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SUBERIN-BASED POLYURETHANES: SYNTHESIS, CHARACTERIZATION AND KINETICS OF THEIR FORMATION

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ABSTRACT

The synthesis and characterization of novel family of polyurethanes prepared by the polycondensation of suberin from *Quercus suber* L. with aliphatic and aromatic isocyanates are reported. A preliminary kinetic study, conducted with the aim of establishing the reactivity of suberin with different mono-, di- and polyisocyanates, showed that the kinetics of these condensations followed the classical second-order behaviour up to conversion of about 90%. The reactivity of different isocyanates followed patterns that could be readily rationalized in terms of steric hindrance and electronic factors associated with each specific structure. The investigation was then extended to the synthesis of the new polymers which were characterized by FTIR and NMR spectroscopy and DSC. These suberin-based polyurethanes were a mixture of linear, branched and crosslinked structures. The proportion of the latter (insoluble fraction) being the highest for the syntheses carried out in stoichiometric conditions, viz. $[NCO]_o = [OH]_o$. The Tg of these materials depended of the diisocyanates used and correlated with their structural stiffness.

1 INTRODUCTION

For several years, we have been engaged in research dealing with the rational exploitation of wastes resulting from the transformation of the outer bark of *Quercus suber* L., commonly known as cork *[1-5]*. In fact, the cork industry produces about 56000 tons/year of dust and wastes without any recognized industrial interest. These rejects are presently burned for energy recovery, regardless of the fact that they could be a source of intersting chemicals or materials *[1-6]*. We have previously shown that an alkaline methanolysis of this by-product gives about 40% of suberin which is a mixture of aliphatic chains bearing carboxylic methyl esters and hydroxyl groups*[1]*. These potential macromonomer were thoroughly characterized by vapour pressure osmometry, which gave a number average molecular weight (Mn) of 800 and by GPC, which showed the existence of a low molecular-weight fraction centered around Mn=550 and a wider fraction with an Mn of about 2000. Based in the results obtained from the determination of the hydroxy number, which was about 160, we calculated an average OH functionality of 2.3 per molecule of methanolyzed suberin. This result incited us to investigate the use of suberin as a polyol in the syntheses of polyurethanes by polycondensation reactions with isocyanates.

This paper first reports a kinetic studies of the formation of urethane functions resulting from the reaction between suberin and conventional aliphatic and aromatic isocyanates. The influence of steric hindrance and electronic factors, linked to the specific structure of each isocyanates could thus be established. The characterization of the suberin-based polyurethanes was then conducted by spectroscopic and thermal analyses.

2 EXPERIMENTAL

The suberin used in this work was obtained by alkaline methanolysis as described in a previous study *[1]*.

Solvents and catalysts were commercial products of the highest purity available. Isocyanates with three different functionalities (F) were used (see Scheme **I**):

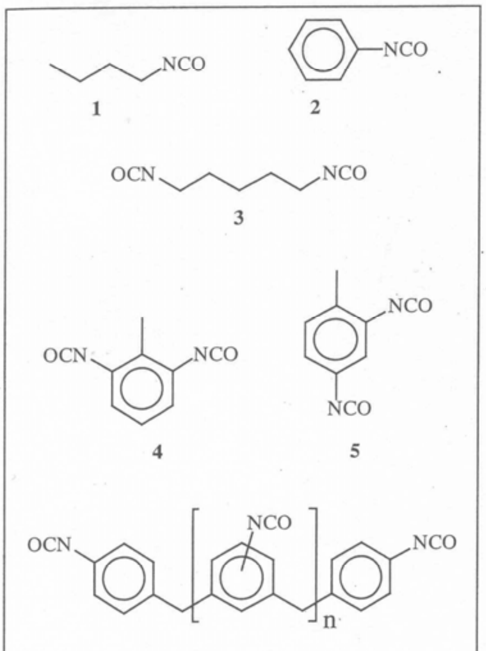
(i) F = 1: namely n-butyl (**1**) and phenyl (**2**) isocyanate;

(ii) F = 2: hexamethylene- (**3**), 2,4- (**4**) and 2,6- (**5**) toluene diisocyanates and their 80:20 w/w mixture and diphenyl methane diisocyanate (**6**);

(iii) F = 2.7: a commercial mixture of diphenyl methane diisocyanates and triphenyl methane triisocyanates (**7**).

