RESEARCH ARTICLE

Novel Cycloaliphatic Cashew Nut Shell Liquid Derivatives and their use as Isocyanate Protective Groups

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ABSTRACT: Cardanol (3-pentadecenyl-phenol), a well-known non-edible natural oil obtained as a by-product of the Cashew Industry, represents a valid alternative to petro-based derivatives, thanks to its peculiar chemical structure. When selected as polymer building block in the synthesis of epoxy curing agents or polyols and diols for polyurethane applications, cardanol can impart unique benefits, like chemical resistance, hydrolytic stability, thermal resistance and balanced mechanical properties. Once used in polyurethane prepolymers, it demonstrates various benefits, including favorable and easily tunable deblocking conditions, lower viscosity of resulting NCO-blocked prepolymers and excellent storage stability in comparison to commonly used phenolic compounds (phenol, nonylphenol, in particular). In this paper, novel cardanol-based fully cycloaliphatic derivatives (e.g. cyclohexanol, oxime, lactam-types) will be presented, investigating their use as innovative isocyanate protective groups with faster reactivity and lower deblocking temperatures than petro-derived benchmarks.

1. INTRODUCTION

Cashew Nut Shell Liquid (CNSL), largely available in the entire sub-tropical area (Brazil, India, Vietnam, Ivory Coast, etc.), is a non-food chain industrial oil found in the honeycomb structure of the cashew nutshell (*Anacardium Occidentale*), typically considered a by-product of the cashew nut industry.

The main product isolated by vacuum distillation of CNSL under proper conditions is cardanol, an USDA certified bio-based (98% bio-content) alkenyl-phenolic product with an average number of two unsaturation on the C_{15} side-chain (Figure 1).
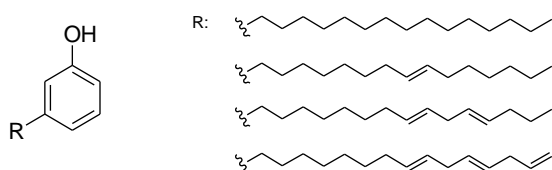

Figure 1: Cardanolstructure

Cardanol represents an interesting and versatile monomer, as it contains three different functional groups (the aromatic ring, the hydroxyl group and the double bonds in the alkyl chain), that can be either selectively or simultaneously modified according to the expected features of final product.

Given its peculiar chemical structure, several chemical routes to cardanol-based derivatives have been reported in the literature, including epoxies, amine curing agents, surfactants, friction particles, phenolic resins [1].

For example, one of the most successful CNSL's applications are epoxy curing agents, a type of derivatives exhibiting good reactivity for fast and low temperature cure, strong adhesion even to damp or poorly prepared surfaces, excellent water resistance, corrosion protection and chemical resistance in epoxy formulations, all properties imparted by cardanol's peculiar chemical backbone.

All the average benefits described above have been also exploited in sectors like polyurethane systems, where cardanol has been described as a useful building block for polyols and derivatives suitable for 2K polyurethane (PU) applications [2], aiming, for example, to improve PU adhesives and coatings durability by imparting hydrophobicity and chemical resistance.

In order to further confirm the versatility of cardanol and its potential applicability in different sectors like 1K PU systems, cardanol and cardanol derivatives have been already described in the literature [3] as possible isocyanate protecting groups, preventing moisture absorption and

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subsequent degradation (Figure 2), providing blocked prepolymers as flexibilizers in epoxy-urethane hybrids or plasticizers in acrylic compositions [4].

Recent studies have also highlighted the possibility of tuning cardanol-protected isocyanates deblocking temperatures by using proper catalysts, nucleophiles or chemical modification of the aromatic ring with electron withdrawing groups [5].

