

THE ROLE OF STIRRING SPEED ON THE PROPERTIES IMPROVEMENT OF BIOPLASTIC COMPOSITE SAGU STARCH MODIFIED WITH CELLULOSE MICROCRYSTAL AND BETEL LEAF EXTRACT

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ABSTRACT

Studies related to making bioplastic composites based on sago starch filled with microcrystalline cellulose and betel leaf extract have several advantages. Among them is the availability of materials that are renewable, biodegradable, resistant to microbial attack, and can improve mechanical properties. The stirring speed effect at the time of mixing the ingredients in producing bioplastic composites has been carried out. The raw materials used were sago starch, microcrystalline cellulose from coconut husk, extract from betel leaves, and glycerol. The composition of the mixture of ingredients is 100 g of sago starch plus 8 %w microcrystalline cellulose, 6%w betel leaf extract, and 20 %w glycerol. The variations made were in the stirring speed of the mixer: 120, 180, 240, and 300 rpm. The process was carried out in a mixer at 70 °C for a duration of 25 minutes. Several analyses were carried out related to density, Fourier transform infrared (FTIR), water absorption, tensile properties, and antimicrobial properties of bioplastic composites. The results obtained showed that all of the bioplastic composite materials were identified in groups in the FTIR spectra. The results also showed that at a stirring speed of 180 rpm, the properties of the bioplastic composite showed the best. Density and water absorption values at 180 rpm speed respectively are 1.25 g/cm³ and 62.5%. While for tensile strength and elongation at break of 1190.643 kPa and 21.1%, respectively. This result is related to the uniform distribution of microcrystalline cellulose as filler in sago starch at a stirring speed of 180 rpm. In the case of antibacterial properties, the stirring speed has no significant effect except at 300 rpm.

Keywords: Sagu Starch, Microcrystalline Cellulose, Betel Leaf Extract, Tensile Strength, Antibacterial.

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INTRODUCTION

Starch is a renewable natural polymer that is derived from various agricultural products. Many previous studies regarding the manufacture of starch-based bioplastics have been carried out, including those using rice, corn, potato, banana peels, and sago starch.^{3,4} One of the plants that have a high starch content is sago. Sago starch has unique characteristics; easily gelatinized and printed, available as a renewable material, inexpensive, and contains a high percent of starch with a value of 82.94%.⁴ Composite bioplastics consisting of starch require a mixture of additives to produce soft and ductile mechanical properties. Additives in the form of plasticizers and fillers are usually used to reduce stiffness and increase the strength of starch. Microcrystalline cellulose is a common filler used in the production of biocomposites. Microcrystalline cellulose is a partially depolymerized cellulose that is obtained by hydrolyzing alpha-cellulose.⁵ Alpha-cellulose is obtained from various sources of pure cellulose, such as coconut husk, with the help of mineral acids to dissolve the amorphous side of the cellulose chain and leave the crystalline side. Coconut husk is a by-product and is the largest part of the fruit head, which is about 35% of the total coconut. Coconut husk is used because it is easy to obtain, cheap, and composed of lignin (29.4%), cellulose (26.6%), hemicellulose (27.7%), water (8%), and other components (8.3%).⁶ Microcrystalline cellulose can be prepared through chemical reactions, such as by strong acid hydrolysis at controlled temperatures. Controlled acid hydrolysis can destroy amorphous regions in cellulose microfibrils, resulting in the formation of single crystals from

intact crystalline segments. Starch-based bioplastics have several weaknesses, such as their O₂ barrier (antioxidant) and poor biological activity (antifungal and antibacterial).^{7,8} Furthermore, one of the functions of packaging is to extend the life of the materials stored in the packaging. So to increase its effectiveness as food packaging, biocomposites can be added with antimicrobial compounds. Antimicrobial packaging is a packaging system capable of controlling, reducing, inhibiting, or slowing the growth of pathogenic microorganisms and reducing surface contamination of food. The use of plant extracts is expected to develop the use of antimicrobials. One of the plants that can be used as an antimicrobial is betel leaf. Betel leaf (*Piper betle*) is a plant commonly used for medicinal purposes. The total flavonoid and tannin content in betel leaf is 5.99% and 20.33%, respectively.⁹ In addition, the antimicrobial activity of the biocomposites revealed that the addition of glycerol and betel leaf extract inhibited the activity of bacteria (*Bacillus cereus*).¹⁰ The study consisted of the manufacture of microcrystalline cellulose from coconut husk, the manufacture of antimicrobials from betel leaf, and the preparation of bioplastic composites based on sago starch. However, when preparing bioplastic composites, the conditions of the mixing process are very important, especially the speed of stirring when mixing the ingredients. This is related to the distribution of fillers in the bioplastic composite.

