

Synthesis and Characterization of Isocyanate-Functionalized PVA-Based Polymers with Applications as New Additives in Lubricant Formulations

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ABSTRACT: This work deals with the incorporation of reactive isocyanate groups into polymer additives, which could be potentially used to modify the rheological properties of lubricating greases by reinforcing the role of traditional thickening agents. Thus, a batch of partially protected poly(vinylalcohol) (PVA) copolymers was successfully synthesized. Some of their —OH groups were blocked as tetrahydropyranyl (THP) ethers (PVA-THP), while the spare hydroxyl groups were further functionalized with —NCO pendant groups by reaction with 1,6-hexamethylene diisocyanate, leading to several isocyanate-functionalized PVA-based polymers (PVA-THP-NCO), which were tested as rheology modifiers of lithium lubricating greases. The highest protection degree of hydroxyl

groups achieved as THP-ether was 58.5% and the recovered polymers were isolated with excellent yields (close to 90% in most cases). NCO-functionalized PVA-based polymers (PVA-THP-NCO) exerted a significant rheological modification in lithium 12-hydroxystearate lubricating greases, increasing the values of the linear viscoelastic functions. The influence of the degree of protection and later functionalization of PVA on the rheological properties of PVA-THP-NCO-additivated lubricating greases is discussed. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 3259–3267, 2012

Key words: functionalized PVA; PVA protection; reactive polymers; lubricant; rheology

INTRODUCTION

The use of reactive groups in oligomer or polymer chains is generally proposed to either achieve certain properties in new materials or produce new active intermediates toward some chemical reactions, which may lead, for instance, to networks or chemically grafted copolymers. Poly(vinylalcohol) (PVA) is a hydrophilic semi-crystalline polymer produced by polymerization of vinylacetate (PVAc), and subsequent hydrolysis of PVAc to PVA. Incomplete hydrolysis reactions result in polymers with different hydroxyl group percentages.¹ Commercial PVA is available in highly hydrolyzed grades (hydrolysis degree above 98.5%) and partially hydrolyzed rates (hydrolysis degree from 80.0 to 98.5%).² Hydrolysis degrees (and hence, acetate group content) of PVAs

has a marked impact on their chemical properties, solubility, and crystallinity.^{2,3}

PVA has been used in direct applications such as membranes, adhesives, paints, printing plates, films, and fibres and may be conveniently modified for other particular applications. Those conversions generally consist of copolymerization reactions and end-group transformations, by means of reactions between hydroxyl groups and reagents such as acyl chlorides, carboxylic acids, and anhydrides. Other alternative routes to functionalize PVA may be accomplished by reaction with diketenes, amines and isocyanates, or by a Michael addition reaction with activated double bond-containing compounds. Thus, for instance, homogeneous grafting reactions can be carried out at moderated and fixed temperatures keeping full control over the final product. PVA modifications are very often performed in solution, being dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and *N*-methylpyrrolidone the solvents most commonly used.⁴

Partial protection of organic materials is a common practice carried out to reduce the reactivity of side functional groups. The preparation of polymers with protected hydroxyl groups was extensively reported in the existing literature; some examples

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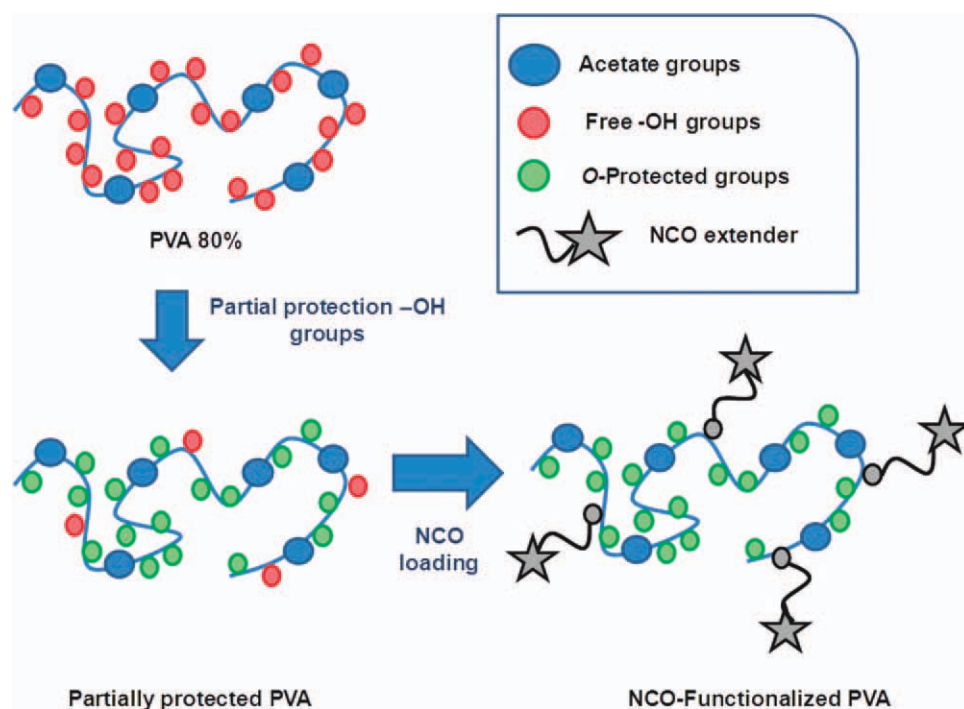


