# Supporting Information (SI) for

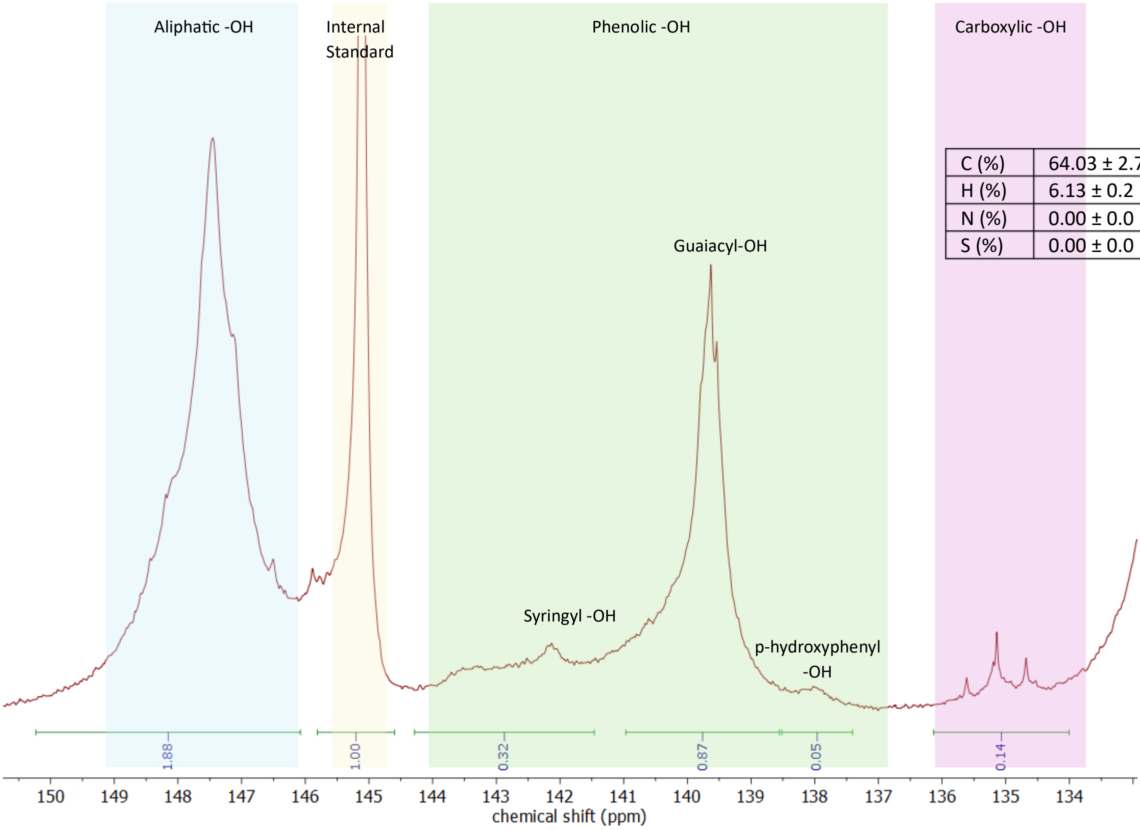
# Fabricating lignocellulosic films as potential biobased plastics

Antonella Rozaria Nefeli Pontillo [a,b], Sirui Chen [b], Diego Freire Ordóñez[a], Niall Mac Dowell[c], Koon-Yang Lee [a] and Tom Welton*[b]

a. Department of Aeronautics, Imperial College London, London, UK.

b. Department of Chemistry, Imperial College London, London, UK.

c. Center for Environmental Policy, Imperial College London, London SW7 2AZ, UK.




| | |
|---|---|
| C (%) | 64.03 ± 2.7 |
| H (%) | 6.13 ± 0.2 |
| N (%) | 0.00 ± 0.0 |
| S (%) | 0.00 ± 0.0 |

Figure S1: $^{31}P$ NMR spectrum and elemental composition (table) of lignin.

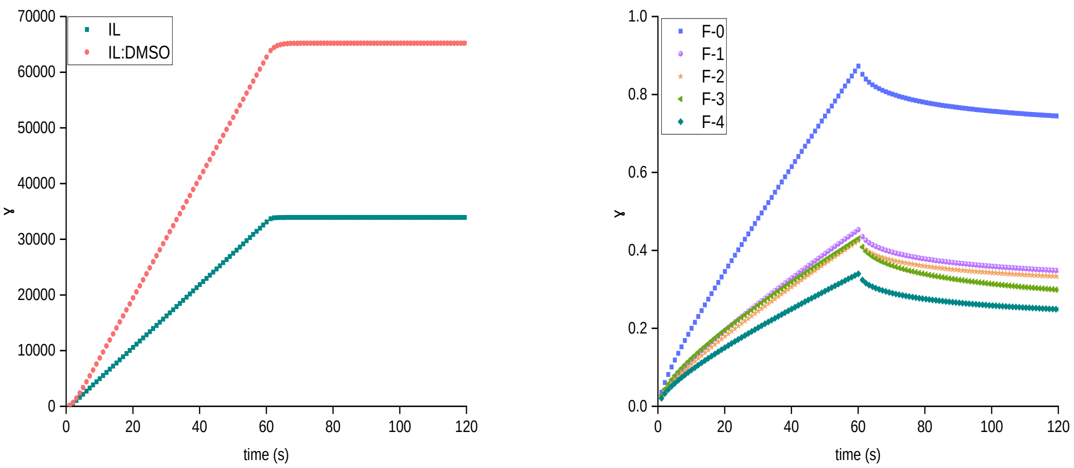



Figure S2: Creep and recovery testing of the ionic liquid and the $[C_2C_1im][OAc]$/DMSO mixture (a) and (b) the five dope solutions (DS)

