

Supplementary Materials for
ENHANCED MECHANICAL AND WATER RESISTANCE PROPERTIES
OF CASSAVA STARCH-PVA NANOCOMPOSITES WITH TiO₂
NANOFILLERS FOR TRIBOELECTRIC NANOGENERATORS FILMS

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Table 1. Composition of The Various Film Nanocomposite Samples.

Table 2. Mechanical Characterization of Nanocomposite Film

1. Fig. S1. Process of making CS-PVA/TiO₂ nanocomposite films.

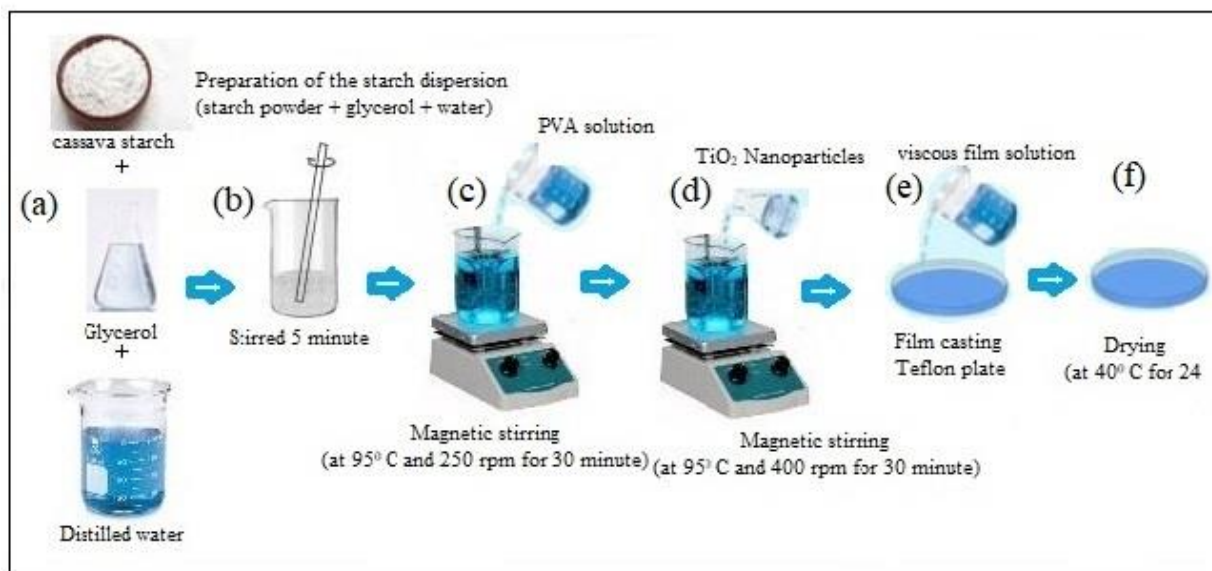


Fig. S1. Preparation of CS-PVA/TiO₂ nanocomposite films by solvent casting method, (a). making a solution of cassava starch (CS), with a composition of cassava starch (4.2 g), and glycerol (3 g) as plasticizer dispersed with distilled water (50 mL) in borosilicate glass, (b). The solution of cassava starch (CS), and glycerol was mechanically stirred for 5 minutes until the solution was completely homogeneous, (c). cassava starch solution (CS) was stirred with a magnetic stirrer at a speed of 250 rpm at a temperature of 95 °C for 30 minutes to obtain a gelatinized starch suspension and added PVA solution while stirring continuously (250 rpm) for 30 minutes until it dissolved completely and a clear solution was formed, (d). CS-PVA clear solution was added with 0.5%, 1%, 3%, 5%, and 7% TiO₂ nanoparticles (based on variations in TiO₂ weight for nanocomposite film samples), and the CS-PVA/TiO₂ solution was stirred continuously using a magnetic stirrer at 400 rpm, and a temperature of 95 °C for 30 minutes. (e). The resulting thick CS-PVA/TiO₂ solution was poured into a Teflon mold (radius 50 mm) with the same pouring volume for each sample (nanocomposite film thickness control), and (f). The drying of the film was carried out in a hot air oven at 40 °C for 24 hours.

