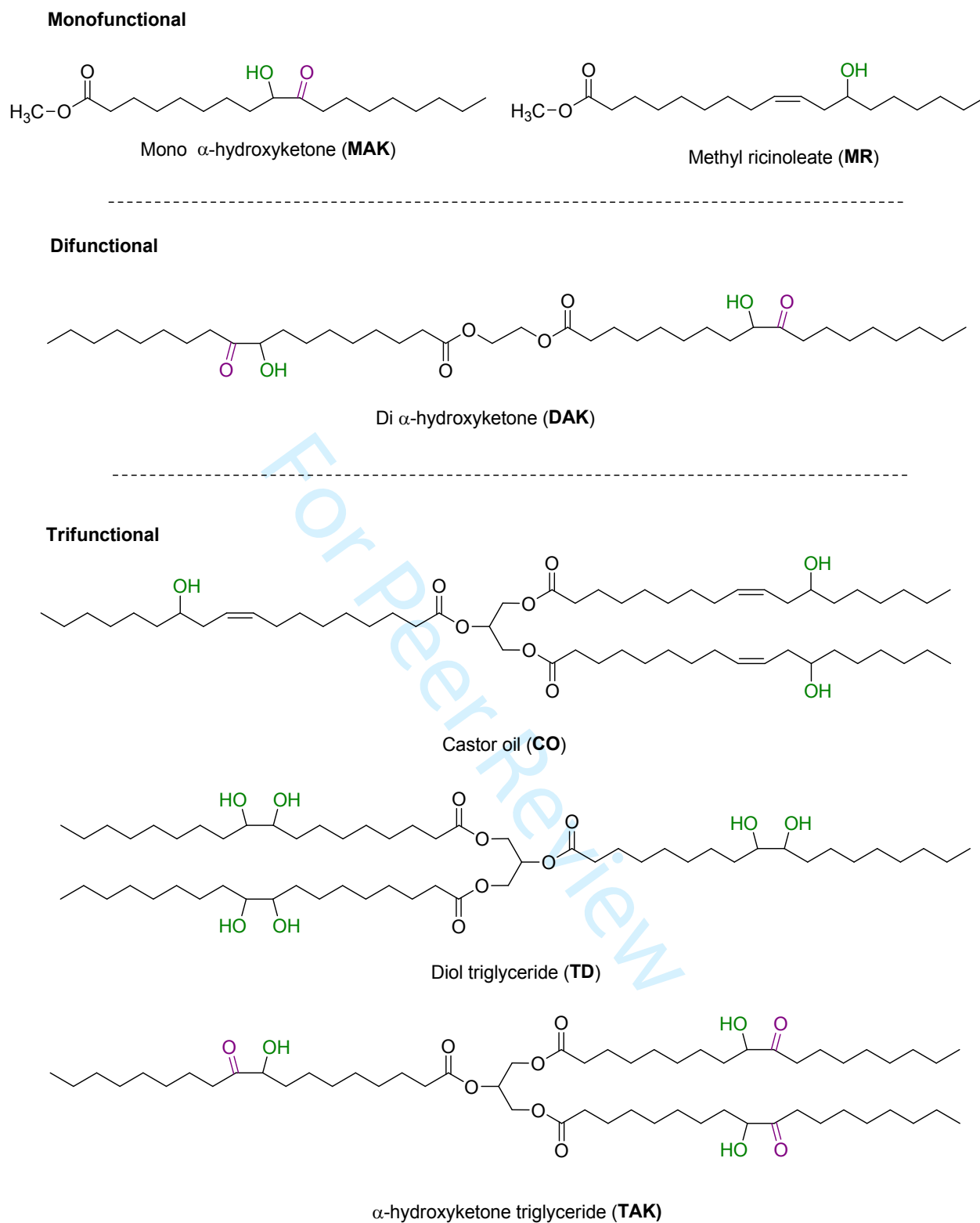


Figure 2. Chemical structure of the lipidic polyols.

Experimental

Materials

Hexamethylene diisocyanate (HDI), Toluene diisocyanate (TDI), methyl ricinoleate (MR), dichloromethane, ethanol and acetone were purchased from Sigma-Aldrich. Castor oil (CO) was purchased on a pharmacy. The α -hydroxyketone fatty acid (MAK), the α -hydroxyketone dimer (DAK), the α -hydroxyketone triglyceride (TAK) and the diol triglyceride (TD) were provided by the ICBMS lab from Lyon and the syntheses were previously described by Vu *et al.* [33].

Kinetics of polyurethane formation

Alcohol (1 eq), HDI (1.1 eq/OH) were mixed using manual agitation for 1 min in a test tube. One drop of the mix was disposed between two KBr pastilles. The kinetic studies were performed at 90 °C during 140 min or 8 h.

Synthesis of polyurethane materials

Polyol (1 mmol) was preheated at 90 °C for 10 min in an aluminum cup. HDI (1.1 eq/OH) was added to the mixture and was stirred manually for 2 min. The mixture was put in an oven at 90 °C for 24h-48h for a total conversion as it is well known for the synthesis of polyurethane thermosets. Hydroxyl moieties were quantified by NMR by monitoring the alcohol peak between 3 and 4 ppm.

