https://dx.doi.org/10.21577/0103-5053.20230049

J. Braz. Chem. Soc., Vol. 34, No. 10, 1373-1379, 2023

Article

Gelation Behavior of Polyacrylamide-Polyethyleneimine: Effects of Diethylenetriamine and Glycerol Addition

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Polymer gel systems find applications in diverse areas, ranging from contact lenses to agriculture and oil production. In general, polyacrylamide (PAM) gels are produced by reaction with metallic (low temperatures) and organic (high temperatures) crosslinking agents. In this paper, given crescent environmental concerns, polyethyleneimine (PEI), an organic reactant, was chosen as the crosslinker of PAM, at 65 ºC. The effects of using a solution of water/glycerol as the solvent for preparing the gels and the addition of diethylenetriamine (DETA), a *n*-alkylamine, on the gelation kinetics and gel stability were evaluated. The data presented in this paper indicate that the solvent mixture provided a more controlled gelling behavior by delaying the gelation time. Also, diethylenetriamine acted both as an efficient anti-syneresis agent, improving gel stability, and by delaying the progress of gel strength.

Keywords: glycerol, PEI, DETA, hydrogel, PAM

Introduction

Polymer hydrogels are three-dimensional water-swollen crosslinked networks with versatile fabrication methods and properties.[1,2] Their hydrophilicity, viscoelasticity, softness, and tunable behavior make them applicable in a large number of areas, such as drug delivery systems, scaffolds in tissue engineering, contact lenses, biosensors, agriculture, heavy metal ions removal and oil recovery.[3-9]

Polyacrylamide (PAM) and its derivatives are water-soluble polymers that can easily form hydrogels by bonding with metallic or organic crosslinking agents. In the oil industry, polyacrylamide hydrogels can find applications from drilling to oil-production and well abandonment, such as in water shutoff, fracturing during production and lost circulation control.[10-13] Gels can be produced either before injection or in the rock formation and the suitable crosslinking system must be selected according to individual field conditions.

The general assumption is using inorganic cross-linkers at low temperature reservoirs, which bind to COO^- groups of partially hydrolyzed polyacrylamide (HPAM) by ionic interactions. At higher temperatures, organic cross-linkers are preferred due to higher stability of covalent bonding. Recently, given crescent environmental concerns, products of low toxicity should be chosen for the gel's formulation. Therefore, typical toxic cross-linkers should be replaced by more eco-friendly ones.[14,15]

Polyethyleneimine (PEI) is a non-toxic and environmentally friendly organic crosslinker that is approved for food contact in the USA.[16] It has been extensively applied to the cross-linking of polyacrylamides at high temperatures.[16,17] However, only a few studies state the gelation behavior of PAM by using PEI as a cross-linker at a mild temperature.[18,19] Alisson and Purkaple,[20] for example, showed that a viscous gel can be quickly formed at room temperature by mixing 0.1% polyacrylamide and 2.5% PEI. Later, Jia *et al.*[21] reported that gelation time and strength at 40 ºC of the HPAM/PEI system can be perfectly adjustable by controlling polymer concentration and molar mass, PEI concentration and total dissolved solids.

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Editor handled this article: Célia M. Ronconi (Associate)

Because of the higher concentration of PEI often needed to form gels at lower temperatures, syneresis may be observed. This is caused by the over-crosslinking effect that leads to the expulsion of water and gel dehydration.[22] In this case, literature has shown that alkylamines can be employed to mitigate this behavior.[23] Likewise, the choice for adding co-solvents to the gel's formulation can modify hydrogen bonding between water and the polymer crosslinked structure, affecting swelling kinetics, stability and viscoelastic properties of the hydrogel.[24] However, no studies were found about the effects of mixing solvents on the behavior of polyacrylamide gels.

Glycerol is a non-toxic and biodegradable compound that has been extensively obtained as a by-product of biodiesel production. The great amount of glycerol generated in this process is still modestly explored and new ways of using this residue have been investigated.[25] One route for using glycerol that can employ pronounced amounts of this product is being used as solvent.[26] The presence of three hydroxyl groups gives to glycerol miscibility in water, allowing the water-glycerol mixture to become a base solvent for the formation of polymeric gels.

