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Short communication

Homogeneous phase synthesis of cellulose carbamate silica hybrid materials using 1-*n*-butyl-3-methylimidazolium chloride ionic liquid medium

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ABSTRACT

Cellulose carbamate silica hybrid materials can be prepared in 78–84% yield using the homogeneous phase reaction of 3-(triethoxysilyl)propyl isocyanate with cellulose dissolved in 1-*n*-butyl-3-methylimidazolium chloride ionic liquid and then using NH_4OH catalyzed hydrolysis of triethoxysilyl groups and the sol–gel process. New cellulose carbamate silica hybrid materials produced were characterized by elemental analysis, FT-IR, and TG-DTA. The hydrophilic affinity of these materials is shown to decrease with the degree of substitution of the cellulose hydroxyl groups with carbamate groups.

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1. Introduction

Cellulose is the most abundant renewable biomass on earth and is widely used as a raw material in numerous applications (Kamide, 2005). Chemical modification of cellulose is a well known process and gives new materials with interesting properties and uses. Generally, these modification reactions are carried out in the heterogeneous phase and involve the substitution of free hydroxyl groups on the carbohydrate polymer with various functional groups like acetyl, carboxymethyl, hydroxypropyl, phthalyl, and carbamate. Recently, researchers have focused their attention on the development of homogeneous functionalization methods (Fischer, Thummler, Pfeiffer, Liebert, & Heinze, 2002; Forsyth, MacFarlane, Thomson, & von Itzstein, 2002; Satge, Granet, Verneuil, Branland, & Krausz, 2004) for cellulose, because more uniform and stable products could be obtained in a homogeneous reaction. However, dissolution of cellulose is challenging due to its complex molecular structure of stiff polymeric molecular chains with close packing via numerous strong, inter and intra-molecular hydrogen bonding, and cellulose is insoluble in all the known common organic solvents and water. Considerable efforts are still being devoted to find good cellulose dissolving solvents and only a limited number of solvent systems such as LiCl–*N*,*N*-dimethylacetamide (Ishii, Tatsumi, & Matsumoto, 2008), urea–sodium hydroxide (Jin, Zha, & Gu, 2007), DMF/N_2O_4, NMNO, molten salt hydrates like $LiClO_4$, and pyridine or imidazole based ionic liquids (Feng & Chen, 2008; Zhu et al., 2006) are known to dissolve cellulose without derivatization. Ionic liquids are particularly attractive among these solvents due to their outstanding dissolution capability, low vapor pressure, and stability. A number of researchers have studied the preparation of carbamate derivatives of cellulose (Kasabo, Kanematsu, Nakagawa, Sato, & Teramoto, 2000; Mormann & Michel, 2002; Yin & Shen, 2007) as the cellulose hydroxyl groups readily react with reactive isocyanates without a catalyst or harsh conditions and usually gives high yields devoid of side reactions. Furthermore, these carbamate derivatives of cellulose have been explored for applications as membrane materials (Diamantoglou, Platz, & Vienken, 1999; Khan, Shiotsuki, Nishio, & Masuda, 2008), and chiral stationary phases (Oliveros, Senso, Franco, & Minguillón, 1998). Even though the usual carbamate derivatizations are carried out under heterogeneous conditions, Schlufter, Schmauder, Dorn, and Heinze (2006) have recently shown that bacterial cellulose with DP $\sim$ 6500 could be efficiently converted to carbamate derivative under homogeneous reaction conditions. In this study they reported the preparation of cellulose phenyl carbamate with a degree of substitution as high as 3.0, by reacting cellulose dissolved in 1-*n*-butyl-3-methylimidazolium chloride ($[bmim]^+Cl^-$) with excess phenyl isocyanate at 80 °C for 4 h.

In an another area of cellulose derived materials, cellulose silica hybrids have attracted interest due to their low environmental impact (Benmouhoub, Simmonet, Agoudjil, & Coradin, 2008), as mimics of biocomposites (Hideaki, Megumi, Toshiki, Takashi, & Shoichiro, 2006), and economical chromatography materials (Chen, Liu, Qin, Kong, & Zou, 2003; Matlin, Grieb, & Belenguer, 1995). In addition, Ikai, Yamamoto, Kamigaito, and Okamoto (2008) has shown that hybrid materials prepared from cellulose 3,5-dimethylphenylcarbamate and tetraethyl orthosilicate can be