Characterizations and measurements

FTIR spectroscopic studies were recorded with a Perkin-Elmer Spectrum 100 spectrometer equipped with an attenuated total reflectance (ATR) crystal (ZnSe). The wavenumber ranges from 4000 to 650 cm^{-1} . Kinetic studies were monitored in real time by FTIR spectroscopy on a Nicolet Nexus apparatus by using OMNIC software. The thermal stability of plasticized PVC films was carried out using a Q50 thermogravimetric analyzer (TGA) of TA instruments®. The experiments consisted in registering the weight loss of the sample under air flow (60 $\text{mL}\cdot\text{min}^{-1}$) in function of temperature ranging from 25 to 500 °C with a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$. Calorimetric analyses were carried out at 10 $^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere using a Star1 differential scanning calorimeter (DSC) from Mettler Toledo. Swelling ratio (Q) and insolubility fraction (I_r) were characterized by gravimetric method.

Polyurethane sample was soaked with an excess of solvent in a pre-weighted tube. After 24 h, the sample was dried at 60 °C for 24 h. Q were calculated from the masses of the wet and dry polymer following equation 1:

$$\text{Equation 1: } Q = \frac{(m_{wet} - m_{dry})}{m_{dry}} \quad (1)$$

Ir was calculated from the masses of the wet and initial polymer following equation 2:

$$\text{Equation 2: } I_r = 100x \frac{m_{dry}}{m_{ini}} \quad (2)$$

The nano-indentation measurements have been performed with an Anton Paar ultra-nano-indenter using a Berkovich diamond tip at room temperature. The space between the indents was set at 30 μm in order to prevent any interaction and the indentation speed was 100 μN min⁻¹ using plane samples of polyurethane. The loading force (P) was measured as a function of the penetration depth (h) curves until a predefined maximum force of 200 μN and subsequently the unloading curves. From the slope (S) at the beginning of the unload curve, the Young modulus (E) of the material was extracted according to the equations 3 and 4.

$$\text{Equation 3 and 4: } E^* = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A_p}} \quad \text{and} \quad \frac{1}{E^*} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (3, 4)$$

where β represented the geometrical constant depending of the shape of indenter (1.034 in the present case), E_i the indenter's Young modulus and ν_i the Poisson ratio of the sample, which has been fixed at 0.6 as a compromise between polymers and elastomers corresponding to the mean behavior of our samples.

The total hardness (H) has been calculated at the maximum force according to equation 5

$$\text{Equation 5: } H = \frac{F}{A_p} \quad (5)$$

where F is the maximum force and A_p is the surface contact area between the indenter and the sample. For each sample, at least 5 nanoindentations were carried out.

Results and discussion

Kinetic studies of urethanisation using α -hydroxyketone model (MAK)

To put in relief the influence of the ketone in α -position of alcohol group on the polyol reactivity in isocyanate-alcohol reaction, a kinetic study was performed on mono-functional molecules: methyl ricinoleate (MR) bearing an isolated alcohol group and α -hydroxyketone fatty ester (MAK). Both kinetic studies proceed in excess of HDI isocyanate 1.1 eq/OH without any catalyst at 90 °C and are monitored by Fourier-transform infra-red spectroscopy (FTIR). As shown in **Figure 3**, the urethanisation, illustrated by the appearance of urethane groups at 1515 and 1720 cm^{-1} , performs in two stages. The reaction starts with a rapid rise of conversion for 2 hours followed by a slower increase for several hours, a well-known phenomenon for PU synthesis[37]. The kinetic of MAK urethanisation is slightly accelerated over these two periods related to MR since after 120 min, 78% of MAK conversion are detected and only 65% for MR. A plateau at 98% conversion is reached for MAK and MR after 6 and 8 hours of reaction, respectively.

