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# Reinforcement of Alginate-Gelatin hydrogels with Bioceramics for biomedical applications: a comparative study

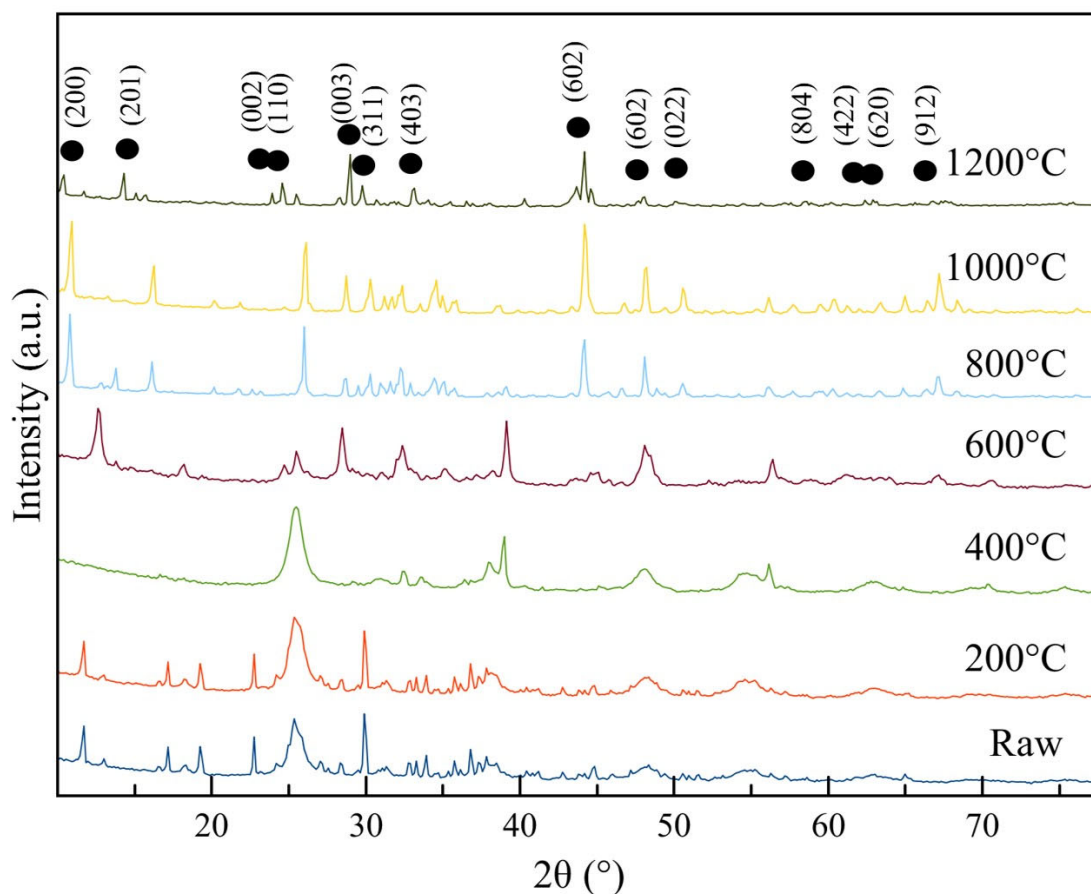
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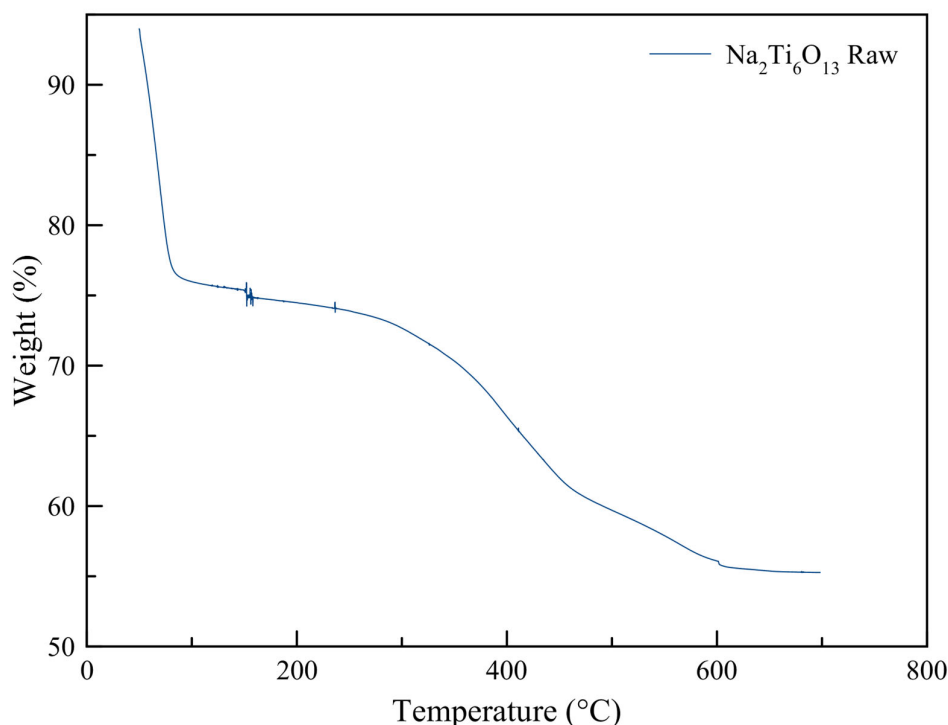
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$\text{Na}_2\text{Ti}_6\text{O}_{13}$

