Supplementary Materials:

An In Situ Wet Chemical Methodology to Fabricate Hydroxyapatite based Nanostructured Biocomposites**

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On the determination of timing of polymer solution addition to the reaction mixture:

The pH of the reaction mixture ($Ca(OH)_2$ + H_3PO_4) is maintained as the acid is added due to the dissolution of non-dissociated $Ca(OH)_2$. The dissolution of $Ca(OH)_2$ is accompanied by the consumption of hydroxyl ions and calcium ions as a result of neutralization and ACP formation. However, the pH of the reaction mixture starts decreasing after the complete dissolution of $Ca(OH)_2$ (event 1) and the ACP starts transforming into crystalline HA (event 2) once the former reaches a critical concentration, C^* (C* is about 10.5 mM at 30 °C and 12.6 mM at 95 °C and would be slightly greater than 12.6 mM at 98 °C)[1S]. Therefore, the polymer solution should be added to the reaction mixture before the ACP particles starts transforming into crystalline HA for maximum interaction between ACP and polymer and just after the pH of the reaction mixture starts to decrease from its initial value to avoid precipitation of, particularly, chitosan. The equation to determine the time at which the pH of the reaction mixture starts to decrease is given below[1S].

$$[Ca(OH)_2] = \left(\frac{k_{sp}}{4}\right)^{\frac{1}{3}} (V_i + fr \cdot t) + \frac{3}{2} C \cdot fr \cdot t \qquad (1S)$$

-where, $[Ca(OH)_2]$ is the total dissolved quantity of $Ca(OH)_2$, (mol), k_{sp} is the solubility product of $Ca(OH)_2$, (the unit for the term $(k_{sp}/4)^{1/3}$ is mol/L), V_i is the initial volume of suspension (L), fr is the acid flow rate (4×10^{-3} L/min), t is the time (min), and C is the concentration of H_3PO_4 (mol/L)[1S].

The k_{sp} of $Ca(OH)_2$ at 98°C is calculated to be 1.60×10^{-6} using the vant Hoff's equation (Eqn. 2S). The k_{sp} of $Ca(OH)_2$ at 25°C is 6.6×10^{-6} and the heat of dissociation, ΔH_r is −17.88 kJ/mol for the reaction, $Ca(OH)_2 \rightarrow Ca^{2+}$ (aq) + $2OH^-$ (aq)[2S].

$$\ln \frac{k_{sp}}{k_{sp}^{25}} = \frac{\Delta H_r}{R} \left(\frac{1}{298} - \frac{1}{T}\right) \qquad (2S)$$

-where, R is the universal gas constant (8.314 J/mol-K) and T is the absolute temperature.

Therefore, in the suspension containing 15mmol $Ca(OH)_2$ in 225mL water at 98°C, about 1.66 mmol of $Ca(OH)_2$ dissociates into Ca^{2+} and OH^- ions. The pH of the reaction mixture starts to

decrease (event 1), in the present study, after approximately 50 minutes (or about 198 mL) of H_3PO_4 addition The ACP concentration in the suspension would be 9.365 mmol/L (or 3.96 mmol in 423 mL) which is well below the critical concentration. Similarly, in a suspension of 15mmol $Ca(OH)_2$ in 150 mL water, the pH start decreasing after adding 143 mL acid and the ACP concentration would be 14.6 mmol/L (or 4.28 mmol in 293 mL). Figure 1S shows a schematic describing the effect of concentration of $Ca(OH)_2$ suspension on the events 1 and 2. The concentration of dissolved $Ca(OH)_2$ and hence the concentration of OH^- ions until the time t_1 can accurately be calculated using Eqn. 1S. After the time t_1, Eqn. 1S can not be used to calculate the concentration of OH^- ions as the consumption of OH^- ions is not only due to the neutralization by H^+ ions, but also due to the formation of crystalline HA from ACP. However, the variation of pH with time after the time t_1 is drawn following the experimentally observed trend of the same[1S]. The increased rate of decrease of conductivity, as a result of consumption of large number of ions after the time t_2 is an indication of the start of ACP $\rightarrow$ HA transformation, via a combination of the following schemes.

$$Ca_3(PO_4)_2 + 2Ca^{2+} + PO_4^{3-} + OH^- \rightarrow Ca_5(PO_4)_3(OH)$$

$$3Ca_3(PO_4)_2 + Ca^{2+} + 2OH^- \rightarrow 2Ca_5(PO_4)_3(OH)$$

$$5Ca_3(PO_4)_2 + 3OH^- \rightarrow 3Ca_5(PO_4)_3(OH) + PO_4^{3-}$$
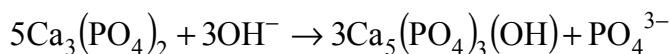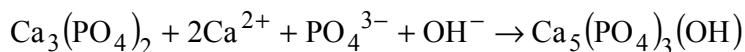
Information related to TGA:

