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Supporting Information for

Mineral plastic hydrogels from the cross-linking of polyacrylic acid and alkaline earth or transition metal ions

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S1 Experimental Section

S1.1 Synthesis of M-PAA hydrogels

All reagents were purchased commercially (Sigma-Aldrich, Merck or Roth) and used without further purification. Into a vigorously stirred 0.1 M aqueous solution of PAA (M_w ~ 100,000 g/mol) and 0.1 M $M^{2+}Cl_2$ (M = Mg^{2+}, Sr^{2+}, Ba^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}), a 0.1 M Na_2CO_3 solution was added dropwise at room temperature with an addition rate of ~3 ml/min. The pH value of reaction mixture was adjusted with the amount of Na_2CO_3 addition. A sticky precipitate gradually formed around the stirring bar accompanied with a turbid solution containing non-gelling fractions. After 1 h, the turbid solution was discarded and the hydrogel was washed with deionized water several times until the supernatant solution was clear. All the hydrogels were air-dried overnight at 50 °C.

S1.2 Synthesis of Ca-PAA hydrogel

By increasing the pH of a vigorously mixed, nitrogen-saturated solution of 0.1 M PAA (M_w ~ 100,000 g/mol) and 0.1 M $CaCl_2$, with 0.1 M nitrogen-saturated sodium hydroxide solution (under inert atmosphere to exclude carbonate development from atmospheric CO_2), complete hydrogel formation (Ca-PAA) was obtained within 1 h with the pH increasing from ~ 2 to ~ 7. The resultant hydrogel was purified as described above and was air-dried for 1 d at 50 °C.

S1.3 Reaction with trivalent metal ions (Fe^{3+} and Al^{3+})

All the attempts to prepare the precursor solution of 0.1 M $FeCl_3$ and 0.1 M PAA (M_w ~ 100,000 g/mol) lead to the precipitation of non-swellable Fe-PAA agglomerates ($pH_{solution}$ ~ 1.6).

In the case of Al^{3+}, into a vigorously stirred 0.1 M aqueous solution of PAA (M_w ~ 100,000 g/mol) and 0.1 M $AlCl_3$, a 0.1 M Na_2CO_3 solution was added at room temperature (addition rate about 3 ml/min). The pH value of the mixture, adjusted by the amount of base addition, was tested in the range of pH = 2-9. All the experiments resulted in non-swellable and non-plastic agglomerates. Also, the usage of 0.1 M NaOH solution instead of Na_2CO_3 in the range of pH = 2-9 showed no hydrogel formation.

S1.4 Staining of Mn-PAA hydrogel with Toluylene red

5 mg of Toluylene red (3-Amino-7-dimethylamino-2-methylphenazine hydrochloride, purchased from Fluka) was added to 10 ml of the mixture of 0.1 M PAA ($M_w \sim 100{,}000$ g/mol) and 0.1 M $MnCl_2$. Then, 5 ml of 0.1 M Na_2CO_3 solution was slowly added ($pH_{solution} \sim 6.4$). The dark red hydrogel gradually formed around the stirring bar and the supernatant solution was discarded. After that, the colored hydrogel was washed with deionized water several times.

S2 Characterizations

Thermogravimetric analysis of dried hydrogels was carried out on a Netsch Jupiter STA 449 F3 by heating from 30 to 1200 °C with a heating rate of 10 K/min under air flow. Energy dispersive X-ray spectra (EDX) were acquired on a Hitachi Table-Top SEM TM3000. ATR-FTIR was carried out on a Perkin Elmer Spectrum100 FTIR (equipped with a diamond ATR crystal). All pH values were measured with a calibrated ELECTRODE BLUELINE 14PH (pH0-14/-5-100°C/3M KCl) from Schott-Instruments. The nanoindentation tests were performed using CSM Instruments Ultra Nanoindentation tester with Vickers indenter. The rheological behavior of hydrogels was investigated by a HAAKE MARS modular advanced rheometer using 25-mm parallel-plate geometry at 25 ºC in the oscillation mode. Atomic absorption spectroscopy for manganese quantification was performed on a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer using a Perkin Elmer Intensitron^{TM} lamp in an acetylene/oxygen flame.