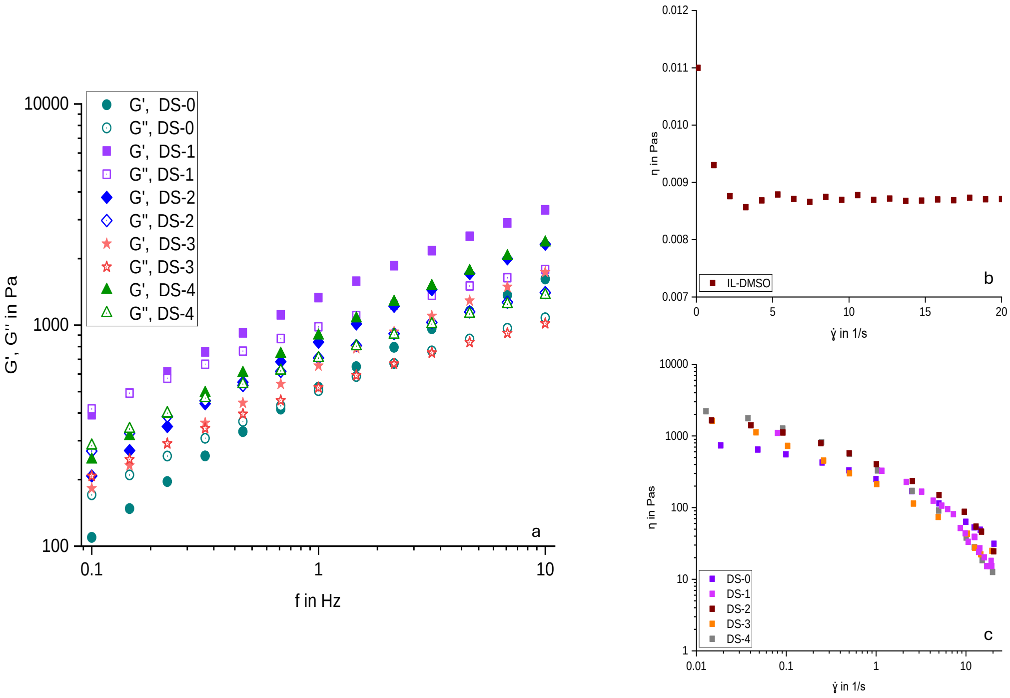



Figure S3: (a) Storage and loss moduli (G' and G'') as a function of the frequency of oscillation for the five dope solutions. (b) Steady shear viscosity as a function of the shear rate for the solvent and the dope solutions (c).

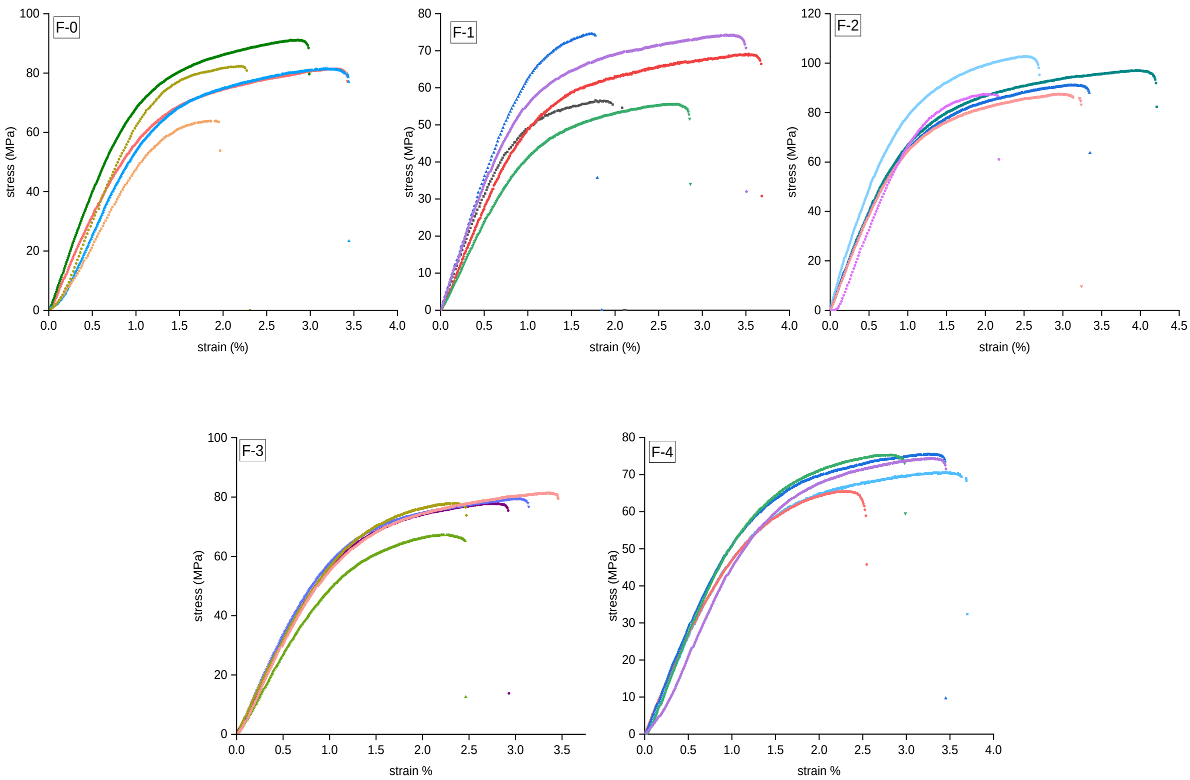
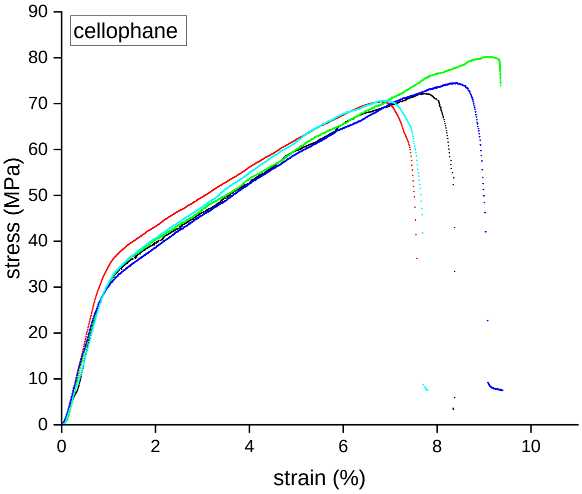



Figure S4: Tensile strength - strain curves of the films.




| | cellophane |
|---|---|
| $\sigma_{max}$ (MPa) | 73.60 ± 4.1 |
| $\varepsilon_{failure}$ (%) | 8.03 ± 0.7 |
| E (GPa) | 3.99± 4.0 |