However, even if a proper selection of processing conditions makes cardanol a suitable raw material to be used in the industrial manufacturing of blocked prepolymers, its

relatively high molecular weight (and subsequent steric hindrance) as well as presence of chromophores (double bonds present on cardanol C_{15} side chain and aromatic ring) could limit cardanol use in applications where relatively low color derivatives, short blocking time and fast deblocking (especially when no catalyst is used) are required. In these cases, as for example polyurethane dispersions (PUDs) or powder coatings, blocking agents like methyl-ethyl ketoxime (MEKO) and ε-caprolactam are commonly used [6].
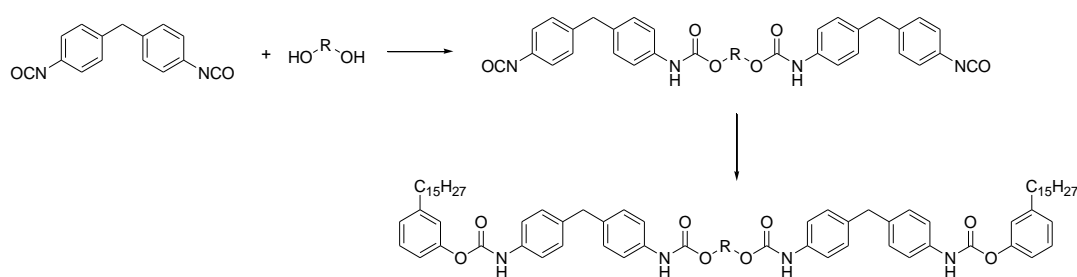

Figure 2: general reaction scheme for 4,4'-methylene diisocyanate (MDI) based prepolymer synthesis followed by blocking reaction with cardanol

However, both methyl-ethyl ketoxime (MEKO) and ε-caprolactam show limitations, as for example toxicity (in the case of MEKO) or high cure temperatures, as in the case of ε-caprolactam blocked prepolymers for powder coatings [7].

On this basis and in order to further extend cardanol applicability as a versatile chemical building block, the present work aims to develop a new generation of aliphatic cardanol-derived isocyanate blocking agents with faster reactivity and lower deblocking temperatures, comparable to currently used petro-based benchmarks.

2 EXPERIMENTAL
2.1 Materials

Cardanol and side chain hydrogenated cardanol were both supplied by Cardolite Corporation under the trade names NX-2026 and NC-510, respectively, and used without any purification.
All reagents (2,2,6,6-Tetramethyl-1-piperidinyloxy TEMPO; periodic acid; sodium thiosulfate; sodium sulfate anhydrous; sodium hydroxide; hydroxylamine hydrochloride; tetrahydrofuran; acetonitrile; trifluoroacetic acid; 1-methoxy-2-propyl acetate, MPA; xylene) were purchased by Sigma-Aldrich and used as received.

Polymeric diolRokopol D2002 (polypropylene glycol MW 2000 Da) was supplied by PCC Rokita. STEPAN DPR 5066-67 (butanediol adipate MW

2000 Da) was supplied by STEPAN. Aromatic isocyanates Ongronat 3050 (4,4'-methylene diisocyanate, MDI) and Desmodur T80 (Toluene diisocyanate,TDI) were supplied by Borsodchem and Covestro, respectively. Aliphatic isocyanates hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) were both supplied by Vencorex.

2.2 Synthesis of 3-pentadecyl-cyclohexanol

In a Parr reactor, cardanol (300 g; 1 mol) is mixed with Ni catalyst (3% w/w with respect to substrate). Temperature is then increased to 160 °C under hydrogen atmosphere (125 psi). After 27 hours under these conditions, catalyst is removed by filtration over Celite® recovering 3-pentadecyl-cyclohexanol, with 85% yield, as a white solid (m.p. 49-51 °C).

2.3 Synthesis of 3-pentadecyl-cyclohexanone

3-pentadecyl-cyclohexanol (62.11 g; 0.2 mol; 1 eq) is dissolved in methylene chloride under gently heating (30-35 °C). TEMPO (3.125 g; 0.02 mol; 0.1 eq) is then added, followed by the addition of periodic acid H_5IO_6 (50.15 g; 0.22 mol; 1.1 eq). The solution turns into a dark red liquid and it's stirred at RT for 4 h. The organic phase is then washed with a saturated solution of $Na_2S_2O_3$, water, brine and dried over anhydrous Na_2SO_4. Solvent is removed under vacuum, giving 58.5 g

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(95%) of a waxysolid (m.p. 42-44 °C). The product can be used as such or further purified by re-crystallization from ethanol.