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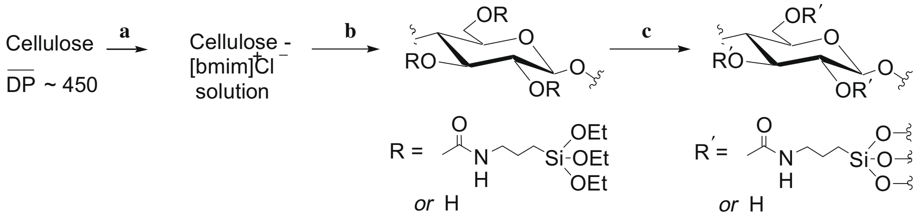

CCS-1,2

a. [bmim]$^+$Cl$^-$, 80 °C, 30 min.
b. $(EtO)_3Si(CH_2)_3$-NCO (2-6 eqv.), 80 °C, 4-48 h
c. i. H_2O, NH_4OH, r.t., 5 days. ii. 90 °C, 24 h

Fig. 1. Synthesis of cellulose carbamate silica hybrid materials **CCS-1** and **2.**

used as efficient chiral stationary phases for enantiomeric separations. In these studies on the preparations of cellulose silica hybrid materials, key reactions were carried out in a heterogeneous phase giving possible non-uniform materials. Our interests in the use of sol–gel process in the preparation of organic–inorganic hybrid materials (Amarasekara, Oki, McNeal, & Uzoezie, 2007; Amarasekara, McNeal, Murillo, Green, & Jennings, 2008) and ionic liquids have led us to develop a new approach for the preparation of cellulose silica hybrid materials in a homogeneous medium using ionic liquid to dissolve cellulose and sol–gel process to produce the silica hybrid. In this communication we report the first application of this methodology, involving the homogeneous reaction of 3-(triethoxysilyl)propyl isocyanate with cellulose dissolved in 1-*n*-butyl-3-methylimidazolium chloride ionic liquid and use of this triethoxysilylpropyl carbamate functionalized cellulose for the preparation of cellulose carbamate silica hybrid materials using sol–gel process, as shown in Fig. 1.

2. Experimental

2.1. Materials and instrumentation

Sigmacell cellulose (DP ~ 450, Cat. No. S6790), 1-*n*-butyl-3-methylimidazolium chloride, and 3-(triethoxysilyl)propyl isocyanate were purchased from Aldrich Chemical Co. FT-IR spectra were recorded on a JASCO-470 PLUS IR spectrometer using KBr pellets. Thermogravimetric-differential thermal analysis (TG-DTA) was carried out on a TA instruments TGA 2050 system. Elemental analysis was performed at QTI laboratories, New Jersey.

2.2. Preparation of cellulose carbamate silica hybrid materials CCS-1 and 2

Sigmacell cellulose (0.30 g, 1.85 mmol glucose units) was dissolved in 2.50 g of 1-*n*-butyl-3-methylimidazolium chloride ionic liquid by heating at 80 °C for 30 min. with stirring using a glass rod to give a clear solution. Then the cellulose solution was transferred to a polystyrene reaction tube with a screw cap and 3-(triethoxysilyl)propyl isocyanate (2–6 equivalents/glucose unit of cellulose) added and the closed tube was heated at 80 °C with magnetic stirring for 4–48 h. The tube was then cooled to room temperature, 3 mL of water and 5 drops of concentrated NH_4OH were added, and the mixture was then left at room temperature undisturbed for 5 days in the closed polystyrene reaction tube for the gel formation. The reaction tube was opened and heated in an oven at 90 °C for 24 h, and the resulting pale yellow solid was cooled to room temperature and purified by soxhlet extraction with ethanol (24 h). The product was dried first at room temperature in air (24 h) and then in an oven at 80 °C for 3 h under a vacuum to give cellulose carbamate silica hybrid materials **CCS-1** and **2** as a pale yellow solids. The samples **CCS-1** and **2** are insoluble in all the common organic solvents including DMSO and DMF. The percent yields, elemental analysis data, and calculated degree of substitutions (DS) of the products are shown in the Table 1.

2.3. Swelling studies of cellulose carbamate silica hybrid materials CCS-1 and 2

The swelling behavior of carbamate silica hybrid materials was determined in order to check their hydrophilic affinity. Typically, carbamate silica hybrid samples (**CCS-1** or **CCS-2**) were cut into thin disks of 8 mm approximate diameter and 2 mm thickness, weighing 0.1–0.15 g. These disks were dried (80 °C) to constant weight (w_i) and immersed in 10–15 mL of deionized water in glass vials at room temperature (23 ± 1 °C) for 6 h. Then the swollen disks were removed from the water, carefully padded with filter papers to dry the surface and weighed (w_s). The disks were immediately returned to water vials and withdrawn after 12, 24, and 48 h of total time, for similar weighings. The percentage degree of swellings after these time periods were calculated using the formula

$$\text{degree of swelling }(\%) = (w_s - w_i) \times 100/w_i$$

The experiments were carried out in duplicate for **CS-1** and **2,** and the results are shown in the Table 2.