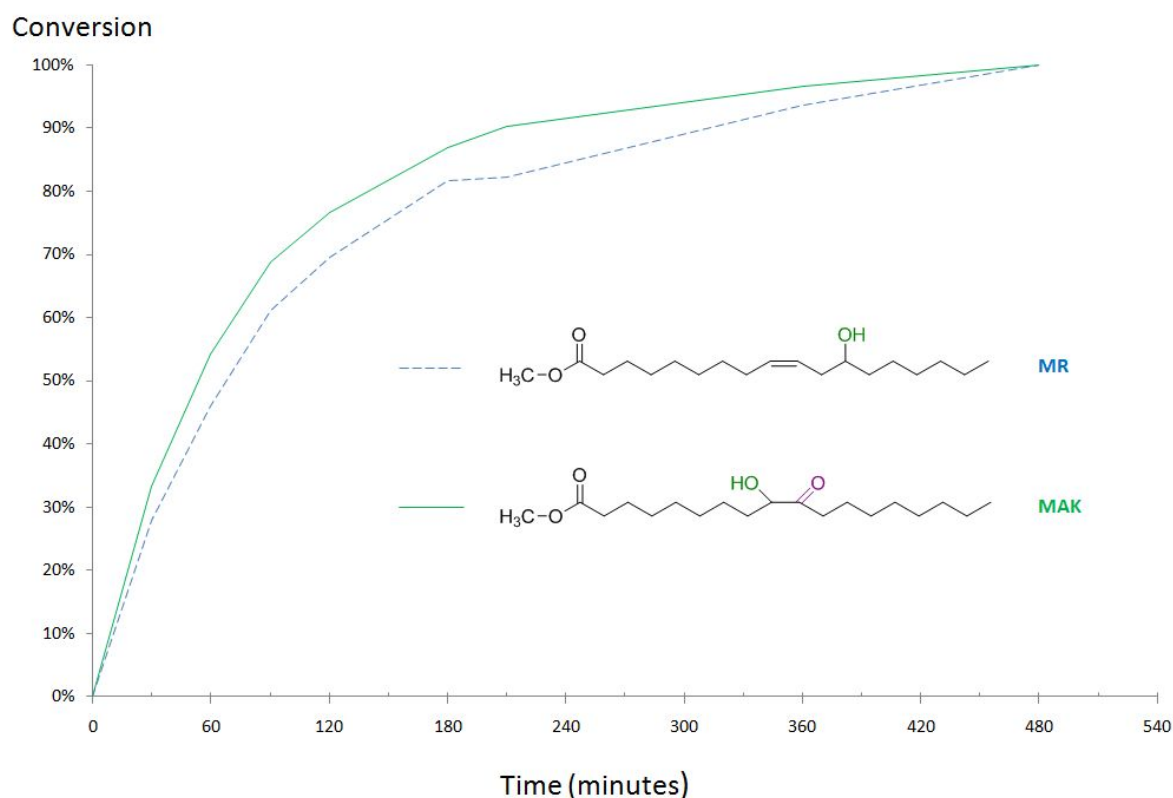


Figure 3. Kinetic curves of MAK and MR reaction with HDI.

This slight increase in reactivity of α -hydroxyketone (MAK) can be explained by the contribution of ketone group during the mechanism of the urethanisation as illustrated in **Figure 4**. The mechanism consists in a nucleophilic addition of an alcohol to a highly electrophilic isocyanate function. The ketone function could weaken the O-H bond of the alcohol by pooling the hydrogen atom between the two oxygen atoms through hydrogen bonding, thus increasing the alcohol nucleophilicity as could a weak base such as triethylamine (one of the most used amine catalyst for polyurethane). In addition, by making the hydrogen atom more acidic, it can also allow a better activation of the isocyanate function.

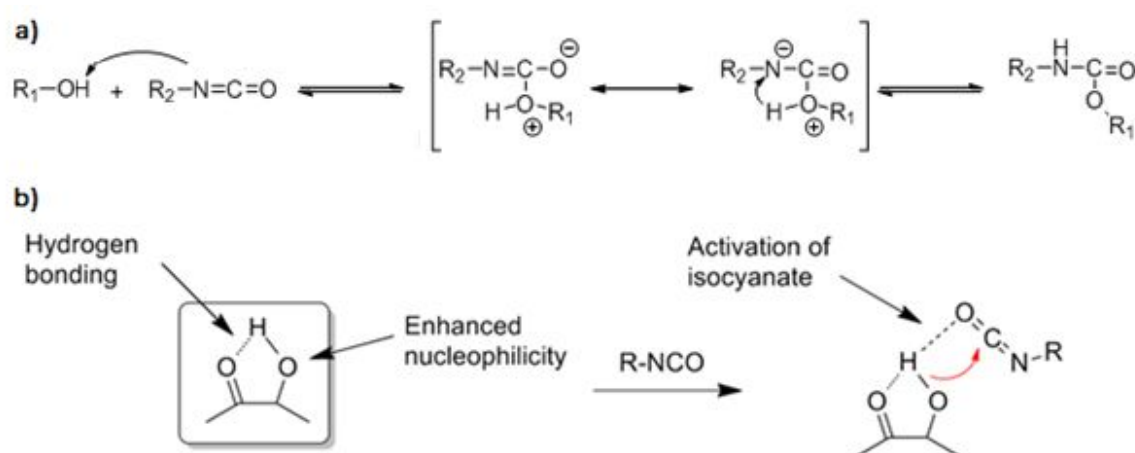


Figure 4. a) Mechanism of nucleophilic addition of alcohol on isocyanate moiety, b) Ketone's effect on the kinetics of urethane formation.

Polyurethane kinetic using α -hydroxyketone triglyceride (TAK) and other triglycerides

The same urethanisation kinetic was carried out on triglyceride polyols using HDI for thermosetting polyurethanes. The reactivity of poly(1,2-diol) (TD) and poly(α -hydroxyketone) (TAK) are compared to that of isolated alcohol of castor oil (CO) using an excess of isocyanate 1.1 eq/OH. As previously described, the conversion achieves in two stages with a fast conversion during the first hour before decelerating as shown in **Figure 4**. The kinetics of TAK and TD are very close and faster than that of CO. For instance, at 60 min of reaction, TAK and TD conversions in urethane are about 88% against 75% for CO. Otherwise, TD and TAK reach the plateau at 98% of conversion after 100 min of reaction while CO requires 140 min. This comparative kinetic of triglyceride polyols (CO and TAK) confirms the results of linear alcohols (RM and MAK). The urethanisation of alcohol is

activated by a ketone function in α position of the alcohol function (α -hydroxyketone). Moreover, the hydroxyl function in α position of the alcohol function (1,2-diol) has a similar effect that of the ketone one.