2. Fig. S2. Results of chemical structure testing with FTIR

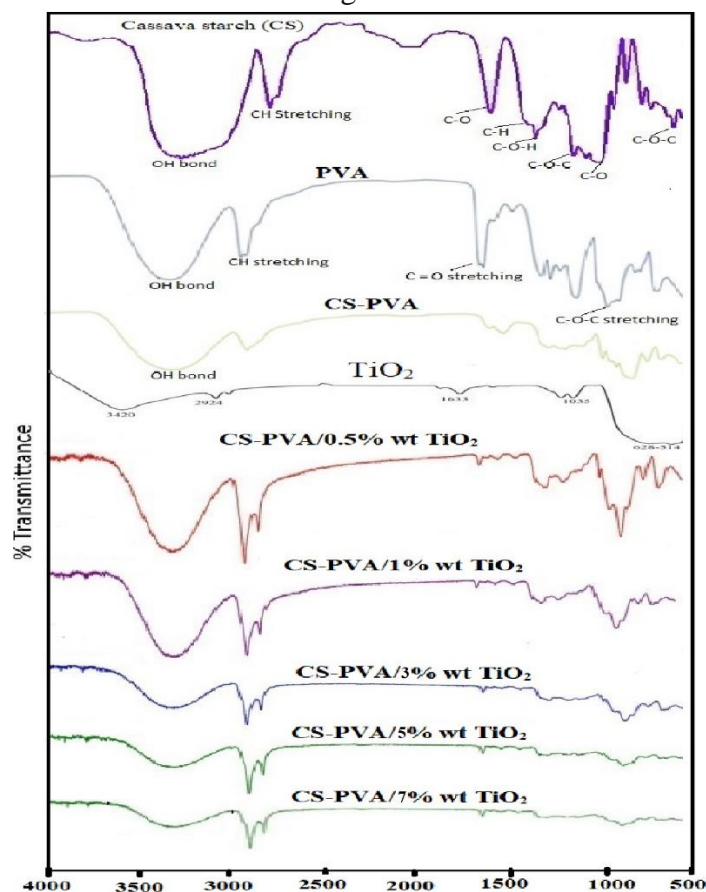


Fig. S2. Testing the chemical structure, crystal structure, morphology, and water resistance of CS-PVA/TiO₂ nanocomposite films. (a) FTIR spectra of cassava starch-PVA/TiO₂, the molecular structure of CS and PVA polymers is rich in hydroxyl groups (the stretching vibration of the hydroxyl group ($-\text{OH}$) in the transmittance band 3285 cm^{-1}). chemical interactions between CS-PVA polymer molecules that cause changes in the spectral peak characteristics of the composite, the C-OH hydrocarbon group is thought to originate from the C-O vibration ($1000\text{--}1250 \text{ cm}^{-1}$), and the $-\text{OH}$ group. the increase in TiO₂ concentration (above 1% TiO₂ wt) showed a slight shift in peak position ($900\text{--}1100 \text{ cm}^{-1}$) associated with the hydrated TiO₂ crystal domain (1000 cm^{-1}) into the CS-PVA polymer.

3. Fig. S3. Results of crystal structure testing with XRD

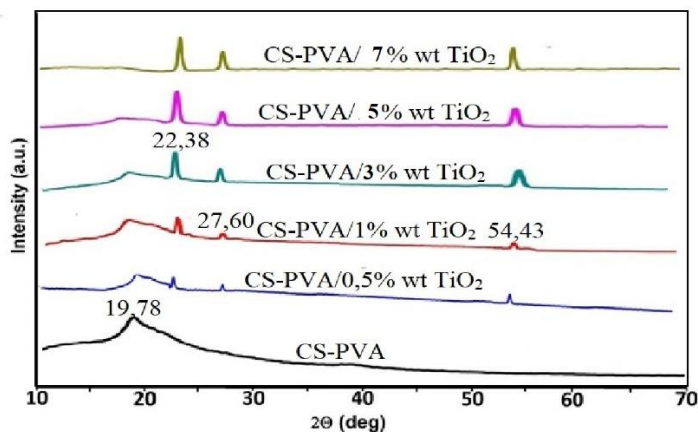


Fig. S3. XRD pattern of cassava starch film produced peaks at $2\theta = 15,73^\circ$, $16,51^\circ$, $17,23^\circ$, $19,69^\circ$, $22,14^\circ$, and $24,37^\circ$. the important diffraction peak is located at $19,69^\circ$ which indicates strong intermolecular and intramolecular hydrogen bonds. The CS-PVA composite showed a change in peak at $2\theta = 13.11^\circ$, 17.21° , 19.76° , and $24,54^\circ$ which could reveal that cassava starch (CS) was dispersed in PVA. TiO_2 dispersion above 1% wt produced peaks at $2\theta = 22,38^\circ$, $27,60^\circ$, and $54,43^\circ$ indicating titanium dioxide embedded in the CS-PVA polymer, and a semicrystalline structure,