EXPERIMENTAL

Preparation of Microcrystalline Cellulose from Coconut Husk

75 g of coconut husk was cut and blended to obtain fine fibers with a size of 150–170 mesh. Fibers were dignified for 2 hours in 500 ml of 2% NaOH at 80 °C. Filtering, then washing with distilled water until the filtrate was neutral. The sample was treated for 30 minutes with 500 ml of a 17.5% NaOH solution at 80 °C. The filtrate was neutralized after it was filtered and the dregs were washed with distilled water. Bleaching with 1.75% NaOCl with a volume of 500 mL at 60 °C for 1 hour. The bleached fiber is filtered, washed with distilled water, and dried for one hour in a 60°C oven. 50 g of alpha-cellulose was put in a beaker glass and hydrolyzed for 15 minutes with HCl at a concentration of 2.5 N at 75 °C. Then, while stirring with a spatula, pour the aquadest into the beaker glass and set aside for 24 hours. The resulting microcrystalline cellulose is washed with distilled water and dried for one hour in a 60°C oven.

Betel Leaf Powder Preparation and Betel Leaf Extraction

Samples of betel leaves were washed with running water until clean. Leaves were cut into small pieces with a size of about 1-2 cm and then dried in an oven at 50°C for 24 hours. The sample was then mashed using a blender and sieved using a 50-mesh sieve. A sample of betel leaf powder was weighed as much as 50 g. 96% ethanol solvent was added with the ratio of ingredients: solvent was 1:5. The sample was extracted for 30 minutes at 40°C and filtered through Whatman filter paper (No.1). The extract was concentrated using a rotary evaporator at 40°C with a rotation speed of 100 rpm.

Preparation of Composite Bioplastics

The starch weighed as much as 100 g. Starch was placed in a mixer and added with distilled water as much as 1000 mL. The solution was heated for 25 minutes at 70°C while stirring with the variation of 120, 180, 240, and 300 rpm. The starch solution added microcrystalline cellulose of 8%w and 20%w of glycerol plasticizer to the solution. Betel leaf extract concentration of 6%v was added. Pour the solution into the acrylic mold. The bioplastic composite was dried for 2 days, then removed from the mold and analyzed.

FTIR (Fourier Transform Infrared) Analysis

Transform of Fourier Infra-Red characterization was considered to identify and show structural changes in functional groups in bioplastic composites. The Shimadzu IR-Prestige 21 was used for the FTIR measurements. The film spectrum is recorded at a wavelength of 500 cm⁻¹ to 4000 cm⁻¹.

Density Analysis

The bioplastic composite was cut to a size of 2 cm by 2 cm, the thickness was measured, and then the volume was calculated. The samples were weighed. The equation can be used to calculate sample density (1).

$$\rho = \frac{m}{v} \quad (1)$$

Where: ρ is sample's density; m is the sample's mass; v is the sample volume

Water Absorption Analysis

The Bioplastic composite was cut to a size of 2 cm by 2 cm and immersed in water, and then the sample was weighed every 2 minutes until a constant mass was obtained.

The following formula was used to calculate water absorption:

$$\text{Water absorption (\%)} = \frac{(M_t - M_0)}{M_0} \times 100\% \quad (2)$$

Where: M_t is the mass of the sample after it has been immersed in water

M_0 is the mass of the sample before it is immersed in water

Tensile Properties Analysis

Tensile properties were determined according to the standard of ASTM 2882-91 using a Universal Testing Machine. A dumbbell-shaped sample of composite bioplastic film was cut from each variance. The table in the tensile test graph calculated the tensile strength value. The percentage elongation is the sample extension expressed as a percentage of its initial length. The percent elongation at the break of the tested object is expressed as a percentage.