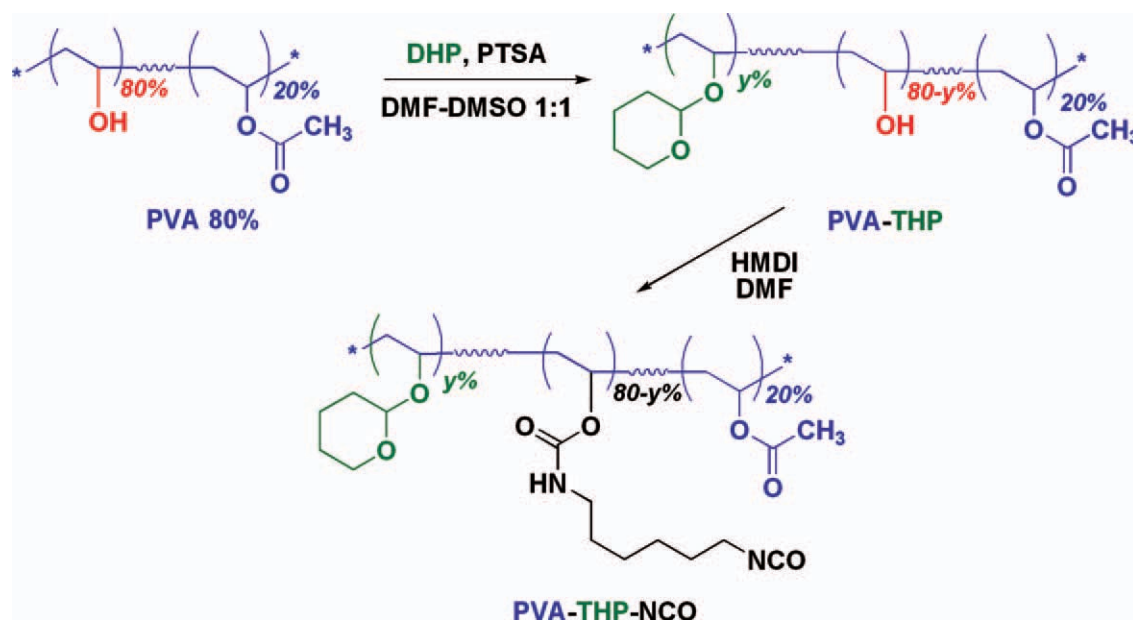
Figure 1 General strategy for the preparation of NCO-functionalized PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

have been selected and included herein. In most cases, the -OH groups from the monomers were previously protected and polymerization was accomplished next. For instance, the -OH s were protected as tetrahydropyranyl (THP) ethers in the production of a soluble, acid-labile, blue luminescent fluorene-based polymer⁵ and in films of polythiophenes.⁶ The THP group could also be found in macromolecular initiators as those ones used for the preparation of functionalized polyethylene oxide for click chemistry.⁷ *Tert*-butyl ethers were employed as protecting group of -OH s in *p*-hydroxystyrene as well. The vinyl monomer was then polymerized and deprotected to provide poly(*p*-hydroxystyrene) derivatives.⁸ Acetyl, *tert*-butoxycarbonyl ethoxymethyl, (2-ethoxy-ethoxy)methyl and methyl groups were utilized to protect *p*-hydroxyacetophenone in the preparation of poly(*p*-hydroxy- α -methylstyrene).⁹

Lubricating greases are highly structured suspensions consisting of a thickener, usually a metal soap, dispersed in mineral or synthetic oil. The most common thickening agent employed is lithium 12-hydroxystereate soap. These lubricating greases usually contain several performance additives.^{10,11} Thus, the incorporation of polymeric materials is a common practice to modify rheological properties of greases by reinforcing the role of the thickening agent.^{12,13} The use of polymers, conveniently functionalized with terminal isocyanate groups, has recently proved to chemically interact with soap net-

works, with the subsequent bulk rheological modifications of greases.^{14,15} Thus, the addition of poly(1,4-butanediol), tolylene-2,4-diisocyanate, and other NCO-terminated prepolymers (prepared from di- and trifunctional polyols and polymeric MDI) leads to significant changes in rheological responses. The effectiveness of such additives is due to the reaction between terminal isocyanate groups—from the macromolecular material—and hydroxyl groups from lithium 12-hydroxystereate soap. However, their performance is highly dependent on two polymeric parameters, free NCO content and molecular weight.

Taking into account the details mentioned above, this work deals with the incorporation of reactive isocyanate groups into polymeric additives, which would potentially modify rheological properties of greases by reinforcing the role of thickening agent. The chosen polymer was the commercially available PVA (80%), which would be conveniently converted into NCO-functionalized additives by partial protection and later functionalization procedure (Fig. 1). Thus, protection process of free hydroxyl groups of PVA 80% by means of reaction with 3,4-dihydro-2-H-pyran (DHP) will be studied and accomplished in different percentages. Second, activation of remaining free -OH groups as NCO-terminated pendant hydrocarbon chains with 1,6-hexamethylene diisocyanate (HMDI) will be carried out and, finally, the efficiency of selected new polymeric additives will be tested as rheology modifier of lubricating greases.



