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Supplementary Material

Ionic liquid mixtures as energy storage materials: a preliminary and comparative study based on thermal storage density.

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Synthetic procedures

1-butyl-3-methylimidazolium bromide ([Bmim][Br])

1-bromobutane (63.03 mmol, 6.8 mL) was slowly added to a distilled *N*-methylimidazole (63.04 mmol, 5 mL) at 0 °C. The reaction mixture was stirred and heated to 80 °C for 12 h under N_2. The obtained viscous liquid was washed with ethyl acetate (3x50 mL) and residual solvents were removed at reduced pressure. The obtained IL was dissolved in CH_3Cl (50 mL) and filtered through diatomaceous earth. Solvent was removed under reduced pressure and the product was dried under vacuum at 70 °C for 12 h. The resulting IL (60.51 mmol, 13.19 g) was collected in 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 0.96 (t, 3H, *J* = 7.4 Hz); 1.39 (sext., 2H, J1 = 7.4 Hz); 1.92 (q, 2H, *J* = 7.4 Hz), 4.14 (s, 3H); 4.36 (t, 2H, J = 7.4 Hz); 7.62 (s, 1H); 7.74 (s, 1H); 10.25 (s, 1H). **^{13}C RMN** (101 MHz, $CDCl_3$): 13,7 (CH3); 19,7 (CH2); 32,4 (CH2); 37,0 (CH3); 50,1 (CH2); 122,6 (CH); 124,1 (CH); 137,4 (CH).

1-butyl-2,3-dimethylimidazolium bromide ([Bdmim][Br])

1-bromobutane (31.16 mmol, 3.36 mL), was slowly added to a 1,2-dimethylimidazole (31.16 mmol, 29.96 g) at 0 °C. The reaction mixture was stirred and heated to 80 °C for 12 h under N_2. The obtained viscous liquid was washed with ethyl acetate (3x30 mL) and residual solvents were removed at reduced pressure. The obtained IL was dissolved in CH_3Cl (30 mL) and filtered through diatomaceous earth. Solvent was removed under reduced pressure and the product was dried under vacuum at 70 °C for 12 h. The resulting IL (28.98 mmol, 6.96 g) was collected in 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 0.96 (t, *J* = 7.4 Hz, 3H); 1.40 (sext., 2H, *J* = 7.4 Hz); 1.82 (q, 2H, *J* = 7.4 Hz); 2.84 (s, 3H); 4.04 (s, 3H); 4.27 (t, 2H, *J* = 7.4 Hz); 7.64 (d, 1H, *J* = 2.0 Hz); 7.80 (d, 1H, *J* = 2.0 Hz).
^{13}C NMR (400 MHz, $CDCl_3$: 11.2 (CH3); 13.7 (CH2); 19.7 (CH2); 32.0 (CH3); 36.4 (CH3); 48.9 (CH2), 121.6 (CH); 123.3 (CH); 143.8 (C).

1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF4])

A round bottom flask equipped with a stirring bar was charged with 1-butyl-3-methylimidazolium bromide (82.11 mmol, 20.29 g) and dissolved in acetone (50 mL). $NaBF_4$ (82.11 mmol, 9.01 g) was added to the solution followed by stirring for 12 h at rt. The white precipitate was allowed to settle, filtered and the solvent was removed at reduced pressure. Residue was dissolved in CH_3Cl (30 mL) and washed with deionized water (6x20 mL). The combined organic layers were dried and filtered through diatomaceous earth. Solvent was removed under reduced pressure and the product was dried under vacuum at 70 °C for 12 h. The resulting IL (78.00 mmol, 17.64 g) was collected in 95% yield.

^{1}H-NMR (400 MHz, DMSO): δ (ppm): 8.87 (s, 1H, C2H); 7.43 (t, *J* = 1.7 Hz, 1H, C4H); 7.42 (t, *J* = 1.6 Hz, 1H, C5H); 4.19 (t, *J* = 7.2 Hz, 2H, NCH2); 3.92 (s, 3H, NCH3); 1.9-1.66 (qt, 2H, CH2CH2CH2); 1.36 (st, 2H, CH2CH2CH3); 0.93 (t, *J* = 7.4 Hz, 3H, CH3).
^{13}CNMR (101 MHz, DMSO): δ (ppm): 136.41 (C2H); 123.59 (C4H); 122.25 (C5H); 48.52 (NCH2); 35.71 (NCH3); 31.35 (CH2CH2CH2); 18.76 (CH2CH2CH3); 13.23 (CH2CH3).