Antimicrobial Activity Analysis

Starter microbes (*Bacillus sp.*) were inoculated on agar media in a petri dish. Bioplastic composite film samples were cut into 6 mm discs and placed on the dish's surface. The plate was then incubated at 37°C for 24 hours. Using a caliper, the inhibition zone, which is marked with a clear colored area around the well, was measured.

RESULTS AND DISCUSSION

Fourier Transform Infra-Red (FTIR)

Figure-1 presents the FTIR results of bioplastic composites filled with microcrystalline cellulose and betel leaf extract based on sago starch. Wavenumbers for each cluster. The FT-IR spectra of different samples of coconut fiber and microcrystalline cellulose were detected in the 4000-500 cm^{-1} range.

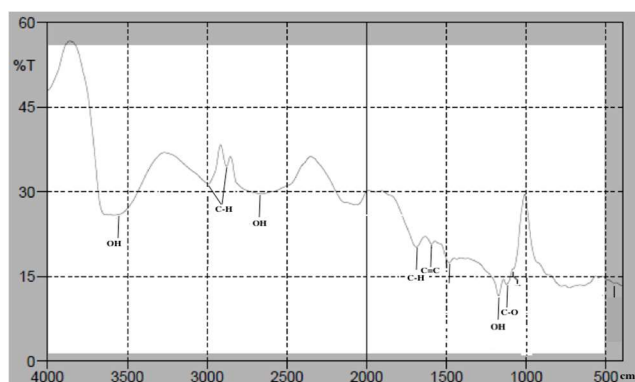


Fig.-1: FTIR Spectra for Bioplastic Composite Based Sagu Starch Modified with Cellulose Microcrystal and Betel Leaf Extract

The absorption peaks indicating the presence of OH groups at wave numbers 3590, 2680, and 1200 cm^{-1} indicated the presence of alcohol and phenolic compounds derived from starch, microcrystalline cellulose, glycerol, and betel leaf extract. Furthermore, the C-H group (alkane) at wave numbers 3000, 2860, and 1745 cm^{-1} was identified by the presence of a stretching C-H group originating from the methyl group found in the cellulose chain. The sharper absorption peaks of the C-H stretching groups are influenced by transformations related to changes in the inter- and intramolecular bonds of cellulose. The presence of the C=C group in the FTIR spectra with a wave number of 1670 cm^{-1} also identified the presence of alkenes derived from the aromatic group of betel leaf extract. Furthermore, the presence of the C-O group at wave number 1175 cm^{-1} confirmed the presence of an ester compound derived from betel leaf extract.

Density of Bioplastic Composites

Figure-2 shows the results of the density of the bioplastic composite with the stirring speed at different preparations of the bioplastic composite. The Fig.-2 shows that as the stirring speed increases, the density of the resulting bioplastic composite also tends to increase.

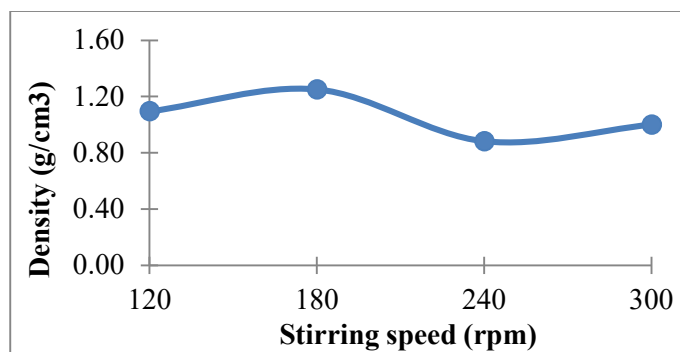


Fig.-2: The Effect of Stirring Speed During Preparation on Density of Bioplastic Composites

The highest density value of the bioplastic composite was obtained at a stirring speed of 180 rpm, which was 1.250 g/cm^3 . while the lowest density value is obtained at a stirring speed of 300 rpm, which is equal to 1.00 g/cm^3 . The graph shows that increasing the stirring speed from 120 to 180 rpm has a tendency to increase density. However, at a stirring speed of 240 rpm, the density decreased again, and at 300 rpm, it increased again to 1 g/cm^3 . This shows that at 180 rpm, the microcrystalline cellulose is spread evenly in the starch, so the density value is not too different from 120 rpm. The stirring speed of 240 and 300 rpm showed a non-uniform distribution of microcrystalline cellulose in the starch, thus allowing the formation of microcrystalline cellulose agglomeration. This can be caused by stirring too fast. Density is directly proportional to the mass of a material, so the greater the mass of a material, the greater the value of density.