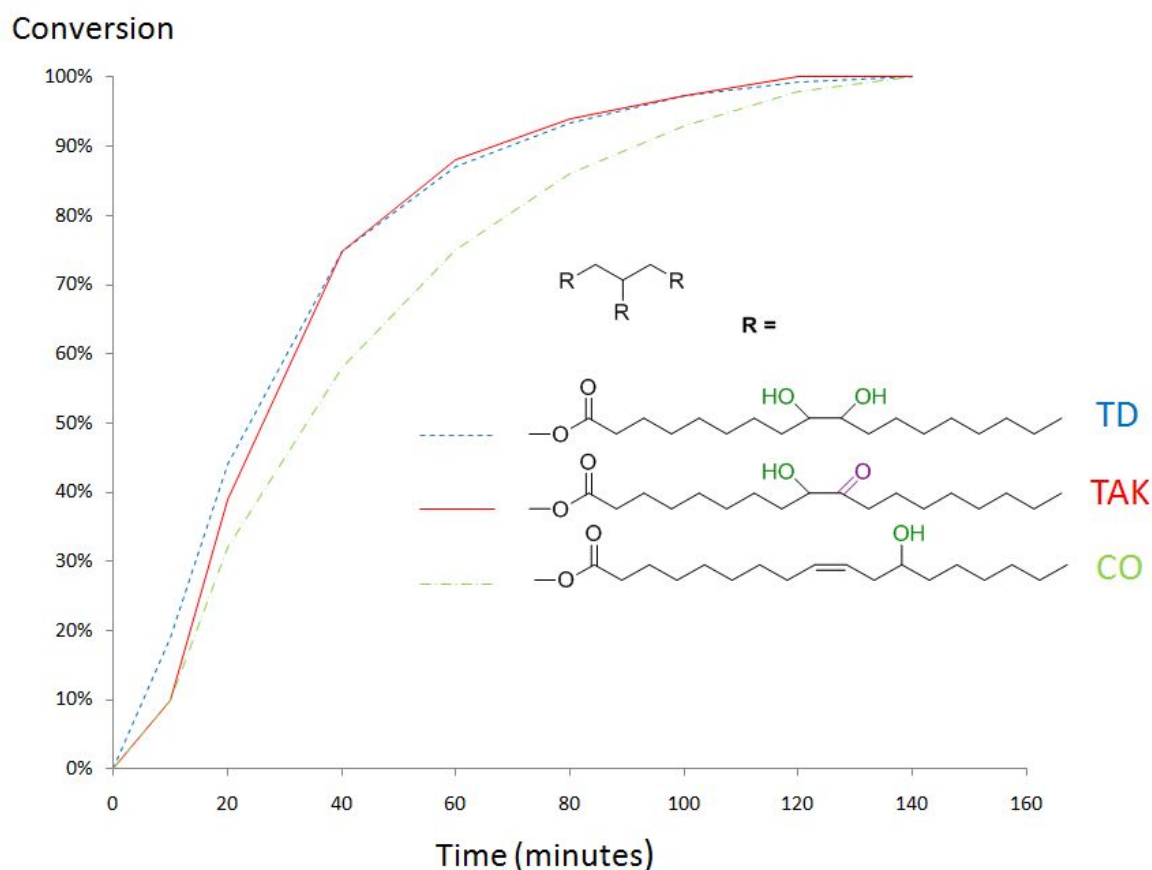


Figure 5. Kinetics of urethanisation between triglycerides (TAK, TD and CO) and HDI.

Deepening the influence of α -hydroxyketone on urethanisation kinetic, the α -hydroxyketone ester (MAK), diester (DAK) and triglyceride (TAK) compounds are compared as illustrated in Figure 1 SI. The di- (DAK) and tri-functional (TAK) polyols are faster than the fatty ester (MAK) with 2h instead of 6-8h to reach the maximum conversion. This phenomenon could be explained by the higher density of alcohol functions in the structure, which gradually brings about an acceleration of the urethanisation. Moreover, the difference between the reactivity of DAK and TAK is probably caused by the higher viscosity of TAK which slows down the polyurethane formation.

Characterization of polyurethane thermosets

The thermal and mechanical properties of polyurethane thermosets are closely connected to the crosslinking density and the size of the network mesh including the presence of interactions inside the network. They are mostly estimated by the swelling test of the materials in water and organic solvents. The influence of ketone group in α position of the urethane function is deduced of the swelling ratio (Q) and the insoluble fraction (Ir) values of the resulting material (**Table 1**). The hydrophobic character of the PU coming from TD (PU-TD) and TAK (PU-TAK) is shown by the low swelling ratio in water close to 1% and, in ethanol - values ranged from 35 to 44%. By contrast, high Q values are observed in dichloromethane without dimensional and surface appearance alterations.