1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([Bdmim][BF_4])

A round bottom flask equipped with a stirring bar was charged with 1-butyl-2,3-dimethylimidazolium bromide (87.00 mmol, 20.88 g) and dissolved in acetone (50 mL). $NaBF_4$ (87.00 mmol, 9.55 g) was added to the solution followed by stirring for 12 h at rt. The white precipitate was allowed to settle, filtered and the solvent was removed at reduced pressure. Residue was dissolved in $CHCl_3$ (30 mL) and washed with deionized water (6x20 mL). The combined organic layers were dried and filtered through diatomaceous earth. Solvent was removed under reduced pressure and the product was dried under vacuum at 70 °C for 12h. The resulting IL (80.91 mmol, 19.43 g) was collected in 93% yield.

^{1}H NMR (400 MHz, DMSO) δ 7.63 (d, *J* = 2.1 Hz, 1H, C2H), 7.59 (d, *J* = 2.0 Hz, 1H, C4H), 4.11 (t, *J* = 7.3 Hz, 2H, NCH2), 3.75 (s, 3H, NCH3), 2.58 (s, 3H, NCH3), 1.78-1.60 (m, 2H, CH2CH2), 1.38-1.21 (m, 2H, CH2CH3), 0.91 (t, *J* = 7.4 Hz, 3H, CH3).

^{13}C NMR (101 MHz, DMSO) δ 144.25 (NCH), 122.27 (CH), 120.84 (CH), 47.30 (NCH2), 34.61 (NCH3), 31.18 (CH2), 18.87 (CH2), 13.36 (CH3), 9.06 (NCH3).

1-buyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6])

A round bottom flask equipped with a stirring bar was charged with 1-butyl-3-methylimidazolium bromide (92.56 mmol, 20.18g) and dissolved in deionized water (50 mL). KPF_6 (92.56 mmol, 17.04 g) was added to the solution followed by stirring for 12 h at rt. Reaction mixture was extracted with CH_2Cl_2 (3x30mL) and the combined organic layers were dried and filtered through diatomaceous earth. Solvent was removed under reduced pressure and the product was dried under vacuum at 70 °C for 12 h. The resulting IL (85.15 mmol, 24.18g) was collected in 90% yield.

^{1}H NMR (400 MHz, DMSO) δ 9.07 (s, 1H, C2H), 7.73 (t, *J* = 1.6 Hz, 1H, C4H), 7.67 (t, *J* = 1.5 Hz, 1H, C5H), 4.16 (t, *J* = 7.2 Hz, 2H, NCH2), 3.85 (s, 3H, NCH3), 1.84-1.71 (m, 2H, CH2CH2), 1.33-1.20 (m, 2H, CH2), 0.91 (t, *J* = 7.4 Hz, 3H, CH3).

^{13}C NMR (101 MHz, DMSO) δ 136.50 (C2H), 123.60 (C4H), 122.25 (C5H), 48.56 (NCH2), 35.71 (NCH3), 31.35 (CH2CH2), 18.78 (CH2CH3), 13.22 (CH3).

1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([Bdmim][PF_6])

A round bottom flask equipped with a stirring bar was charged with 1-octyl-2,3-dimethylimidazolium bromide (64.78 mmol, 15.55g) and dissolved in deionized water (50 mL). KPF_6 (64.78 mmol, 11.93g) was added to the solution followed by stirring for 12 h at rt. Reaction mixture was extracted with CH_2Cl_2 (3x30mL) and the combined organic layers were dried and filtered through diatomaceous earth. Solvent was removed under reduced pressure and the product was dried under vacuum at 70 °C for 12 h. The resulting IL (58.30 mmol, 17.37g) was collected in 90% yield.