2.4 Synthesis of 3-pentadecyl-cyclohexane oxime

A solution of NaOH (2.86 g, 71.5 mmol) and hydroxylamine hydrochloride (4.97 g, 71.5 mmol) in 15 mL of water at 40 °C is added with a solution of 3-pentadecyl-cyclohexanone (20 g, 64.8 mmol) in 160 mL of THF under vigorous stirring. After stirring at 40 °C overnight THF is removed under reduced pressure and the residue is diluted with ethyl acetate. The organic phase is washed with water, brine and dried over anhydrous Na_2SO_4. Solvent is removed under reduced pressure giving 18 g (85%) of a brownish solid (m.p. 65-67 °C). The product can be used as such or further purified by re-crystallization from acetone or di-isopropylether.

2.5 Synthesis of pentadecyl-azepan-2-one

In a sealed flask 3-pentadecyl-cyclohexane oxime (5 g, 15 mmol) is dissolved in 100 mL of 10% w/w acetonitrile in trifluoroacetic acid and heated under stirring at 60 °C for 2h. Solvent is removed under vacuum giving 4.5 g (93%) of brownish solid (m.p. 43-46 °C).The product can be used as such or further purified by re-crystallization from acetone or di-isopropylether.

2.6 ^{13}C-NMR and HPLC data

^{13}C-NMR spectra have been recorded on a VARIAN Inova 500 MHz, using deuterated chloroform as solvent (with tetramethyl silane as stabilizer).High Performance Liquid Chromatography (HPLC) results have been collected on a HITACHI Chromaster 5160 dual piston pump, equipped with a HITACHI Chromaster 5410 UV detector (wavelength set to 280 nm), a HITACHI Chromaster 5450 RI detector, a HITACHI Chromaster 5310 Oven (set at 25 °C) and a HITACHI Chromaster 5260 Auto-sampler, using an acetonitrile/water 95/5 with 10% tetrahydrofuran mixture as eluent in isocratic mode at 1 ml/min flow rate.

2.7 Isocyanate content determination

Isocyanate content has been determined accordingly to ASTM D2572 on a METTLER TOLEDO T50 automatic titrator. In a typical experiment, sample (about 1 gram weighed on an analytical scale) was dissolved in 25 ml of mono-chlorobenzene and 20 ml of methyl ethyl ketone (MEK), added of 5 ml of a 2N di-isobutylamine solution in mono-chlorobenzene and titrated using HCl 1N in methanol. A blank is measured under the same conditions.

2.8 Preparation of prepolymers, blocked isocyanates and blocked prepolymers

Prepolymers are prepared starting from commercially available diols (polyester, polyether) according to the following procedure: to a weighed amount of isocyanate pre-heated at 50 °C and stirred under nitrogen atmosphere, the selected diol is added dropwise, keeping mixture temperature around 65-70 °C. Once the addition is completed, the system is stirred under nitrogen atmosphere at the same temperature, monitoring prepolymer formation by isocyanate content titration. When the target NCO content is obtained, the prepolymer is then blocked by adding the selected blocking agent portion-wise under stirring, keeping reaction temperature around 65-70 °C under nitrogen flush and monitoring NCO disappearance by titration. A similar procedure has been used to make isocyanate-blocking agents adducts, still monitoring full NCO capping by automatic titration.

2.9 Determination of deblocking temperature

Deblocking temperatures have been determined by Differential Scanning Calorimetry on a METTLER TOLEDO DSC1 STAR System equipped with a HUBER TC45 thermostat, heating the sample (10 mg) from 25 °C to 250 °C at 10 °C/min under nitrogen. Initial deblocking temperature corresponds to a change in the baseline slope.

3 RESULTS AND DISCUSSION

The peculiar cardanol structure, with an aromatic ring that provides excellent rigidity and thermal stability and the long chain at the meta position imparting outstanding hydrophobicity, over the last decades has prompted the development of several derivatives like amines, epoxies, polyols, amides, antioxidants, flavors, foods, lubricants, polymers, rubbers. Chemical modifications of cardanol are traditionally obtained by alkylation, condensation, nitration, halogenation, while a number of other chemical transformations have all been used with different degrees of success for the selective functionalization of cardanol and its isolated components [8].