For the uncatalyzed reactions, the isocyanate was added to a solution of suberin in pure dry tetrahydrofuran (THF). The initial concentration of both reagents was 0.2 M and the stoichiometric conditions were kept equal to unity, i.e. $[NCO]_o = [OH]_o$. For the catalyzed reactions, a 10^{-2} M solution of the catalyst (dibutyltin dilaurate, DBTD) in dry THF was prepared and stored in a dry atmosphere. The suberin was dissolved in the catalyst solution before adding the isocyanate under vigorous stirring. For kinetic studies the resulting mixture was quickly poured into an FTIR liquid cell and thereafter spectra recorded at regular intervals. Between spectra, the cell was kept at the desired constant temperature. A gentle stream of dry nitrogen was maintained in all experiments. The course of the reactions were controlled by monitoring the NCO peak around 2250 cm^{-1} in the FTIR spectra and each run was stopped after total consumption of the isocyanate moieties had been reached.

Both the kinetic study and the actual preparation of polyurethane with different isocyanates were carried out in the same conditions, except for the reaction temperature for the materials' synthesis which was 70±1°C. The polyurethanes thus obtained were extracted in soxhlet apparatus with methylene chloride, for 12 hours and the soluble and insoluble fractions weighed and examined.



Scheme I. Chemical structure of the isocyanates used in this work.

The FTIR spectra were recorded with a Perkin- Elmer Paragon 1000 spectrometer whereas the ^{1}H-NMR spectra was taken with a Brucker AMX-300 spectrometer using deuterated chloroform as the solvent of the soluble fractions and tetramethylsilane (TMS) as internal standard. The chemical shifts (δ) are given in ppm down field from TMS.

Differential scanning calorimetry (DSC) analyzes were made in sealed aluminium capsules with a Setaram DSC 92 in a stream of dry nitrogen. Sample for DSC weighed ca. 10 mg. The oven was maintained in a dry nitrogen atmosphere. Annealing was carried out by plunging the capsules in liquid nitrogen. Heating cycles were made between -150°C and +150°C, at a rate of 10°C per minute and cooling cycles with 15°C per minute.

3 RESULTS AND DISCUSSION

3.1 Kinetic studies

The second-order treatment was the most adequate way of representing the kinetic data of these systems with all the isocyanates investigated *[5]*. The Lambert-Beer law was applied to the variation of the intensity of the FTIR NCO peak according to the second-order kinetic equation *[5]*:

$$(A_0\text{-}A)/A = k\,[NCO] \qquad \text{(I)}$$

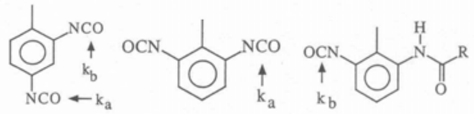
The experimental data thus obtained, processed according to equation **I**, showed good linearity of the second-order treatment, up to 90% conversion. In some cases, a deviation was observed at higher conversion. This phenomenon is well-documented in the literature attributed to an autocatalytic effect induced by the urethane functions and/or to the consumption of NCO by side reactions like the formation of allophanates *[7]*.

The second-order rate constants for the uncatalyzed reactions between suberin and **1** or **2**, at room temperature, were 0.25×10^{-4} and 1.5×10^{-4} l mol^{-1} s^{-1}, respectively. The modest reactivity of the aliphatic isocyanate compared with that of phenyl homologues and the present quantitative difference agrees with those reported in previous studies *[8]*. The catalyzed reactions displayed the same trends, albeit with a smaller difference in reactivity, as shown in Table I.

Table I: Second-order rate constants and activation energies for the catalyzed reactions between suberin and different isocyanates in THF at different temperatures, with $[NCO]_o$ = $[OH]_o$ = 0.2 M.

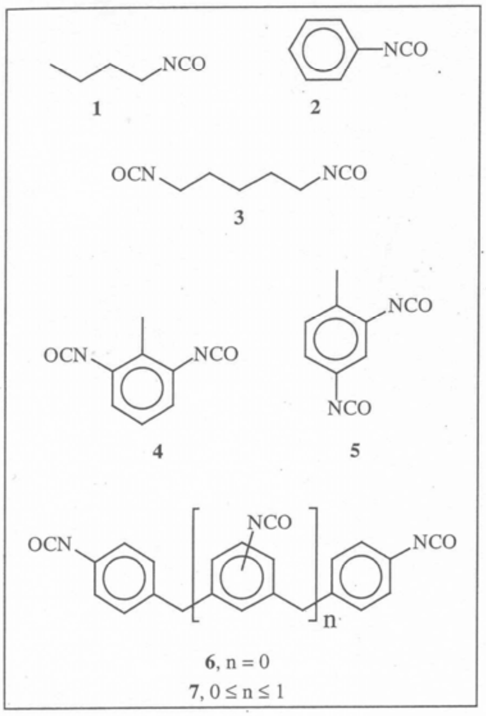
Isocyanate	Temperature (°C)	10^4 k (l mol^{-1} s^{-1})	Ea (kJ mol^{-1})
	23	16.3	
1	35	22.8	18.7
	45	27.5	
6	23	16.1	
2	23	5.75	
	23	5.2	
3	35	6.6	30.6
	45	12.6	

The second-order plots of asymmetric diisocyanate **5** gave two straight lines with a break in the slope (Figure 1). Therefore, the kinetic study of asymmetric diisocyanates were treated according to the competitive consecutive second-order model *[9]*. Two rate constants were determined, corresponding respectively to the reaction of the NCO groups at the *para* and *ortho* positions as given in Table II.