Table 1
SiO_2 residue% from TGA, degree of substitution (DS), percent yields, and elemental analysis data of cellulose carbamate silica hybrid materials **CCS-1** and **2.**

Sample	Molar ratio[a]	Reaction conditions (°C/h)	SiO_2 residue[b] %	DS[c]	Yield[d] %	Elemental analysis[e]		
						%C	%H	%N
CCS-1	1:2	80/4	11.9	0.43	78	42.32 (42.68)	5.61 (5.84)	2.97 (2.77)
CCS-2	1:6	80/48	32.8	2.95	84	39.28 (39.57)	4.92 (5.17)	7.88 (7.65)

[a] Glucose unit of cellulose: 3-(triethoxysilyl)propyl isocyanate.
[b] From TGA.
[c] Degree of substitution (DS) was determined using the % of residual SiO_2 in the TGA.
[d] % yield based on glucose unit of cellulose.
[e] CHN% calculated based on degree of substitution (DS) values are shown in the parenthesis below.

Table 2
Changes in the degree of swelling (%) with time (h) for cellulose carbamate silica hybrid materials **CCS-1** and **2.**

Sample	Time (h)	Swelling (%)[a]
CCS-1	6	30
CCS-1	12	36
CCS-1	24	41
CCS-1	48	41
CCS-2	6	7
CCS-2	12	9
CCS-2	24	11
CCS-2	48	11

[a] Degree of swelling (%) = $(w_s - w_i) \times 100/w_i$; w_s = weight of swollen solid, w_i = weight of dry solid. Hybrid material disks (diameter ~ 8 mm, thickness ~ 2 mm) were used in water at room temperature (23 ± 1 °C). Average from duplicate experiments.

3. Results and discussion

3.1. Synthesis of cellulose carbamate silica hybrids CCS-1 and 2

In the initial experiment, cellulose dissolved in 1-*n*-butyl-3-methylimidazolium chloride was reacted with 3-(triethoxysilyl)propyl isocyanate for 4 h at 80 °C, following the reported procedure (Schlufter et al., 2006) for homogeneous phase reaction of cellulose with phenyl isocyante, but this experiment gave a product (**CCS-1**) with poor degree of substitution (0.43). This may be due to the fact that alkyl isocyanates are less reactive than phenyl isocyanate. Therefore much longer reaction time of 48 h and excess of 3-(triethoxysilyl)propyl isocyanate was used in the second experiment to ensure all the possible hydroxyl groups react with the isocyanate.

3.2. Structural characterization of cellulose carbamate silica hybrids CCS-1 and 2

3.2.1. TG–DTA and elemental analysis

Cellulose carbamate silica hybrid materials **CCS-1** and **2** were characterized using thermogravimetric-differential thermal analysis, elemental analysis, and FT-IR spectroscopy. Thermogravimetric-differential thermal analysis of the hybrid material **CCS-2** is shown in Fig. 2. The SiO_2 residue left after burning all the organic fraction in the structure corresponds to 32.8% residual weight. The repeating unit formula for the cellulose carbamate silica hybrid is $C_{6+4n}H_{10+6n}N_nSi_nO_{5+2n}$ where *n* is the degree of substitution. Thus, *n* can be calculated using the formula:

$$(SiO_2)_n/C_{6+4n}H_{10+6n}N_nSi_nO_{5+2n} = \text{fraction of the residual weight in TGA}$$