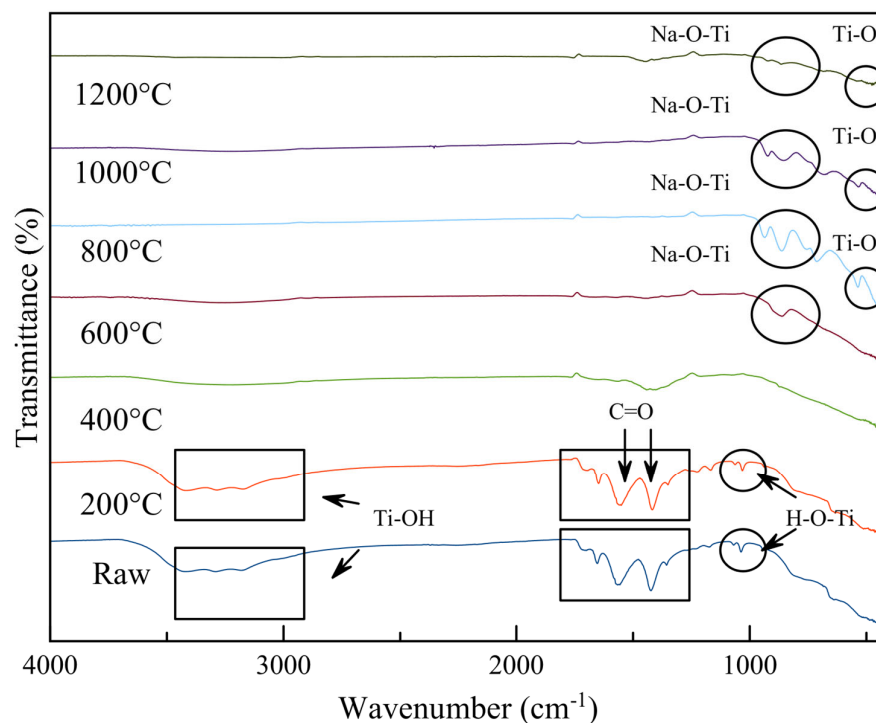
Figure S1. X-ray diffractogram of  $\text{Na}_2\text{Ti}_6\text{O}_{13}$  synthesis with different temperatures of calcination until 1200°C