Scheme 1 Partial protection and further functionalization of PVA 80%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

Common reagents and solvents were purchased from Sigma-Aldrich and used as received. Solvents were dried and purified, when necessary, by appropriate standard procedures. The polymer poly(vinyl alcohol) (PVA) used was purchased from Sigma-Aldrich (typical $M_w = 9000$ – $10,000$) with 20 mol % poly(vinyl acetate) in its structure.

For the preparation of lithium 12-hydroxystearate lubricating greases (14% w/w soap), 12-hydroxystearic acid, lithium hydroxide, and a naphthenic mineral lubricating oil (density at 20°C: 916 kg/m³; kinematic viscosity at 40°C: 115 mm²/s) were used. All components were kindly supplied by Verkol, S.A. (Spain).

General methods

Protection and functionalization reactions (Scheme 1) were performed using standard Schlenk techniques, in the absence of humidity, under inert atmosphere. All glassware was heated overnight at 80°C before use, and was further heated under vacuum to eliminate surface moisture after assembly. Poly(vinyl alcohol) (PVA 80%) was freeze-dried before use. HMDI and 3,4-dihydro-2-*H*-pyran were stored at 4°C and handled under inert atmosphere.

Elemental analyses were determined at the Microanalyses Laboratories of the CITIUS Service, University of Seville. IR spectra (films or KBr discs) were recorded with a JASCO FT/IR-410 spectrometer. NMR spectra were recorded at 300 K on either a

Bruker Advance AV-500 or a Bruker AMX-500. Chemical shifts (δ) are reported as parts per million downfield from Me₄Si. Thermogravimetric analyses were performed under nitrogen atmosphere (flow rate 100 mL min⁻¹) with a Universal V4.3A TA Instrument at a heating rate of 20°C min⁻¹.

Rheological measurements were carried out in a controlled-strain (ARES, Rheometric Scientific, UK) rheometer, using plate–plate geometries (25-mm diameter, 1-mm gap). Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, in a frequency range of 10⁻²–10² rad/s. At least two replicates of each test were carried out on fresh samples.

Protection reaction of PVA 80% with DHP (PVA-THP)

The general method for protection of PVA 80% hydroxyl groups is described below. Reaction conditions for the different assays are listed in Table I.

In a typical procedure (preparation of PVA-THP-D), PVA 80% (10.0 g, 0.15 mol of vinyl alcohol residues) was dissolved in a mixture of DMF–DMSO (1 : 1 volume, 50 mL). The polymer and solvents were stirred for not <1.5 h. When PVA 80% was completely dissolved, the reaction solution was cooled down to 0°C and DHP (14.6 mL, 0.19 mol) was added, followed by the incorporation of the catalyst [*p*-toluenesulfonic acid (PTSA), 0.350 g, 1.84 mmol]. The reaction proceeded at 0°C for 1 h and then warmed up at 25°C for further 5 h. The reaction mixture was poured into distilled cold water and the partially protected polymer precipitated. The

TABLE I
Synthetic Data for the Protection Reaction of PVA 80% (Synthesis of PVA–THP Polymers)

Polymer	Reaction conditions ^a		Protection degree (mol %) ^b		Molar composition of final PVA–THP (%) ^c			Δ% ^d		Residual solvent (%)
	DHP (mequiv)	Reaction time 0°C/25°C (hr)	¹ H NMR	Elemental microanalysis	VAc	VA	VA–THP	C	H	
PVA	–	–	–	–	20	80	0	0.01	0.01	3.1
PVA–THP-A	1.0	1.0 / 0.5	1.0	1.3	20	79	1	0.25	0.33	2.8
PVA–THP-B	1.0	1.0 / 1.0	3.5	4.0	20	77	3	0.21	0.30	2.8
PVA–THP-C	1.0	2.0 / 5.0	30	26	20	59	21	0.11	0.33	2.3
PVA–THP-D	1.25	1.0 / 5.0	46	49	20	41	39	0.26	0.50	1.8
PVA–THP-E	1.25	2.0 / 5.0	60.5	58.5	20	33	47	0.00	0.02	0.5

^a [PVA]₀ = 15–20% w/v in 1 : 1 DMF/DMSO; Catalyst: *p*-toluenesulfonic acid (10 mol %).

^b Mol % of VA repeating units protected as VA–THP calculated by ¹H NMR and elemental microanalysis.

^c Calculated values from elemental microanalysis data.

^d Differences between theoretical and experimental elemental microanalysis data.

solid was filtered out, washed with distilled water and then with cold diethyl ether. The pure polymer (white amorphous solid) was freeze-dried for 2 days and stored in a desiccator. (16.3 g, 87% yield). Degree of protection: by ¹H NMR: 46%, by Elemental microanalysis: 49%.