In this scenario, this work aims to explore the effects of adding an alkylamine, diethylenetriamine (DETA), and a water-glycerol mixture on the gelation behavior of PAM-PEI gels at 65 ºC.

Experimental

Materials

Non-ionic polyacrylamide (PAM, weight average molecular weight (Mw) = 9.5×10^5 g mol^{-1}, number average molecular weight (Mn) = 2.5×10^5 g mol^{-1}, Figure S1, Supplementary Information (SI) section), was gently donated by Floerger (France). Polyethyleneimine (PEI, Mw = 7.5×10^5 g mol^{-1}, Mn = 6.0×10^4 g mol^{-1}), branched, provided as a 50 wt.% aqueous solution and diethylenetriamine (DETA) were acquired from Sigma-Aldrich (Brazil). Glycerol was purchased from Dinâmica (Brazil). All the materials were analytical grade and used without further purification.

Preparation of the gellant systems

PAM and PEI were separately added to distilled water and left dissolving under magnetic stirring for 24 h, before they were blended together for more 2 h. Some of the formulations were also composed by DETA and glycerol. For those cases, DETA was added to the PEI solution, and stirred for another 1 h. Next, glycerol was added to the PAM solution, followed by the mixture of these systems for 2 h. The formulations of the gellant are depicted at Table 1.

Table 1. Formulations of the gellant solutions

Sample	PAM / ppm	PEI / ppm	DETA / ppm	Water/ glycerol
PPW	5000	5000	–	100/0
PPWD	5000	5000	2500	100/0
PPWG	5000	5000	–	40/60
PPWGD	5000	5000	2500	40/60

PAM: polyacrylamide; PEI: polyethyleneimine; DETA: diethylenetriamine.

Bottle tests

A volume of 50 mL of each formulation was poured into a 100 mL bottle and then placed into an oven at 65 ºC. Gelation kinetics was monitored by the Sydansk's code, which consists of a visual evaluation of the formulation behavior upon the sealed vial inversion.[27] The strength of gellants is expressed as an alphabetic code of A-J: A = no visually detectable gel formed; B = highly flowing gel; C = flowing gel; D = moderately flowing gel; E = slightly flowing gel; F = highly deformable non-flowing gel; G = moderately deformable non-flowing gel; H = slightly deformable non-flowing gel; I = rigid gel; and J = rigid ringing gel.

Rheology

A Thermo Haake Mars rheometer (Germany) equipped with a DG41Ti coaxial cylinder sensor and Accel 500 LT temperature controller was used to obtain the viscosity curves of the samples at different times of aging. The measurements were made at a shear rate ranging from 0.1 to 1000 s^{-1}, at 30 ºC.

Viscoelastic behavior was obtained with a Thermo Haake Mars rheometer (Germany) equipped with a C60/1° Ti cone-plate geometry sensor and Accel 500 LT temperature controller. The samples were scanned from 0.1 to 10 Pa, at a frequency of 1 Hz, to find the region of linear viscoelasticity. Then, the frequency changed from 0.1 to 10 Hz, at 0.2 Pa (within the linear viscoelastic region). All measurements were performed at 65 ºC.

Results and Discussion

Bottle tests

Transamidation is the process of transforming one amide into another via amide-amide or amide-amine reactions.[28] In this paper, amine groups from PEI or PEI and DETA may react with amide groups from PAM to originate new amide linkages. Because of the great number of amide groups on PAM and of amine groups on PEI/DETA, a tridimensional crosslinked gelled structure is formed with time of reaction.

Gelation time is generally defined as the time needed to reach specific gel strength and many methods can be applied to determine this parameter. By using the Sydansk's code, gelation time of each formulation is usually considered to occur when the gel strength code changes from A to C.[29] A recent work[30] has demonstrated that PEI with high molar mass provides a faster gelation time than a PEI with low molar mass. Then, the choice for a PEI of high molar mass, such as the one applied in this study, provides a gelation time within a few hours, but not so fast to overload pumping into the oil well. Table 2 exhibits the Sydansk's codes of the samples with time and Figure 1 shows representative pictures of the gelation progress. The one-way analysis of variance (ANOVA) and Tukey's multiple comparison test were used to verify statistical differences at significance level of 0.05. No statistical difference on the gelation time was detected between PPWG and PPWGD either between PPW and PPWD. For all the other combinations, the samples exhibited statistical differences on the gelation time.

