Polyurethane/poly (Ionic Liquids) Cellulosic Composites and their Evaluation for Separation of CO$_2$ from Natural Gas

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The development of both versatile and inexpensive sorbents for CO$_2$/CH$_4$ separation has become one of the greatest challenges to the environment and natural gas processing. This study reports the preparation and characterization of polyurethane (PU)/cellulose based poly(ionic liquid)(CPIL) composites for CO$_2$/CH$_4$ separation. PU matrix was reinforced with CPIL in the range of 10-30 wt%. Several characterization techniques (TGA, DSC, DMTA and FESEM) were used to study the physical properties of composites when the PU matrix is reinforced with cellulose based poly(ionic liquids) (CPIL) up to 30%. CO$_2$ sorption, reusability and CO$_2$/CH$_4$ selectivity were assessed by pressure-decay technique. Results showed that CPIL addition in PU matrix promoted the increase in both thermal stability and mechanical properties when compared to PU. The best result for CO$_2$ sorption (35.0 mgCO$_2$/g) was obtained for PU/CPIL-TBP 10% which presented a higher sorption value when compared to PU (24.1 mgCO$_2$/g) and PU/CELLULOSE 10% (26.8 mgCO$_2$/g). PU/CPIL-TBP 20% demonstrated higher CO$_2$/CH$_4$ selectivity. PU/CPIL composites appear as promissory materials for CO$_2$ capture. These compounds combine the benefits of ionic liquids (ILs) (high ionic conductivity, chemical and thermal stability) and cellulose (thermal stability) with PU properties (mechanical stability, processing and tunable macromolecular design).

Keywords: Carbon dioxide, natural gas, composites, polyurethanes, cellulose-based poly(ionic liquids).

1. Introduction

Carbon capture technologies from natural gas appear as one of main strategies to mitigate global warming, meet fuel performance requirements for a given application and prevent corrosion problems in pipeline$. The development of both versatile and inexpensive sorbents for CO$_2$ capture has been one of the most relevant challenges in this field$. Chemical absorption processes using aqueous alkanolamine solutions have been extensively used in industry during the recent years$. Using these solvents in capture processes have shown some drawbacks, including amine degradation/evaporation, equipment corrosion and high energy penalty for solvent regeneration$. It has been demonstrated that the use of solid adsorbents e.g. Poly(ionic liquid)s (PILs) present advantages compared to aqueous alkanolamine solutions as such as elimination of corrosion problems, reversible CO$_2$ sorption/desorption performance and low energy for sorbent regeneration$. However, high cost is the main drawback as compared with alkanolamines.

Poly(ionic liquid)s (PILs) are an emerging new subclass of polyelectrolytes containing each repeated ionic unit connected through a polymeric backbone to form a macromolecular structure$. PILs syntheses are generally performed via direct ionic liquid monomer polymerization or chemical modification of existent polymers through ion exchange$. Our previous work$^a$ reported the chemical modification of cellulose fibers extracted from rice husk with different ionic liquid cations (imidazolium, phosphonium, ammonium and pyrrolidinium). These cellulose based poly(ionic liquids) (CPIL) obtained from agroindustrial residues (rice husk) can be a promising alternative for CO$_2$ capture because they combine the benefits of ILs (high ionic conductivity, chemical and thermal stability) with waste reduction. The counteraction introduction into cellulose structure promoted CO$_2$ sorption increase and a completely reversible CO$_2$ sorption/desorption process.

Polyurethanes (PUs) are an important class of polymers containing urethane group as the major repeating unit. Nevertheless other groups such as esters, urea, ethers and aromatic may also be present in the structure. PUs are versatile materials and widely used in industry$. Literature describes that the introduction of polar groups (usually O, N) into the polymer structure may be an effective way to promote CO$_2$ affinity$^a$.
PU formulation can be tuned to deliver desirable properties in specific applications. Furthermore, composites may also be used as alternative to improve mechanical and thermal properties of PU. The use of cellulose as reinforcing filler in PU to promote improvements of both mechanical and thermal properties have been reported. Cellulose based poly(ionic liquid) use aiming to obtain PU/CPIL composites are not described in literature needing further studies.