The weight fraction of nHA in composite films is measured using Equation 1 given in the experimental section, whose derivation is given below. It is assumed that the weight loss in composite films is only from the polymers, which is true as HA does not degrade temperatures below 650°C.

$$W_p + W_c = W_{cp} \tag{3S}$$

$$W_{ash} + W_c = W_r \tag{4S}$$

-where, W_p is weight of polymer, W_{ash} is weight of residue in pure polymer films after heating, W_c is weight of nHA, W_{cp} is weight of composite and W_r is weight of residue in the composite. By subtracting Eqn. 4S from Eqn. 3S, we eliminate the weight of HA in both the composite and the residue. Thus,

$$W_p - W_{ash} = W_{cp} - W_r \qquad \text{or} \quad \frac{W_p - W_{ash}}{W_p} = \frac{W_{cp} - W_r}{W_p} \qquad \text{or} \quad W_p = \frac{W_{cp} - W_r}{f} \tag{5S}$$

-where $f = (W_p - W_{ash})/W_p$ is essentially the weight loss in pure polymer film. Equation 5S estimates the weight of polymer in the composite. The final nHA content in the composite is given by Eqn. 6S.

$$\frac{W_c}{W_{cp}} = \frac{W_{cp} - W_p}{W_{cp}}$$

(6S)

By substituting Eqn. 5S for Wp in Eqn. 6S, we get

$$\frac{W_c}{W_{cp}} = 1 - \frac{W_{cp} - W_r}{f W_{cp}} = 1 - \frac{\% \text{ wt. loss in composite}}{\% \text{ wt. loss in polymer}}$$

(7S)
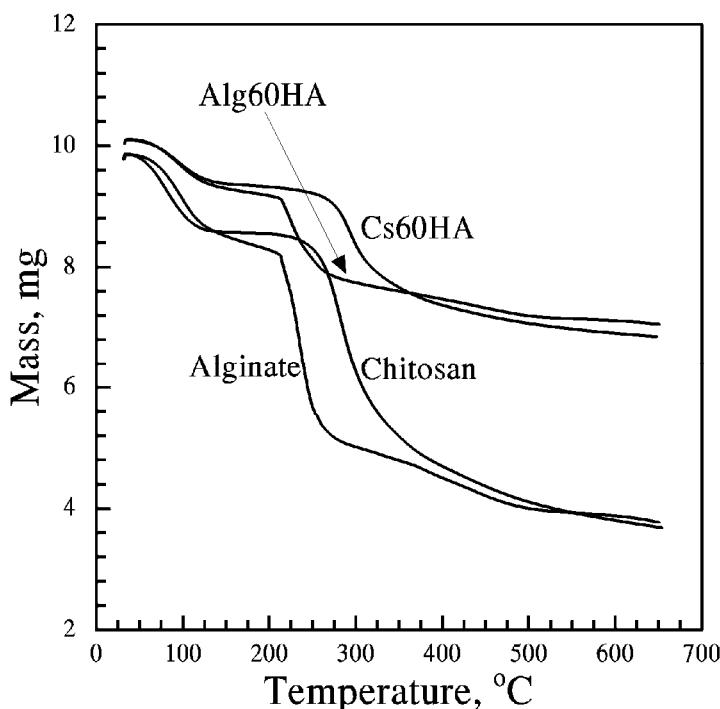
Figure 1S. TGA thermograms of polymers and hybrid films.

Table 1S: Weight loss and weight fraction of HA measured via TGA thermograms of films.

Material	Weight loss (%)	Estimated nHA content, (Wt. %)
HCHO treated chitosan	63.5	0
CS-60nHA	27.8	56.2
Sodium Alginate	64.5	0
SA-60nHA	28.9	55.2