The pronounced peaks of figure S1 indicate the XRD patterns of the samples synthesized from sodium acetate and titanium butoxide (IV), which are indexed to  $\text{Na}_2\text{Ti}_6\text{O}_{13}$  phase (monoclinic structure) space group. Prominent peaks belong to Anatase ( $\text{TiO}_2$ ) in lower temperatures, indicating the starting materials have been almost turning into  $\text{Na}_2\text{Ti}_6\text{O}_{13}$  products at  $1200^\circ\text{C}$ . At lower temperatures below  $1000^\circ\text{C}$  it can be seen different peaks corresponding to Anatase ( $\text{TiO}_2$ ), which peaks crystal structure (2theta) at  $25^\circ$ ,  $39^\circ$  and  $47^\circ$ , obtained from ICSD (01-071-1168), and Rutile ( $\text{TiO}_2$ ) since  $600^\circ$  with  $27^\circ$ ,  $48^\circ$  and  $56^\circ$ , before the desired crystal at the  $1200^\circ\text{C}$  of calcination(1) (2).



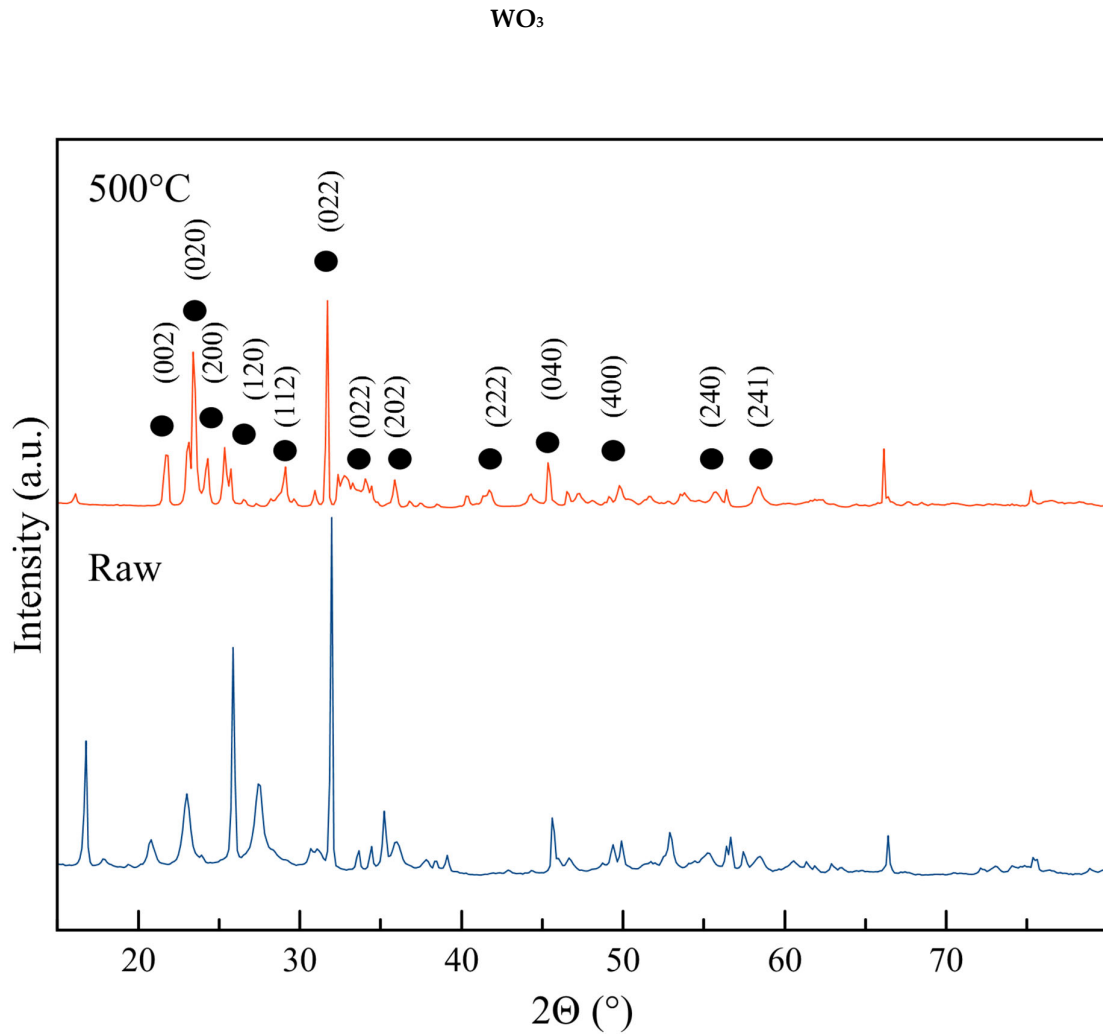
**Figure S2.** Thermogravimetric analysis spectra from pre-calcined  $\text{Na}_2\text{Ti}_6\text{O}_{13}$