Figure 1. Illustration of the gelation progress of the gels. PPWG changing from strength A (left), to C, E, and H (right).

Gelling solutions prepared without glycerol (PPW and PPWD) reached the gelation time with only 3 h of aging. The presence of DETA on PPWD promoted a slight decrease on gel strength, since the maximum code reached was H, whereas PPW reached code I after only 19 h. However, DETA gave better stability to PPWD, while syneresis followed by gel breakage was observed for PPW formulation.

The literature[23] has described that DETA analogous chemicals, such as ethylenediamine and *n*-hydroxyethylethyenediamine respectively behave as delaying agents, increasing gelation time, as well as efficient anti-syneresis agents, increasing gel stability. The amine groups on DETA compete with PEI for the reaction with PAM, delaying the increase on gel strength after code H is reached. When the amount of DETA was increased from 2500 to 5000 ppm (Table S1, SI section), the progress of gelation was delayed. After 19 h, the gel with 2500 ppm of DETA (PPWGD) exhibited gel code H, whereas, with 5000 ppm of DETA, the code was G. Then, even if PEI has much more amino groups than DETA, the high molar mass of PEI hinders its mobility. The low molecular weight DETA reaches more easily the amide groups of PAM, delaying the progress of PAM-PEI crosslinking. The presence of DETA also gives a greater number of hydrophilic groups on the gel structure, enabling more hydrogen-bonding with water molecules, diminishing the water release, and then increasing the stability of the gels.

Samples with glycerol (PPWG and PPWGD) exhibited a longer gelation time and code C was observed only after 6 h of aging. Hopkins *et al*.[31] stated that when polyacrylamide is dispersed in glycerol, the polymer chains acquire a more locked-in structure, whereas in water the chains have more flexibility. In this sense, the lower mobility of polymer chains in glycerol leads to a decrease on gelation kinetics. Once again, the presence of DETA delayed the progress of gelling and promoted a higher stability of the gel: the sample without DETA reached code I more quickly (19 h), but the gel got broken after 120 h; on the other hand, the sample with DETA took 72 h to reach code I, but it was stable after 120 h of aging.

Rheology

Given that samples with glycerol exhibited a more controllable gelling process and notable stability, they were

Table 2. Sydansk's code of the gelling solutions with time of aging at 65 ºC

Sample	Sydansk's code								
time / h	0	3	6	19	24	48	72	96	120
PPW	A	C	H	I[a]	I[a]	I[a]	I[b]	I[b]	I[b]
PPWD	A	C	H	H	H	H	H	H	H
PPWG	A	A	C	I	I	I	I	I	I[b]
PPWGD	A	A	C	H	H	H	I	I	I

[a]Free water; [b]broken gel. A: no visually detectable gel formed; C: flowing gel; H: slightly deformable non-flowing gel; I: rigid gel.

chosen to quantitative determinations of the gelling process. Figure 2 shows the apparent viscosity as a function of shear rate of formulations PPWG and PPWGD with different times of gel maturation.

Both formulations exhibited a pseudoplastic behavior, i.e., decrease in viscosity with increasing shear rate. At lower shear rates, the greater resistance to flow can be attributed to the macromolecules entanglements, crosslinking, and hydrogen-bonding. On the other hand, the lower viscosities at higher shear rates were due to disruption of entanglements and intermolecular associations. This behavior is desirable to guarantee an easier displacement of the fluid by the pump. For drilling fluids, for example, low viscosities at higher shear rates protect the pump from overload during injection, whereas higher viscosities at lower shear rates imply on better carrying of cuttings and avoid cutting accumulation.

It is interesting to note that when the shear rates are above 1 s^{-1}, the PPGW (formulation without DETA) exhibited higher viscosity at 6 h than at 19 or 24 h of aging. However, at lower shear rates, the viscosities are higher at 19 and 24 h of gel maturation. This behavior shows that higher shear rates are strong enough to disturb the gelled network and promote the disruption of associations. On the other hand, the formulation with DETA (PPGWD) showed higher viscosities at 19 and 24 h for the entire shear rate range applied. These results reveal that DETA has a decisive impact on the rheological properties of the gels.