Otherwise, regarding the Ir and Q_{ethanol} values of TAK and TD, an excess of isocyanate is required for a complete crosslinking (low Q_{ethanol} and high Ir). This can be explained by the presence of water which can react with HDI and limit the cross-linking step, leaving free OH moiety. We noted that for the same NCO/OH equivalent: TD 0.5 eq (one in two hydroxyl group of 1,2-diol) and TAK 1 eq, and with almost the same Ir, PU-TAK as a higher Q value related to PU-TD (300% against 189%). This result means that, for the same crosslinking ratio, bigger mesh sizes exist in PU-TAK network because ketone groups interact less than free alcohol groups of PU-TD network. Moreover, for PU-TD, the reaction of all the alcohol groups with isocyanate (1.1 eq) avoids hydrogen bonds coming from residual alcohols and induces weaker swelling in CH_2Cl_2 (110 instead of 189%) and higher crosslinking (0.95 instead 0.87).

The isocyanate/alcohol stoichiometry and the presence of ketone or hydroxyl group in α position of urethane group have the same influence on the thermal and mechanical properties of the resulting material as illustrated with the glass transition temperature (T_g) and Young's modulus (E) values (**Table 1** and **Figure 2, SI**). We noted the increase of T_g (from -19 to -3 °C) with the insoluble ratio and the NCO eq/OH. Moreover, the presence of weak interactions in the network such as with ketone, produces less flexible materials (T_g of -19 °C) than PU-CO (T_g of -35 °C) while more rigid materials are elaborated with stronger interactions such as hydrogen bonds with alcohol groups (T_g of 4 °C) and urethane groups (T_g of 32 °C).

Table 1. Characterization of the PU networks.

Polyol/eq isocyanate	Q _{Water} (%)	Q _{Ethanol} (%)	Q _{Dichloromethane} (%)	I _{rDichloromethane}	T _g (°C)
TAK 1 eq	3	44	300	0.91	-19
TAK 1.1 eq	- ^a	- ^a	176	0.94	-3
TD 0.5 eq	1	35	189	0.87	4
TD 1.1 eq	- ^a	- ^a	110	0.95	32
CO 1.1eq	- ^a	- ^a	1128	0.89	-35

^a: not measured.

Thermal stability of PU thermosets

Polyurethane materials degrade mainly in two stages in thermogravimetric analysis (TGA). The first step is the degradation of the hard segments of the PU corresponding to the breaking of urethane bonds around 330 °C. The second step concerns the degradation of the polyol present in the material, followed by a release of HCN between 420 and 460 °C [26, 38]. For castor oil based polyurethane, the two steps of degradation are observed, with values slightly higher than expected. The degradation of urethanes is around 342 °C (10% mass loss, **Table 2** and **Figure 5**). The degradation of the lipid polyol portion occurs at around 440 °C. For PU-TD (1.1 eq/OH), the degradation of the urethanes is located at 317 °C (10% mass loss) which is close to the values of other PU elaborated by Dien *et al.* using triol and pentaol synthesized by thiol-ene/yne[26] (**Figure 6**). The higher thermal stability of PU materials concerns TAK polyol-based PU with 338 °C for 10% mass loss and 79% at 400 °C without notable difference in value with the ratio of isocyanate. Regarding the residual weight of the sample at 500 °C named CHAR, we noted higher values for TD, 15% against around 5% for TAK and CO. These values have already been described for flame retardant additives based on triglyceride functionalized by phosphate (COFPL)[39] (**Figure 6**).

The first derivative of the TGA curves (DTG) related to **Figure 7 (Figure 3, SI)** permit a deep analysis of the effect of the interactions in hard segments of PU on the thermal stability. For PU-TAK, the lower intensity of the first degradation at 340 °C than PU-TD (1.1 eq/OH)

and PU-CO and inversely the higher second degradation after 400 °C can be explained by a stabilization in temperature of PU materials by ketone-urethane groups (TAK) related to urethane groups (CO), hydroxy-urethane groups TD (0.5 eq/OH) and urethane-urethane groups TD (1.1 eq/OH). In other words, the increasing thermal stabilizing effect of the polyols is the following: poly(1,2-diol), isolated alcohol (castor oil) and poly(α -hydroxyketone).