However, the majority of cardanol derivatives reported in the literature are based on cardanol as mixture of isomers, with subsequent potential lack of reproducibility, UV instability, with limited average type of functional groups and applicability in sectors where color and purity are key aspects (e.g. 1K polyurethane; thermoplastics).

Above cardanol limitations and the need of safer and affordable alternatives to commonly used isocyanate blocking agents widely used in coatings and adhesives [9], prompted us to select high

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purity cardanol (>99%) as starting substrate and

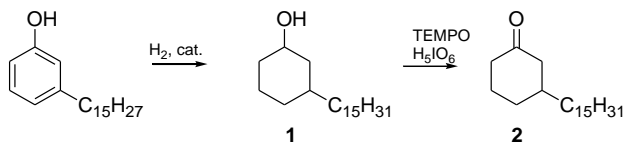convert it into fully aliphatic structures.

Figure 3: reaction scheme to convert cardanol into 3-pentadecylcyclohexanone2

In particular, cardanol was catalytically hydrogenated to 3-pentadecylcyclohexanol **1**[10], then oxidized under known conditions [11] to 3-pentadecyl-cyclohexanone**2** (Figure 3), whose chemical structure has been confirmed by ^{13}C-NMR (Figure 4).

The recovered cardanol-derived ketone **2**was then further modified by reaction with hydroxylamine or, more preferably for safer handling, hydroxylamine hydrochloride, under the same conditions typically applied to cyclohexanone [12], allowing the recovery of 3-pentadecyl-cyclohexane oxime **3**.Other examples of cardanol-derived oximes are reported in the literature [13], but in these cases the oxime group derives from an aldehyde group introduced either on C$_{15}$ side chain*via* ozonation or on cardanol's aromatic ring by carbonylation. On the contrary, the use of 3-pentadecyl-cyclohexanone **2**as substrate for the oximation reaction allows the recovery of a cardanol-derived oxime that can either be used as such or further converted into a lactam by a Beckmann rearrangement with
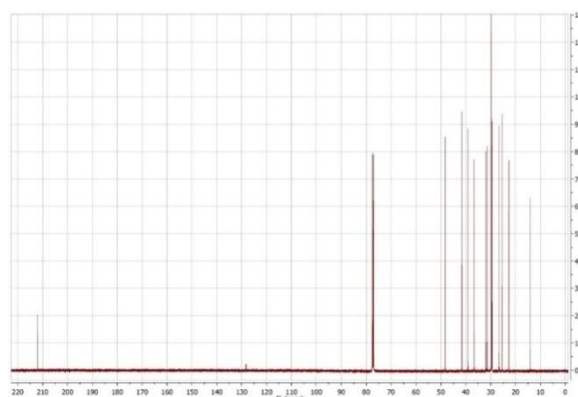

Figure 4: ^{13}C-NMR spectra of 3-pentadecyl-cyclohexanone

trifluoroacetic acid [14].The resulting cardanol-derived lactam is recovered as an about equimolar mixture of the two regio-isomers 4-pentadecyl-azepan-2-one**4a** and 7-pentadecyl-azepan-2-one **4b** (Figure 5).

The conversion from cardanol-derived 3-pentadecyl-cyclohexanone **2** to3-pentadecyl-cyclohexane oxime **3** has been monitored by HPLC, highlighting the presence of two peaks with a retention time around 10 minutes and corresponding to two stereoisomers. Applying the same analytical conditions, the conversion for cardanol-derived oxime to pentadecyl-azepan-2-one**4a** and **4b** as a mixture of two regio-isomers has been confirmed (Figure 6).
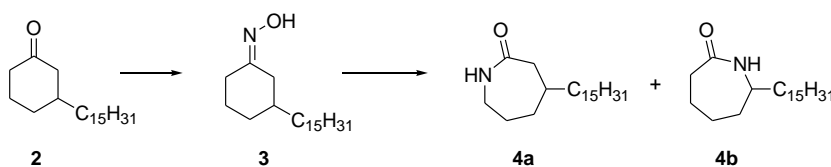

Figure 5: synthesis of 4-pentadecyl-azepan-2-one and 7-pentadecyl-azepan-2-one from 3-pentadecyl-cyclohexanone2

To further assess the full conversion of 3-pentadecylcyclohexanone **2** into derivatives **3** and **4**, their ^{13}C-NMR spectra have been collected as well, with signals at 160 ppm and 181-182 ppm corresponding to oxime carbonyl and lactam-carbonyl carbons, respectively (Figure 7).