Figure S5: Tensile strength - strain curves of a commercial cellophane film

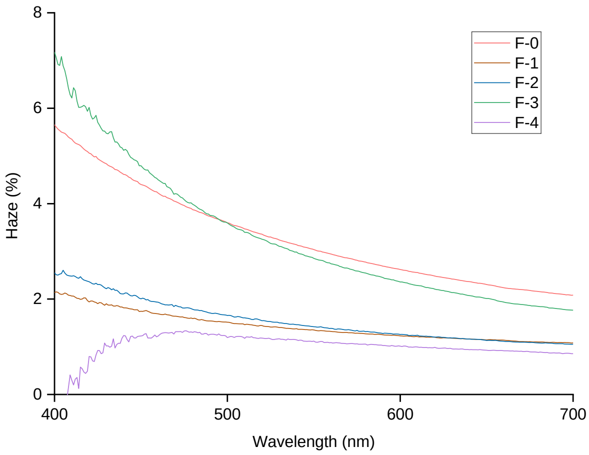



Figure S6: Optical properties of the films: haze of films in the visible spectrum.

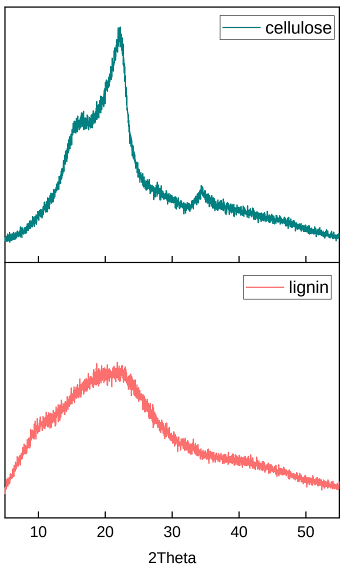



Figure S7: XRD patterns of cellulose (top) and lignin (bottom).

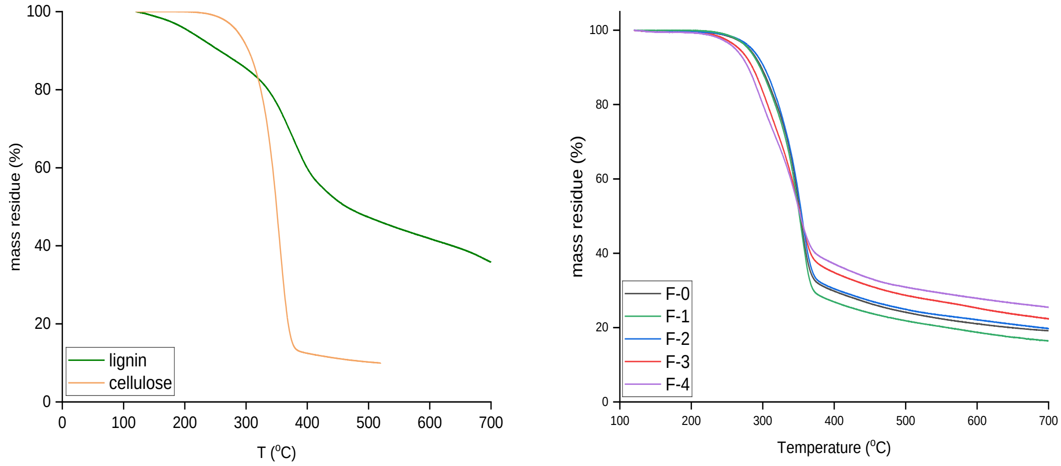
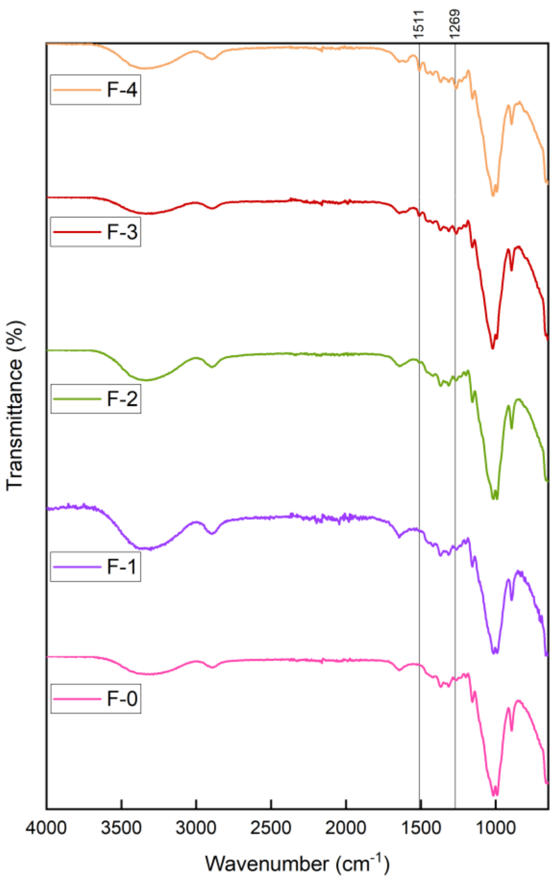



Figure S8: TGA curves of the two polymers (left) and the five samples (right).




| | F-1 |
|---|---|
| C | 45.09 ± 0.24 |
| H | 7.25 ± 0.05 |
| N | 0 |

| F-0 |
|---|
| 46.00 ± 0.08 |
| 6.49 ± 0.35 |
| 0 |

Figure S9: FTIR spectra of the films and elemental analysis of samples F-0 and F-1.