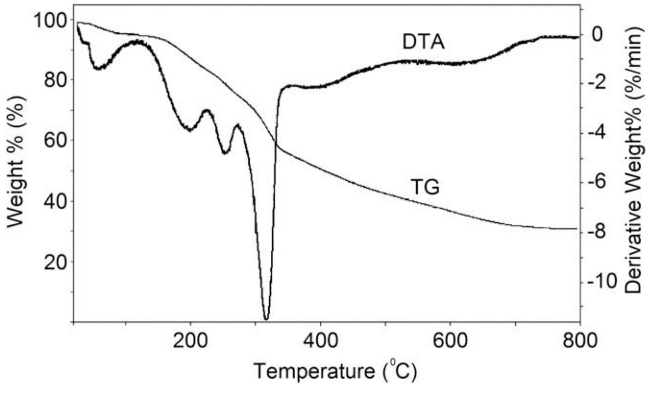

Fig. 2. TG/DTA of cellulose carbamate silica hybrid **CCS-2.**

The calculated *n* or the degree of substitution for **CCS-2** is 2.95, showing that practically all the free hydroxyl groups in cellulose are substituted with carbamate groups (Table 1). The DTA curve of **CCS-2** (Fig. 2) shows three endothermic peaks at 200, 250, and 317 corresponding to 13%, 8.7% and 18.3% weight losses during the burning of the organic polymer structure. In addition, elemental analysis (Table 1) calculated using this degree of substitution value are within ±0.36% of the experimental results, and this is a reasonable agreement when taking into account the complex nature of the polymeric structure. The sample **CCS-1** also showed similar behavior in the TG-DTA (not shown in the figures), and showed 11.9% residual weight for SiO_2. This residual weight percentage corresponds to a degree of substitution of 0.43 (Table 1), showing that only a small fraction of free hydroxyl groups are reacting when two equivalents of 3-(triethoxysilyl)propyl isocyanate are used and allowed to react for 4 h. Furthermore, elemental analysis for **CCS-1** were also in agreement with the calculated CHN% using the degree of substitution data, as shown in Table 1. The difference in chemical structures between the samples **CCS-1** and **2** is in the degree of substitution by carbamate groups. The sample **CCS-1** prepared in a shorter reaction time gave a lower degree of substitution of 0.43, whereas a much longer reaction time, and excess of 3-(triethoxysilyl)propyl isocyanate produced sample **CCS-2** with the higher degree of substitution of 2.95.

3.2.2. FT-IR

FT-IR Spectrum of the sample **CCS-2** is shown in Fig. 3. The strong absorption at 1702 cm^{-1} can be attributed to the C═O absorption of the carbamate groups. Other characteristic peaks at 3365 and 2928 cm^{-1}, can be assigned to the NH and CH absorptions. The Si–O absorptions of the hybrid structure can be observed as two strong peaks at 1039 and 1132 cm^{-1} in the IR spectrum. The related cellulose carbamate silica **CCS-1** also showed similar FT-IR spectrum (not shown in the figures) with relatively weaker absorptions for C═O, CH, and NH groups showing the lower degree of substitution in the carbohydrate polymer.

3.3. Degree of swelling and cross linking nature of cellulose carbamate silica hybrid materials CCS-1 and 2

The hydrophilic affinity and cross linking nature of the hybrid polymer can be studied by the swelling experiment using water as the solvent. This experiment showed that samples **CCS-1** and **2** reached the equilibrium degree of swellings of 41% and 11%, respectively, after 24 h in water at room temperature (Table 2).

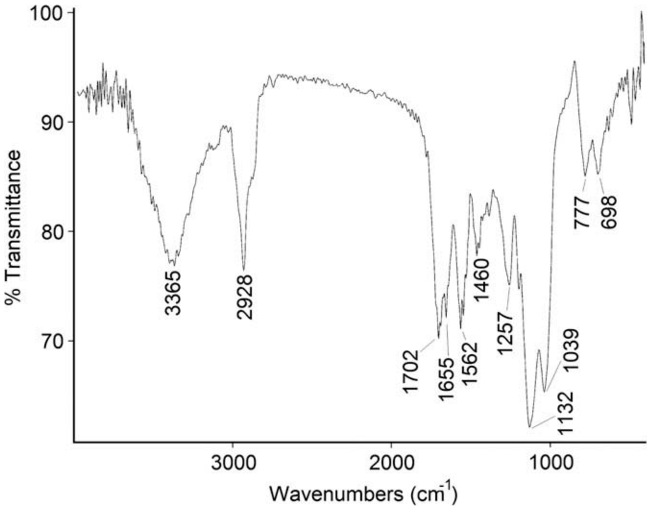

Fig. 3. FT-IR spectrum of cellulose carbamate silica hybrid **CCS-2.**

The sample **CCS-1** with the lower degree of substitution (DS = 0.43) and cross linking showed the higher hydrophilic affinity due to unreacted hydroxyl groups in the carbohydrate polymer and visibly displayed the swelling of the polymer when placed in water. The sample **CCS-2** with DS = 2.95 showed much smaller swelling and hydrophilic affinity as practically all the hydroxyl groups are substituted with carbamate groups.

4. Conclusion

In summary, we have shown that cellulose carbamate silica hybrid materials with different degree of substitutions can be efficiently prepared in homogeneous medium reactions using 1-*n*-butyl-3-methylimidazolium chloride ionic liquid as the solvent. The new organic–inorganic hybrids were characterized by elemental analysis, FT-IR, and TG-DTA. The hydrophilic affinity of these materials is shown to decrease with the degree of substitution with carbamate groups.

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