IR: ν (cm⁻¹) 3375 (OH), 2916 (C–H aliph), 1731 (C=O acetate), 1240 (C–OH), 1018 (CO–C). ¹H NMR (DMSO-*d*₆, 500 MHz): δ (ppm) 6.14 (d, 1H, O–H, *J* 5.1 Hz), 5.35–3.30 [m, 6H, 3 CH (VA, VAc, VA–THP repeating units), CH–O (THP ring), 1 CH₂–O (THP ring)], 1.95 [s, 3H, CH₃ (VAc)], 1.85–1.05 [m, 12H, 3 CH₂ (VA, VAc, VA–THP repeating units), 3 CH₂–O (THP ring)], ¹³C NMR (DMSO-*d*₆, 125 MHz): δ (ppm) 169.7 [C=O (VAc)], 93.4 [CH–O (THP ring)], 73.2, 72.5, 71.9 [CH (VAc)], 67.8, 66.7, 65.7, 63.7 [CH (VA, VA–THP repeating units)], 60.6 [1 CH₂–O (THP ring)], 45.9, 45.7, 45.6, 45.4, 39.5, 39.2, 38.6, 37.0, 34.4, 30.32 [CH₂–O (VA, VAc, VA–THP repeating units)], 32.3, 25.1, 20.4 [3 CH₂–O (THP ring)], 20.7 [CH₃ (VAc)].

Elemental Microanalysis Calcd. for [(C₄H₆O₂)₂₀ (C₂H₄O)₄₁ (C₇H₁₂O₂)₃₉ (C₃H₇NO)_{0.5} (C₂H₆OS)_{1.5}]: C, 60.81; H, 8.88. Found: C, 61.07; H, 8.38].

Functionalization reaction of partially protected PVA–THP with HMDI (PVA–THP–NCO)

For a representative procedure, the partially protected PVA–THP-E polymer (12.0 g, 0.043 mol of vinyl alcohol residues) was loaded in a round-bottomed flask with an inlet of Argon/vacuum. The system was treated with three cycles of vacuum-argon before the addition, via cannula, of dried DMF (50 mL). The mixture was stirred to homogenization, and HMDI (7.0 mL, 0.043 mol) was added under argon atmosphere, followed by catalyst (dibutyltin dilaurate, one drop) and the reacting mixture was stirred for further 12 h, at 25°C. The solution was

then freeze-dried to remove solvent. The functionalized product (PVA–THP–NCO) was purified by stirring with cold, dried diethyl ether (200 mL) to remove remaining reagents. The pure polymer (white solid) was dried under vacuum for 2 days and stored at 4°C (9.2 g, 67% yield). Degree of functionalization: by ¹H NMR: 23%, by Elemental microanalysis: 24%.

IR: ν (cm⁻¹) 3428 (N–H), 3375 (O–H), 2931 (C–H aliph), 2268 (N=C=O), 1735 (C=O acetate), 1694 (C=O urethane), 1534 (N–H urethane), 1241 (C–OH), 1022 (C–OC). ¹H NMR (DMSO-*d*₆, 500 MHz): δ (ppm) 6.05 (bs, 1H, O–H), 5.35–3.30 [m, 8H, 3 CH (VA, VAc, VA–THP repeating units), 2 N–H, CH–O (THP ring), 1 CH₂–O (THP ring)], 3.13 (bs, 4H, CH₂–NH), 1.95 [s, 3H, CH₃ (VAc)], 1.85–1.05 [m, 20H, 3 CH₂ (VA, VAc, VA–THP repeating units), 3 CH₂–O (THP ring), 2 CH₂–CH₂NH], 1 CH₂–NCO, 1 CH₂–CH₂CH₂NH]. ¹³C NMR (DMSO-*d*₆, 125 MHz): δ (ppm) 169.5 [C=O (VAc)], 121.5 (NCO), 94.5 [CH–O (THP ring)], 73.1, 72.7, 71.5 [CH (VAc)], 67.9, 66.6, 65.8, 64.0 [CH (VA, VA–THP repeating units)], 60.4 [1 CH₂–O (THP ring)], 45.8, 45.7, 45.3, 39.6, 38.7, 37.1, 34.6, 30.31 [CH₂–O (VA, VAc, VA–THP repeating units)], 40.91 (CH₂–NH), 32.1, 25.6, 20.5 [3 CH₂–O (THP ring)], 29.8, 29.6 (CH₂–CH₂NH, CH₂CNO), 26.3 CH₂–CH₂CH₂NH], 20.5 [CH₃ (VAc)].

Elemental Microanalysis Calcd. for [(C₄H₆O₂)₂₀ (C₂H₄O)₄₁ (C₇H₁₂O₂)₃₉ (C₃H₇NO)_{0.5} (C₂H₆OS)_{1.5}]: C, 60.81; H, 8.88. Found: C, 61.07; H, 8.38].

Preparation of lubricating greases with PVA–THP–NCO as additives

The processing of greases was performed in a small mixing reactor (batches: 34 g), using an anchor impeller by applying a rotational speed of 60 rpm. Typical lubricating grease formulation evaluated

includes 83% (w/w) naphthenic oil, 14% lithium 12-hydroxystearate (w/w), and 3% (w/w) polymeric additive (PVA-THP-NCO). Processing details and procedure have been extensively described elsewhere.^{16,17} Once saponification was completed, the mixture was heated up to a maximum temperature of 180°C, to induce the phase transition of soap crystallites into a waxy phase, and complete the dehydration process, as previously reported.¹⁷ Afterwards, a controlled cooling ramp down to room temperature was imposed. The addition of isocyanate-functionalized PVA-based polymer (PVA-THP-NCO-E), dissolved in DMF, was carried out at 150°C, during the final cooling step. More details on this type of reactions can be found elsewhere.¹⁶ The whole manufacturing process generally occurred over a period of 18 h. A final homogenization treatment (rotational speed: 8800 rpm; homogenization time: 7 min), using a rotor-stator turbine (Ultra Turrax T-25, Ika, Staufen, Germany), was applied at room temperature to reduce crystal size.

