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Polyurethane/poly (Ionic Liquids) Cellulosic Composites and their Evaluation for Separation of CO_2 from Natural Gas

Franciele Longaray Bernard[a]***, Leonardo Moreira dos Santos***[a]***, Fabiana Willers Cobalchina***[a]***,***
Marina Barbieri Schwab[a]***, Sandra Einloft***[a,b]*

[a]*Escola Politécnica, Pontifícia Universidade Católica do Rio Grande do Sul (PUCRS), Porto Alegre, RS, Brasil*
[b]*Programa de Pós-Graduação Engenharia e Tecnologia de Materiais (PGETEMA), Pontifícia Universidade Católica do Rio Grande do Sul (PUCRS), Porto Alegre, RS, Brasil*

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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[1]. The development of both versatile and inexpensive sorbents for CO_2 capture has been one of the most relevant challenges in this field[2].

Chemical absorption processes using aqueous alkanolamine solutions have been extensively used in industry during the recent years[3–5]. Using these solvents in capture processes have shown some drawbacks, including amine degradation/ evaporation, equipment corrosion and high energy penalty for solvent regeneration[3–5]. 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[2,6–11]. 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[12,13]. PILs syntheses are generally performed via direct ionic liquid monomer polymerization or chemical modification of existent polymers through ion exchange[11–15].

Our previous work[16] 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 countercation 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[17,18]. 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[19,20].

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*e-mail: einloft@pucrs.br

PU formulation can be tuned to deliver desirable properties in specific applications[21]. Furthermore, composites may also be used as alternative to improve mechanical and thermal properties of PU[21–23]. The use of cellulose as reinforcing filler in PUs to promote improvements of both mechanical and thermal properties have been reported[21–23]. 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 [16]. ILs cations TBPB, TBAB, BMPYRR and BMIM were inserted into the cellulose structure in contents of 1.16×10^{-4} mol/g, 0.68×10^{-4} mol/g, 1.57×10^{-4} mol/g and 0.5901×10^{-4} mol/g, respectively[16]. Surface area values obtained for CPLIs 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[16].

PU was synthesized following procedures adapted from literature[24]. 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 methyl ethyl ketone (50 mL) (MEK, P.A Dinâmica) in a five-necked flask. Then, hexamethylene diisocyanate (HDI, ≥98.0%, Sigma Aldrich) (0.153 mol) was slowly added to the reaction mixture by a dropper funnel and stirred at 60°C for 90 min to obtain NCO-terminated polyurethane prepolymer. The NCO/OH ratio of 1.7 (0.153 mol HDI/0.09 mol OH) was used. The solid content was quantified as well as the polymer NCO free isocyanate (%NCO). In order to neutralize the NCO free isocyanate content, the system was cooled to 55°C and chain extender (1,6-Hexanediol) was charged into the reactor. Molecular weight (Mn) of 68000 g/mol and DPI = 1.5 was acquired from a Gel Permeation Chromatograph (GPC), equipped with a Waters 1515 pump and a Waters 2412 refractive index detector, using THF as eluent at a flow rate of 1 mL/min. PU/CPIL composites were labeled as PU/CPIL-X-Y, where X is cation, Y is CPIL concentration, For example, PU/CPIL-TBP-10% means TBP cation, 10%wt CPIL in PU matrix.

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). In another glass bottle a suspension of CPILs was obtained using magnetic stirring in dimethylformamide for 6 h (Fig.2II).The mixtures were magnetically stirred for one day (Fig.2III). They were then 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°C–170°C, or 200°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 CO2 sorption by pressure-decay technique[25]. The experiments were carried out in triplicate. Samples ($W_s \approx 1g$) 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 [26–28]. 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.