Water Absorption of Bioplastic Composites

The effect of stirring speed on the preparation of bioplastic composites on water absorption can be seen in Fig.-3. It presents the effect of the stirring speed when providing bioplastic composites on the water absorption capacity of starch-based bioplastic composites at constant weight starting from the 10th to the 12th minute. The duration of this time is when the bioplastic composites have been saturated to absorb water. The results showed that at a stirring speed of 180 rpm, the percentage of bioplastic composites showed the lowest value. This is related to the very good distribution of cellulose in sago starch, which means that it can withstand the penetration of water into the material. The addition of microcrystalline cellulose causes a decrease in the hydrophilic nature of starch due to the characteristics of cellulose, which is not soluble in water. The more homogeneous the distribution (spread) of the added microcrystalline cellulose, the lower the water absorption value. Furthermore, polyphenolic compounds (flavonoids and tannins) in betel leaf extract form a strong bond with sago starch molecules, resulting in hydrophobic interactions in sago starch bioplastics when betel leaf extract is added. Polyphenolic and tannins compounds in gelatinized starch engage with amylopectin and amylose molecules. Because of the increased swelling of the amylopectin and amylose chains, polyphenolic compounds can bind particularly to starch molecules via hydrogen bonds, resulting in hydrophobic interactions.

Tensile Properties of Bioplastic Composites

Figure-4 presents the influence of the mixing speed when providing bioplastic composites on the tensile strength test profile. From the figure, it can be seen that the stirring speed of 180 rpm for providing bioplastic composite shows the highest load and elongation values among the other stirring speeds. This shows that this speed results in a uniform distribution of microcrystalline cellulose in the starch so that when the tensile load takes place, the stress distribution in the material takes place properly. When compared with the stirring speed of 120 rpm used to provide bioplastic composites, the load required for the material to break is relatively low, as is its elongation. This is influenced by the uneven distribution of microcrystalline cellulose filler in the starch, which causes the stress distribution to be poor when the tensile load is applied. At a speed of 300 rpm, the same thing also happened: because the stirring speed was too high, the distribution of microcrystalline cellulose was uneven in the bioplastic composite.

In this case, the load and elongation also tend to be lower than the speed of 180 rpm. For the speed of 240 rpm, the tendency for a greater load was probably caused by the accumulation of microcrystalline cellulose in the tested sample, but it can be seen that the elongation is low.

