Study of the Applicability of pH Mediators in Bioplastic Formulations for Use in Food Packaging

Camille Victória Carvalho[1*], Gabrielle Honorata Barbosa[1], Joaquim Dantas[1], Wendel Costa[1], Ingrid Lessa Leal[1], Paulo Romano[1], Tatiana Vale[1]

[1]SENAI CIMATEC University; Salvador, Bahia, Brazil

This work proposes the manufacture of bioplastics for food packaging using starch, carboxymethylcellulose, and green coconut waste (*Cocos nucifera*), with the addition of acid-base mediators to indicate the pH of the food. The method was based on experimental research, in which films were produced using the casting technique and incorporated mediators at a concentration of 1% (v/v). The results showed a high percentage of solubility, with an average of 95.09%, and low moisture content on a dry basis, with an average of 0.95%, and presented visually noticeable colorimetric changes in the pH ranges from 2 to 9. The research highlights the importance of using biodegradable materials and valorizing waste, which aligns with circular economy and sustainability practices.

Keywords: Bioplastics. Renewable Resources. Smart Packaging.

Economic development and urbanization are changing human behavior and the production of goods, leading the food industry to create packaging that guarantees the quality and safety of food on a large scale. However, the growing use of oil-based polymers has increased waste generation and damaged the environment, highlighting the need for better solid waste management strategies. In response, innovative packaging made of biodegradable polymers with pH indicators, such as corn starch, carboxymethylcellulose, and green coconut fiber, is emerging, improving food preservation by detecting spoilage and reducing the environmental impacts of conventional plastics.

Packaging production has been fundamental to the development of commerce and urban growth since human sedentarization, which led to the creation of artifacts to preserve and store food. With the First Industrial Revolution, there was an increase in industry and innovation in packaging to maintain product quality, using advanced materials and technologies [1]. According to ABRE (Brazilian Packaging Association), in partnership with FGV [2], in 2022, the gross value of packaging production in Brazil was R$123.2 billion, an increase of 3.9% compared to 2021. The food and packaging sector constantly evolves to reduce losses, reuse by-products, and increase food safety. Scarce resources and rising food costs drive demand for sustainable packaging that ensures product quality and safety.

Economic development, population growth, urbanization, and the technological revolution have changed consumption and production patterns, significantly increasing solid waste from various sources [3]. Excessive consumption and improper disposal of packaging saturate landfills and dumps, hinder waste degradation, cause environmental pollution, and favor the proliferation of diseases [4]. In Brazil, the National Solid Waste Policy (PNRS), established by Law No. 12.305/2010 [5], is crucial for managing this waste, promoting shared responsibility, and encouraging sustainable practices to meet ecological and social challenges.

Biodegradable Polymers

Polymers are macromolecules with a chemical structure and covalent intra- and intermolecular interactions. They can be derived from organic and inorganic matter, being highly malleable and moldable through heat and pressure to manufacture various products. Biodegradable

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Address for correspondence: Camille Victória Carvalho. SENAI CIMATEC University. Avenida Orlando Gomes, 1845. Zipcode: 41650-010. Salvador, Bahia, Brazil. E-mail: camille.carvalho@ba.estudante.senai.br.

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polymers, as defined by ISO 1472:1998 [6], are films that undergo significant changes in their chemical structure under specific environmental conditions due to the action of microorganisms and are a sustainable and viable alternative to replace conventional plastics in production.

The size of the global bioplastics market is expected to grow from around 1.78 million tonnes in 2023 to 3.95 million tonnes by 2028, with a CAGR of 17.25% during the forecast period [7], presenting itself as a field in development, making it an area of great potential for studies to make its use viable. The application of polymer materials of natural origins, such as starch and cellulose derivatives, can generate continuous, naturally abundant, renewable, non-toxic, and biodegradable matrices, demonstrating thermoplastic behavior, presenting advantages over conventional plastics in terms of cost and functionality, reducing energy consumption, and making manufacturing cheaper [8], characteristics of industrial interest.