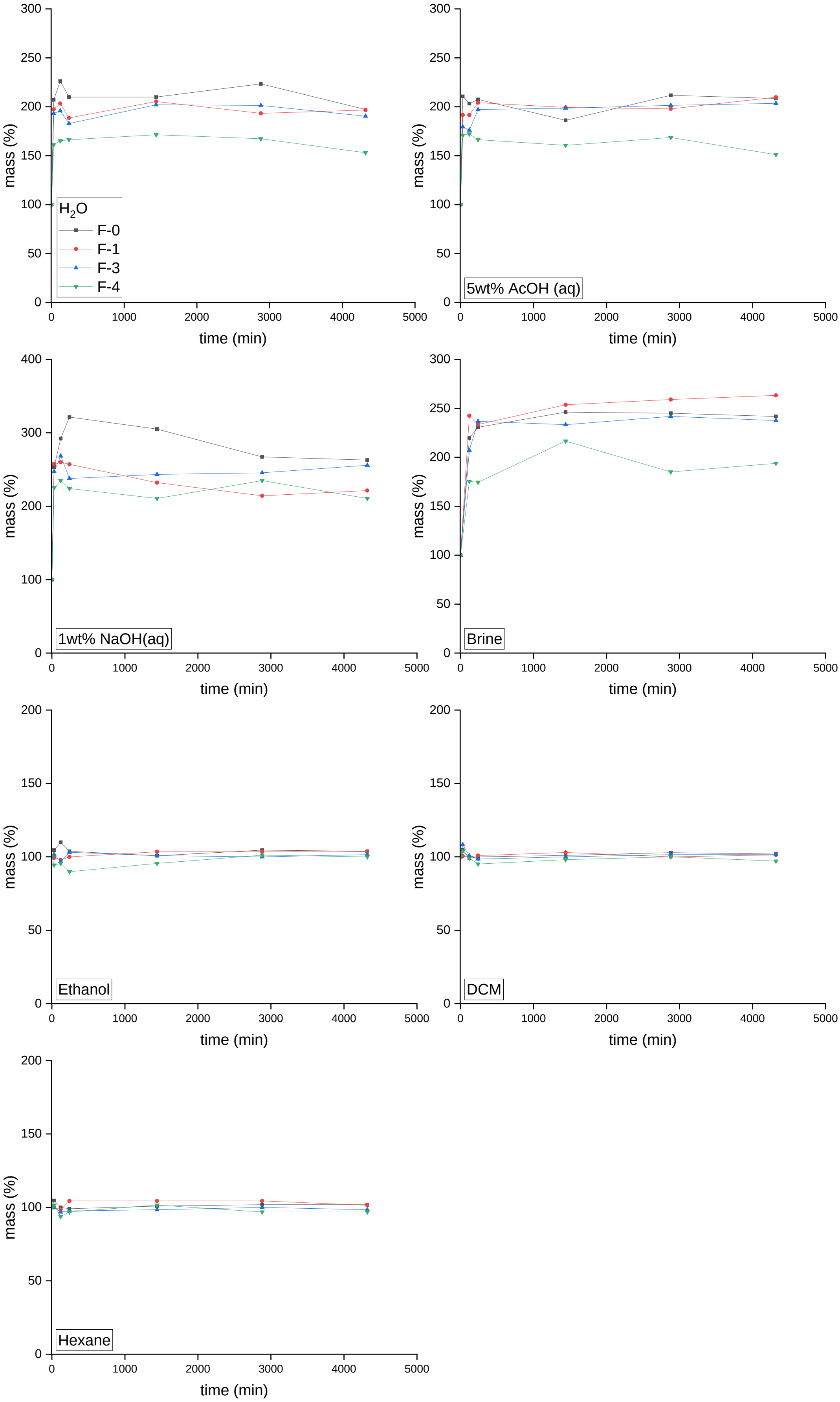


Figure S10: Swelling behaviour of the films in water, 5wt% acetic acid (aq), 1wt% sodium hydroxide (aq), brine, ethanol, dichloromethane and hexane.

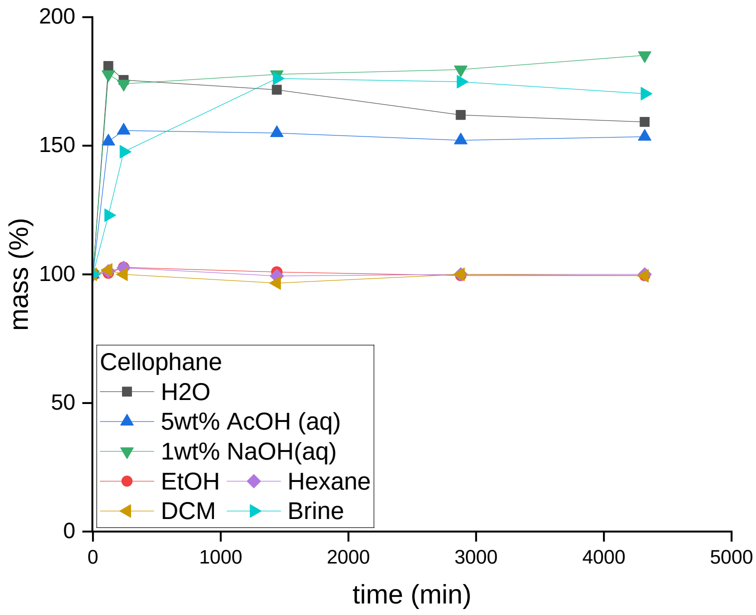



Figure S11: Swelling behaviour of cellophane in different solvents.

Table S1: Stability tests of the films F-0, F-1, F-3, F-4 and a commercial cellophane sample in different solvents.

| | **Change in mass (%)** | | | | |
|---|---|---|---|---|---|
| | **F-0** | **F-1** | **F-3** | **F-4** | **cellophane** |
| **$H_2O$** | 1.4 | 1.3 | -0.7 | -3.1 | -6.5 |
| **EtOH** | 1.5 | 1.4 | 0.8 | -6.7 | -4.5 |
| **5wt% AcOH (aq)** | 0.0 | 0.7 | 0.0 | -3.6 | -5.7 |
| **1wt% NaOH (aq)** | 1.7 | -4.3 | -13.4 | -27.2 | -13.3 |
| **Hexane** | -0.9 | 0.7 | -3.2 | -4.7 | -3.8 |
| **DCM** | 0.0 | -0.4 | 0.0 | -1.9 | -5.7 |
| **Brine** | -3.3 | 12.2 | 12.1 | 0.0 | 6.0 |