Herein, we report for the first time the preparation and characterization of PU/CPIL composites. The effect of cation present in CPILs structure (1-butyl-3-methylimidazolium (BMIM), tetrabutylammonium (TBA), tetrabutylphosphonium (TBP) and 1-butyl-1-methylpyrrolidinium (BMPYRR) as well as CPIL concentration on the CO$_2$ sorption capacity, and both thermal and mechanical properties of the composites were studied. Our study also investigated CO$_2$/CH$_4$ separation.

2. Experimental

2.1 Materials

Synthesis and characterization of cellulose-based poly(ionic liquids) (CPILs) (1-butyl-3-methylimidazolium - CPIL-BMIM, tetrabutylammonium-CPIL-TBA, tetrabutylphosphonium-CPIL-TBP and 1-butyl-1-methylpyrrolidinium-CPIL-BMPYRR), were previously described by our group. ILs cations TBPB, TBAB, BMPYRR and BMIM were inserted into the cellulose structure in contents of 1.16 x 10$^{-4}$ mol/g, 0.68 x 10$^{-4}$ mol/g, 1.57 x 10$^{-4}$ mol/g and 0.5901 x 10$^{-4}$ mol/g, respectively. Surface area values obtained for CPILs TBP, TBA, BMPYRR and BMIM were extremely small (0.6430 m$^2$/g, 1.7370 m$^2$/g, 0.5901 m$^2$/g, 0.6984 m$^2$/g respectively)

PU was synthesized following procedures adapted from literature. Poly(tetrahydrofuran) polyol (PTMG-2000 g/mol, Sigma aldrich) (0.09 mol) and 0.1% wt of dibutyltin dilaurate (DBTDL, 95% Sigma aldrich) were dissolved in 50 mL methyl ethyl ketone (MEK, P.A Dinâmica) were dissolved in dimethylformamide (DMF, P.A Dinâmica) (0.09 mol) and 0.1% wt of dibutyltin dilaurate (DBTDL, 95% Sigma aldrich) (0.09 mol). The solution was prepared by dissolving 7.5 g PU into 25 ml dimethylformamide (DMF, P.A Dinâmica) via magnetic stirring until PU was completely dissolved. In another glass bottle a suspension of CPILs was obtained using magnetic stirring in dimethylformamide for 6 h.

2.2 Preparation of composites

The PU and CPILs (PU/CPILs) were mixed in different ratios to obtain dry films of 0.15 mm thickness with CPILs content ranging up to 30 wt%. CPILs and PU chemical structures can be seen in Fig.1. Initially, 30%wt PU solution was prepared by dissolving 7.5 g PU into 25 ml dimethylformamide (DMF, P.A Dinâmica) via magnetic stirring until PU was completely dissolved (Fig.2I). The mixtures were magnetically stirred for one day (Fig.2II). Then, they were sonicated by means of high power ultrasound disperser during 20 min (Fig.2IV). Finally, films with a thickness close to 0.15 mm were produced by casting and dried under vacuum at 60°C for 72 h (Fig.1IV).

2.3 Characterization

Samples were characterized by Universal Attenuated Total Reflectance sensor (UATR-FTIR) using a Perkin-Elmer Spectrum One FTIR Spectrometer, 4000 - 650 wavenumber range. Field emission scanning electron microscopy (FESEM) was performed using a FEI Inspect F50 equipment in secondary electrons (SE) mode. Differential Scanning Calorimetry (DSC) thermograms were attained by using a TA Instrument Q20 differential scanning calorimeter in the range of $-90^\circ$C–$170^\circ$C, or $200^\circ$C at a heating rate of 10°C/min under nitrogen. Thermogravimetric Analysis (TGA) was performed using a TA Instrument SDT-Q600 between 25°C and 600°C at a heating rate of 20°C/min in a nitrogen atmosphere. Tensile tests (stress x strain curves) were carried out at 25°C with rectangular shape films (12 mm long; 7 mm wide) with a thickness close to 0.15 mm, on a DMTA equipment (model Q800, TA Instruments) with 1 N/min. The Young Modulus of materials was determined according to ASTM D638. The analyses were carried out in triplicate.