Having confirmed their purity and chemical structures, the novel cardanol derived oxime**3** and lactam(used as mixture of isomers**4a** and **4b**) werethen validated in polyurethane systems as isocyanate blocking agents (Figure8). In fact their

structures showchemical features similar to reference methyl ethyl-ketoxime (MEKO) and ⍰-caprolactam, respectively.

Both MEKO and ɛ-caprolactam are widely used in polyurethane systems to block prepolymers for CASE applications [15], protecting isocyanates groups from hydrolysis and side reactions. However, both methyl-ethyl ketoxime (MEKO) and ɛ-caprolactam show limitations, as for example toxicity (in the case of MEKO) or high cure

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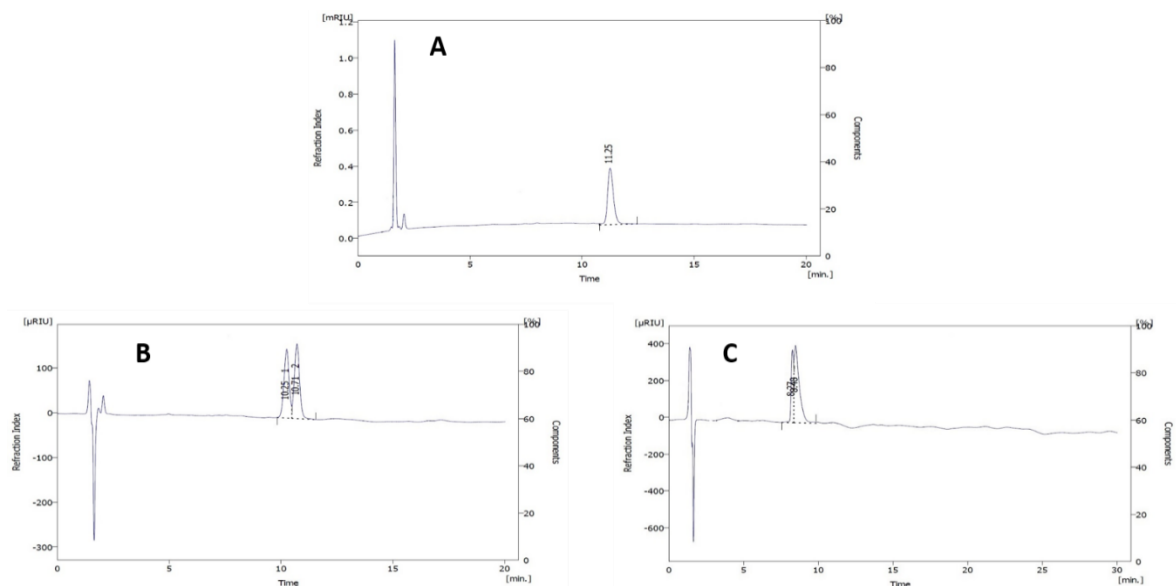temperatures, as in the case of ε-caprolactam blocked prepolymers for powder coatings [16].