RESULTS AND DISCUSSION

Synthesis and characterization of highly functionalized isocyanate-based PVA

PVA 80% was chosen as starting material in this work for several reasons: first, the environmental interest of PVAs as biodegradable materials for further industrial applications; second, the presence of vinyl acetate units (VAc) enhances the solubility of PVA 80% in organic solvents, what ensures subsequent copolymer transformations in solution; and finally, the chemical transformations to carry out over the polymer is guaranteed by the high alcohol groups content, to transform PVA 80% into novel additives in the manufacture of lubricating greases.

We aimed to prepare new PVA-based materials in which isocyanate moieties will be introduced into it to strengthen their role as thickening agent. The ratio of NCO groups may be a key factor in the final performance of these additives and hence, its study is addressed in this work. As cross-linking reactions should be avoided to get linear and soluble polymers for further industrial applications and, taking into account that HMDI can react either once or twice due to its two terminal -NCO groups, the reaction by only one of its edges is required. With this target in mind, the synthesis of PVA-NCO derivatives was conducted as follow: first, a partial protection of PVA hydroxyl groups is recommended to lessen the ratio of available free hydroxyl units to quickly react with HMDI. The protection to a degree of pendant hydroxyl groups was performed by reaction with DHP as THP ethers. Second, the use of a molar excess of NCO groups referred to alcohols

units (molar ratio 2 : 1) would prevent, in some extension, network formation. The anchorage of HMDI residues to the polymer was carried out via urethane bonds by reaction between the spare -OH units in the protected polymer and one of the -NCO groups in HMDI. So, PVA-THP-NCO polymers would contain hexamethylene chains with pendant isocyanate moieties at each end, which can later react with the hydroxyl groups of the hydroxystearate salt in grease formulations.

Protection of hydroxyl groups as THP-ether (repeating unit formed: VA-THP) was performed with DHP in the presence of PTSA as catalyst, at room temperature, following the method described by Holdcroft et al. for the synthesis of 9,9-di(2-(2-tetrahydropyranloxy)ethyl)fluorine monomer in the preparation of luminescent polyfluorenes⁵ (Scheme 1). The choice of THP ether as protecting groups was due to its simple and well-known associated chemistry,⁵ as well as the aliphatic nature of THP ethers, which resembles not only the lipophilic nature of PVA polymer backbone but also of the NCO-based new additives that would be employed later on. This lipophilic character is of crucial relevance in additives, as they should be miscible with the oil used to guarantee the homogeneity of lubricant formulation. In addition, THP ethers are stable at basic pH and high temperatures and they are not affected by the presence of highly basic species such as LDA and sodium hydride or alcoholates such as potassium *t*-butoxide or sodium methoxide. These ethers are also stable at high temperatures (150°C) and may be altered in some degree at 200°C or above. Those aspects are of relevance for their later use as additives.¹⁸

The different degrees of protection of vinyl alcohol repeating units (VA) achieved are displayed in Table I were calculated by ¹H NMR and elemental microanalysis. Exact percentage of VAc units in PVA 80% was determined from elemental microanalyses; they revealed an 80 : 20 mol ratio of VA/VAc units, and this value was fixed for further calculations. The DHP ratio incorporated into the polymer backbone as THP ether was then calculated by elemental microanalysis and ¹H NMR spectroscopy. The calculated ratios of VAc, VA, and VA-THP repeating units were obtained by comparing the integrals of two regions: the first one includes the overlaid peaks assigned to CH_2 protons in the polymer backbone as well as the peaks corresponding to the protons adjacent to an oxygen atom in THP ring (from ~ 5.4 to 3.2 ppm); the second region displays the peak due to the CH_3 protons from VAc repeating units (~ 1.95 ppm). The scrutiny of these results highlighted the good agreement between the experimental values determined by both techniques (¹H NMR and elemental microanalysis). Thus, the actual

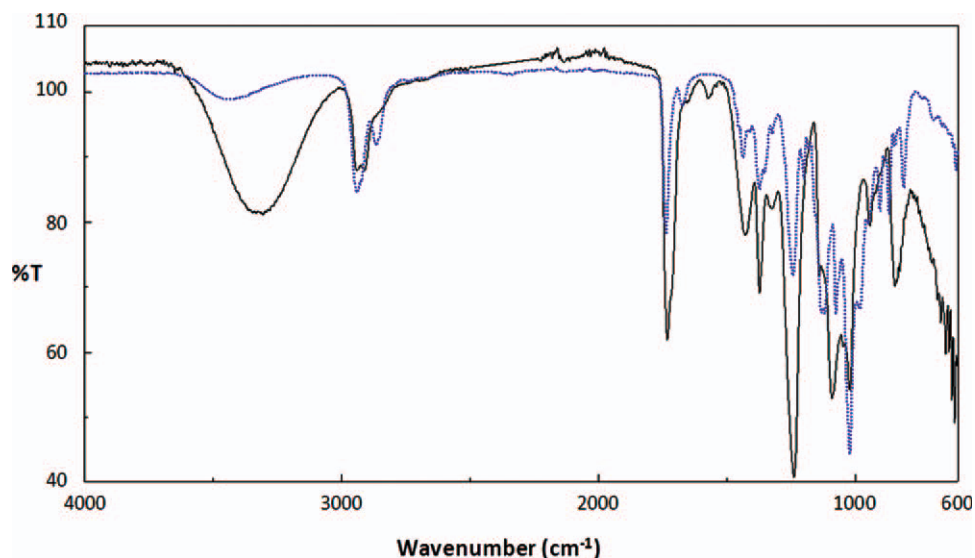


Figure 2 IR comparative curves of the commercial polymer PVA (solid line) and PVA-THP-E, with 39% molar protection of the VA units as VA-THP acetals (dotted line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copolymer compositions calculated by both methods turned to be quite similar with no more than ± 4.0 mol percentage of difference.