The evolution of gravimetric loss is elucidated in the range from around  $90^\circ\text{C}$  to  $150^\circ\text{C}$  the last of 25% of weight due to the loss of water and hydroxyl groups that are coordinated to the initial pre-calcined samples due to solvents as tert-butanol, deionized water, and coordinated water bonds from sodium acetate that are used in thermal synthesis step before calcination at high temperatures. A second weight-loss of 30% from  $250^\circ\text{C}$  to  $600^\circ\text{C}$  represents the loss of carbonyl from sodium acetate and by the rearrangements and loss of oxygen atoms until getting the desired structure (3).



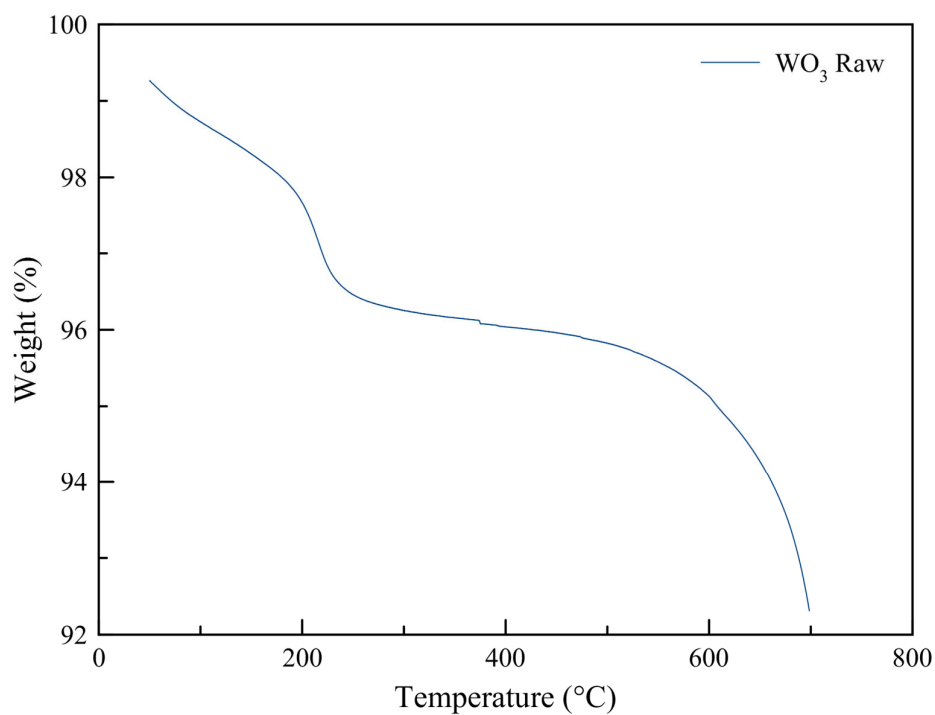
**Figure S3.** FT-IR spectra from pre-calcined raw  $\text{Na}_2\text{Ti}_6\text{O}_{13}$  material to calcined higher temperatures