Starch is a plant polysaccharide characterized by semi-crystalline granules of different sizes and shapes. In recent years, corn starch has been the predominant raw material for producing biodegradable polymers as it is one of the primary sources of starch produced worldwide - approximately 64% [9]. Among the advantages of using biodegradable packaging made from starch are the following characteristics: transparency, barrier against oxygen and carbon dioxide, biodegradability, and compatibility with most materials during production.

Carboxymethyl cellulose (CMC) is an anionic biopolymer derived from cellulose, obtained by the alkaline reaction and etherification of cellulose with alkali and monochloroacetic acid successively. It is widely used in the food and pharmaceutical industries because it is biodegradable, soluble in cold or hot water, and transparent when in solution [10]. Its excellent properties, such as high water content, biocompatibility, and permeability, make it promising for the production of food packaging. Brazil is one of the largest global producers of green coconuts. Still, large-scale consumption generates up to 70% of the waste in coastal urban areas, mainly due to the fruit'sfruit's fibrous husks, which are bulky and heavy, making it challenging to manage municipal solid waste and negatively impacting the helpful life of landfills due to their slow decomposition. This waste is rich in lignin, hemicellulose, and cellulose and is used in various applications due to its strength and durability, similar to natural wood. Green coconut fiber has potential as a raw material for biodegradable bioplastics, offering a sustainable alternative for managing solid urban organic waste [11].

Smart Packaging

According to ABRE (Brazilian Packaging Association), the packaging is designed to store products in a way that prolongs their durability, protects them, and facilitates their distribution and consumption. In the case of food packaging, it preserves food against environmental factors such as light, humidity, gases, and microorganisms, keeping it unchanged during transportation and storage [12]. Oxidation by microorganisms reduces the shelf life of food, affecting taste and nutritional quality and generating toxic compounds [13].

The WHO [14] points out that millions of people fall ill and die every year from water- and food-borne diseases, underlining the importance of effective systems for handling and sanitizing packaging. Interest in intelligent packaging, such as biodegradable films with pH indicators, is growing to monitor food quality and safety [15]. Controlling the growth factors of microorganisms is essential in the production, transport, storage, and marketing of perishable foods to maintain the quality of these products [16].

Indicators are devices capable of transmitting information to consumers about food quality, considering the development of microorganisms [17].Real-time monitoring of specific characteristics, such as the absence or presence of biological or chemical compounds, can be carried out through, for example, visible colorimetric change using acid-base indicators

such as anthocyanin, bromothymol blue, or phenolphthalein. This simple technique quickly detects signs of food deterioration through pH change.

Materials and Methods

The study adopted an experimental qualitative-quantitative approach, starting with bibliographical research and preliminary topic analysis. Data collection was based on relevant scientific articles, including studies by Sugimoto (2000) [18], Leow and colleagues (2022) [19], Vedove (2019) [20], and Guglielmi and colleagues (2008) [21].

The following materials will be used in this work: corn starch, Carboxymethylcellulose - CMC, green coconut fibers (obtained from establishments in Salvador and São Sebastião do Passé - BA - used as a matrix for bioplastic formulations – separate as Sample A and B, respectively), distilled water, Glycerin P.A, citric acid, bicarbonate, Petri dishes, anthocyanin (extracted from red cabbage), phenolphthalein (from ACS Científica) and bromothymol blue (from Êxodo Científica) - used as pH indicators in an experiment in the Biotechnology Laboratory at SENAI CIMATEC. To obtain the bioplastic formulations, the solutions were obtained by the casting method (Tables 1 and 2), spread on glass plates, and left to dry at room temperature for 72 hours.

The CMC film solutions were prepared by heating and stirring the polymer containing water and glycerol as plasticizing agents. The films were obtained by casting, spread on glass plates, and left to dry at room temperature for 72 hours.