The factors involved in the degree of protection achieved were not only the mequiv of DHP used (from 1.00 to 1.25 mequiv) but also the reaction time at 0°C and 25°C (from 30 min to 5 h). Total protection of hydroxyl groups was prevented by steric hindered effect of highly bulk THP groups. This was crucial as the remaining —OH groups would subsequently react with the less bulky reagent HMDI, leading to a set of new additives functionalized in different degrees. In our hands, the highest degree of protection obtained was accomplished with 1.25 mequiv of DHP and the longest reaction times tested (2.0 h at 0°C and 5.0 h at 25°C) (Table I, entry PVA-THP-E). The recovered polymers were isolated with excellent yields (close to 90% in most cases). Residual solvent was found in all of them, with lower percentages in highly protected materials.

Infrared spectra of new copolymers were in concurrence with their chemical structure. The absence of a band at $\approx 1660\text{ cm}^{-1}$ (due to DHP-vinyl ether bond) confirmed the lack of unreacted DHP in the new materials (See Fig. 2). The incorporation of DHP into the polymers as saturated THP rings was confirmed by the band at 1018 cm^{-1} . It is significant that the reduction of the band at 3375 cm^{-1} (attributable to the OH— moieties) from the starting material to the PVA-THP polymers, since the incorporation of the protecting groups into the PVA-THP polymers reduced the percentage of free hydroxyl groups in polymer chains.

Thermal degradation behavior of commercial PVA 80% and new PVA-THP polymers turned to be

quite different. For commercial PVA 80%, thermal degradation under nitrogen atmosphere occurred in two steps, at 319 and 431°C, with higher weight loss at 319°C (83%, Table II). For partially protected PVA-THP polymers, the introduction of THP rings into the polymer structures reduced their thermal stabilities in great extend due to the acetal groups, with marked impact in highly THP-content polymers, as expected (Fig. 3 and Table II). Similarly, the thermal degradation pattern exhibited by DHP was clearly different to those displayed by the new PVA-THP polymers, corroborating the chemical incorporation of THP rings into the polymer structures.

Several attempts were made to synthesize functionalized-based PVA (PVA-THP-NCO polymers) using partially protected PVA-THP copolymers as starting material. The reactions proceeded at room temperature for 12 h under anhydrous, inert

TABLE II
Thermal Properties of the New PVA-THP Copolymers

Polymer	TGA		
	T_{d0} (°C) ^a	T_d (°C) ^b	ΔW (%) ^c
DHP	101	169/ 300 /449	53/37/6
PVA	306	319 /431	83/12
PVA-THP-A	236	220/271/ 330 / 456	15/17/30/35
PVA-THP-B	237	229/279/ 327 /452	13/14/35/31
PVA-THP-C	210	207 /247/326/449	29/23/18/22
PVA-THP-E	200	206 /339/449	58/14/22

^a Onset temperature.

^b Decomposition temperatures measured at the peaks of the derivative curves; major peaks in bold.

^c Loss weight at the end of the decomposition step.

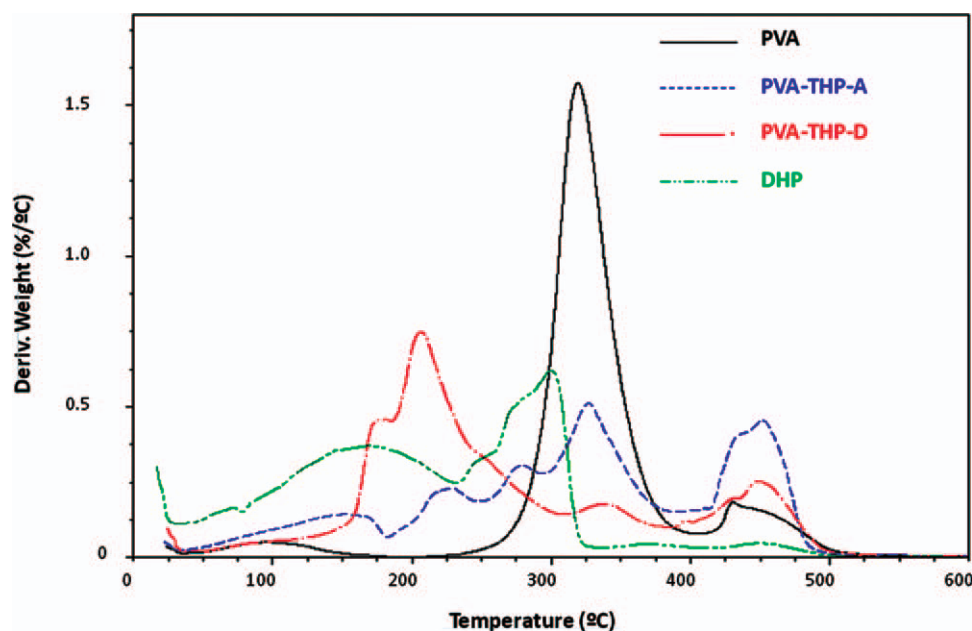


Figure 3 Thermal degradation curves, under inert atmosphere, of PVA-based polymers with different protection degree (Derivative of Weight loss (%/°C) vs. Temperature). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