4. Fig. S4. Results of testing the surface morphology film with SEM

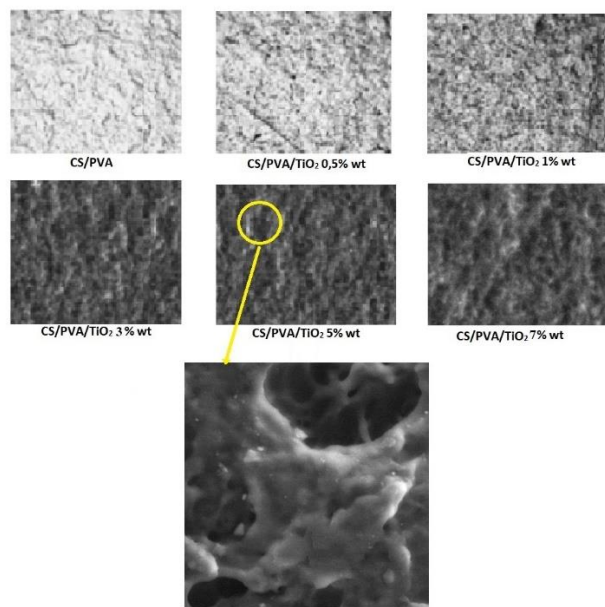


Fig. S4. The SEM results showed that the morphology of the CS-PVA nanocomposite film had heterogeneous surface relief. TiO_2 filler particles were evenly distributed in the polymer matrix, and the addition of TiO_2 concentration of more than 3% wt showed an increase in density, the surface roughness of the film, and an increase in tortuous paths in the nanocomposite film,

5. **Fig. S5.** Water resistance test method and The results water resistance test