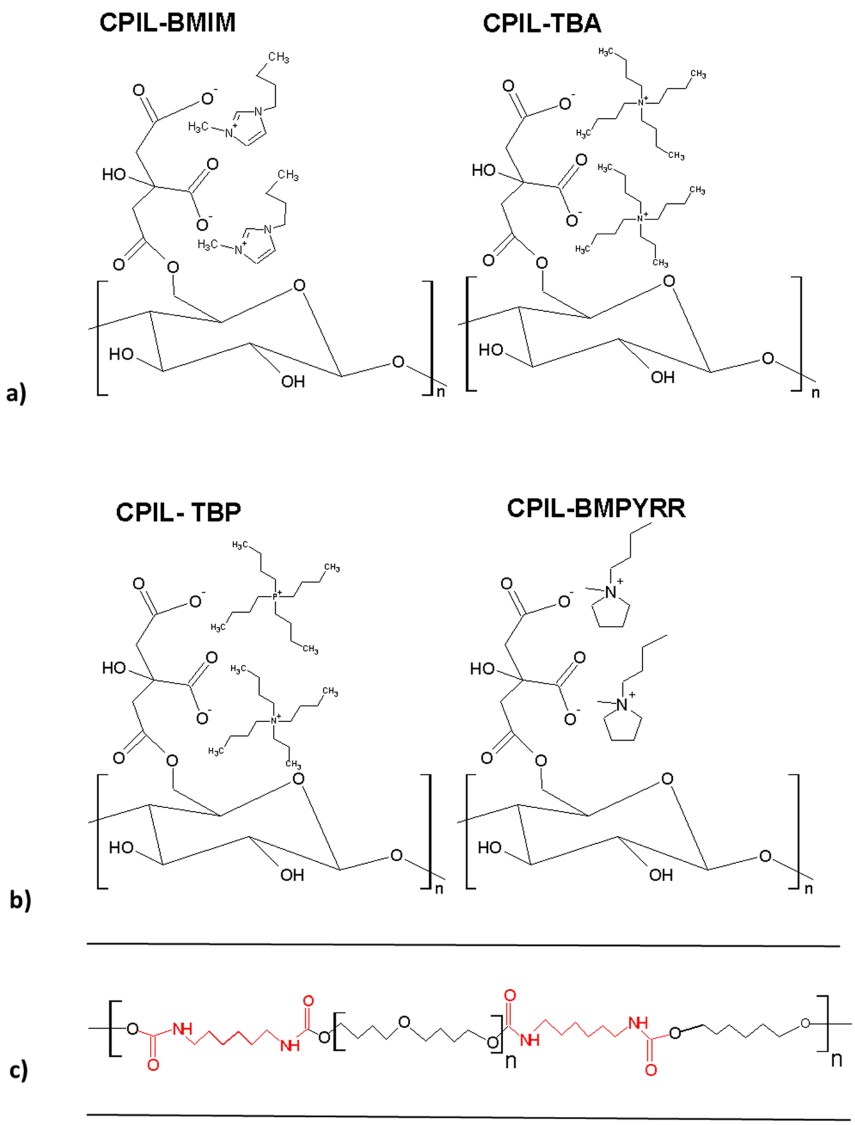

Figure 1. CPILs (a) and PU (a) chemical structure.

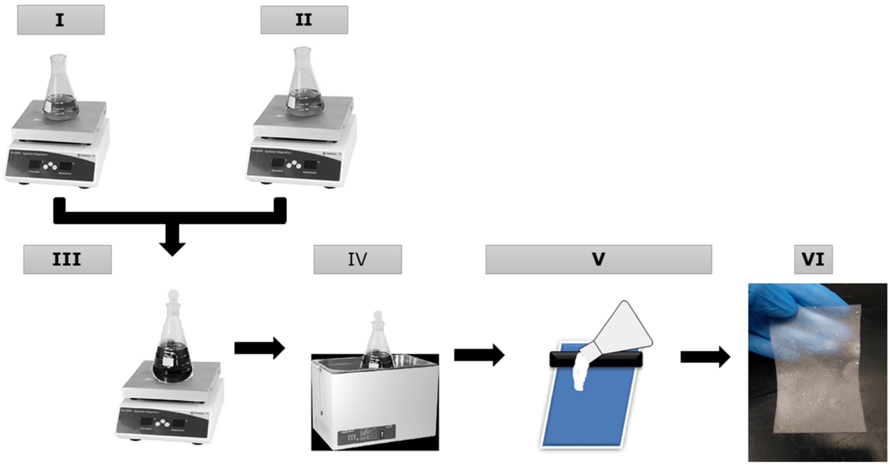

Figure 2. Preparation scheme of composites

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 [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 [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[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[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[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)[37–39] and cellulose/ CPIL structure[16]. T_{1onset} 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)[40]. $T_{2\ onset}$ 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.