^{1}H NMR (400 MHz, DMSO) δ 7.62 (d, *J* = 2.1 Hz, 1H, C2H), 7.59 (d, *J* = 2.0 Hz, 1H, C4H), 4.10 (t, *J* = 7.3 Hz, 3H, NCH3), 3.74 (s, 3H, CCH3), 2.57 (s, 1H), 1.79 –-1.59 (m, 2H, CH2CH2), 1.40 - 1.19 (m, 2H, CH2CH3), 0.91 (t, *J* = 7.4 Hz, 3H, CH3).

^{13}C NMR (101 MHz, DMSO) δ 144.22 (NCH), 122.29 (CH), 120.84 (CH), 47.30 (NCH2), 34.62 (NCH3), 31.16 (CH2), 18.87 (CH2), 13.36 (CH3), 9.05 (NCH3).

1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Bmim][Tf_2N])

A round bottom flask equipped with a stirring bar was charged with 1-butyl-3-methylimidazolium bromide (11.79 mmol, 25.7g) and dissolved in deionized water (50 mL). A aqueous solution of Li[Tf_2N] (11.79 mmol, 33.85g), was slowly added to the solution followed by stirring for 12 h at rt. Reaction mixture was extracted with CH_2Cl_2 (3x30mL) and the combined organic layers were dried and filtered through diatomaceous earth. Solvent was removed under reduced pressure and the product was dried under vacuum at 70 °C for 12 h. The resulting IL (11.55 mmol, 4.85) was collected in 98% yield.

^{1}H NMR (400 MHz, DMSO) δ 9.10 (s, 1H, C2H), 7.75 (t, *J* = 1.7 Hz, 1H, C4H), 7.69 (t, *J* = 1.6 Hz, 1H, C5H), 4.16 (t, *J* = 7.2 Hz, 2H, NCH2), 3.85 (s, 3H, NCH3), 1.85-1.69 (m, 2H, CH2CH2), 1.36-1.18 (m, 2H, CH2CH3), 0.91 (t, *J* = 7.4 Hz, 3H, CH3).

^{13}C NMR (101 MHz, DMSO) δ 123.60 (C2H), 122.25 (C4H), 121.11 (C5H), 117.91 (CF3), 48.54 (NCH2), 35.70 (NCH3), 31.35 (CH2CH2), 18.75 (CH2CH3), 13.16 (CH3).

1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ([Bdmim][Tf_2N])

A round bottom flask equipped with a stirring bar was charged with 1-butyl-3-methylimidazolium bromide (17.13 mmol, 4.11) and dissolved in deionized water (50 mL). A aqueous solution of Li[Tf_2N] (17.13 mmol, 4.92g), was slowly added to the solution followed by stirring for 12 h at rt. Reaction mixture was extracted with CH_2Cl_2 (3x30mL) and the combined organic layers were dried and filtered through diatomaceous earth. Solvent was removed under reduced pressure and the product was dried under vacuum at 70 °C for 12 h. The resulting IL (16.27 mmol, 7.05g) was collected in 95% yield.

^{1}H NMR (400 MHz, DMSO) δ 7.63 (d, *J* = 2.1 Hz, 1H, C4H), 7.60 (d, *J* = 2.1 Hz, 1H, C5H), 4.10 (t, *J* = 7.3 Hz, 2H, NCH2), 3.75 (s, 3H, NCH3), 2.58 (s, 3H, CCH3), 1.78-1.61 (m, 2H, CH2CH2), 1.37-1.20 (m, 2H, CH2), 0.91 (t, *J* = 7.4 Hz, 3H, CH3).

^{13}C NMR (101 MHz, DMSO) δ 144.20 (C2H), 122.29 (C4H), 120.84 (C5H), 117.90 (CF3), 47.31 (NCH2), 34.61 (CH3), 31.16 (CH2), 18.86 (CH2), 13.29 (CH3), 9.06 (CH3).