Some papers[32,33] have described the use of viscosity measurements to gelation time determinations.The point with an abrupt increase on viscosity with time corresponds to the onset of gel formation. The samples in this paper displayed an abrupt increase on viscosity at 6 h of aging, demonstrating the formation of a gelled structure (insert, Figure 2). This behavior agrees with Sydansk's codes presented in Table 1.

A strain sweep was performed to determine the linear viscoelastic region (LVR) of the formulations at different times of aging. It consists of the region from which the storage modulus (G') and the loss modulus (G") do not change with increase in deformation. At the LVR, the structure of the gel remains intact, and the sample only undergoes reversible deformations. G' and G" were constant at all times of aging studied in the 0.1-1.0 Pa range (Figure 3). Samples with aging time higher than 3 h exhibited a higher stability and the G' and G" kept constant up to 10 Pa.

Literature[34] states that kinetics of cross-linking and gel stability can be quantitatively expressed by the tan(delta), obtained by the G"/G' ratio. Tan(delta) ≥ 1 is obtained for materials at a viscous liquid state; samples with tan(delta) < 1 exhibit a gel character, with lower values associated with higher rigidity; and samples with tan(delta) < 0.1 can be classified as strong gels. Figure 4 exhibits the tan(delta) of PPWG and PPWGD at different times of aging.

According to tan(delta) parameters, no gel was detected within 3 h of aging. It shows that there is still a great amount of free polymer chains, with few points of crosslinking, which contributes to the viscous modulus (G"), displacing the tan(delta) to values above 1. Gel state was formed with 6 h of aging for both formulations, as evidenced by the tan(delta) < 1. A strong gel was obtained with 19 h of aging and gel strength increased with time. However, after 120 h, PPWG presented an increase on tan(delta), revealing a decrease on gel strength. This data agrees with the visual observation highlighted on Table 2: the gel was broken. At the same time, PPWGD kept stable properties, as no significant changes on Sydansk's code either on tan(delta) curve were detected. It was verified by the one-way ANOVA with Tukey test that the addition of DETA significantly influenced these results at the times of 6, 19 and 120 h (significance level = 0.05).

The behavior exhibited by formulations with DETA is similar to the ones observed by other gels with reinforcing

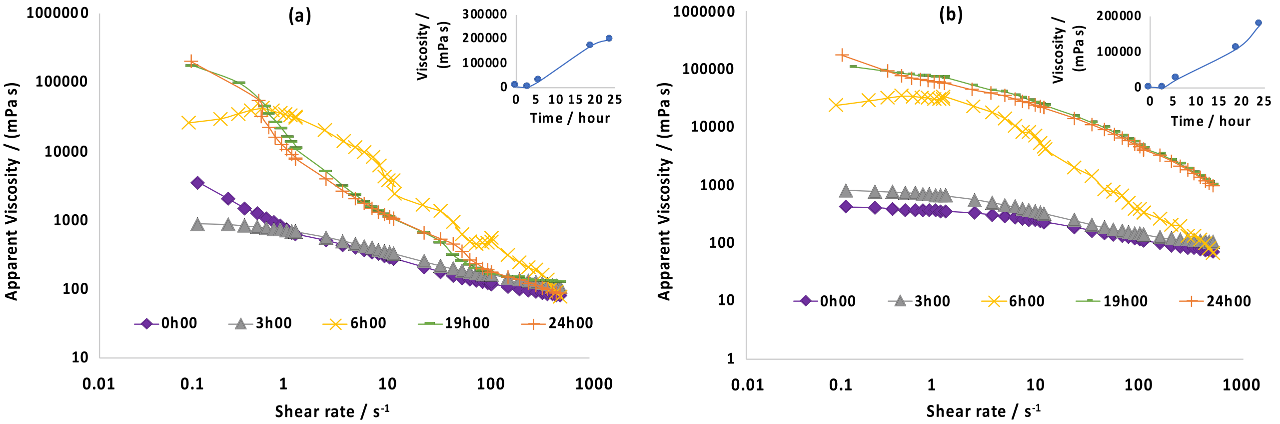

Figure 2. Viscosity curves for (a) PPWG and (b) PPWGD and their respective viscosity *versus* time curves (insert) at 0.1 s^{-1}.

