Flexible and high performing polymer electrolytes obtained by a UV-induced polymer-cellulose grafting

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SUPPORTING INFORMATION

S1. XPS Survey spectra

XPS analysis was performed and the results for the G-SW40 grafted sample were compared to those obtained for both the pristine SW-40 cellulose handsheet and the pure GA after UV-irradiation. Figure S1 shows the survey spectra obtained by scanning the binding energies between 0 and 1200 eV. Oxygen (peak at 531 eV) and Carbon (peak at 285 eV) are the two species detected in all the samples.

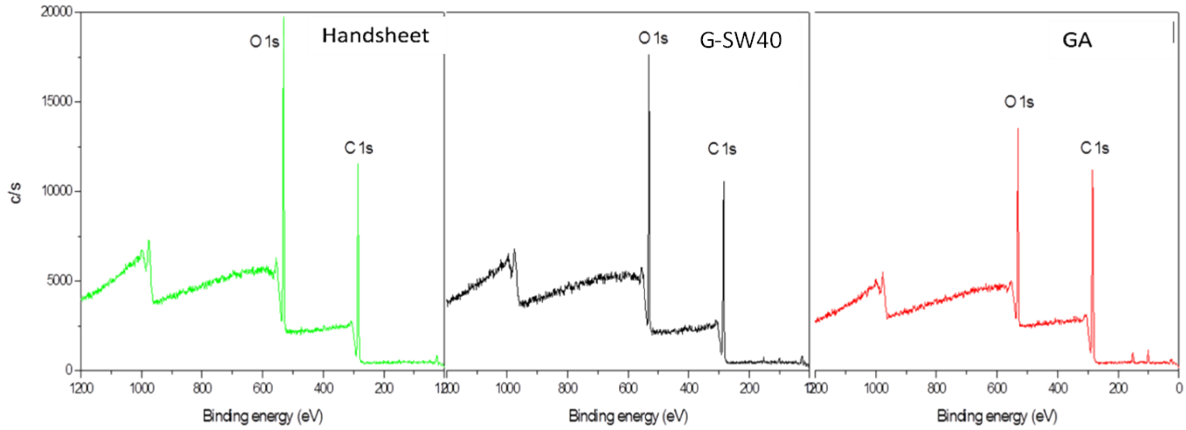

Figure S1. XPS survey spectra obtained for the pristine SW-40 cellulose handsheet (left-hand plot), G-SW40 grafted sample (black line, middle plot) and pure GA (red line, right-hand plot).

Table 1 reports the atomic concentration relative to the peaks O1s ans C1s and their ratio, together with the values calculated on the basis of the molecular formula. The structure of the glucose ring in cellulose was considered for the handsheet sample while the structure of GA was considered for the third sample.

Table S1 Carbon and Oxygen content in the three samples analyzed by XPS. The O/C ratios, both measured and calculated on the basis of the chemical structure, are also shown.

Sample	C 1s	O 1s	O/C measured	O/C calculated
SW-40	63.5	36.5	0.57	0.83(pure cellulose)
G-SW40	66.5	33.5	0.50	-
GA	71.0	29.0	0.41	0.50

The relative intensity of the Oxygen signal, thus the measured O/C ratio, decreases when GA is grafted to the handsheet. Comparing the experimental values with those calculated on the basis of the molecular formulae, one can observe that the O/C values obtained from the measurement were lower than those expected. The major differences between the experimental and the calculated value were obtained for the pristine handsheet, which was quite expected. Indeed, being the handsheet a material of natural origin its composition is variable, thus we calculated the O/C value by considering the structure of the pure cellulose but it is known from the literature[1-3] that lower values of this ratio can be attributed to the presence of lignin.

S2. Kinetic plots of the reactive group conversion in the G-SW40 grafted formulation

The percentage of conversion of the double bond of the acrylic groups and the opening of the epoxy rings of the monomers, during the UV exposure was evaluated by kinetic studies using real-time FT-IR technique. The influence of the PIs was evaluated. The overall reactions were monitored during irradiation through the change in the intensity of the absorption band of the methacrylic groups at around 1634 cm^{-1} and the epoxy ring at 910 cm^{-1} (only for samples B and C); the C=O bond at 1730 was used as an internal standard. Conversion curves are shown in Figure S2.