Adjustment parameters of heat capacities (Cp)

Polynomic adjustment: $Cp = A0 + A1 \cdot T + A2 \cdot T^2$

IL or mixture	A0	A1	A2	R^2
IL1	-0,00005	0,04	-6,253	0,969
IL2	-0,000048	0,043	-7,855	0,994
IL3	0,000007	0,002	-0,2699	0,976
IL4	0,000005	0,001	0,599	0,998
IL5	-0,000067	0,058	-10,555	0,975
IL6	-0,000032	0,035	-7,098	0,998
M1	-0,00007	0,062	-11,84	0,988
M2	-0,000017	0,033	-8,339	0,923
M3	-0,000081	0,065	-11,6	0,965
M4	-0,000035	0,03	-5,122	0,978
M5	-0,00001	0,008	-0,005	0,958
M6	-0,000045	0,037	-6,344	0,944
M7	-0,00005	0,04	-6,329	0,905
M8	-0,000014	0,0033	2,2161	0,965
M9	-0,000002	0,005	-0,2	0,932
M10	-0,00008	0,068	-12,85	0,985
M11	-0,000243	0,201	38,54	0,998
M12	-0,000138	0,104	-17,783	0,964
M13	0,000012	-0,005	1,8755	0,997
M14	-0,000123	0,103	-18,979	0,995
M15	0,00003	-0,018	4,693	0,947

Experimental densities of ionic liquids and mixtures

Experimental density (kg/m^3)

	293.15 K	**313.15 K**	**323.15 K**	**333.15 K**	**355.15 K**
IL1	1205.9	1191.2	1184.0	1176.9	1162.9
IL2	1373.1	1356.0	1347.6	1339.3	1322.9
IL3	1436.6	1417.3	1407.7	1398.3	1379.6
IL4	1190.3	1176.3	1169.3	1162.5	1148.9
IL5	---	1332.3	1324.2	1316.2	1298.1
IL6	1414.5	1395.5	1386.2	1376.9	1358.4
M1	1342.5	1324.1	1314.6	1311.3	1294.4
M2	1291.9	1276.8	1268.1	1260.3	1245.1

M3	1405.4	1387.1	1378.0	1369.0	1351.0
M4	1325.5	1308.6	1300.2	1291.9	1274.9
M5	1272.6	1257.3	1249.7	1242.1	1226.9
M6	1380.8	1362.8	1354.0	1345.2	1327.8
M7	1201.7	1187.3	1180.3	1173.3	1159.5
M8	1355.4	1338.7	1330.3	1322.1	1305.9
M9	1423.8	1404.6	1395.2	1385.8	1367.2
M10	1280.6	1265.0	1257.4	1249.8	1234.8
M11	1335.1	1317.9	1309.5	1301.1	1284.4
M12	1279.7	1264.1	1256.4	1248.8	1233.7
M13	1395.6	1377.5	1368.5	1359.6	1341.8
M14	1333.5	1316.4	1307.9	1299.5	1282.8
M15	1396.5	1378.5	1369.6	1360.7	1343.2

Adjustment parameters of densities of ionic liquids and mixtures

Polynomic adjustment: $\rho = A0 + A1 \cdot T + A2 \cdot T^2$

	A0	A1	A2	R^2
IL1	1461.4	-1.001	0.004	1
IL2	1663.7	-1.121	0.0004	1
IL3	1756.8	-1.2115	0.0004	1
IL4	1422	-0.8746	0.0003	1
IL5	1353.1	0.6305	-0.0022	0.9999
IL6	1719.1	-1.1268	0.0003	1
M1	1817.3	-2.3159	0.0024	0.9918
M2	1537,9	-0.8845	0.0002	0.9996
M3	1691.9	-1.0372	0.0002	1
M4	1568.6	-0.8194	0.00004	1
M5	1501.9	-0.8	0.00006	1
M6	1676.4	-1.1137	0.0004	1
M7	1444.6	-0.9337	0.0004	1
M8	1633	-1.0485	0.0003	1
M9	1737	-1.1737	0.0004	1
M10	1541.1	-0.9937	0.0004	1
M11	1613.3	-1.0368	0.0003	1
M12	1537.5	-0.9741	0.0003	1
M13	1679.2	-1.0272	0.0002	1
M14	1608.2	-1.0142	0.0003	1

M15	1687.6	-1.0808	0.0003	1

Thermal gravimetric analysis (TGA-DTA) of ionic liquids and mixtures

Figure S1: TGA thermograms for the six inicial ILs.