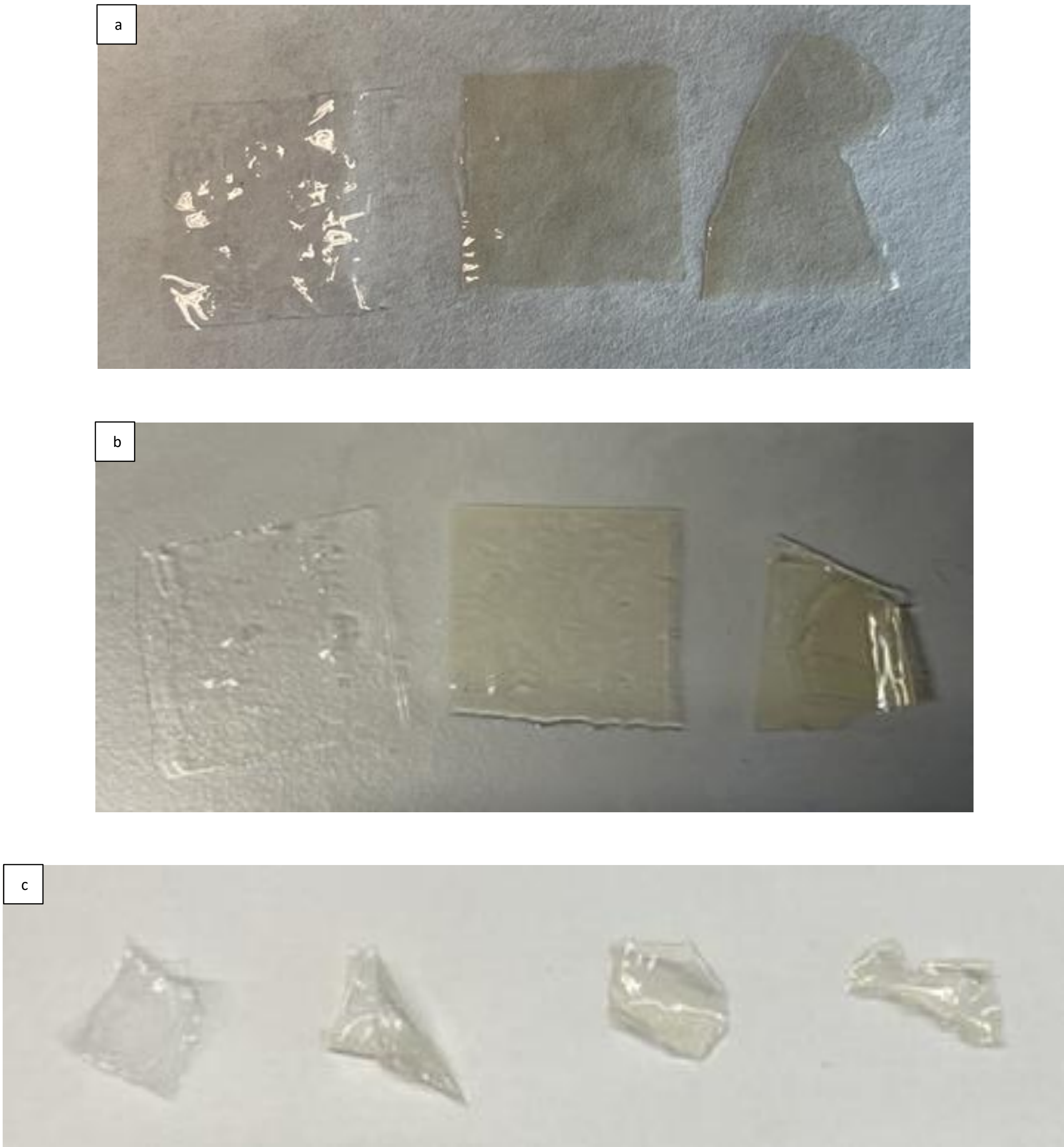



Figure S12: Films F-0, F-3 and F-4 (a) 30 s and (b) 24 h after submerged in 1% NaOH solution. (c) Films F-0, F-1, F-3 and F-4 72 h after submerged in 1% NaOH solution.