2.4 Sorption experiments

2.4.1 CO$_2$ sorption measurements

A dual-chamber gas sorption cell was used to measure CO$_2$ sorption by pressure-decay technique. The experiments were carried out in triplicate. Samples (W$_S$=1g) were previously degassed at 70°C (343.15K) during 2 h. CO$_2$ sorption measurements were carried out at 25°C (298.15 K) and 0.1 MPa. A detailed description of sorption apparatus and measuring procedure can be found in previous works. Five CO$_2$ sorption/desorption cycles were also performed in PU/CPIL composites. CO$_2$ sorption was evaluated at 25°C (298.15 K) and 0.1 MPa with desorption following each cycle using heating 70°C (343.15K) during 2h.
Figure 1. CPILs (a) and PU (a) chemical structure.

Figure 2. Preparation scheme of composites
2.4.2 CO$_2$/CH$_4$ separation selectivity

The separation of CO$_2$ from CO$_2$/CH$_4$ gas mixture (35 mol % of CO$_2$ and CH$_4$ balance) also was determined using a dual-chamber gas sorption cell by pressure-decay technique which has been previously described in detail\textsuperscript{27,29–31}. Samples (Ws≈1g) were also previously degassed at 70°C (343.15K) during 2 h. Selectivity experiments were also carried out in triplicate at 25°C and 2.0 MPa.

3. Results and Discussion

PU/CPIL-TBP composites were chosen to be characterized and to study the effects of CPIL addition in PU on both thermal and mechanical properties due to higher CO$_2$ sorption capacity compared to PU. The PU/CELLULOSE 10% composite was also characterized for comparative purposes.

FTIR analysis was used to identify polymer formation and the effect of CPIL presence in PU matrix. The FTIR spectra of PU, PU/CELLULOSE-10% and PU/CPIL-TBP composites are shown in Fig.3. The completion of urethane reaction can be observed by the absence of band at about 2270 cm$^{-1}$ corresponding to free NCO group stretching vibration\textsuperscript{32,33}. The N-H absorption region in spectrum indicates the presence of band at about 3322 cm$^{-1}$ associated with the N-H stretching of bonded hydrogen\textsuperscript{34,35}. Band area at 3322 cm$^{-1}$ tends to increase with both the incorporation and concentration of fillers in PU matrix. Bands at about 1720 and 1693 cm$^{-1}$ are attributed to “free” C=O stretching and 'bonded hydrogen' C=O stretching, respectively\textsuperscript{34}. The band area increase at about 1693 cm$^{-1}$ upon the filler addition suggests a hydrogen bond formation increase. Band area at about 1693 cm$^{-1}$ of PU/CPIL-TBP is higher than PU/CELLULOSE 10%. FTIR analysis also showed others characteristic PU and cellulose adsorption bands\textsuperscript{36}: 2936 - 2840 cm$^{-1}$ (C-H), 1532 cm$^{-1}$ (HN), 1246 cm$^{-1}$ (C-N and C-O of urethane), 1100 cm$^{-1}$ (C-O-C).