atmosphere. Equimolar amounts of HMDI were added referred to calculated VA ratio in the reactant used, which would ensure the presence of —NCO moieties in the final PVA-THP-NCO polymers. However, total functionalization of VA units was prevented probably due to the highly bulk substituents in PVA-THP. It was also observed that the higher the protection degree of the starting material, the lower the NCO percentage (Table III). Although PVA 80% was effectively functionalized by reaction with HMDI, a significant percentage of insoluble cross-linked materials (62%) was obtained, as expected. The remaining soluble PVA-NCO displayed a 75% of functionalization; in contrast, only a 24% mol content of the hydroxyl groups in PVA-THP-E reacted with HMDI but no insoluble aggregates were found in this case. In general terms, when PVA-THP-NCO macromolecules were synthe-

sized, it was observed that the higher the rate of THP protecting groups in the reactants, the lower the cross-linked residue content was found, and hence, better soluble properties were achieved.

The formation of PVA-THP-NCO polymers was confirmed by different techniques. Figure 4 represents the IR curves of a PVA-THP polymer with 4% molar protection (PVA-THP-B, solid line) and its further functionalization with HMDI (dotted line). It is significant the reduction in intensity of the band at 3375 cm^{-1} (attributable to the OH— moieties in VA repeating units) since they reacted with isocyanate groups of HMDI leading to urethane linkages (see Scheme 1). Second, the urethane bands were present at 3428 (N—H) , $1694\text{ (C=O urethane)}$, and $1534\text{ cm}^{-1}\text{ (N—H urethane)}$. Moreover, the intense peak at 2268 cm^{-1} confirmed the presence of unreacted isocyanate groups, as expected.

TABLE III
Synthetic Data for the Functionalization of Partially Protected PVA-THP

Polymer	PVA-THP used ^a	Functionalization degree (mol %) ^b		Molar composition of initial PVA-THP (%) ^c			Molar composition of final PVA-THP-NCO (%) ^c			
		¹ H NMR	Elemental microanalysis	VAc	VA	VA-THP	VAc	VA	VA-THP	VA-NCO
PVA-NCO	PVA	—	75	20	80	0	20	20	0	60
PVA-THP-NCO-B	PVA-THP-B	—	69	20	77	3	20	24	3	53
PVA-THP-NCO-D	PVA-THP-D	38	41	20	41	39	20	24	39	17
PVA-THP-NCO-E	PVA-THP-E	23	24	20	33	47	20	25	47	8

^a [Reactant]₀ 20–24% w/v in DMF.

^b Mol % of VA repeating units functionalized as VA-NCO calculated by ¹H NMR and elemental microanalysis.

^c Calculated values from elemental microanalysis data.