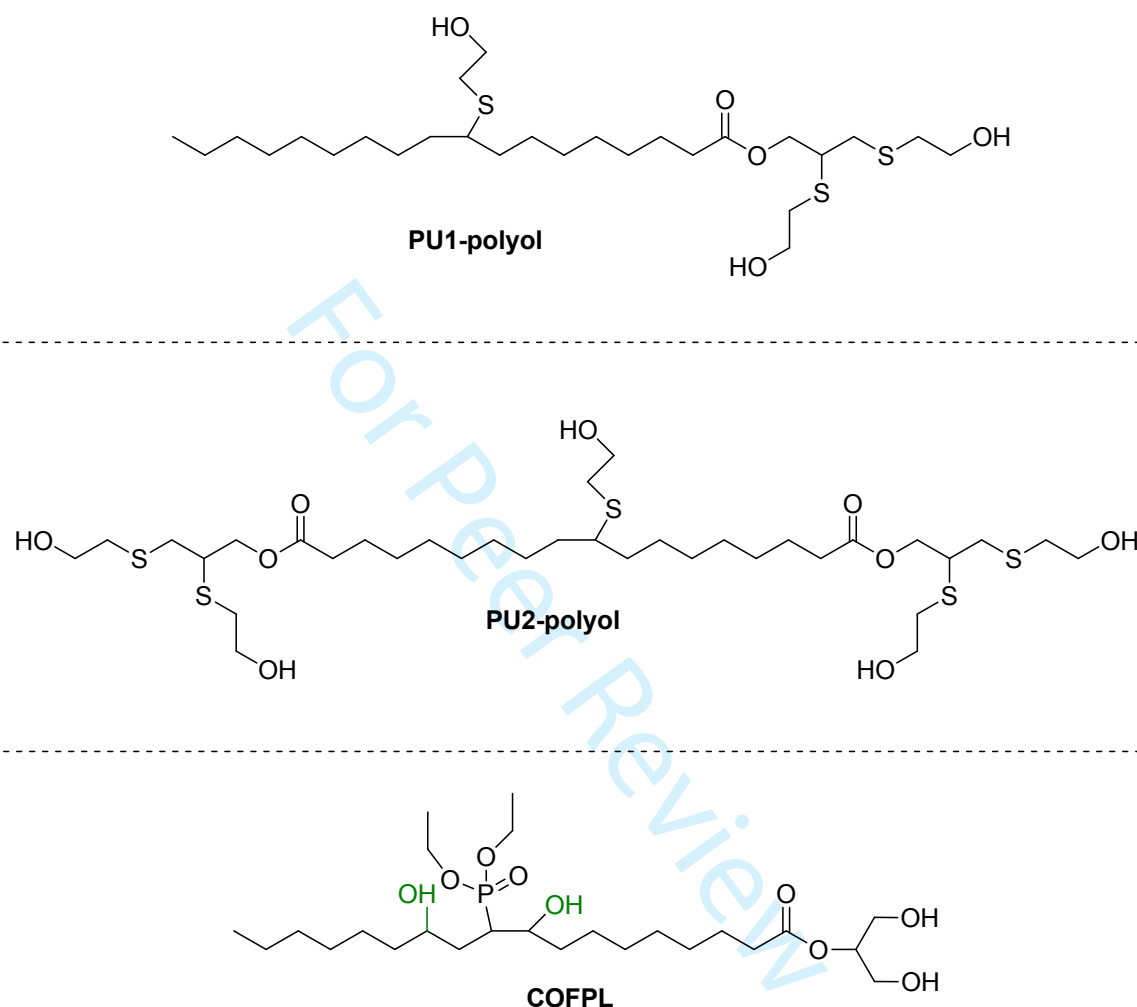


Figure 6. Chemical structure of PU1-polyol[26], PU2-polyol[26] and COFPL[39].

Table 2. TGA values of PU thermosets.

Polyol	T _{10%} (°C)	W _{400°C} (%)	CHAR _{500°C} (%)
TAK 1 eq	335	78	5
TAK 1.1 eq	338	79	5
TD 0.5 eq	330	44	14

TD 1.1 eq	317	47	15
PU1 ^a 1.1 eq	310	22	3
PU2 ^a 1.1 eq	295	35	6
COFPL ^b 1.3 eq	250	61	16
CO 1.1 eq	342	51	9

^a: ref:[26] ; ^b: ref:[39].