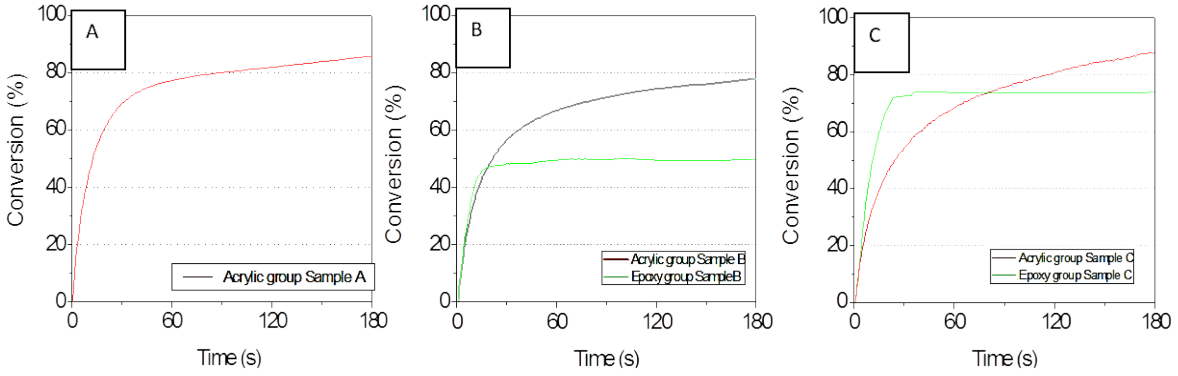

Figure S2. Kinetic plots of the conversion of the acrylic and epoxy (when present) groups in: a) sample A composed of BEMA:PEGMA in the 50:50 ration along with the addition of 3% of RPI, b) sample B composed of BEMA:PEGMA:GA in the 47.5:47.5:5 ratio along with the addition of 3% of RPI, and c) sample C composed of BEMA:PEGMA:GA in the 47.5:47.5:5 ratio along with the addition of 3% of RPI and 2% of CPI.

As visible in plot a) of Figure S2, the double bond reaction was very fast in the presence of RPI and reached the 70% in about 30 sec, resulting in more than 80 % after 3 min. The conversion was not quantitative as PEGMA-1100 is highly viscous and tends to crystallise. In fact, it is a waxy solid material at ambient temperature and was solubilised in BEMA by heating. However, after polymerisation, the longer pendant –EO– chains tend to recrystallize[4, 5].

As shown in plot b) of Figure S2, when GA is added to the BEMA:PEGMA mixture in the presence of RPI, the speed of conversion of the double bond of the acrylic group decreased, reaching the 80% after 3 min. At the same time, the epoxy ring also partially reacted by thermal reaction even if CPI was not present. In fact, being the acrylic reaction exothermic, the heat produced may trigger the polymerisation of epoxides.(20) As shown in plot c), when both CPI and RPI were added to the mixture, the double bond conversion decreased with respect to what observed for samples A and B. nevertheless, it quantitatively increased up to ~ 90%, due to the presence of CPI which generates radicals upon UV-irradiation. In the presence of both the PIs the epoxy ring opening was also faster, and a quantitatively higher conversion was reached, that is up to 70 % after less than 30 sec.

S3. TGA Analysis

The thermal stability of sample CRPE-D was assessed by TGA measurements and the profile is shown in Figure S3. The first decomposition step (below 200 °C) was linked to the presence of the organic solvent that evaporated at relatively low temperatures.

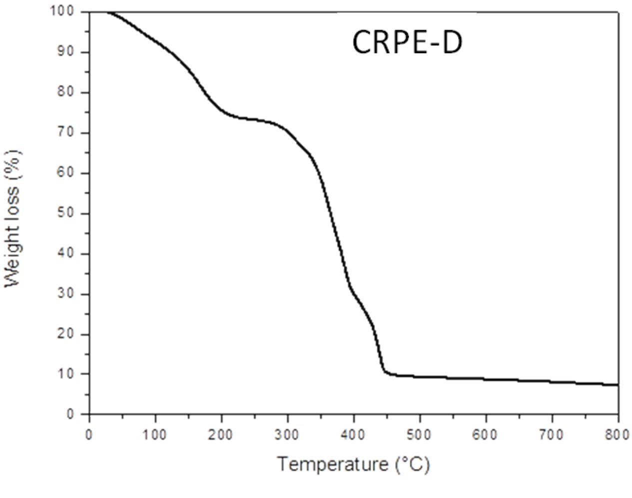

Figure S3. TGA plot of sample CRPE-D used for electrochemical testing.

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