*Stress vs. Strain curves of polymer and composite films:*
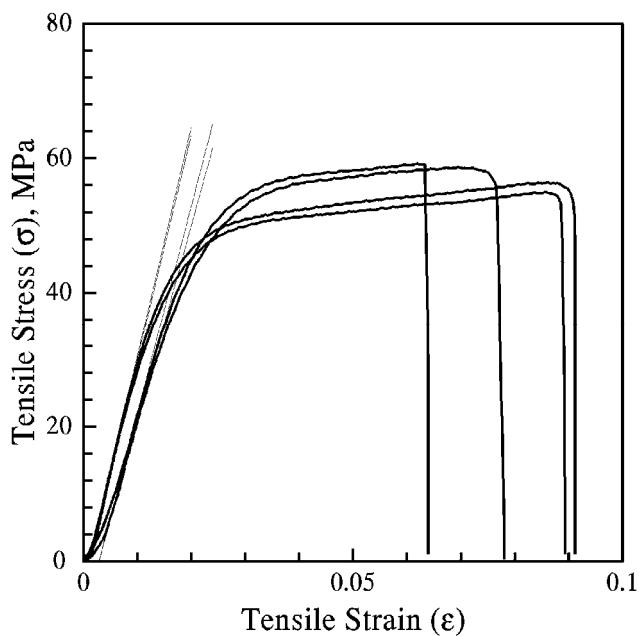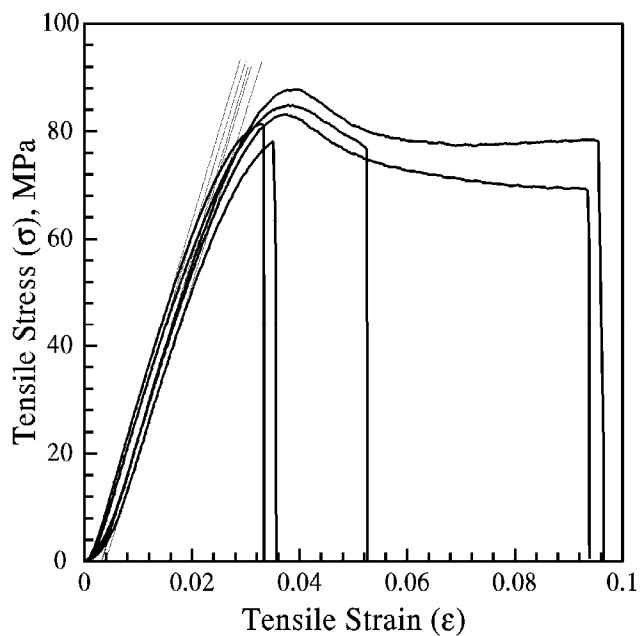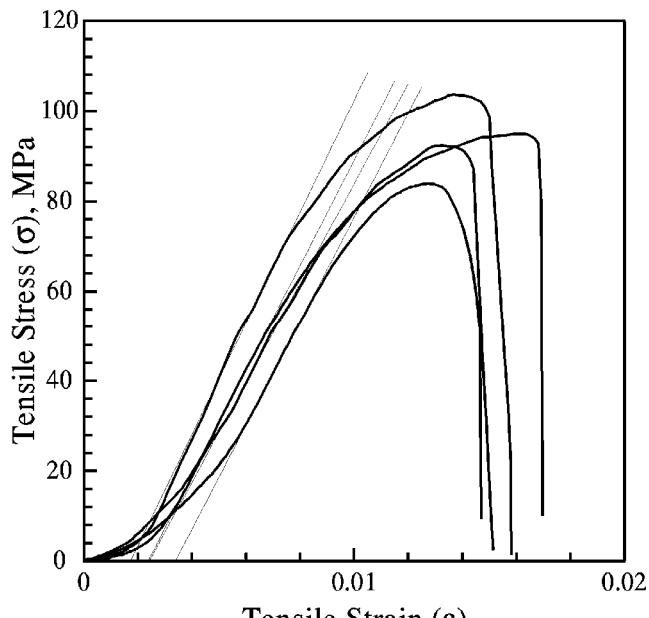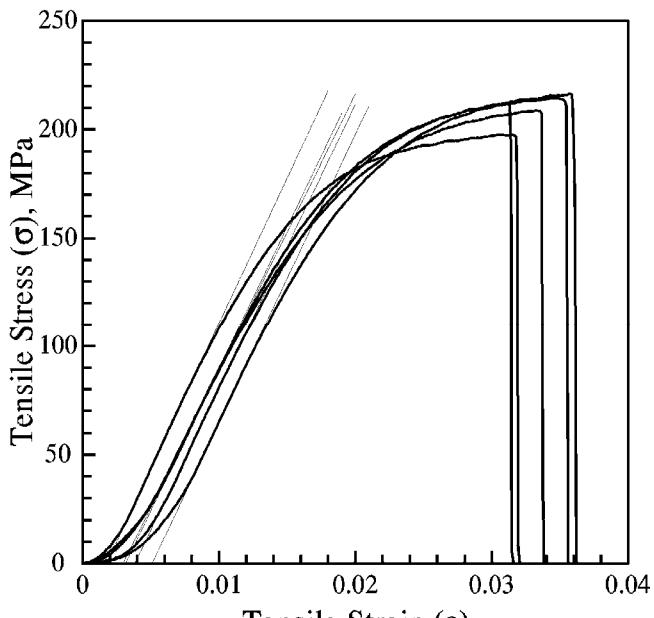
Figure 2S: Stress vs. Strain curves of (a) sodium alginate, (b) formaldehyde treated chitosan, (c) SA-60nHA and (d) CS-60nHA films. Note the changed x- and y- axes scale.

Reference

1S. Prakash, K. H.; Kumar, R.; Ooi, C. P.; Cheang, P.; Khor, K. A. *J. Phys. Chem. B* **2006**, *110*, 24457-24462.

2S. Thomas J. J.; Rothstein, D.; Jennings, H. M.; Christensen, B. J. *Cement and Concrete Res.* **2003**, *33*, 2037-2047.