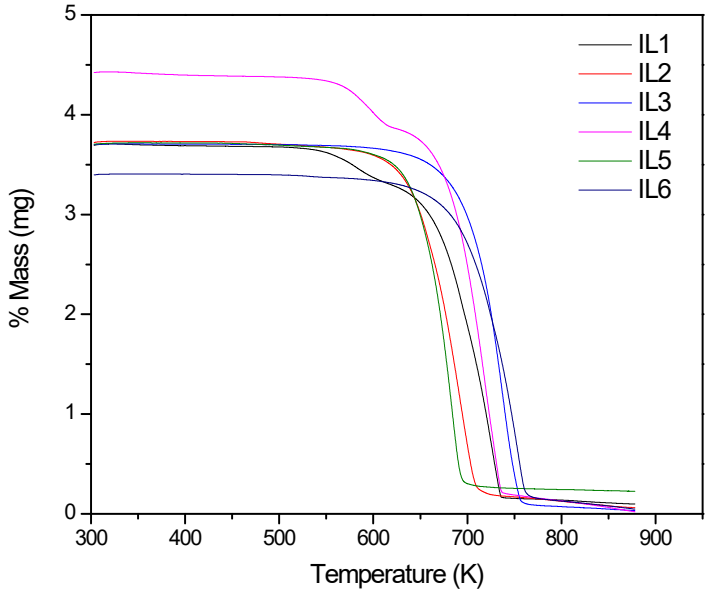


Figure S2: TGA thermograms for the binary mixtures of ILs.

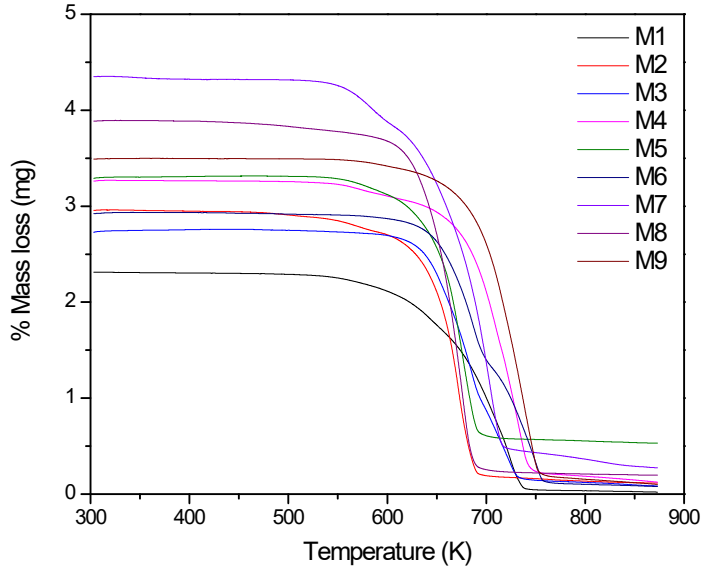
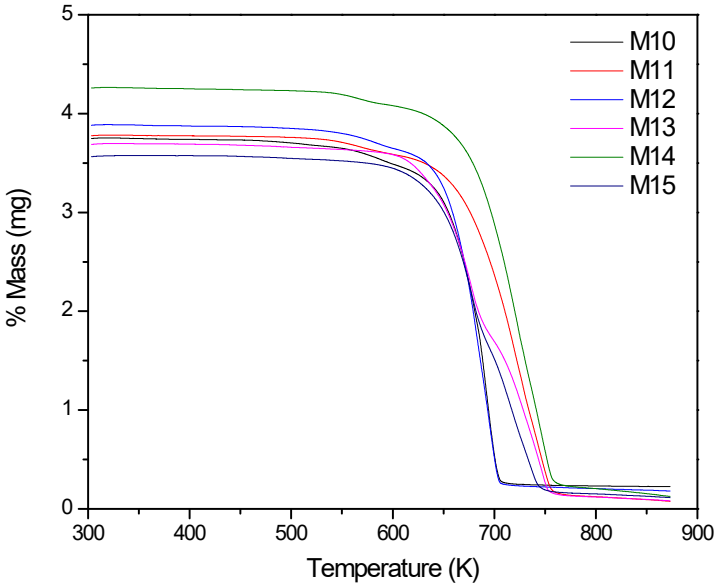


Figure S3: TGA thermograms for the reciprocal binary mixtures of ILs.



Examples of thermograms analyzed by DTA

Figure S4: IL2 - TGA thermogram.