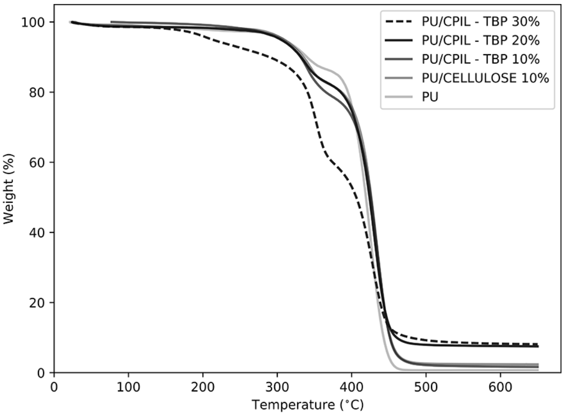

Figure 4. TGA thermograms of PU and PU composites.

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[41,42].

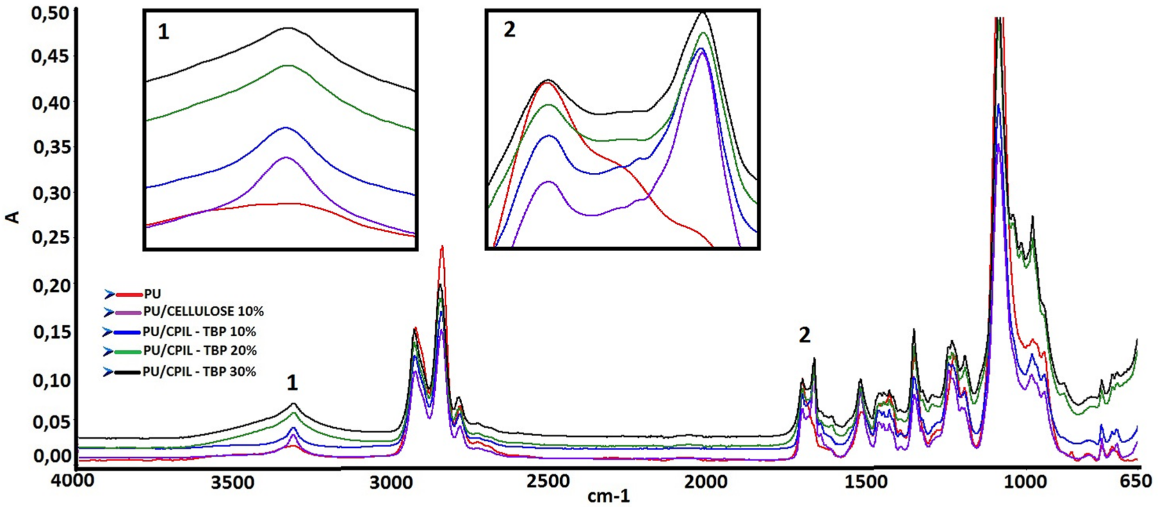

Figure 3. FTIR spectra of PU and PU composites

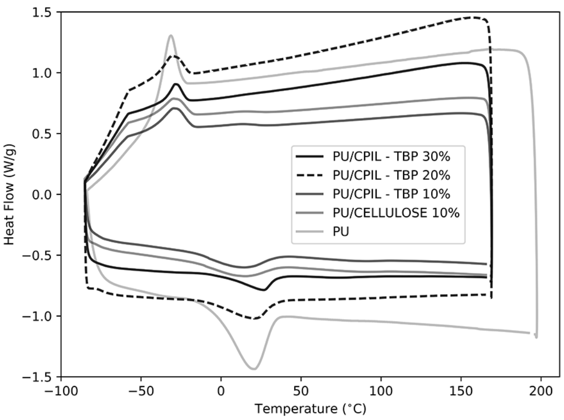

Figure 5. DSC thermograms obtained for PU and PU composites.