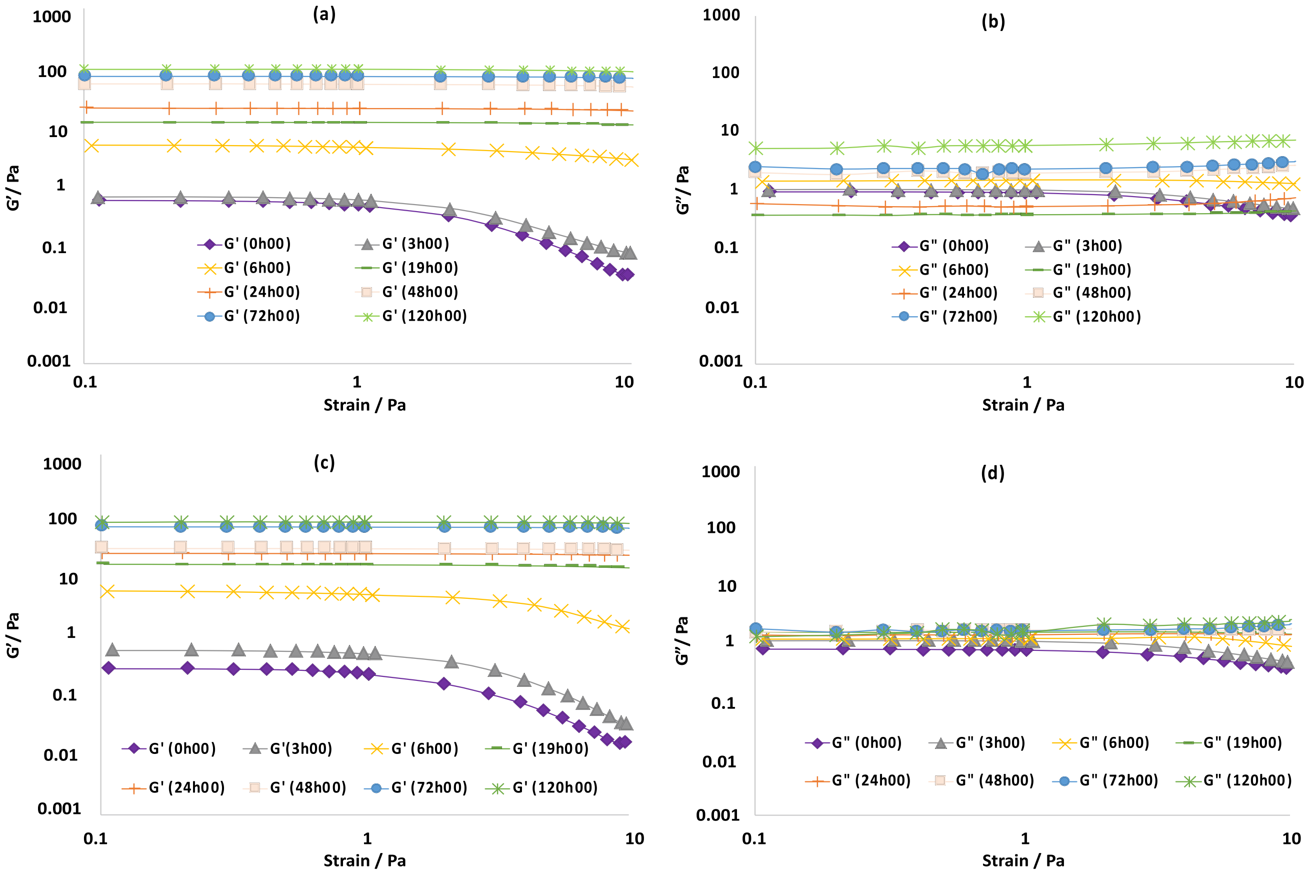

Figure 3. Strain sweep for (a,b) PPWG and (c, d) PPWGD.