S2.1 Energy Dispersive X-Ray Spectroscopy (EDX)

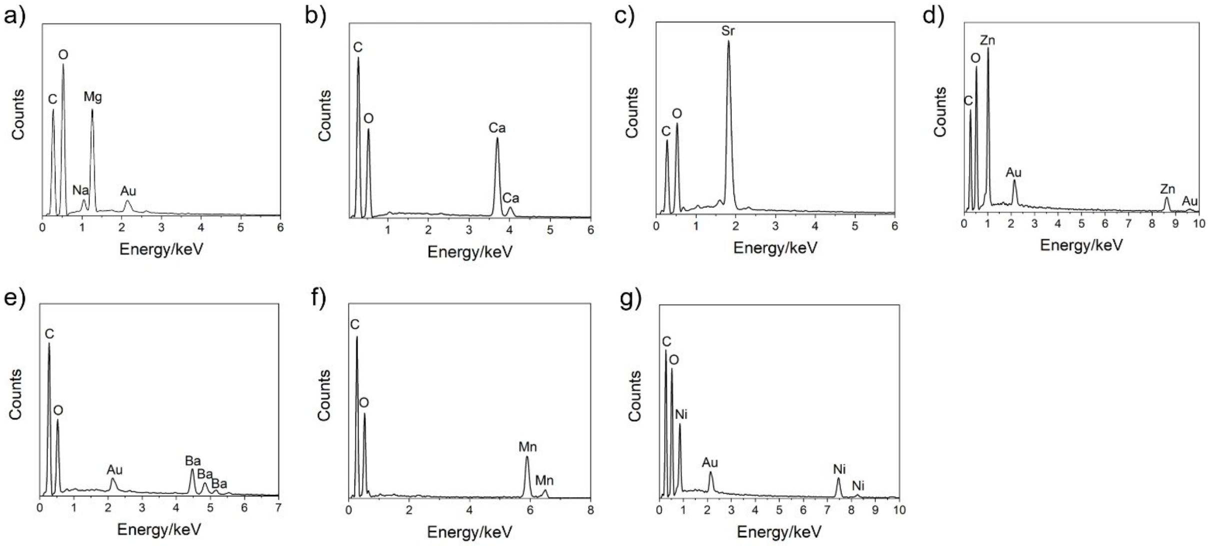


Figure S2.1 EDX spectra of all synthesized hydrogels in the dry state: a) Mg-PAA, b) Ca-PAA, c) Sr-PAA, d) Zn-PAA, e) Ba-PAA, f) Mn-PAA, g) Ni-PAA. Mg-PAA contains traces of sodium due to its oil-like texture which hinders processing. Note that presence of Au results from gold-covering of the sample (Mg-PAA, Ba-PAA, Ni-PAA and Zn-PAA).