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 ΔHc= 15.2 J/g; PU/CPIL-TBP 30% ΔHm= 15 J/g and ΔH_c = 9.24 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[43,44]. 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 CO_2 sorption capacity at 0.1 MPa and 298.15 K is shown in Fig.9. PU exhibited a CO_2 sorption capacity of 24.1mgCO_2/g (1 bar) due to polar groups into the polymer structure that may promote CO_2 affinity [19,20]. CO_2 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 CO_2[16,26]. PU/CPIL CO_2 sorption capacity was higher than PU/CELLULOSE 10%, indicating that the carboxylate ion and IL countercation present in CPIL promote CO_2 sorption in PU matrix. The best result was found for PU/ CPIL-TBP 10% (35.0 mgCO_2/g). Computational studies showed that TBP cation exhibit weaker coordination of carboxyl group promoting CO_2 sorption through electrostatic binding of CO_2 and carboxylate ion [16,45].

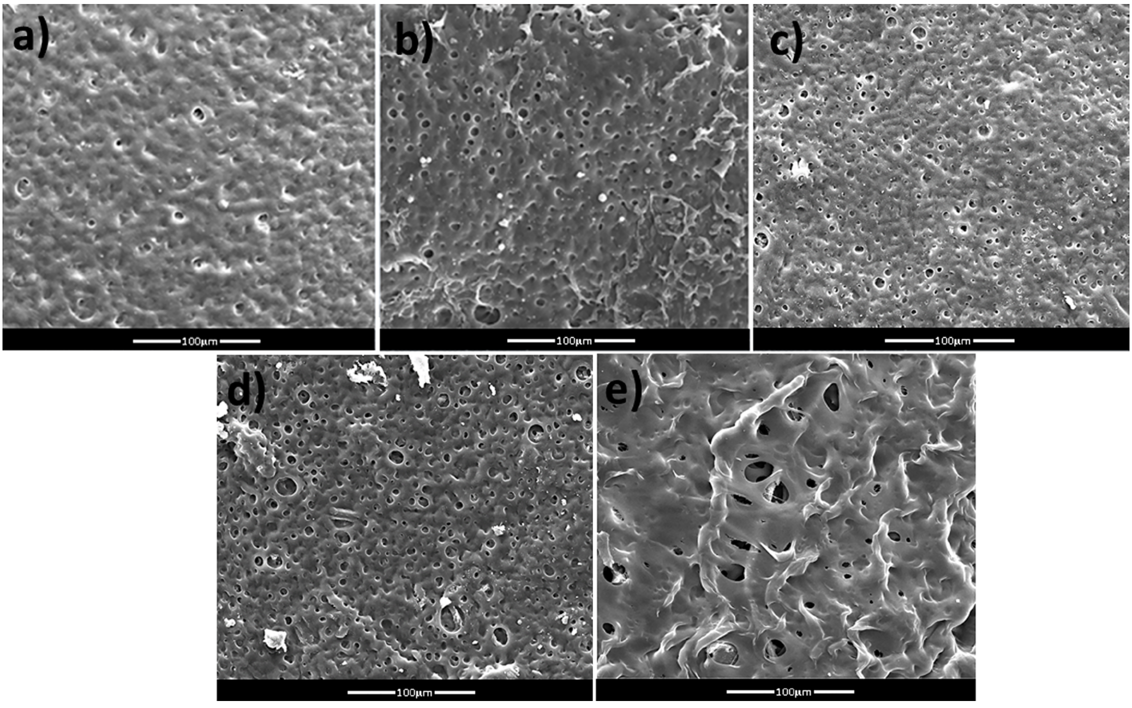

Figure 6. Micrographs obtained for PU and PU composites. (a)PU, (b) PU/CELLULOSE 10%, (c) PU/CPIL-TBP 10%, (d) PU/CPIL-TBP 20% and (d) PU/CPIL-TBP 30%