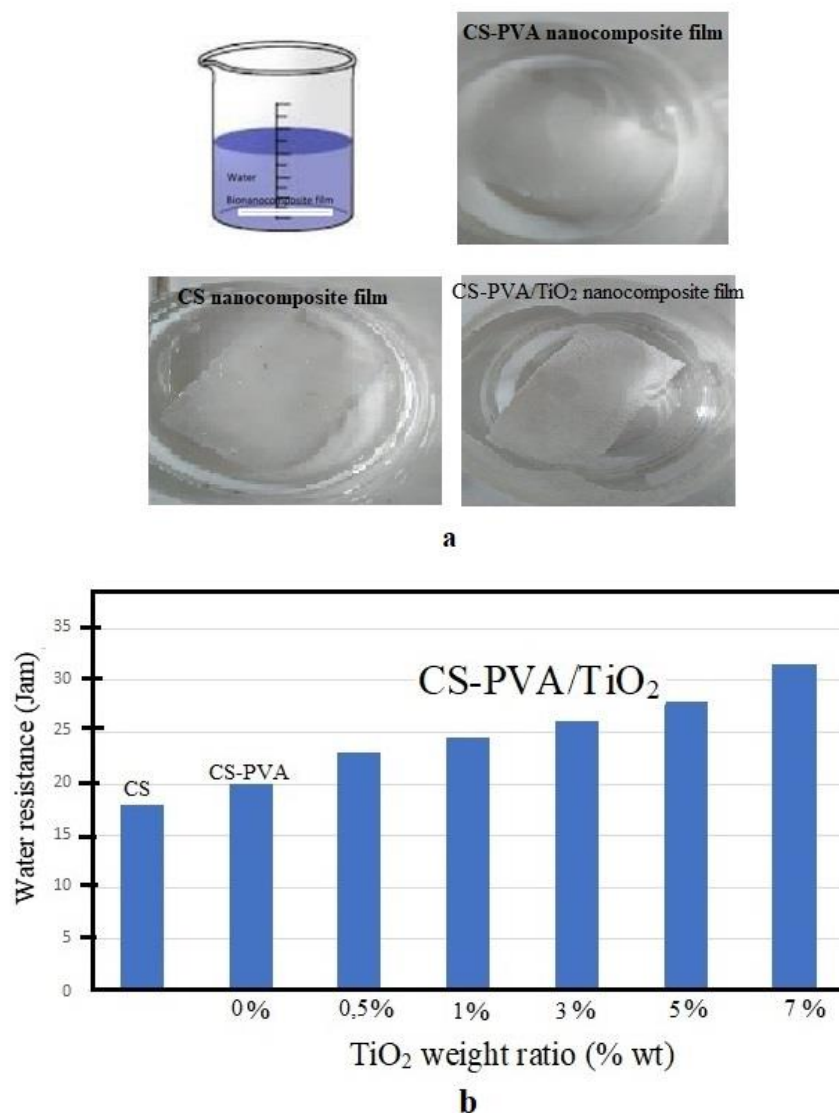


Fig. S5. a- Water resistance testing is carried out to identify the level of film damage to water. The film samples (length \times width \times thickness = 100 mm \times 20 mm \times 0.5 mm) were immersed in deionized water; **b-** The water resistance of CS/PVA nanocomposite films with TiO₂ nanofiller increased 2-fold compared to that without TiO₂. where, the water resistance of the CS film for 17 hours, CS/PVA increased for 20 hours, and the optimal water resistance of the SC/PVA-TiO₂ nanocomposite film for 32 hours with the addition of 7% by weight of TiO₂. The resistance of CS films is influenced by the number of hydroxyl groups in the polymer molecule, where the hydroxyl groups bind to water molecules by forming hydrogen bonds

6. Fig. S6. Water contact angle

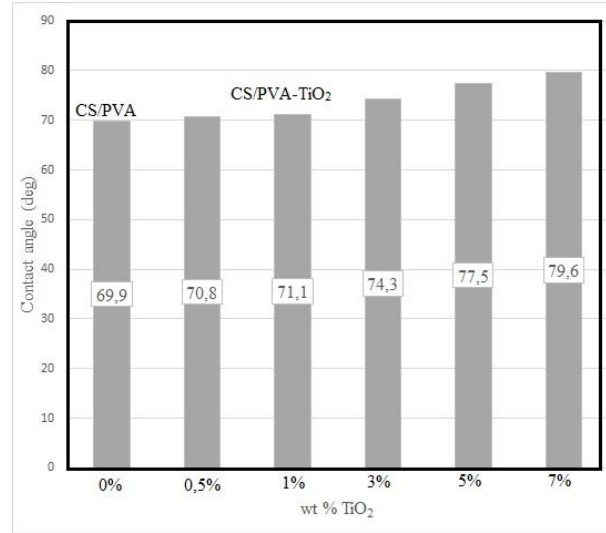


Fig. S6. The CS/PVA composite film sample yielded a value of 69,9° indicating hydrophilic properties. The addition of TiO₂ to the CS/PVA composite with the addition of 0.5 wt% to 7 wt% TiO₂ nanoparticles showed a trend of increasing the contact angle of the film surface (70.8°, 71.1°, 74.3°, 77.5°, 83.6°). Increasing the contact angle can increase the hydrophobicity of the CS/PVA-TiO₂ film due to an increase in the surface roughness of the film due to the distribution of TiO₂ particles.

7. Fig. S7. Design and structure of RDF-TENG

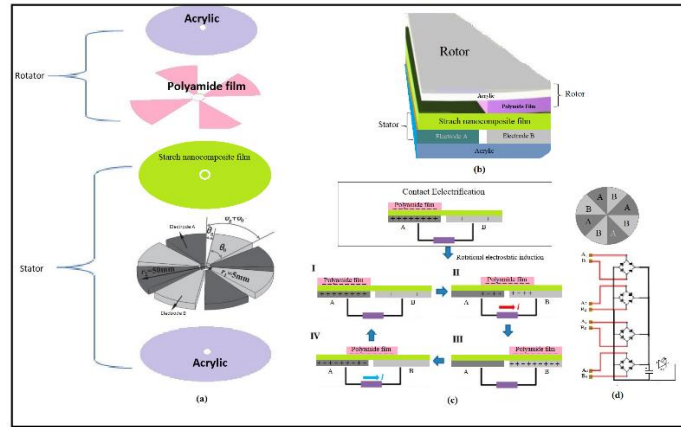


Fig. S7. Rotary-disk freestanding triboelectric nanogenerator (RDF-TENG) mode. The TENG structure uses Rotary-disk freestanding (RDF-TENG) mode. Rotor structure parameters with the number of film segments (n) = 4, outer radius (r_2) = 50 mm, inner radius (r_1) = 5 mm, and made of commercial polyimide thin film (0.03 mm) as a triboelectric film glued to an acrylic surface (radius = 50 mm). Meanwhile, the stator structure parameters consisting of CS-PVA/TiO₂ nanocomposite films were cut to form an equal interval electrode model with the number of film segments (n) = 8, outer radius (r_2) = 50 mm, inner radius (r_1) = 5 mm, and the nanocomposite film thickness was 100 μ m. Next, the cut nanocomposite film was glued to the copper foil (electrode film A, and B).