To obtain the bioplastic formulations from green coconut fiber, formulations from the Sugimoto patent (2000) [18] were adapted by processing the mesocarp of the green coconut (Table 3).

As materials used, the green coconut (Coccus Nucifera L) was obtained from establishments after use for manual separation of the Exocarp, Mesocarp, and Endocarp of the green coconut, separately stored and preserved in refrigerators at 4º C, avoiding the proliferation of microorganisms. The green coconut mesocarp was washed with distilled water and subjected to acid hydrolysis

Table 1. Bioplastic formulations from cornstarch by casting method.

Formulations	Components
F1	Starch; Water; Glycerol; Sodium hydroxide; Hydrochloric acid.
F2	Starch; Water.
F3	Starch; Water; Glycerol.
F4	Starch (4%); Water; Glycerol; Sodium Bicarbonate.
F5	Starch (5%); Water; Glycerol; Sodium Bicarbonate.
F6	Starch; Glycerol; Citric Acid.

Table 2. Bioplastic formulations from carboxymethyl cellulose by casting method.

Formulations	Components
F1	CMC; Water.
F2	CMC; Water; Glycerol.
F3	CMC; Water; Starch; Glycerol.
F4	CMC; Water; Glycerol; Sodium Bicarbonate.
F5	CMC; Starch; Water; Citric Acid.

Table 3. Bioplastic formulations from coconut fiber by casting method.

Formulations	Components
F1	Coconut fiber; Water; Carboxylic Acid; Starch.
F2	Coconut fiber; Water; Glycerol; Carboxylic Acid.
F3	Coconut fiber; Water; CMC.
F4	Coconut fiber; Water; Glycerol; Starch; CMC.

for 4 to 8 hours in a 6% (m/v) NaOH solution to delignify and remove impurities. After soaking, the suspended fibers were washed with distilled water until they reached a neutral pH and dried in an oven at 100ºC for 24 hours to lighten and reduce humidity. The fibers were then ground and sieved to obtain powdered fibers.

Hemicellulose quantification was performed on green coconut fiber mesocarp samples adapted from the patent from Leow and colleagues (2022) [19]. The process involved weighing 1g of dried green coconut fiber mesocarp and adding it to a 0.5 M NaOH solution in a Shaker Incubator for 4 hours at 500 rpm. After cooling to room temperature, the sample was vacuum-filtered and washed with distilled water until it reached a neutral pH. The remaining residue was dried in an oven at 100°C until the following day. The difference between the initial weight and the weight of the dried residue determined the hemicellulose content of the sample. Lignin quantification was performed on green coconut fiber mesocarp samples adapted from the patent from Leow and colleagues (2022) [19]. To do this, 1g of dried green coconut fiber mesocarp was added to a solution of 8 ml of 72% sulfuric acid and 7 ml of distilled water in a Shaker Incubator for 4 hours at 500 rpm. After cooling to room temperature, the sample was vacuum-filtered and washed with distilled water until it reached neutral pH. The remaining residue was dried at 100°C until the following day, and the weight of the dried residue was used to determine the lignin content of the sample.

The selected biofilms were prepared and dried for 72 hours at room temperature for the solubility test. After drying, the films were placed in Erlenmeyer flasks containing 50 mL of distilled water, then placed in a shaker with 80 rpm agitation at 25°C for 24 hours. After that, they were dried in an oven at 70°C for 24 hours to determine the final mass. The films were weighed before and after to obtain the initial and final mass. The solubility was calculated using Equation 1.

$$S = \frac{Wi - Wf}{Wi} \times 100 \quad (1)$$

Moisture content, on a dry basis, was determined according to AOAC method 930.04 [22] is determined by quantifying the mass before and after being dried in an oven at 105° C for 24 hours. The moisture content is obtained by calculation using Equation 2.

$$M = \frac{Wi - Wf}{Wi} \quad (2)$$

The mechanical tests were carried out using the EMIC Universal Shear and Tensile Testing Machine for adhesives (ASTM), provided by the Microscopy Laboratory at SENAI CIMATEC. Four specimens, F1 (CMC), F3 (CMC), F3 (coconut fiber), and F4 (coconut fiber), with an area of 5.5 mm2, were used.