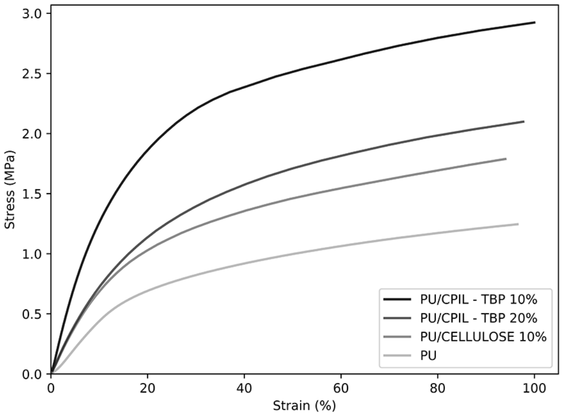

Figure 7. Stress/strain curves obtained for PU and PU composites.

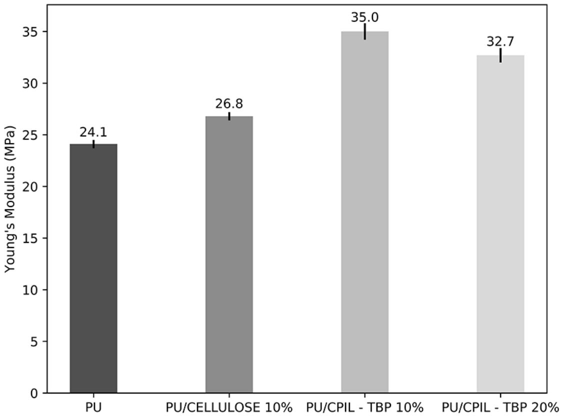

Figure 8. Young moduli of PU and PU composites.

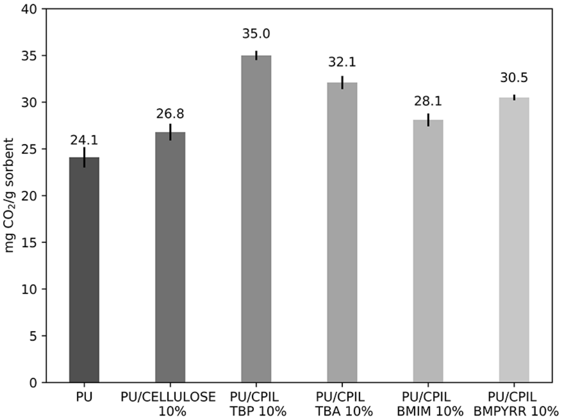

Figure 9. PU and PU composite CO_2 sorption capacity values at 0.1 MPa and 298.15 K.

The effect of filler concentration increase in PU matrix on CO_2 sorption capacity is shown in Fig.10. CO_2 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−CO_2 interactions.

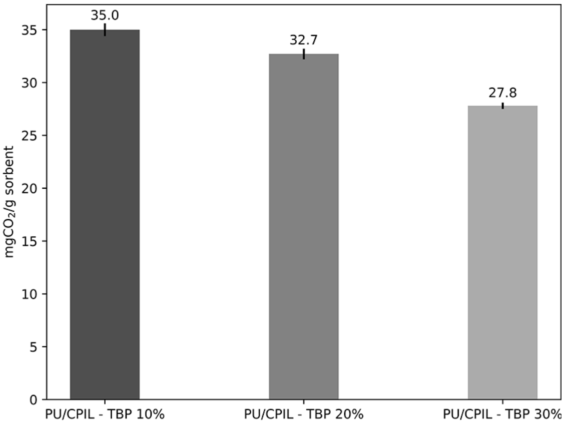

Figure 10. PU/CPIL-TBP composites CO_2 sorption capacity values at 0.1 MPa and 298.15 K.