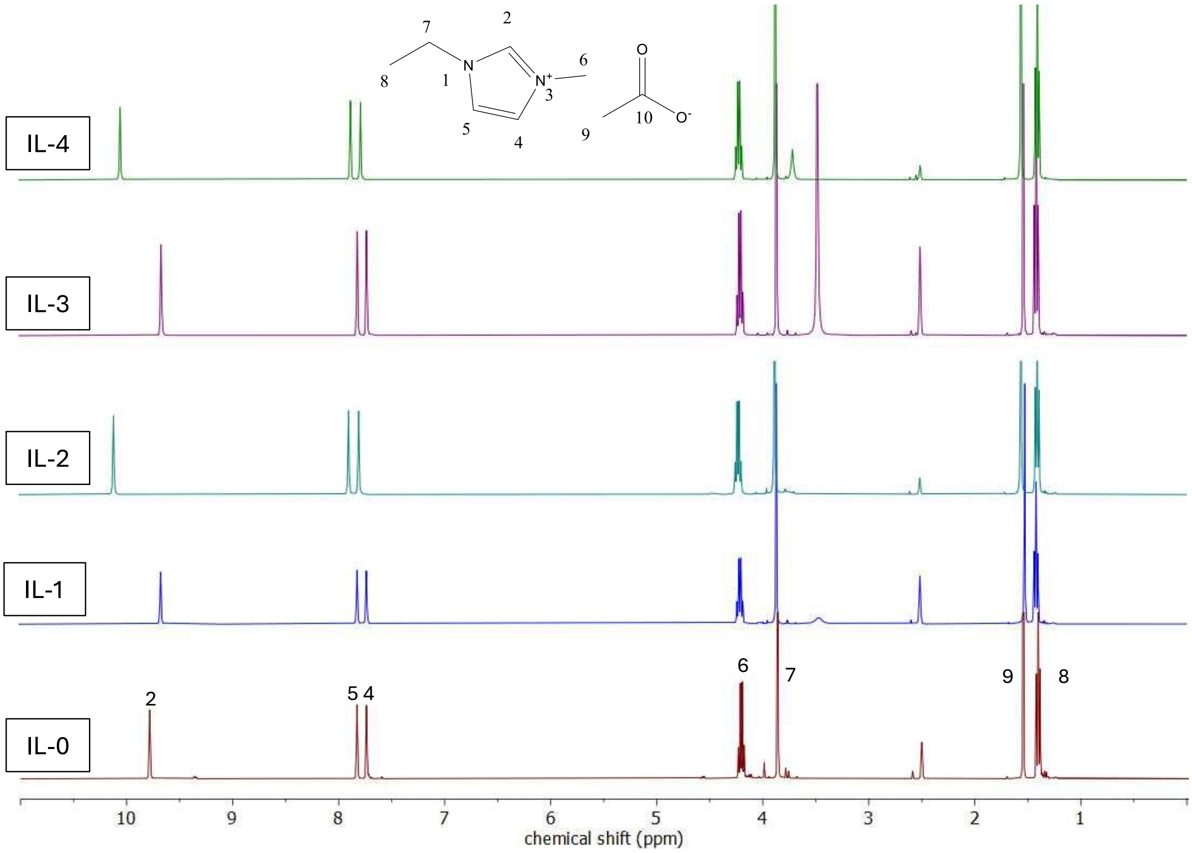


Figure S13: $^{1}H$ NMR spectra of the freshly synthesised (IL-0) and recycled ionic liquid.

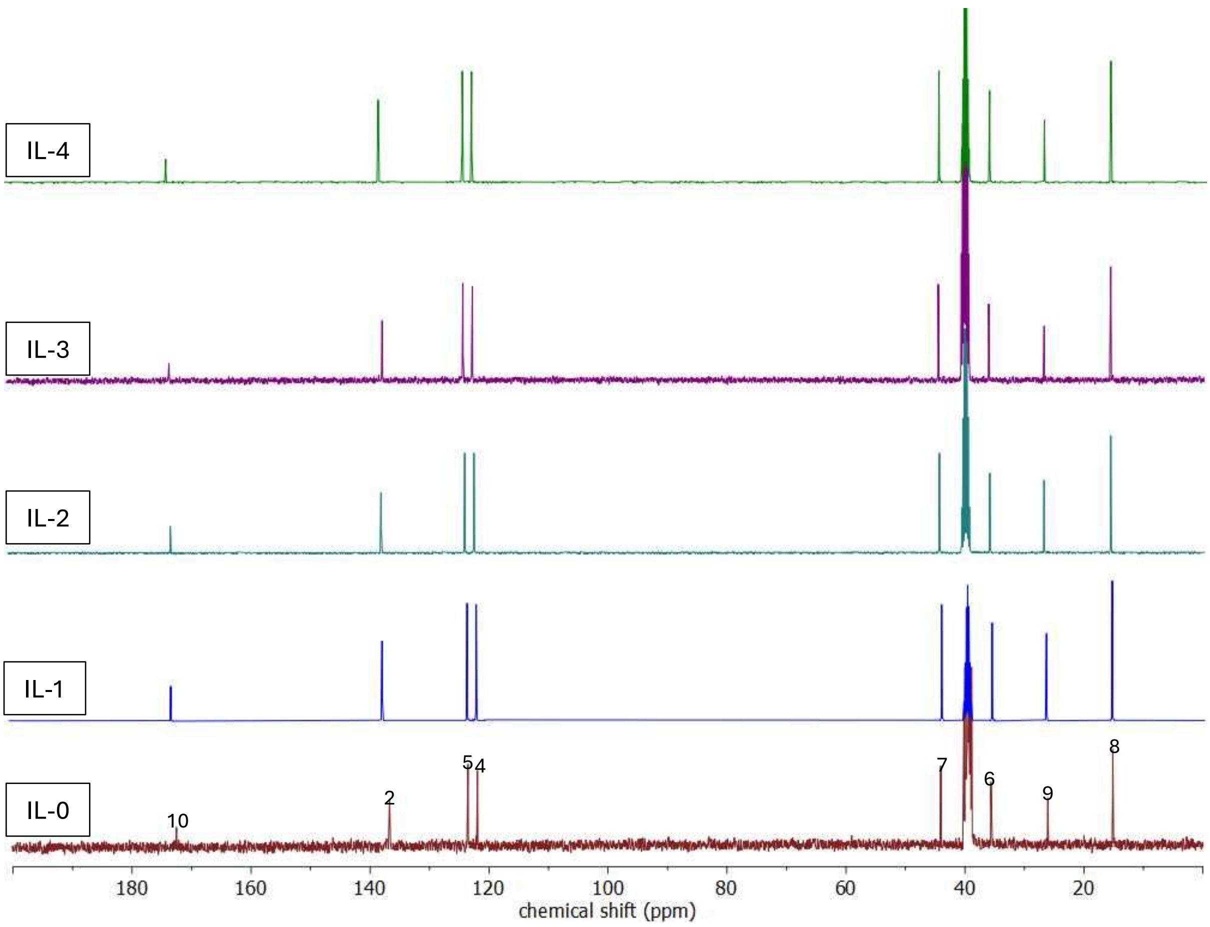


Figure S14: $^{13}C$ NMR spectra of the freshly synthesised and recycled ionic liquid.

**Freshly synthesised ionic liquid (IL-0):**

$^{1}$H NMR (400 MHz, DMSO-d$_6$) $\delta_H$ (ppm): 9.78 (s, 1H, imC(2)**H**), 7.78 (d, *J* = 35.8 Hz, 2H, imC(4)**H,** -C(5)**H**), 4.20 (q, *J* = 7.3 Hz, 2H, imC(6)**H$_2$**), 3.86 (s, 3H, imC(8)**H$_3$**), 1.54 (s, 3H, acetate-C**H$_3$**), 1.40 (t, *J* = 7.3 Hz, 3H, imC(7)**H$_3$**)

$^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta_H$ (ppm): 172.53 (acetate-C(10)), 136.73 (imC(2)), 123.54 (imC(5)), 121.95 (imC(4)), 44.06 (imC(7)), 35.63 (imC(6)), 26.06 (acetate-C(9)), 15.15 (imC(8))

**Ionic liquid retrieved after the 1$^{st}$ cycle of recycling (IL-1):**

$^{1}$H NMR (400 MHz, DMSO-d$_6$) $\delta_H$ (ppm): 9.67 (s, 1H), 7.77 (d, *J* = 35.2 Hz, 2H), 4.20 (q, *J* = 7.3 Hz, 2H), 3.86 (s, 3H), 1.51 (s, 3H), 1.40 (t, *J* = 7.3 Hz, 3H)