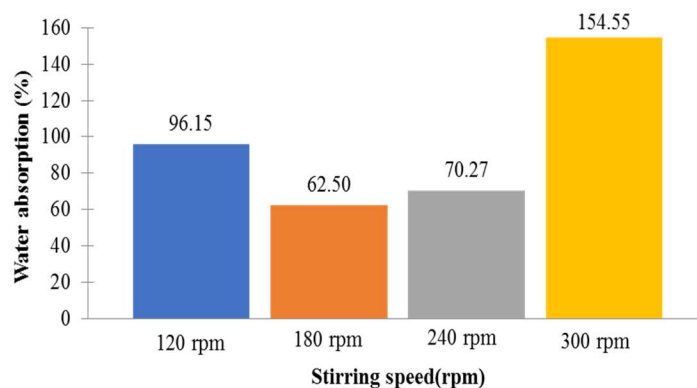


Fig.-3: The Effect of Stirring Speed on Water Absorption of Bioplastic Composite

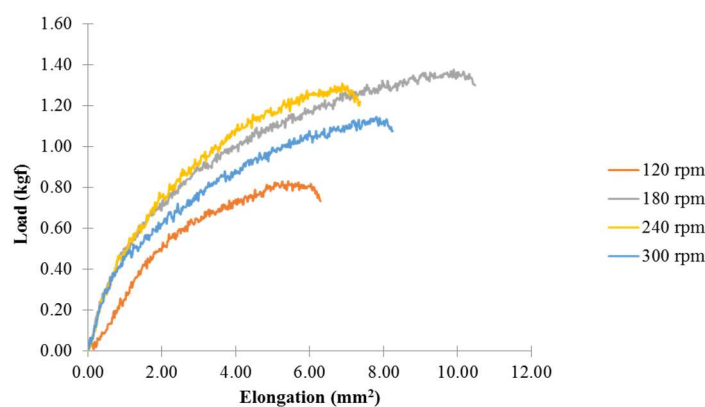


Fig.-4: Load vs Elongation of Bioplastic Composite with Different Stirring Speed

Figure-5 presents the effect of stirring speed when providing bioplastic composites on the tensile strength of sago starch-based bioplastic composites. The highest tensile strength was achieved at the mixing speed of providing the bioplastic composite at 180 rpm, which is 1190.643 kPa. This could be due to the strong interfacial interactions between the microcrystalline cellulose and starch embedded in the matrix, which results in efficient stress transfer. The interaction between the matrix and filler phases will be enhanced by the homogeneous distribution of microcrystalline cellulose.

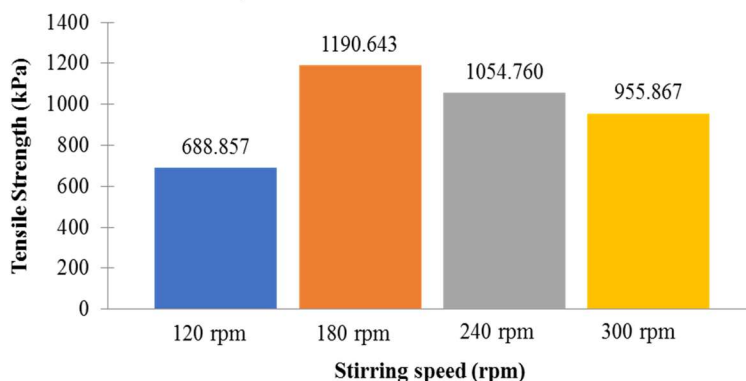


Fig.-5: The Effect of Stirring Speed on Tensile Strength of Bioplastic Composite

The presence of the extract of betel leaf containing water and glycerol in the bioplastic composite also increases the homogeneity of the dispersion of microcrystalline cellulose because both of them function as plasticizers. Meanwhile, in bioplastic composites filled with microcrystalline cellulose and stirred at other speeds (120, 240, and 300 rpm), the distribution of microcrystalline cellulose in sago starch was not homogeneous, resulting in an inefficient transfer of stress from the matrix to the filler during the test. Figure-6 shows the effect of the speed of stirring provided by the bioplastic composite on the elongation at

the break of the material. From the Figure, it can be seen that the elongation at break has the highest value at 180 rpm stirring variation, which is 21.1%.

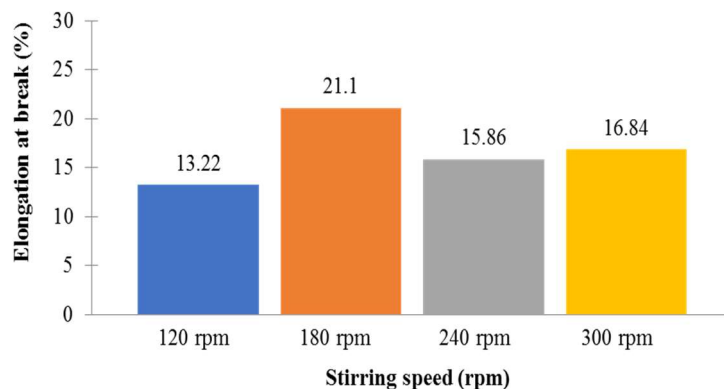


Fig.-6: The Effect of Stirring Speed on Elongation at Break of Bioplastic Composite

This is because the tensile strength is also the highest at the same speed. As seen in the previous tensile test profile picture (Fig.-6), at a speed of 180 rpm, the elongation of the material is highest compared to the other speeds (120, 240, and 300 rpm). This proves that the homogeneous distribution of microcrystalline cellulose in sago starch greatly affects the elasticity of the material. In addition, the presence of the extract of betel leaf and glycerol also influenced the interactions between the components in the bioplastic composite.¹¹ Because the repulsive charge of the acids present in the betel leaf extract increases the mobility of the polymer chains, the chemical disposition of the phenolic acids and flavonoids from the betel leaf extract with adjoining glycerol and amylose chains molecules loosens the intermolecular interactions of the starch.