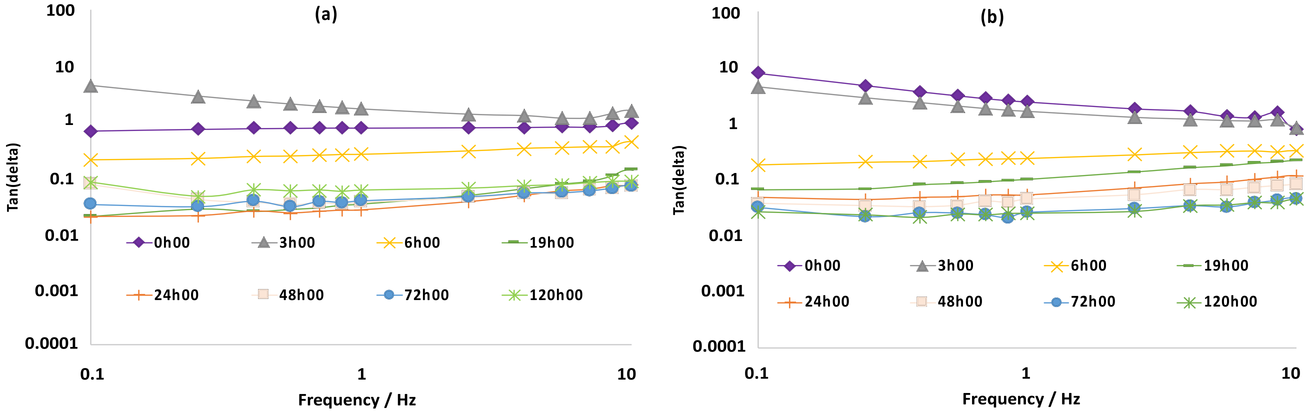

Figure 4. Tan(delta) for (a) PPWG and (b) PPWGD.

fillers like nanosilica, metallic oxides and coal fly ash.[34-36] The low tan(delta) and stability of the gels were attributed to a greater number of interaction sites promoted by the reinforcing fillers.

The experimental observations allowed us to describe the effects of DETA and glycerol on the gelation process of PAM-PEI formulations (Figure 5). The amine groups on DETA resulted in an increase in hydrogen bonds with water, which consequently reduced the loss of water from the gels and made syneresis difficult. At the same time, DETA is involved in transamidation reaction with amide groups on PAM, allowing a competition between DETA and PEI, controlling the progress on gel strength. The high viscosity of glycerol/water medium promotes a lower mobility for polyacrylamide chains, PEI and DETA molecules, leading to a decrease on gelation kinetics. The three hydroxyl groups on glycerol also increase the number of hydrogen bonds with water molecules, trapping them inside the gelled crosslinked structure, promoting greater stability to the formulations.

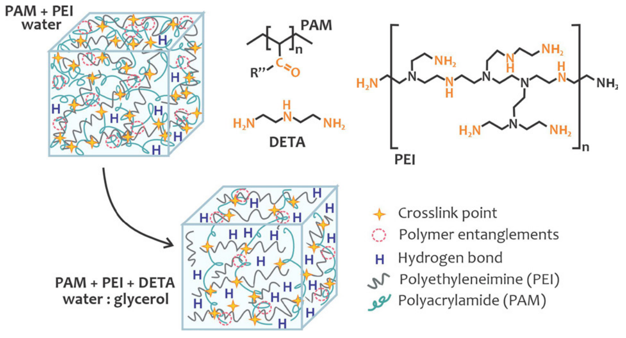

Figure 5. Representation of PPW and PPWGD.

Conclusions

In this paper, PAM-PEI hydrogels were prepared in combination with DETA, in water and water/glycerol media, and their maturation, at 65 ºC, was investigated by the Sydansk's code and rheological measurements. A lower mobility of the polyacrylamide chains in glycerol led to a decrease on gelation kinetics and the formulation without glycerol reached the gelation time more quickly (3 h) than the ones with glycerol in their composition (6 h). On both water and glycerol/water solutions, DETA delayed the gelation progress and gave higher stability to the gels. The amine groups on DETA compete with PEI for the reaction with PAM, retarding the increase on gel strength. Also, the presence of DETA and glycerol provides a greater number of hydrophilic sites on the gel structure, enabling more hydrogen-bonding with water molecules, increasing their stability. The semiquantitative and quantitative results certified that glycerol and DETA can modify the gelation kinetics and stability of the gels at a mild temperature, turning into interesting components for PAM-PEI formulations.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

The authors are grateful to PETROBRAS S/A (SAP 4600580022 and 4600568098) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq grant 304339/2019-9) for their financial support. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

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Submitted: December 16, 2022