8. **Fig. S8.** RDF-TENG testing instrument installation

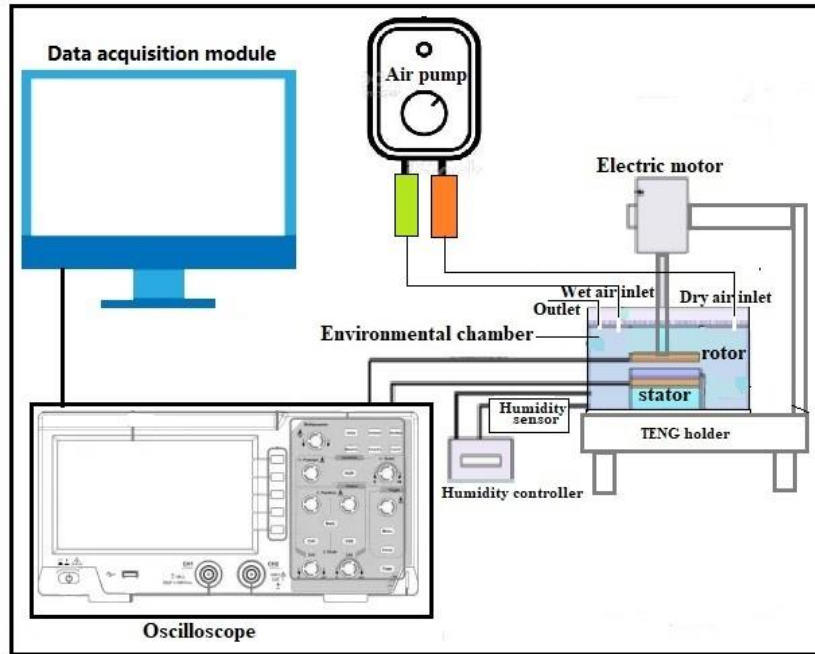


Fig. S8. RDF-TENG testing installation scheme in the form of a cylindrical chamber equipped with one exhaust duct and two inlets for dry air intake and wet air for humidity control in the cylinder chamber. cylinder chamber is equipped with a humidity regulator to condition the humidity of the cylinder chamber as expected. external energy RDF-TENG uses a 24 Volt DC electric motor whose rotational speed can be controlled. The output voltage and current are measured using an oscilloscope equipped with a PC device.

Fig S9. performance of RDF-TENG CS/PVA-TiO₂ nanocomposite films under different humidity (RH: 15% and 95%)

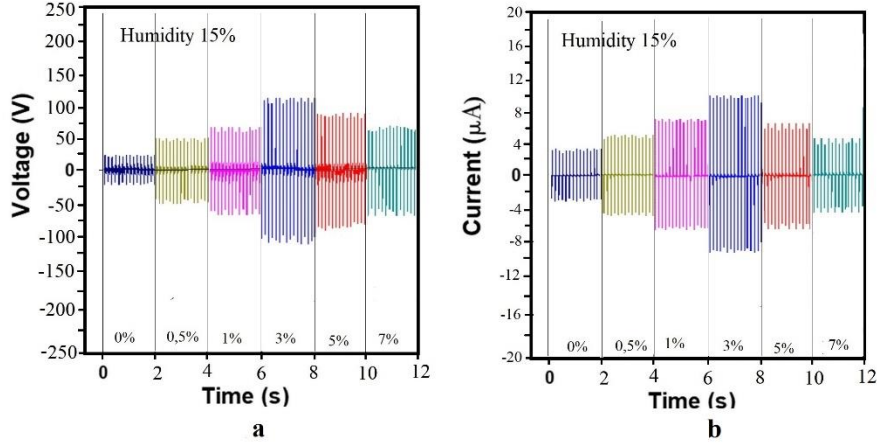


Fig S9. Performance of RDF-TENG CS/PVA-TiO₂ nanocomposite films under different humidity 15%, The results of the output voltage and current output voltage and current ~25.5 V and ~3.6 μA without addition of TiO₂ in CS-PVA nanocomposite matrix. Meanwhile, the addition of TiO₂ in the weight ratio (0% to 7 % wt TiO₂) showed a linear increase in voltage and current, respectively. The optimal output voltage and current were achieved at a concentration of 3%wt TiO₂ with a value of 112.5 V and 10.2 μA. This increase in output voltage and current is due to an increase in the value of the dielectric constant due to the presence of TiO₂ in the CS-PVA polymer mixture which can increase the triboelectric of the film.