Antibacterial Activity of Bioplastic Composites

Figure-7 shows the presence of antibacterial activity from all variations of bioplastic samples, as indicated by the clear zone formation around the sample. Both glycerol and betel leaf extract have a role in inhibiting bacterial growth. The largest diameter of the inhibition zone obtained in composite bioplastic samples is 23.3 mm at a stirring speed of 180 rpm. While the diameter of the smallest inhibition zone was obtained in composite bioplastic samples with stirring speeds of 300 rpm, which is 11.3 mm.

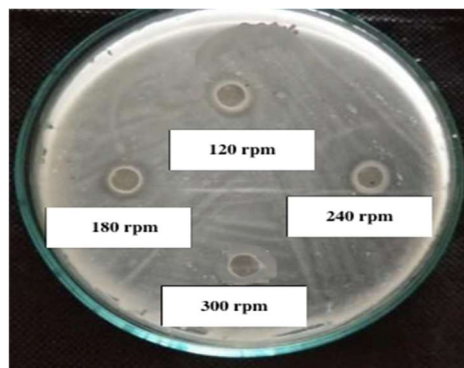


Fig.-7: Antibacterial Activity on Bioplastic Composite with Different Stirring Speed

Bacillus is a rod-shaped bacterium that can be found in soil and water. Some cells produce extracellular enzymes that can hydrolyze complex proteins and polysaccharides. Bacillus is a gram-positive, aerobic bacterium that is commonly called a decomposer. The inhibitory properties of these bacteria were influenced by the addition of glycerol and betel leaf extract. Betel leaf extract contains polyphenolic compounds such as tannins and flavonoids, which play a role in inhibiting the activity of microorganisms. Meanwhile, glycerol is also a polyol compound that has bactericidal properties at certain concentrations. Tannins' antibacterial action is accomplished by causing bacterial cells to lyse. This occurs because tannins have a target on the bacterial cell wall's polypeptide wall, causing the cell wall formation to be incomplete

and the bacterial cell to die.¹² Tannins can also prevent proteins from passing through the inner lining of cells by inactivating bacterial enzymes. Table-1 displays the diameter of the bioplastic composite's inhibitory zone at various stirring speeds.

Table-1: Diameter of Inhibitory Zone of Bioplastic Composite

Stirring speed (rpm)	Diameter of Inhibitory Zone (mm)
120	22.4
180	21.5
240	23.3
300	11.3

This can be seen from the formation of clear zones with almost the same diameter values for stirring speeds of 120, 180, and 300 rpm. This shows that the stirring speed does not affect the distribution of betel leaf extract in the bioplastic composite. However, at a speed of 300 rpm, the inhibitory zone diameter decreased drastically, to 11.3 mm. This was related to the uneven distribution of the extract of betel leaf in the starch, so it was possible that the sample that was applied contained very little extract.

CONCLUSION

The presence of all the components making up the bioplastic composite, such as starch, microcrystalline cellulose, and betel leaf extract, can be seen from the spectra shown by FTIR. The effect of stirring speed on the characteristics of sago starch bioplastic composites filled with microcrystalline cellulose and betel leaf extract showed significant value. From the properties and characteristics analyzed, it was shown that a stirring speed of 180 rpm produced the best bioplastic composites. This can be seen in the density, water absorption, tensile strength, elongation at break, and antibacterial properties. Analysis of the results obtained showed that the speed of 180 rpm during the process of preparing the biopolymer composite resulted in a uniform distribution of microcrystalline cellulose as filler in the starch as well as the betel leaf extract. The uniform distribution of filler in the matrix causes the stress distribution during the tensile test to be maximized. Likewise, the water absorption capacity of bioplastic composites with a stirring speed of 180 rpm has succeeded in reducing the percentage of water absorption when compared to other speeds. Meanwhile, for the antibacterial properties, the stirring speeds of 120, 180, and 240 rpm did not show any different results. However, at a speed of 300 rpm, the inhibition zone diameter showed a significant decrease.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

AUTHOR CONTRIBUTIONS

All of the authors made significant contributions to this manuscript, took part in the review/editing process, and granted the final version for publication. The following ORCID ids can be used to verify the authors' research profiles:

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