$^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta_H$ (ppm): 173.26, 137.80, 123.53, 122.01, 43.87, 35.41, 26.29, 15.25

**Ionic liquid retrieved after the 2$^{nd}$ cycle of recycling (IL-2):**

$^{1}$H NMR (400 MHz, DMSO-d$_6$) $\delta_H$ (ppm): 10.10 (s, 1H), 7.83 (d, *J* = 38.3 Hz, 2H), 4.21 (q, *J* = 7.3 Hz, 2H), 3.87 (s, 3H), 1.55 (s, 3H), 1.39 (t, *J* = 7.3 Hz, 3H)

$^{13}$C NMR (101 MHz, DMSO-d$_6$) δH (ppm): 172.82, 137.51, 123.48, 121.92, 43.92, 35.48, 26.38, 15.20

**Ionic liquid retrieved after the 3$^{rd}$ cycle of recycling (IL-3):**

$^{1}$H NMR (400 MHz, DMSO-d$_6$) $\delta_H$ (ppm): 9.66 (s, 1H), 7.77 (d, *J* = 35.2 Hz, 2H), 4.20 (q, *J* = 7.3 Hz, 2H), 3.86 (s, 3H), 1.53 (s, 3H), 1.40 (t, *J* = 7.3 Hz, 3H)

$^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta_H$ (ppm): 172.65, 137.02, 123.51, 121.93, 44.01, 35.58, 26.30, 15.18

**Ionic liquid retrieved after the 4$^{th}$ cycle of recycling (IL-4):**

$^{1}$H NMR (400 MHz, DMSO-d$_6$) $\delta_H$ (ppm): 10.05 (s, 1H), 7.83 (d, *J* = 38.0 Hz, 2H), 4.21 (q, *J* = 7.3 Hz, 2H), 3.87 (s, 3H), 1.55 (s, 3H), 1.39 (t, *J* = 7.3 Hz, 3H)

$^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta_H$ (ppm): 172.99, 137.54, 123.50, 121.95, 43.93, 35.48, 26.34, 15.24

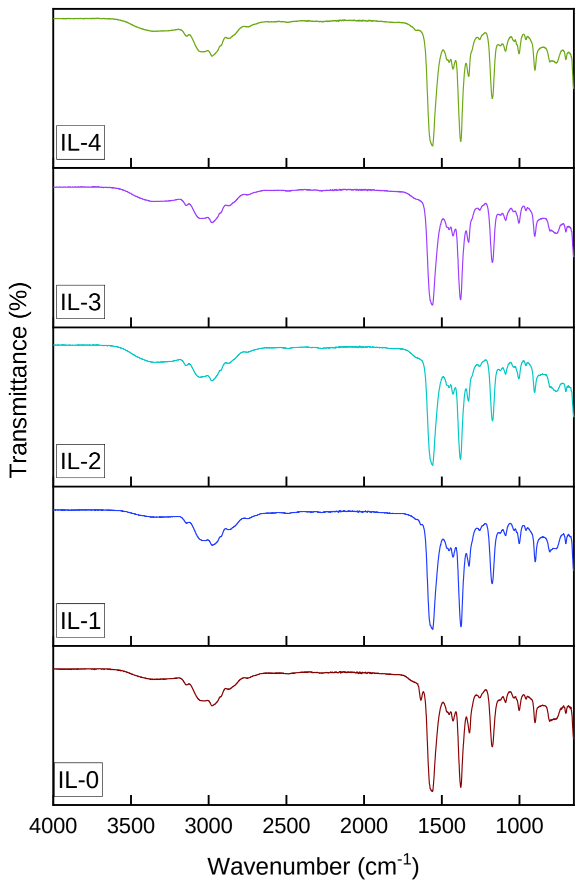



Figure S15: FTIR spectra of the freshly synthesised and recycled ionic liquid.