Figure 6: HPLC profiles of cardanol-derived 3-pentadecyl-cyclohexanone 2 (A),3-pentadecyl-cyclohexane oxime 3 (B) andpentadecyl-azepan-2-one (C)
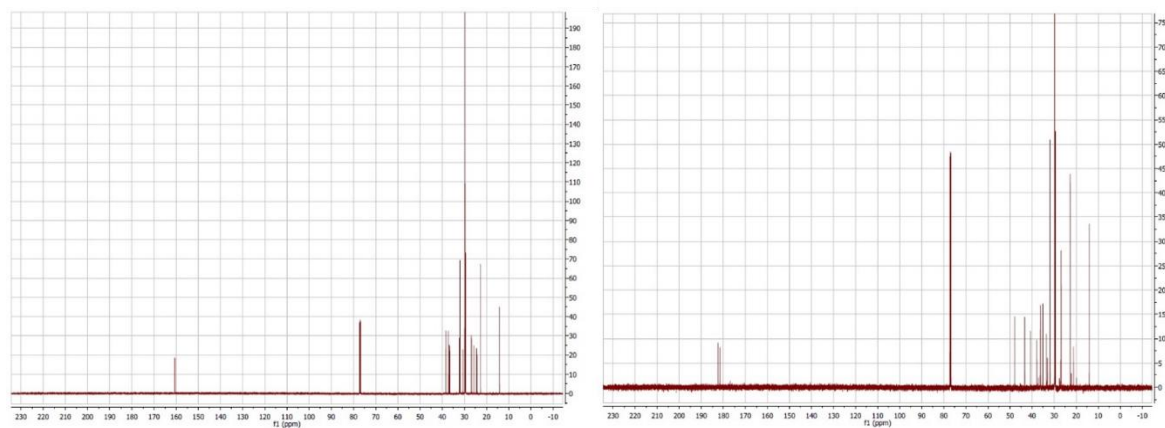

Figure 7: ^{13}C-NMR spectra (in CDCl$_3$)of 3-pentadecyl-cyclohexane oxime 3 (left) andpentadecyl-azepan-2-one as mixture of isomers (right)
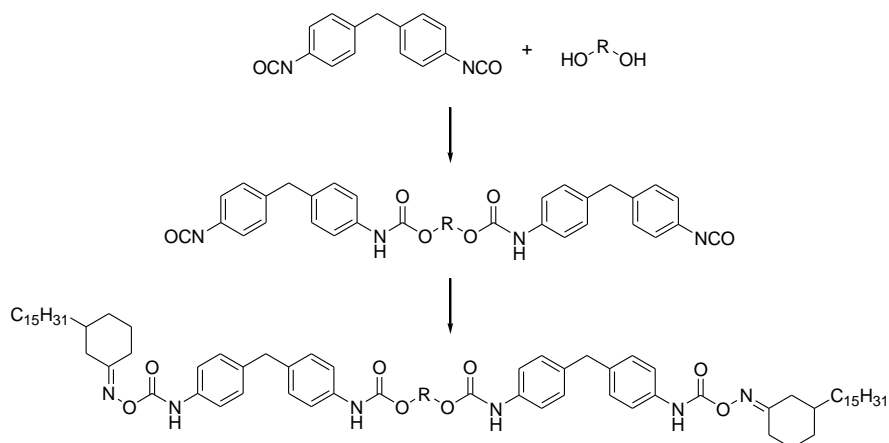

Figure 8: a non-limiting example of 3-pentadecyl-cyclohexane-oxime blocked MDI-based prepolymer

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In order to have a first indication on cardanol behavior as NCO blocking agent, model isocyanate-cardanol adducts were prepared, using both aromatic (TDI, MDI) and aliphatic (HDI, IPDI) isocyanates at a cardanol-derivative/isocyanate stoichiometric ratio. Similar adducts have been prepared with the reference petro-based benchmarks mentioned above (MEKO, ε-caprolactam), but also with other cardanol derivatives (high purity cardanol used as starting raw material and side chain hydrogenated cardanol, both commercially available from Cardolite as NX-2026 and NC-510, respectively), to have a broader comparison and a better understanding of the validity of the approach.

The resulting adducts have been then characterized for their deblocking temperatures (Table 1).Among all the analytical techniques (IR, TGA, UV-Vis, NMR, GC, GC-MS, titration, CO_2 evolution, Gel Time, X-Ray Photoelectron Spectroscopy) applicable to estimate deblocking temperatures of blocked prepolymers [17], Differential Scanning Calorimetry (DSC) was selected, due to easy and quick sample preparation, wide range of screening temperatures and method sensitivity [18].
In a typical DSC experiment, blocked isocyanates were heated from 25 °C to 250 °C at 10 °C/min undernitrogen.The new cardanol-based blocking agents not only show comparable reactivity to MEKO and ε-caprolactam during the isocyanate blocking reaction, but also faster deblocking kinetic when characterized by Differential Scanning Calorimetry, showing average deblocking temperatures lower than references, including cardanol andside chain hydrogenated cardanol.Comparable reactivity during blocking step, lower deblocking temperatures, presence of the $C_{15}H_{31}$ residue that offers flexibility as well as hydrophobicity are all unique features that allow the applicability of 3-pentadecyl-cyclohexane-oxime **3** and pentadecyl-azepan-2-ones **4a**, **4b** as novel isocyanate blocking agents with a broader spectrum of applications than traditional products, along with safer handling due to reduced volatility.