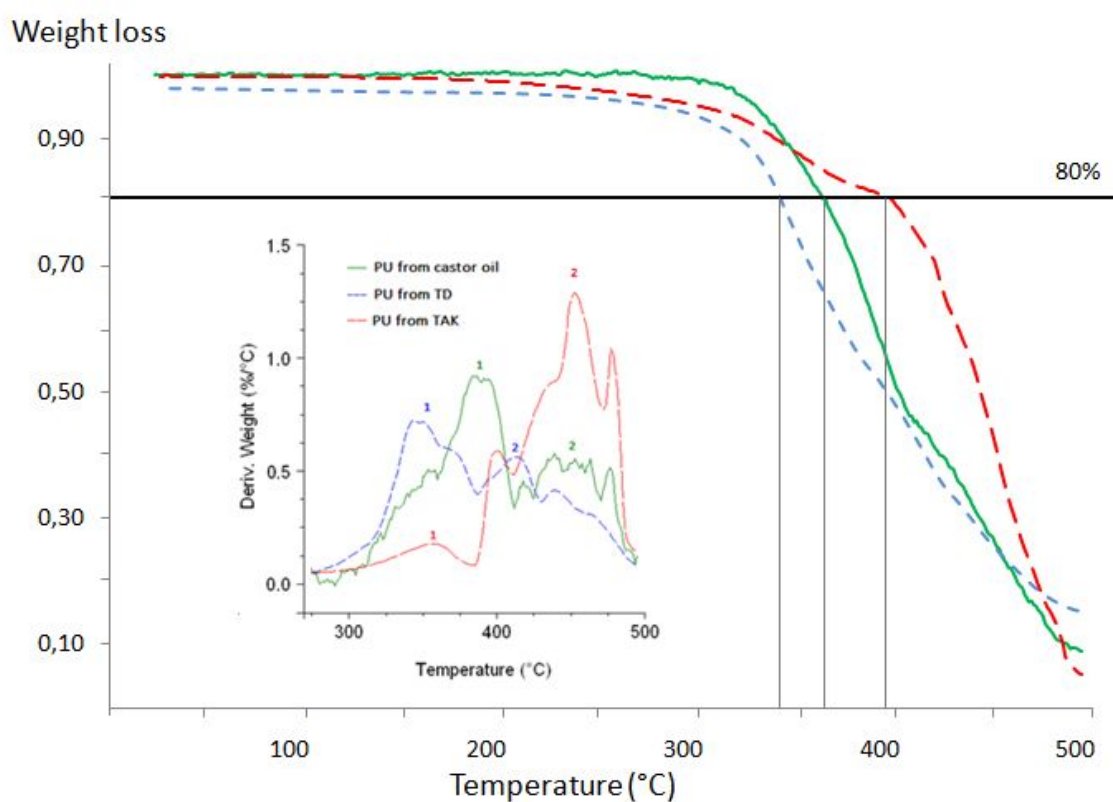


Figure 7. TGA and DTG curves of the cross-linked PU materials.

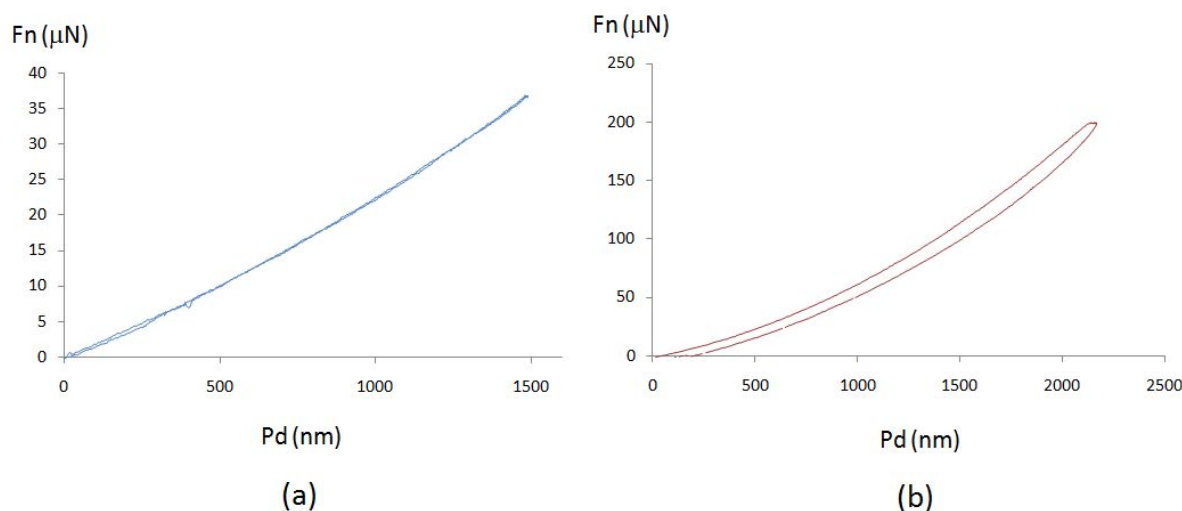
Mechanical properties of PU thermosets

Mechanical behavior of PU-TD and PU-TAK made with hexamethylene diisocyanate (HDI) or toluene diisocyanate (TDI) was measured by nanoindentation. As summarized in **Table 3**,

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3 PU-HDI young modulus (E) and hardness (H) values both corresponded to the behavior of a
4 soft material. Nevertheless, PU-TAK material was characterized by a lower young modulus
5 than PU-TD. This trend was confirmed when HDI was replaced by TDI. The gap between
6 PU-TAK (3.7 MPa) and PU-TD values (890 MPa) was exacerbated with TDI, demonstrating,
7 in this case, a real gain of softness with the presence of a α -ketone function in the
8 polyurethane structure. The nanoindentation load-displacement curves of (a) PU-HDI-TAK
9 (b) and PU-HDI-TD display a typical elastic behavior of the material, specifically for PU-
10 HDI-TAK where both curves are clearly stackable as illustrated in **Figure 8**. PU performed
11 with TDI have another mechanical behavior, typical plastic one (**Figure 9**). We noted the
12 quite close young moduli for both PU-TAK even if PU-HDI-TAK has elastomeric behavior
13 by contrast with PU-TDI-TAK.
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24 **Table 3.** Young modulus and hardness values of PU thermosets obtained by nanoindentation.