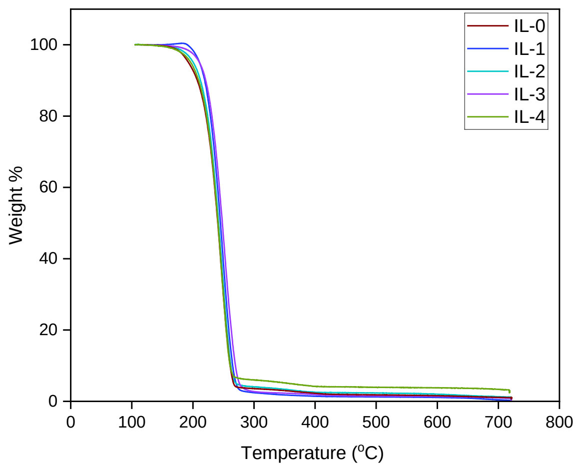



Figure S16: TGA curves of the freshly synthesised and recycled ionic liquid

Table S2: Main properties of different biogenic and conventional films

| | PLA | Chitosan | High Density Polyethylene (HDPE) | Low Density Polyethylene (LDPE) | Cellophane | PVA | starch | pvc | pcl | gelatin | pbat | pbs | Polyethylene terephthalate (PET) | polypropylene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **biobased** | Yes | Yes | Yes/No | Yes/No | Yes | No | Yes | No | No | Yes | No | Yes/No | Yes/ No | Yes/No |
| **Biodegradable** | Yes | Yes | No | No | Yes | Yes | Yes | No | Yes | Yes | Yes | Yes | No | No |
| **mechanical properties** | E = 3.0 ± 0.2 GPa TS = 69.1 ± 0.1 MPa EB = 126.3 ± 14.6 % [1]<br>TS = 20 MPa EB = 68 % E = 445 MPa[2]<br>E = 2.24 ± 0.04 GPa TS = 58.0 ± 2.8 MPa EB = 3.6 ± 0.2%[3] | TS = 6.64 ± 0.77 MPa EB = 79.13 ± 1.81 %[4]<br>TS = 55.2 - 64.3 MPa EB =11.9 - 13.7 %[5]<br>E = 4.5 - 6.41 MPa [6]<br>E = 3.1 GPa [7] | TS = 23 – 28 MPa EB = 7.5 - 10 mm/mm [9]<br>TS = 29.9 ± 2.4 MPa E = 609 ±34 MPa EB = 770± 45 %[10] | TS = 10 - 24 MPa EB = 129 - 591 % [11]<br>TS = 22 - 40 MPa EB = 393 - 734 E= 231 - 270 MPa[12] | TS = 73.60 ± 4.1 MPa EB = 8.03 ± 0.7 % E = 3.99± 4.0 GPa<br>TS = 40 - 125 MPa EB = 8% E = 0.9 - 3 GPa[13]<br>TS = 30.2 MPa EB = 372.3 % Ym = 892.1 MPa[14] | TS = 6MPa[15]<br>TS = 28.5 ± 3.0 MPa EB = 220%[16]<br>TS = 19.80 MPa E = 250 MPa EB = 145 %[17]<br>TS = 97.9 - 152.8 MPa E = 2.98 - 4.14 GPa EB =7.5 - 25 %[18] | TS = 3MPa EB = 15%[19] | TS = 26 - 32 MPa EB = 163 - 246 E = 76 - 99 MPa[12]<br>TS = 45.39 ± 4.64 MPa EB = 22.18 ± 2.53%[20] | TS = 17.94 ± 2.69 MPa E = 131.3 ± 12.4 MPa EB = 605.6 ± 43.95 %[21]<br>TS = 23.9 ± 5.0 MPa E= 129 ± 11 MPa EB = 8.0 ± 0.7%[22]<br>E = 225 MPa TS = 15 MPa[23] | TS = 82.69 ± 3.21 MPa E = 708.2 ± 10.54 MPa EB = 3.6 ± 1.45 %[21]<br>TS = 29.5 - 135.2 MPa EB = 1.32 - 10.20 %[24] | TS = 17.7 - 15.9 MPa EB = 637 - 547[25]<br>E = 81.0 ± 2.5 MPa EB = 689.5 ± 110.3% TS = 20.1 ± 2.4 MPa[26]<br>E = 75 MPa TS = 14 MPa EB = 800 %[23] | E = 725.6 ± 15.6 MPa EB =7.1 ± 0.3% TS = 29.6 ± 1.5 MPa[27] | E = 2.016 × 10 GPa TS = 50.45 MPa [27]<br>TS = 55 - 60 MPa E =2.8 - 3 GPa EB = 280 - 320 %[28] | TS = 20.32 MPa E =1015 MPa[29]<br>EB = 1000% E = 32 MPa TS = 14 MPa[30] |
| **OP (**$cm^3$ $m \cdot d^{-1} \cdot m^{-2} \cdot Pa^{-1}$**) / OTR** | $2.12*10^{-7}$ [31] | | $1.18*10^{-6}$ [10]<br>$5.4*10^{-7}$ [32] | $1.95*10^{-2}$ [33]<br>$2.1*10^{-6}$ [32]<br>$(13.4 \pm 2)*10^{-4}$ [12] | | $(2.65 - 141.7)*10^{-12}$ [18] | | $(6.5 \pm 1.1)*10^{-4}$ [12] | $25*10^{-6}$ $cm^2 \cdot STP/cm \cdot h \cdot bar$[23] | $(1.8 – 6.2)*10^{-9}$ [24] | $(8.54 \pm 0.02)*10^{-7}$ [26]<br>$7.5*10^{-6}$ $cm^2 \cdot STP/cm \cdot h \cdot bar$[23] | $(1.90 \pm 0.02)*10^{-7}$ [26] | $(1.18–2.8)*10^{-8}$ $cm^3$ $m \cdot d^{-1} \cdot m^{-2} \cdot Pa^{-1}$[25]<br>$4.62*10^{-8}$ $cm^3$ $m \cdot d^{-1} \cdot m^{-2} \cdot Pa^{-1}$ | $(565 \pm 0.9)*10^{-9}$ [34] |
| **WVP (**$g \cdot d^{-1} \cdot m^{-1} \cdot Pa^{-1}$**) / WVTR** | $3.45*10^{-6}$ [2]<br>$<2.6*10^{-7}$ [3] | $(0.23 \pm 0.002)*10^{-6}$ [4]<br>$(1.6 – 3.5)*10^{-4}$ [8] | $1.18*10^{-4}$ $g \cdot m^{-1} \cdot d^{-1}$ [32] | $0.21*10^{-6}$ [33]<br>$3.78*10^{-4}$ $g \cdot m^{-1} \cdot d^{-1}$ [32]<br>$(20 \pm 4)*10^{-3}$ | $14*10^{-6}$ [36] | $0.60*10^{-6}$ [17] | $0.65*10^{-7}$ $g \cdot m^{-1} \cdot d^{-1}$ [19] | $0.78 \pm 0.1$ $g \cdot m^{-1} \cdot d^{-1}$ [12] | $(1.54 \pm 0.04)*10^{-6}$ [35] | $(22.4 – 45.2)*10^{-6}$ [37] | $(11.0 \pm 0.12)*10^{-6}$ [26] | $(4.3 \pm 0.02)*10^{-6}$ [26] | $(9.5 \pm 0.8)*10^{-8}$ $g \cdot d^{-1} \cdot m^{-1} \cdot Pa^{-1}$ | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | (4.74 ± 0.05)*$10^{-6}$ [35] | | $g \cdot m^{-1} \cdot d^{-1}$ [12] | | | | | | | | | | |
| **$T_m$ ( °C)** | 146[2]<br>140.8 - 163.4 [31] | | 134 [32]<br>130[38] | 113[32]<br>107.6 [38]<br>106.3[33] | | | 141.61[19] | | | | 120.9[26] | 101.8, 113.6 [26] | 250.2[39]<br>245[31] | 140[40] |
| **$T_g$ ( °C)** | 61[2]<br>66.1 - 71.4[31] | 171 – 175[5] | | | | | | 93.5[20] | | | | | 60 - 84[28]<br>78.98[39] | |
| **Wca (º)** | 79.7 - 81.2 [1] | | | 72[11] | 12/35[41] | | | | 84.8 ± 3.4[21] | | | | | 92[40] |
| **$T_d$ ( °C)** | 384.8[42] | 107, 292[4] | 460[10] | 456.2[11] | | 250, 450[14] | 250-270[19] | 287.7, 453.8[20] | 380[22] | | 407[26] | 402[26] | | |

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