Table 1 presents the comparison of CO_2 sorption capacity of PU/CPIL - TBP -10% with competitive PILs described in literature. At comparable temperatures and pressures, PU/CPIL-TBP 10% CO_2 sorption capacity is higher when compared to reported PILs. Results suggest that PU/CPIL-TBP 10% presents potential for CO_2 capture.

PU/CPIL-TBP 10% stability was evaluated over five CO_2 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 CO_2 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 CO_2/CH_4 selectivity results are presented in Fig.12. PU/CPIL-TBP composites showed higher selective response than PU/ CELLULOSE 10%. Preferential affinity of CO_2 for PU/CPIL-TBP composites compared to PU/ CELLULOSE 10% is probably due to strong interactions between CO_2 and carboxylate ion of CPIL -TBP [45].

Table 1. Comparison of PU/CPIL - TBP -10% CO_2 sorption capacity values with competitive PILs.

Sorbent	CO2 sorption (mg/g)	Conditions (P, T)	Ref.
P[VBIH][PF_6]	3.22	0.079 bar, 295.15K	6
P6 [BIEMA][acetate]	12.46	0.1 MPa, 278.15K	46
P[VBTEA][PF_6]	14.04	0.1 MPa, 278.15K	47
PIL-8.1.BF_4	24.76	0.1 MPa, 273.15K	48
PU-TBP	15.70	0.082 MPa, 303.15K	45
PUIS-02-TBP	26.70	0.082 MPa, 303.15K	28
PU/CPIL-TBP-10 %	35.00	0.082 MPa, 298.15K	This study

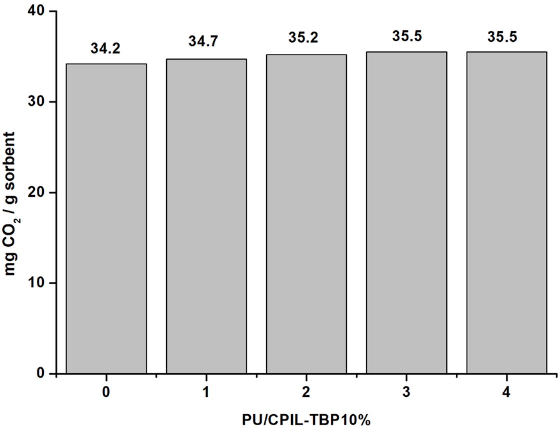

Figure 11. PU/CPIL-TBP 10% CO_2 sorption/desorption cycles.

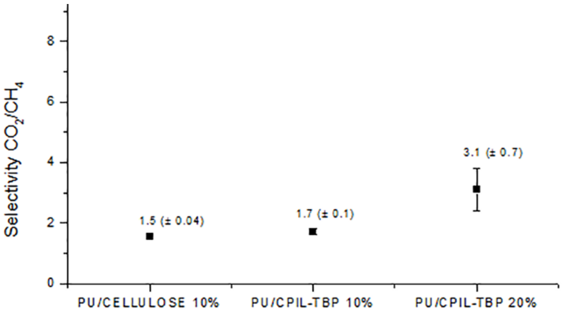

Figure 12. PU composites CO_2/CH_4 selectivity values at 2.0 MPa and 298.15 K.

Results provide evidence that the addition of CPIL-TBP can increase the selectivity of PU for CO_2 over CH_4. PU/CPIL-TBP 20% composite presented higher CO_2/CH_4 selectivity as compared with polyurethane-based poly(ionic liquid) s (PILPC-TBP: CO_2/CH_4 selectivity of ~2.22 at 303.15 K and 2 MPa)[49] and PU foam/ILs composite (PUF BF4 40: CO_2/CH_4 selectivity of 1.42 at 3 MPa)[29].

4. Conclusions

PU/ CPIL composites for CO_2 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 CO_2 sorption result was obtained for PU/CPIL - TBP -10%. PU/CPIL - TBP 10% CO_2 sorption capacity is highest then competitive PILs described in literature. PU/CPIL - TBP 20% Selective capacity for CO_2/CH_4 was higher than PU/CPIL - TBP 10%.

5. Acknowledgments

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6. Reference

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