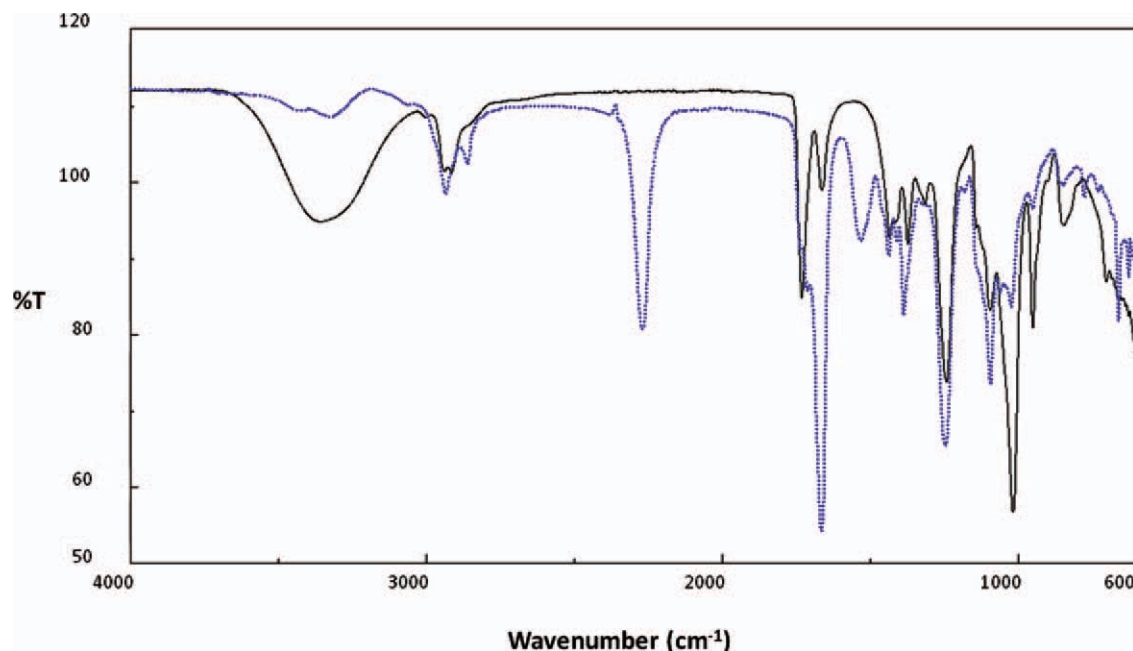


Figure 4 IR comparative curves of polymer PVA-THP-B (4% molar protection of the VA units as VA-THP acetals, solid line) with functionalized polymer PVA-THP-NCO-B (dotted line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Regarding TG tests, all NCO-functionalized copolymers exhibit similar tendencies with onset temperatures close to 300°C and maximum decomposition temperatures at around 325 and 460°C. Therefore, the maximum degradation step shifts to temperature values lower than those displayed by PVA-THP copolymers.

Rheological properties of lubricating greases modified with isocyanate-functionalized PVA-based polymers

Selected isocyanate-functionalized PVA-based polymers, with high and low functionalization degree, respectively (PVA-NCO and PVA-THP-NCO-E), have been tested as additives to enhance the viscoelastic functions of lithium 12-hydroxystearate lubricating greases. Thus, lubricating greases modified with those polymers were prepared and compared with both, additive-free lubricating grease and that containing a non-reactive PVA-based polymer (PVA-THP-D). Figure 5 shows the linear viscoelastic response of these greases. In all cases, the mechanical spectra are qualitatively similar, being the values of the storage modulus, G' , significantly higher than those found for the loss modulus, G'' , in the whole frequency studied. The so-called "plateau region" was always noticed, where G' slightly increases with frequency and G'' displays a clear minimum. This mechanical spectrum corresponds to the typical evolution of other commercial and model lubricating greases previously studied.^{14,15,19} As can be

observed in Figure 5, the values of the SAOS functions of grease containing the non-reactive PVA-based polymer were lower than those obtained with the additive-free lubricating grease. On the contrary and as expected, grease formulations modified with functionalized polymers showed a significant increase in the values of both viscoelasticity functions, in comparison with the reference formulations. The rheological modification exerted by PVA-THP-NCO-E, with a relatively low functionalization degree (Table III), mainly affected the G' values, i.e.,

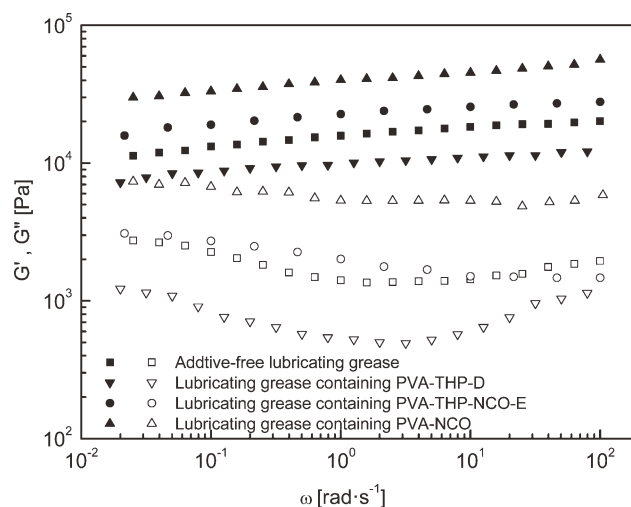


Figure 5 Frequency dependence of the storage and loss moduli for lubricating greases modified with different PVA-based polymers (G' full symbols, G'' open symbols).

the elastic response. On the other hand, the lubricating grease containing PVA–NCO, with 75% of functionalization degree, showed a more remarkable increase of both viscoelastic moduli respecting the additive-free lubricating grease and hence affecting both, the elastic and viscous characteristics. However, this formulation was much more heterogeneous due to the presence of the more insoluble additive (PVA–NCO). In general, the rheological modifications achieved with these functionalized PVA-based polymers were similar, or slightly larger, than those previously found in greases modified with terminal isocyanate linear prepolymers depending on the functionalization degree.¹⁵

CONCLUSIONS

A batch of partially protected PVA copolymer were successfully synthesized and further functionalized with –NCO pendant groups by reaction with HMDI. In that sense, several isocyanate-functionalized PVA-based polymers were prepared and some of them tested as rheological modifier of lithium lubricating greases. The excellent agreement between the experimental copolymer compositions established by both, elemental analyses and ¹H NMR data was confirmed.

The highest degree of protection of hydroxyl groups as THP–ether (58.5%) was achieved at the longest reaction times tested and with a 25% molar excess of DHP and the recovered polymers were isolated with excellent yields (close to 90% in most cases). The highly bulk THP–ethers prevented full functionalization of the remaining free hydroxyl groups in PVA–THP polymers, with NCO-incorporation values ranging from 75 to 24%. Although it was expected that the higher the degree of functionalization the better their performance as additives in lubricating greases, PVA–THP–NCO polymers with low VA–NCO units displayed better solubility in organic solvents than their highly reactive counter-

parts, which turned to be essential for further applications.

NCO-functionalized PVA-based polymers exerted a significant rheological modification in lithium 12-hydroxystearate lubricating greases, increasing the values of the linear viscoelastic functions. This modification was more important as the NCO content increased.

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