5 **4**

5 is an intrinsically asymmetric diisocyanate which always displays two distinct rate constants for the reaction of each functional group. **4** is symmetric in terms of chemical structure, but can become "asymmetric" after one of its NCO group has reacted because the urethane moiety and the attachment of bulky substituent can alter the reactivity of the remaining NCO moiety. This is particularly relevant here because the condensation with OH function of a suberin macromonomer chain certainly introduces steric problems for the reaction of the second NCO of **4**. Table II gives the second-order rate constants and the values of the two slopes, as measured from Figure 1 for the reaction of apparatus with methylene chloride, for 12 hours and the soluble and insoluble fractions weighed and examined.



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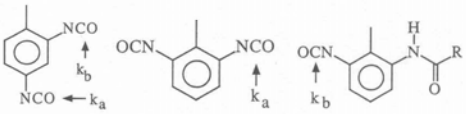

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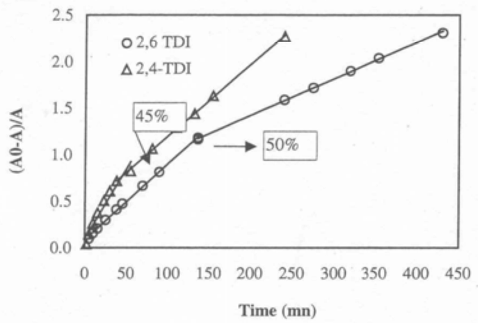

Figure 1: Second-order plot for the reaction **4** and **5** with suberin in the conditions specified in Table I at 23°C.

Table II: Second order-rate constants (l mol^{-1} s^{-1}) and slopes of the straight lines for the reactions showed in Figure 1, according to Frost and Schwemer model.

	Frost and Schwemer model *[9]*			
	k_a	k_b	k_a/k_b	$k_a + k_b$
4	18.1	2.1	8.6	20.2
5	11.1	1.4	7.9	12.5
	Graphic data (Slopes)			
	1	**2**	**1/2**	**1 + 2**
4	15.3	6.7	2.3	22.0
5	6.9	3.3	2.1	10.2

The values of the slopes 1 and 2 (l mol^{-1} s^{-1}), determined graphically, are not directly related to the individual rate constants, which are instead provided by the Frost-Schwemer treatment. However, the sum of the two slopes must be the same as the sum of k_a and k_b (see Table II).

3.2 Synthesis and characterization of products

The monourethane obtained by the reaction of suberin and **2** was with a yield of about 90% a viscous liquid. FTIR spectroscopy showed the presence of the peaks characteristic to the urethanes moieties, namely: NH, C=O and O=C-O at 3345, 1735 and 1220 cm^{-1}, respectively and the absence of those specific to the NCO groups of **2**. ^{1}H-NMR spectrum displayed mainly three groups of resonances, respectively in the regions: (i) 1.2 - 2.2 ppm corresponding to the aliphatic protons of suberin, (ii) 2.2 - 2.6 ppm representing protons of ester groups of suberin ($-OCH_3$); and (iii) at 6.9 - 7.5 ppm, corresponding to the aromatic protons from **2**. The DSC thermogram of this product showed an endothermic peak centered at 42°C, representing the melting point of the cristalline fraction of this suberin-based monourethane.

The use of isocyanates with functionality higher than unity, gave a mixture of linear, branched and crosslinked polymers. The extraction of these materials gave two fractions corresponding to linear and branched structures on the one hand and to the crosslinked ones, on the other hand. The influence of the *[NCO]*/*[OH]* ratio for the reaction of suberin with **6** was studied in detail. As shown in Table III, of all the polymers prepared, that corresponding to the synthesis carried out at the stoichiometric conditions *[NCO]* = *[OH]* gave the highest amount of insoluble fraction.

The thermal analyses of the insoluble fractions of these suberin-aromatic polyurethanes (see Table III) showed that the glass transition temperature, Tg, reached a maximum value of 98°C again when the polymer had been prepared at stoichimetric conditions. Figure 2 shows the DSC thermogram of this suberin-**6** polyurethane before extraction and those of its soluble and insoluble fractions. The lower Tg of pristine products (about 60°C which is nearly 40°C below that corresponding to the insoluble fraction), arises from the plasticizing effect of the soluble product which has a Tg of only 42°C.