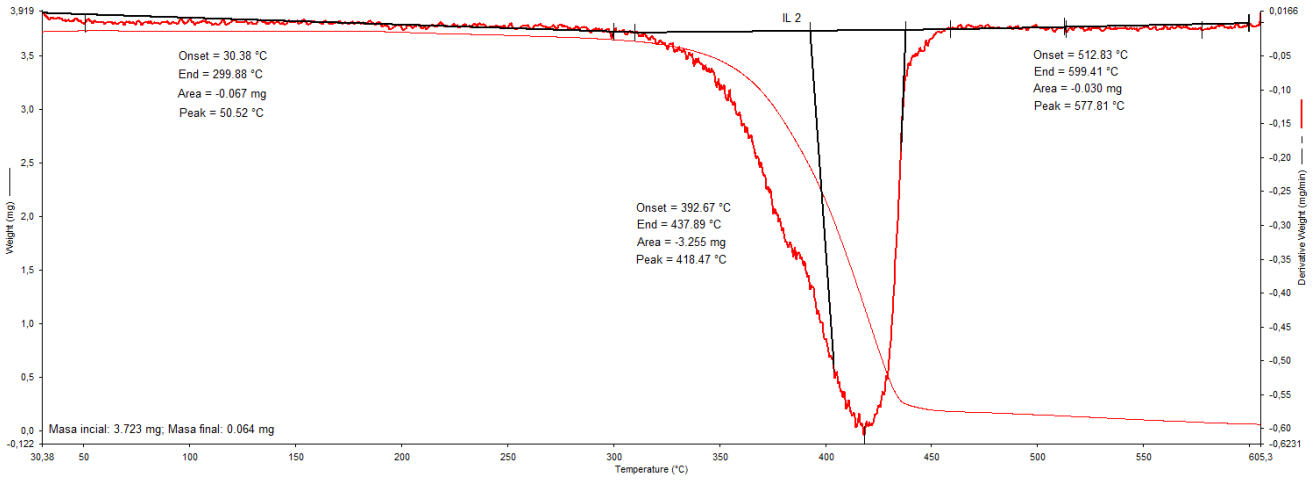


Figure S5: IL5 - TGA thermogram.

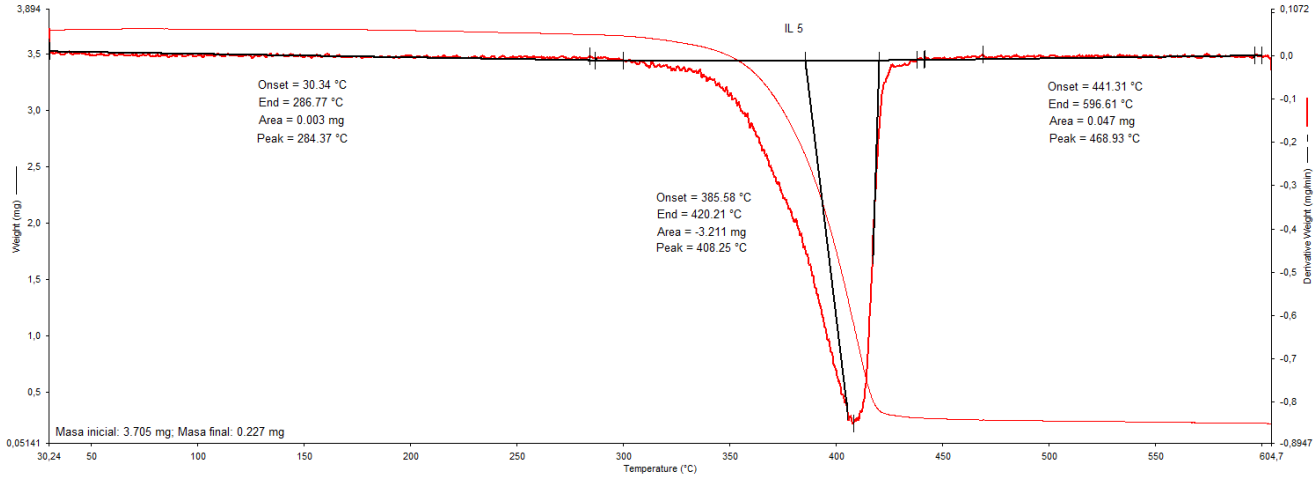


Figure S6: M8 - TGA thermogram.