FT-IR studies from figure S5 show that the bands at  $1730\text{ cm}^{-1}$  and  $3150\text{ cm}^{-1}$  are related to the bending and stretching modes of the chemisorbed or interlamellar water molecules. It is essential to mention that the shoulder at  $2900\text{ cm}^{-1}$  belongs to the interaction between Ti-OH ions at temperatures below  $400^\circ\text{C}$ . When the temperature increases in post-synthesis, that the signal from water was removed, and the Ti-OH bonds were modified. Sodium titanates contain Ti-O and Ti-OH is stretching and bending vibration bands with different intensities in the region  $500\text{--}1000\text{ cm}^{-1}$ . The peak at  $910\text{ cm}^{-1}$  corresponds to Na-O-Ti, and bonds in  $\text{TiO}_6$  octahedra appear at  $600^\circ\text{C}$  and above this temperature. The small peak at  $974\text{ cm}^{-1}$  is due to the bending vibrations of Ti-OH non-bridging bonds in the as-made sample. The alkali-oxygen vibrations usually provide absorption bands at  $1440$ ,  $1370$ ,  $1060$ , and  $880\text{ cm}^{-1}$ . The short peaks near  $500\text{ cm}^{-1}$  correspond to Ti-O when achieving calcination up to  $600^\circ\text{C}$  or higher temperatures until  $1200^\circ\text{C}$ . The sharp peak at  $1460\text{ cm}^{-1}$  of the dehydrated sample is attributable to new alkali-oxygen (Na-O). The low-intensity broadband in the  $3200\text{--}3600\text{ cm}^{-1}$  region and the band centered at  $1625\text{ cm}^{-1}$  are assigned to O-H stretching and deformation vibrations of weakly bound water, giving evidence for the existence of Ti-OH or Ti=O groups due to Titanium(IV) butoxide, that was used in the synthesis protocol as the precursor of titanium ions meanwhile the two bands with high intensity at raw, and  $200^\circ\text{C}$  correspond to carbonyl groups which are from the sodium acetate that disappear at higher temperatures. Peaks corresponding to the bending vibrations of the Ti-O groups at  $506$  and  $448\text{ cm}^{-1}$  converge into a broader peak centered at around  $480\text{ cm}^{-1}$  seen from  $800^\circ\text{C}$  to  $1200^\circ\text{C}$ ; this by the elimination of hydration and the rearrangement of atoms. The shoulder at  $878\text{ cm}^{-1}$  is characteristic of the Na-O bending of the Na-O-Ti bond of sodium titanates, whereas the minimal signal at  $1061\text{ cm}^{-1}$  can be attributed to the respective bending vibration H-O-Ti of the hydroxyl titanates (4, 5), (6), (7).