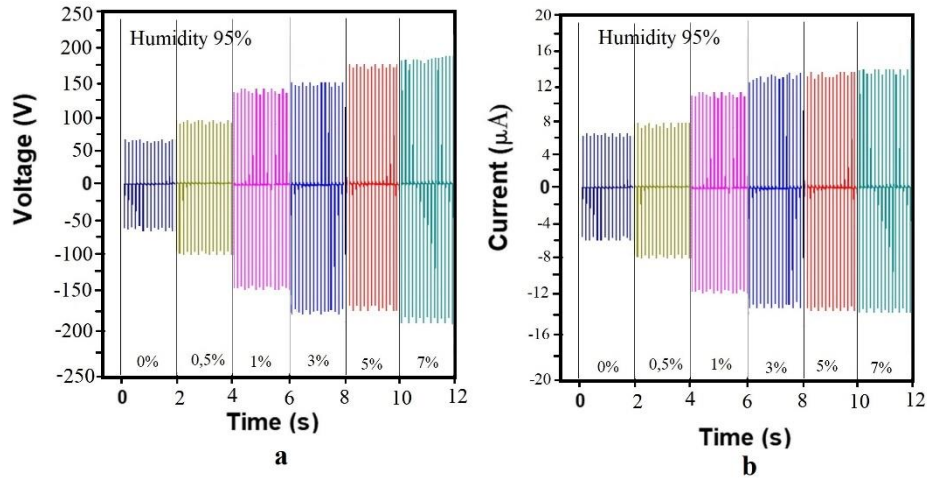


Fig S9. Performance of RDF-TENG CS/PVA-TiO₂ nanocomposite films under different humidity 95%, The RDF-TENG optimal output voltage and current when humidity is high (RH, 95%) with a concentration of 7% TiO₂ wt can reach 1.6-fold from ~112.5 V to ~180 V, and the current increases 1.4-fold from ~10.2 μA to ~13.7 μA. The increase in RDF-TENG output voltage and current is caused by the formation of hydrogen bonds between hydroxyl groups and water molecules (when humidity is high) on the surface of the CS-PVA/TiO₂ nanocomposite film increasing the positive triboelectrification properties of the film.

Table 1. Composition of The Various Film Nanocomposite Samples.

Nanocomposite Sample	Composition		
	Cassava strach (CS)	PVA	TiO ₂ (% wt)
CS-PVA	70	30	0
CS-PVA/0,5 TiO ₂ wt%	70	30	0,5
CS-PVA/1 TiO ₂ wt%	70	30	1
CS-PVA/3 TiO ₂ wt%	70	30	3
CS-PVA/5 TiO ₂ wt%	70	30	5
CS-PVA/7 TiO ₂ wt%	70	30	7

Table 2. Mechanical Characterization of Nanocomposite Film

Composite Sample	Mechanical Characterization		
	Ultimate Tensile Strength (Ts), MPa	Elongation at the break (Eb), %	Young's Modulus (My), MPa
CS-PVA	14.23±2.25	112.13±2.28	70.27±4.12
CS-PVA/0,5 TiO ₂ wt%	19.11±1.35	80.45±9.25	113.38±4.57
CS-PVA/1 TiO ₂ wt%	21.20±2.52	78.20±17.12	75.45±6.59
CS-PVA/3 TiO ₂ wt%	10.13±1.26	81.43±4.22	73.27±8.53
CS-PVA/5 TiO ₂ wt%	9.27±1.60	76.23±2.55	75.83±8.12
CS-PVA/7 TiO ₂ wt%	9.50±1.75	73.23±15.54	74.76±9.35

Description Table 2. The addition of TiO₂ particles into the CS/PVA composite showed a significant increase in the Tensile Strength value for the CS/PVA/TiO₂ film sample – 0.5 wt% increased from 14.23 MPa to 19.11 MPa. While the addition of TiO₂ – 1 wt% showed the optimal Tensile Strength of 21.20 MPa. However, the effect of TiO₂ on the CS/PVA composite caused the elongation at break value of the CS/PVA-TiO₂ nanocomposite to decrease. The addition of TiO₂ nanoparticles above 3 wt% shows that the Tensile Strength tends to decrease and the elongation at break tends to decrease. The possibility of adding more than 3 wt% of nanoparticles causes TiO₂ particles to agglomerate and spread unevenly.