Table III: Amounts of soluble and insoluble products of the reaction between suberin and **6**, as a function of *[NCO]*/*[OH]* ratio and glass transition temperature of the corresponding CH_2Cl_2-insoluble fractions.

[NCO]/ *[OH]*	Soluble products (%)	Insoluble products (%)	Tg of insoluble products (°C)
0.5	78.9	20.1	58
0.7	50.7	42.1	76
0.8	43.1	55.6	88
0.9	36.8	62.0	91
1	29.0	70.3	98
1.2	55.2	44.0	68
1.3	66.4	33.1	50

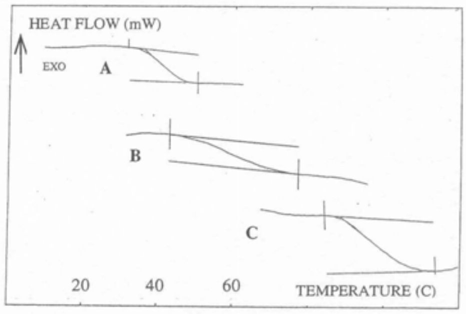

Figure 2: DSC Termograms of the reaction products of suberin with **6** for *[NCO]*/*[OH]*=1 (A: soluble fraction, B: before extraction; C: insoluble fraction).

The reaction of suberin with the other isocyanates gave different polyurethanes as summarized in Table IV. The amounts of insoluble fractions are similar for all the isocyanates used, except for **7**, which has a functionality of 2.7, with which a slightly higher yield of insoluble product was observed.

Table IV: Proportions of soluble and insoluble fractions of the polyurethanes prepared from suberin and various polyisocyanates (*[NCO]*$_o$ = *[OH]*$_o$) and Tg of the corresponding insoluble fractions.

Isocyanates	Soluble products (%)	Insoluble products (%)	Tg of insoluble fraction (°C)
4+5 (80:20)	27.7	71.5	105
6	29.0	70.3	98
7	25.1	73.9	97
3	28.6	71.0	25

The FTIR spectra of these polyurethanes showed the presence of the peaks which arise from urethane functions (NH, C=O and O=C-O at 3345, 1735 and 1220 cm^{-1}, respectively) and the absence of peaks from possible residual NCO groups. For suberin-**3** polyurethane, a strong peak corresponding to the hexamethylene moiety was detected at 2960 cm^{-1}, whereas for suberin-aromatic counterparts, the presence of the specific peaks corresponding to the differently substituted aromatic rings was ascertained in each spectrum. Figure 3 show typical FTIR spectra for suberin-**6** soluble and insoluble polyurethanes. It was systematically observed that the relative intensity of the aliphatic peaks corresponding to the soluble products were higher than those of the insoluble counterpart, comparatively to the intensity of urethane (NH peak at ca. 3350 cm^{-1}). This results from the fact that the soluble fractions of all these polyurethanes were mainly made up by the suberin macromonomer bearing *fewer* OH groups.

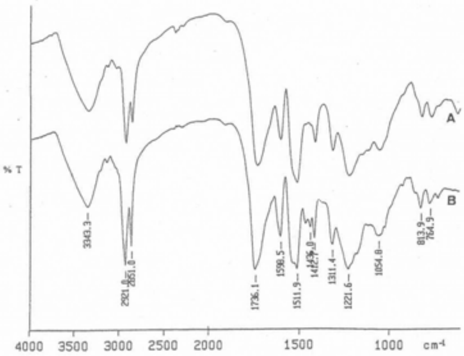

Figure 3: FTIR Spectra of the products of the reaction of suberin with **6**: (A) insoluble and (B) soluble fraction.

Table IV also shows the glass transition temperature of the insoluble products corresponding to various suberin-based polyurethanes. The glass transition temperature of an amorphous polymer is an excellent probe of its chain stiffness. The presence of flexible of aliphatic chains in diisocyanate **3** is therefore accompanied by a logical decrease in the Tg of the corresponding crosslinked polyurethane compared with those around 100°C, of all the aromatic-based counterparts.

4 CONCLUSION

The results obtained in the kinetic study of the polycondensations of suberin polyols with different isocyanates showed that these natural macromonomers behave in a straightforward manner in this specific context. The ensuing polyurethanes contained both thermoplastic and thermoset topologies because of the variable number of OH groups born by the suberin fragments. Depending on the type of diisocyanate used their glass transition temperature varied, thus providing the possibility of modulating their properties in accordance with the applications envisaged for these novel materials based on renewable resource.

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