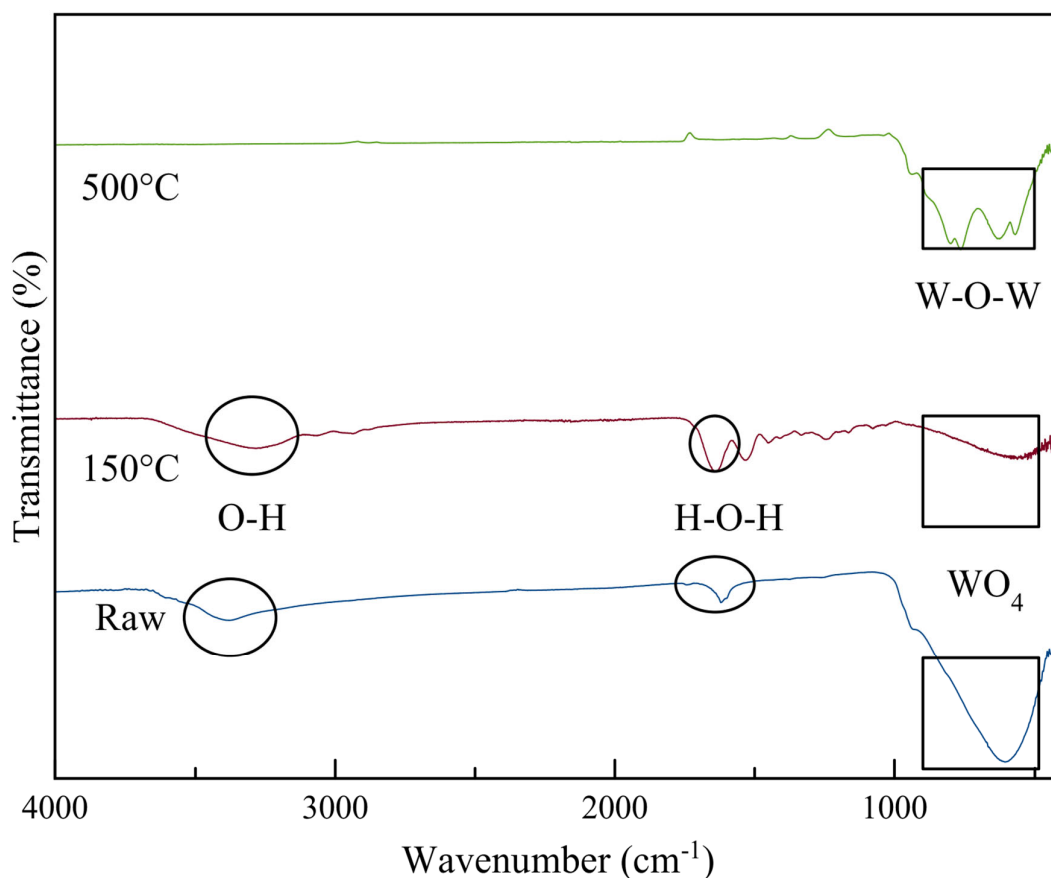
**Figure S4.** X-ray diffraction from the synthesis of raw pre-calcined and 500 °C calcination of  $\text{WO}_3$

From the XRD pattern of Fig S2,  $\text{WO}_3$  particles calcined at 500°C are monoclinic crystals has their highest (022) peak was at 34° with low intensity of (020) at peak 23° peak, while a peak with increased intensity of  $\text{WO}_3$  (200) at 24°. The previous information is obtained from ICSD (00-024-0747).  $\text{WO}_3$  showed balanced peak intensity among all three samples, indicating the crystal's presence (8), (9). In the case of the structure of the raw pre-calcinate material showing residues of  $\text{NaWO}_3$  dehydrated, that is presented in the 2 $\theta$  16° and 27° (10).



**Figure S5. Thermogravimetric analysis spectra from pre-calcined  $\text{WO}_3$**

In the thermogravimetric analysis from figure S4 of  $\text{WO}_3$ , before 200°C the decay of the slope corresponds to the elimination of the coordinated water molecules attached initially by the sodium tungstate dihydrate precursor. There is a constant behavior until the degradation at 600°C. Therefore, while synthesizing the particles at 500°C, the final structure does not lose a significant percentage of weight from 200°C to 600°C (11).



**Figure S6.** FT-IR from  $\text{WO}_3$  pre-calcined and with different temperatures of calcination

The higher bands at the  $3700\text{--}3100\text{ cm}^{-1}$  region are observed due to OH groups and adsorbed water. Specifically, the broad bands at  $3450$  and  $3692\text{ cm}^{-1}$  are due to various O–H stretching modes and a sharp mode at  $1620\text{ cm}^{-1}$  is the H–O–H bending mode. Conversely, no bands were observed in the region  $3400\text{--}3700\text{ cm}^{-1}$  or at  $1620\text{ cm}^{-1}$  when calcined at higher temperatures. The shallow or superficial shoulder, located around  $600\text{ cm}^{-1}$  in the pre-calcined powders, can refer to the initial  $\text{WO}_4$  from the tungstate precursor. The W–O peak shifts towards higher wavenumbers, at  $813\text{ cm}^{-1}$ , where this shift corresponds to the formation of W–O–W crystalline bonds that gives information about the changes, from raw to calcined powders  $500^\circ\text{C}$  (12) (13).

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