PU and PU composites thermal stability was investigated by thermogravimetric analysis (TGA) (Fig.4). PU thermal stability tended to increase with the addition of cellulose/CPIL in PU matrix. TGA curves showed two stages of thermal degradation. The first thermal event is due to degradation of both hard segment (urethane bond)\textsuperscript{37–39} and cellulose/CPIL structure\textsuperscript{16}. $T_{1\text{onset}}$ for PU, PU/CELLULOSE 10%, PU/CPIL-TBP 10%, PU/CPIL-TBP 20% and PU/CPIL-TBP 30% occurred at 306.6°C, 344.2°C, 311.1°C, 311.0°C and 333.2°C, respectively. The second weight loss is associated to dissociation of soft segments (PTMG polyol)\textsuperscript{40}. $T_{2\text{onset}}$ for PU, PU/CELLULOSE 10%, PU/CPIL-TBP 10%, PU/CPIL-TBP 20% and PU/CPIL-TBP 30% occurred at 450.6°C, 456.13°C, 458.6°C, 451.5°C and 447.6°C, respectively.

DSC curves (Fig. 5) obtained for PU and PU composites showed an endothermic peak ($T_m$) (PU =19°C, PU/CELLULOSE 10% = 12°C, PU/CPIL-TBP 10% = 13°C, PU/CPIL-TBP 20% = 21°C and PU/CPIL-TBP 30% = 21°C) associated to the melting of crystalline microphase due to molecular weight (Mn= 2000) of soft segments (PTMG) promoting crystallization\textsuperscript{41,42}. 
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DSC curves also showed an exothermic peak related to crystallization of microphase (T_c) was also observed for all samples (PU = -32.0°C, PU/CELLULOSE 10% = -29.0°C, PU/CPIL-TBP 10% = -30.0°C, PU/CPIL-TBP 20% = -31°C and PU/CPIL-TBP 30% = -29°C). Melting and crystallization enthalpy tended to decrease with the addition of cellulose/CPIL in PU matrix (PU ΔH_m = 36.5 J/g and ΔH_c = 36.4 J/g; PU/CELLULOSE 10% ΔH_m = 18.4 J/g and ΔH_c = 14.6 J/g; PU/CPIL-TBP 10% ΔH_m = 20.4 J/g and ΔH_c = 17.8 J/g; PU/CPIL-TBP 20% ΔH_m = 23.3 J/g and ΔH_c = 15.2 J/g; PU/CPIL-TBP 30% ΔH_m = 15 J/g and ΔH_c = 9.2 J/g).

Homogeneous structures with a relatively uniform dispersion were obtained in PU composite filled with a fiber concentration up to 10 wt% (Fig.6). Holes (pores) were also observed after the filler addition in PU matrix.

Tensile properties and Young moduli are presented in Figs 7 and 8. Mechanical properties increased with the filler addition in PU matrix. PU/CPIL-TBP 10% showed higher Young moduli than PU/CELLULOSE 10%. The presence of hydrogen bonding tends to enhance the mechanical properties of PU. FTIR band areas associated with the bonded hydrogens in PU/CPIL-TBP were higher than PU/CELLULOSE 10% (see Fig.3). However, the Young moduli reduced from 35 MPa in PU/CPIL-TBP 10% to 32.7 MPa in PU/CPIL-TBP 20%, probably due to homogeneity reduction observed by FESEM analysis (Fig.6). PU/CPIL-TBP 30% demonstrated fragility to perform tensile tests.

PU and PU composite CO₂ sorption capacity at 0.1 MPa and 298.15 K is shown in Fig.9. PU exhibited a CO₂ sorption capacity of 24.1 mg CO₂/g (1 bar) due to polar groups into the polymer structure that may promote CO₂ affinity. CO₂ sorption increased after the filler addition in PU matrix. The cellulose structure also has polar groups (ether, ester and hydroxyl groups) that may promote interactions with CO₂. PU/CPIL CO₂ sorption capacity was higher than PU/CELLULOSE 10%, indicating that the carboxylate ion and IL countercation present in CPIL promote CO₂ sorption in PU matrix. The best result was found for PU/CPIL-TBP 10% (35.0 mg CO₂/g). Computational studies showed that TBP cation exhibit weaker coordination of carboxyl group promoting CO₂ sorption through electrostatic binding of CO₂ and carboxylate ion.