Even if suitable for a first screening, basic isocyanate-blocking agents adducts are not truly representative of the polymeric substrates used in 1K PU applications. For this reason, some derivatives (NX-2026; MEKO; cardanol-derived oxime **3**) were tested in model blocked prepolymers (Table 2).

Model prepolymers were prepared under the same process conditions, using polypropylene glycol (MW 2000) as starting polymeric diol, MDI as isocyanate source and targeting a 4% free NCO content prior to full blocking. The resulting blocked-prepolymers were then characterized for their deblocking temperatures under the same conditions as for adductsby Differential Scanning Calorimetry (Table 2).

Table 1: deblocking temperatures of a cardanol-derivatives blocked isocyanates

Isocyanate	Blocking agent	Deblocking T (°C)
TDI	NX-2026	~115
	NC-510	~160
	MEKO	~70
	ε-caprolactam	~150
	3	~70
	4	~130
MDI	NX-2026	~145
	NC-510	~150
	MEKO	~90
	ε-caprolactam	~145
	3	~77
	4	~125
HDI	NX-2026	~155
	NC-510	~185
	MEKO	~120
	ε-caprolactam	~180
	3	~82
	4	~144

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IPDI	NX-2026	~130
	NC-510	~180
	MEKO	~110
	ε-caprolactam	~185
	3	~86
	4	~142

Table 2: deblocking temperatures of PPG$_{2000}$/MDI-blocked prepolymers

Substrate	Blocking agent	Deblocking T (°C)
PPG$_{2000}$-MDI	NX-2026	~165
	NC-510	~125
	MEKO	~98
	3	~83

Table 3: deblocking temperatures of aliphatic polyester diol/TDI-blocked prepolymers

Substrate	Blocking agent	Deblocking T (°C)
Polyester diol-TDI	NC-510	~120
	ε-caprolactam	~140
	4a,4b	~130

A similar approach (Table 3) was used for the other blocking agents (ε-caprolactam; cardanol-derived lactams **4a**,**4b**), using a polyester diol based on adipic acid andbutane-diol (MW 2000), TDI as isocyanate source and targeting a 4% free NCO content prior to full blocking. Given the nature of the starting polymeric diol (solid at RT) and the general increase in viscosity when blocked prepolymer are produced, a 1/1 v/v mixture of 1-methoxy-2-propyl acetate/xylene has been used as solvent (dry residue 70%).

As evident from above results, the same trend observed for basic isocyanate adducts is observed on model prepolymer, where cardanol-derived oxime **3** and cardanol-derived lactams**4a,4b** show favorable deblocking conditions, with average comparable or lower deblocking temperatures than both petro- and other cardanol-derived references.

All these results confirm the validity of the chemical approach herein described towards the development of novel cycloaliphatic cardanol-derivatives, without necessarily using a catalyst or a nucleophile to tune their deblocking temperatures, as it normally happens with petro-based blocking agents (e.g. MEKO) and as sometimes required by cardanol when used as isocyanate protective group.

4 CONCLUSIONS

Cardanol is one of the most promising bio-based materials used in the thermoset industry, due to its multiple chemical functional sites amenable to derivatization (through the aromatic ring, the phenolic OH andthe side chain double bonds). This paper describes the applicability of high purity cardanol as a valid substrate for the development of a series of cycloaliphatic derivatives that can be successfully used as protectives groups for both neat isocyanates as well as isocyanate-terminated prepolymers. These derivatives, once compared to standard petro-derived blocking agents with similar reactive groups (e.g. methyl-ethyl ketoxime, ε-caprolactam), show comparable, or even lower, deblocking temperatures, therefore representing versatile chemical tools to adhesive and coatings Formulators. Future work will be addressed to collect more application data on cardanol-derived oxime and cardanol-derived lactam as suitable blocking agents for coil stoving and powder coating applications.

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