S2.2 Thermogravimetric Analysis

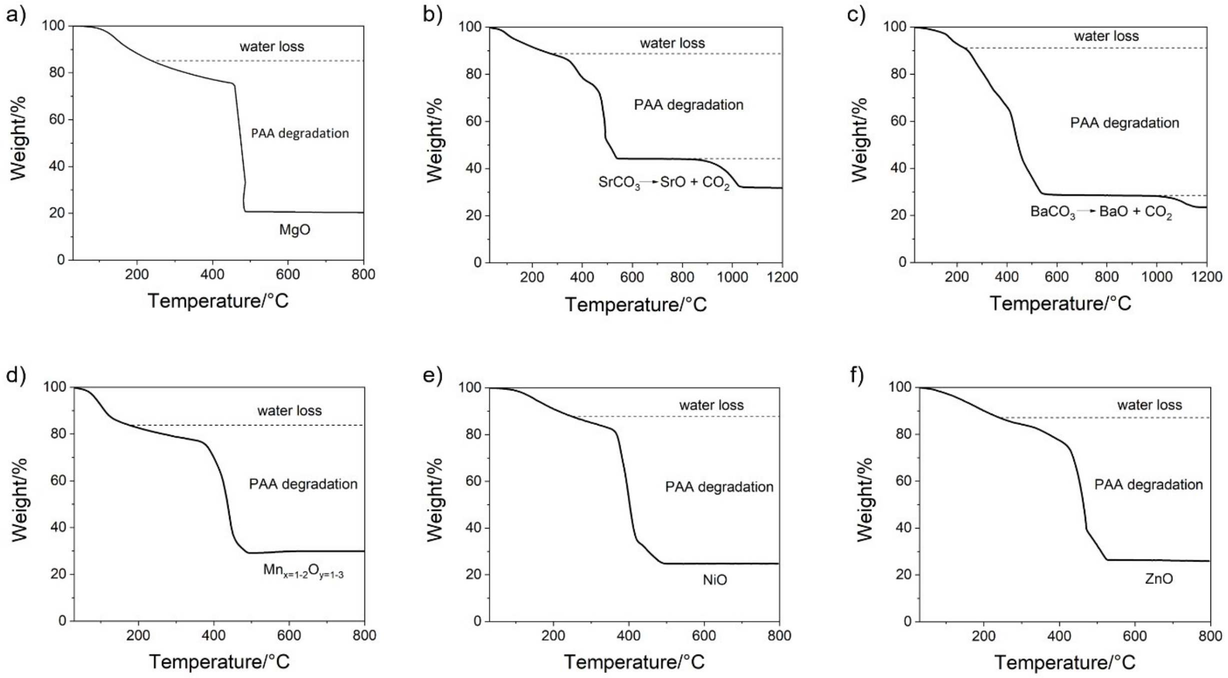


Figure S2.2 TGA traces of all synthesised hydrogels in the dried state. As temperature increases, loss of water and PAA degradation occur successively. Analogous to ACC-PAA, b) Sr-PAA and c) Ba-PAA exhibits definite decay of $SrCO_3$ and $BaCO_3$, respectively. In contrast, a) Mg-PAA, d) Mn-PAA, e) Ni-PAA and f) Zn-PAA show no distinct decomposition (step) of respective metal carbonate due to the decomposition temperatures in the region of PAA degradation. The metal content was calculated via the finally formed respective metal oxide. Note that, several possible oxidation states in the case of manganese were considered which results in an expanded uncertainty.

S2.3 Rheology measurements

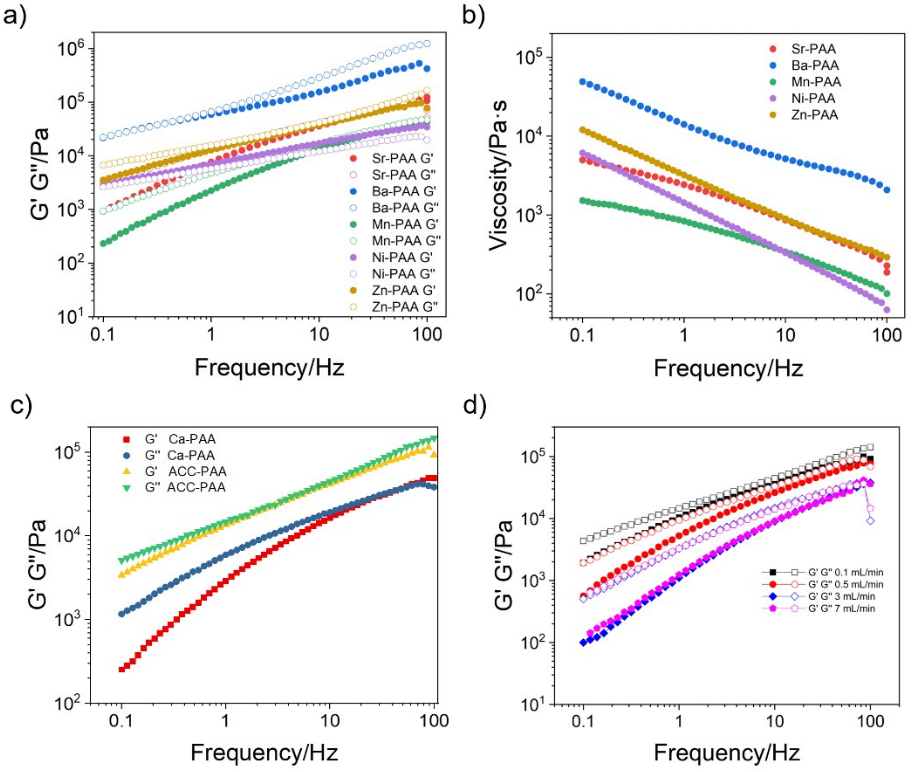
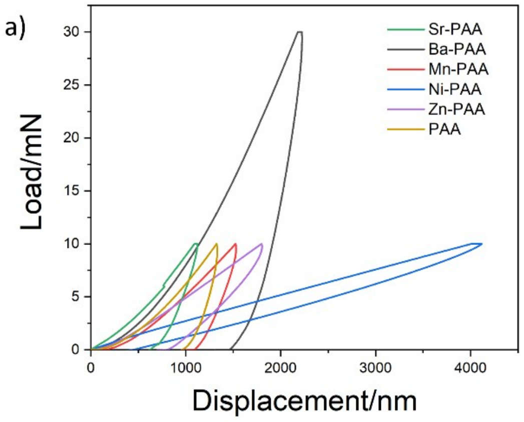