Diisocyanate	HDI		TDI	
Polyol	TD	TAK	TD	TAK
E	14	7	890	3.7
H	4.7	4	101	0.5



53 **Figure 8.** Nanoindentation curves of (a) PU-HDI-TAK and (b) PU-HDI-TD.
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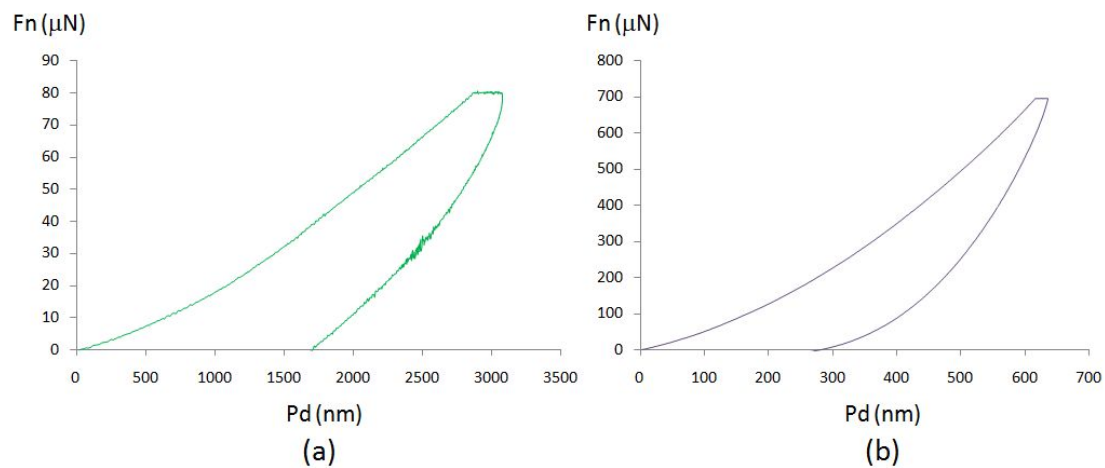


Figure 9. Nanoindentation curves of (a) PU-TDI-TAK and (b) PU-TDI-TD.

For Peer Review

Conclusion

The catalyst-free reaction of various triglyceride polyols with HDI demonstrated the slight activation of alcohol-isocyanate reaction in presence of ketone in α position of alcohol group by hydrogen bond assistance. We noted the slower urethanisation rate of α -hydroxyketone derivatives when the function is borne by a fatty ester related to fatty diester or triglyceride structure. Otherwise, for the same crosslinking ratio, the bigger mesh sizes in PU-TAK network compared to PU-TD can be explained by the fewer interactions between urethane and ketone groups than between urethane and free alcohol groups. The presence of weak interactions such as urethane-ketone in the hard segments of PU thermosets also produced flexible materials while more rigid materials were elaborated with stronger interactions (hydrogen bonds) such as between urethane and residual alcohol group and between urethane groups. Among the PU obtained from polyols bearing isolated alcohol (PU-CO), 1,2-diol (PU-TD) and α -hydroxyketone (PU-TAK), the latter offers better thermal stability as illustrated in TGA study showing the stabilizing effect of the ketone groups in the hard segments of PU. It would subsequently be interesting to extend the study of the α -hydroxyketone polyols to flexible polyurethane foams.

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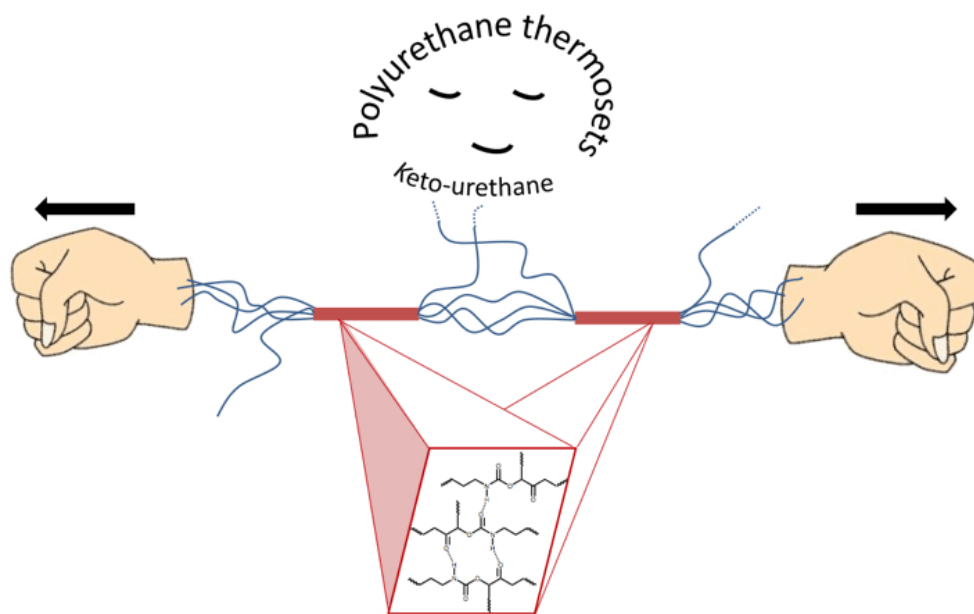
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For Peer Review

alpha-hydroxyketone function at the service of polyurethane reactivity and properties

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