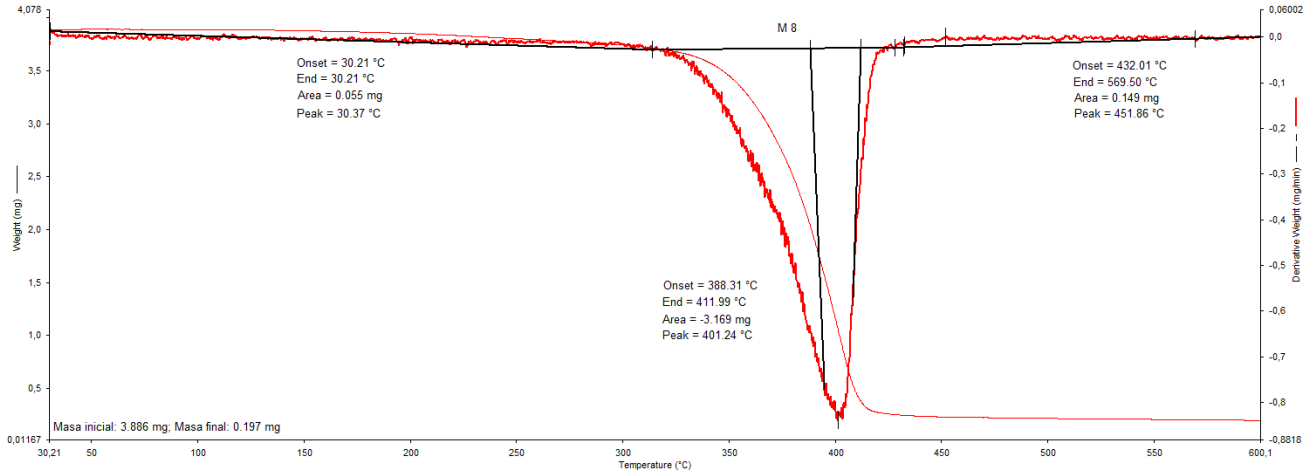


Figure S7: M6 - TGA thermogram.

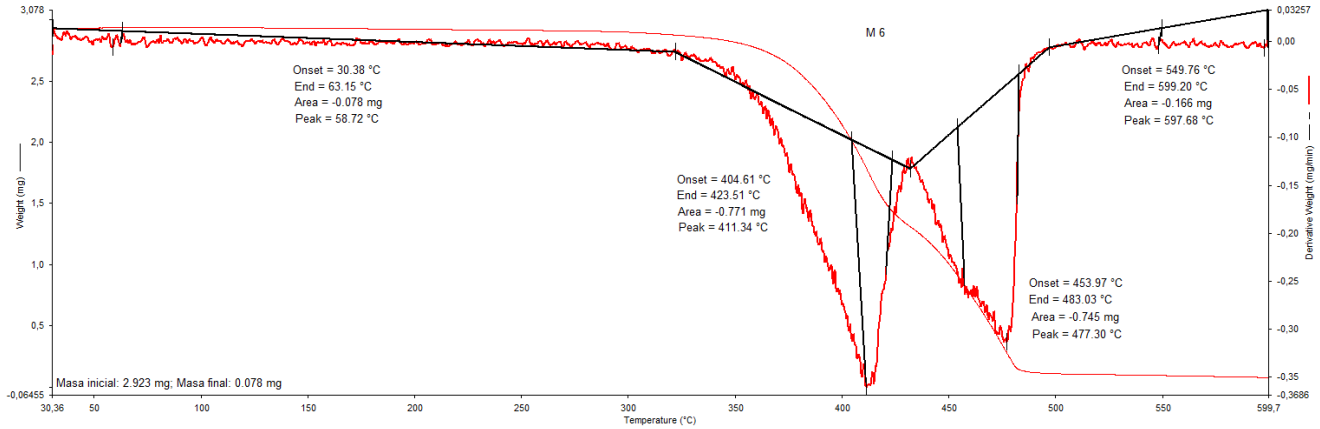


Figure S8: M15 - TGA thermogram.