Figure 5. DSC thermograms obtained for PU and PU composites.

Figure 6. Micrographs obtained for PU and PU composites. (a)PU, (b) PU/CELLULOSE 10%, (c) PU/CPIL-TBP 10%, (d) PU/CPIL-TBP 20% and (d) PU/CPIL-TBP 30%
The effect of filler concentration increase in PU matrix on CO₂ sorption capacity is shown in Fig. 10. CO₂ sorption decreased with the increasing content of CPIL-TBP in PU matrix. This behavior can be associated with increase of hydrogen bonds (see Fig. 3) and/or homogeneity reduction of PU composite (see Fig. 6) that may reduce PU–CO₂ interactions.

Table 1 presents the comparison of CO₂ sorption capacity of PU/CPIL-TBP -10% with competitive PILs described in literature. At comparable temperatures and pressures, PU/CPIL-TBP 10% CO₂ sorption capacity is higher when compared to reported PILs. Results suggest that PU/CPIL-TBP 10% presents potential for CO₂ capture.

PU/CPIL-TBP 10% stability was evaluated over five CO₂ sorption/desorption cycles (Fig. 11). PU/CPIL-TBP 10% sorption capacity was constant for all cycles indicating that PU/CPIL-TBP 10% sorbent offers necessary stability for CO₂ capture processes. This result evidences a typical behavior of a physical sorbent. Moreover, the advantage in this case is the low temperature needed for desorption process.

PU composites CO₂/CH₄ selectivity results are presented in Fig. 12. PU/CPIL-TBP composites showed higher selective response than PU/CHELULOSE 10%. Preferential affinity of CO₂ for PU/CPIL-TBP composites compared to PU/CHELULOSE 10% is probably due to strong interactions between CO₂ and carboxylate ion of CPIL-TBP.

| Sorbent        | CO₂ sorption (mg/g) | Conditions (P, T) | Ref. |
|----------------|---------------------|-------------------|------|
| P[VBIH][PF₆]   | 3.22                | 0.079 bar, 295.15K| 6    |
| P6 [BEMA][acetate] | 12.46             | 0.1 MPa, 278.15K  | 46   |
| P[VBEA][PF₆]   | 14.04               | 0.1 MPa, 278.15K  | 47   |
| PIL-8.1.BF₄    | 24.76               | 0.1 MPa, 273.15K  | 48   |
| PU-TBP         | 15.70               | 0.082 MPa, 303.15K| 45   |
| PU/IS-02-TBP   | 26.70               | 0.082 MPa, 303.15K| 28   |
| PU/CPIL-TBP-10%| 35.00               | 0.082 MPa, 298.15K| This study |
Results provide evidence that the addition of CPIL-TBP can increase the selectivity of PU for CO₂ over CH₄. PU/CPIL-TBP 20% composite presented higher CO₂/CH₄ selectivity as compared with polyurethane-based poly(ionic liquid)s (PILPC-TBP: CO₂/CH₄ selectivity of ∼2.22 at 303.15 K and 2 MPa)⁴⁹ and PU foam/ILs composite (PUF BF4 40: CO₂/CH₄ selectivity of 1.42 at 3 MPa)²⁹.

4. Conclusions

PU/CPIL composites for CO₂ capture from natural gas were successfully prepared. PU/CPIL composites showed improvement in both thermal stability and mechanical properties when compared to PU. The best CO₂ sorption result was obtained for PU/CPIL - TBP -10%. PU/CPIL - TBP 10% CO₂ sorption capacity is highest then competitive PILs described in literature. PU/CPIL - TBP 20% Selective capacity for CO₂/CH₄ was higher than PU/CPIL - TBP 10%.

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6. Reference

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