Figure S2.3 Rheological behaviour of swollen hydrogels. a) The diagram shows frequency dependencies of the storage (G’) and loss (G’’) moduli of all the hydrogels. b) Illustration of their viscosity as a function of shear rate. c) Frequency dependence of storage (G’) and loss (G’’) moduli of ACC-PAA hydrogel compared with Ca-PAA hydrogel. d) Frequency dependence of storage (G’) and loss (G’’) moduli of Mn-PAA hydrogels at different addition rates of Na_2CO_3.

S2.4 Nanoindentation measurements



b)

	Hardness/ MPa	Modulus/ GPa
Sr-PAA	451	7.5
Ba-PAA	405	13
Mn-PAA	201	6.0
Ni-PAA	69	0.25
Zn-PAA	148	2.4
PAA	271	9.7

Figure S2.4 a) The diagram shows the loading-unloading nanoindentation curves of dried mineral plastic films (Sr-PAA, Ba-PAA, Mn-PAA, Ni-PAA, Zn-PAA and pure PAA for comparison). b) The summary of hardness and reduced modulus determined by nanoindentation measurements of the dried films is given in the table on the right side.

S2.5 Fe^{3+}-PAA and Al^{3+}-PAA agglomerates

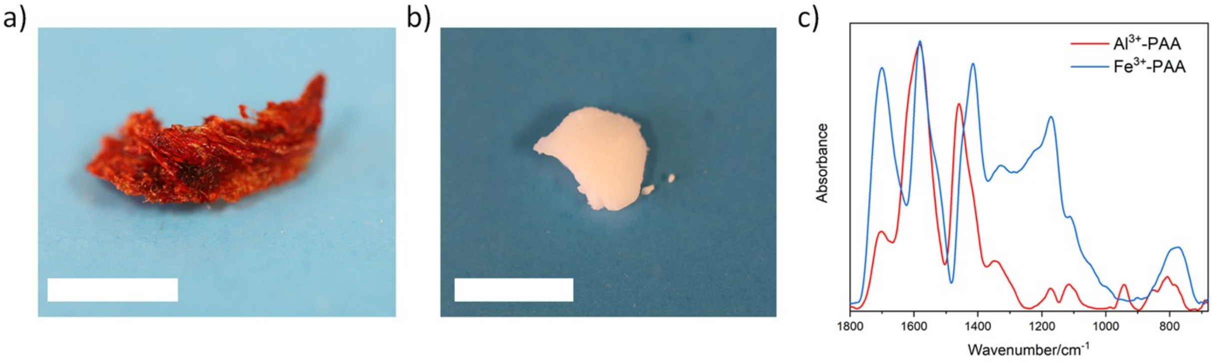


Figure S2.5 a) Image of dried Fe^{3+}-PAA and b) dried Al^{3+}-PAA agglomerates. The formed agglomerates are non-plastic and non-swellable. Scale bar = 1 cm. c) Normalized ATR-FTIR spectra of Al^{3+}-PAA and Fe^{3+}-PAA agglomerates. Low degree of deprotonated PAA for Fe^{3+}-PAA results from the agglomeration at low pH of the reaction mixture. Both spectra indicate the complexation between carboxylates and respective trivalent metal ions (around 1580 cm^{-1}).