For the pH colorimetric transition test, formulations were prepared in triplicate for each bioplastic sample using the indicators Anthocyanin, Phenolphthalein, and Bromothymol Blue at a concentration of 1% (v/v). These formulations were developed during the production of the bioplastics at room temperature. After formulation, the samples were placed in glass Petri dishes in a controlled environment for drying, without constant lighting and with air circulation. After

drying, the colorimetric transition test was carried out by adding 2 mL of buffer solutions (from ACS Científica) with pH 2, 7, and 9 at a concentration of 1 M. This procedure allowed visible color changes to be observed as the acidic, neutral and basic substances were added to the samples.

Results and Discussion

The study of bioplastic formulations with corn starch and CMC revealed that citric acid caused changes to the surface, making film formation incompatible. In contrast, sodium bicarbonate gave the formulations more elasticity and moisture, making them biocureatives. After drying, only two formulations containing starch showed positive results (F4 and F5) with smooth and adherent surfaces. The formulations with CMC (F1, F2, F3, and F4) exhibited the appearance of conventional plastics and desirable characteristics such as transparency, resistance, lightness, and malleability. The formulations with green coconut fiber (F3 and F4) were also successful, showing resistance and rigidity despite the lack of transparency (Figure 1).

The results of the extraction of samples revealed the removal of soluble lignin-cellulose components, resulting in a reduction in the total mass of the samples (Tables 4 and 5). Previous studies have indicated variations in the lignin and cellulose content of different green coconut cultivars, ranging from 37.2 ± 0.8%to 43.9±0.7% and from 31.5±0.1% to 37.4±0.5% for the lignin and cellulose content, respectively [23]. The concentration of hemicellulose and lignin in the residual samples was evaluated in comparison with non-residual green coconut fibers, showing that waste in the manufacture of composites remains within the natural values of the original raw material.

The results of the mechanical tests were analyzed based on the Stress at Maximum Breaking Strength, Specific Deformation at Breaking, and Modulus of Elasticity, shown in Figures 2, 3, and 4, respectively. Two used 2 samples each of the formulations that exhibited the appearance of conventional plastic, with the main characteristics desired for the experiment: resistance, lightness, and malleability, observed in the samples F1 (CMC), F3 (CMC), F3 (coconut fiber) and F4 (coconut fiber) – described the formulations in the Tables 2 and 3 – showed greater rigidity, indicated by the higher values of Modulus of Elasticity and lower elastic deformation under tension.

Figure 1. Developed formulations with desirable characteristics.

Table 4. Hemicellulose quantification.

	Starting weight (g)	Final Weight (g)	Hemicellulose Content (g)	Hemicellulose Percent (%)
Sample A	1,1855	0.8506	0.2979	29.79
Sample B	1,0678	0.6846	0.2999	29.99

Table 5. Lignin quantification.

	Starting weight (g)	Final Weight (g)	Lignin Percent (%)
Sample A	1,0683	0.3349	33.49
Sample B	1,0201	0.3842	38.42

Previous studies have highlighted the superior mechanical strength of formulations with CMC and water due to the specimens' smaller grain size and more excellent compaction [21]. However, due to the limited number of samples and the lack of structural uniformity, discrepancies were observed in the results, suggesting the need for more samples and more excellent uniformity for future studies.

The moisture and solubility results for the films with satisfactory visual results made with starch, CMC, and coconut fiber powder are indicated in percent as 0,95% and 95,09%, respectively Table 6). The presence of plasticizers, such as glycerol, contributes to an increase in the amorphous regions of bioplastics, making them easier to permeate with water. Due to the high solubility of CMC in water, it was possible to observe that the

Figure 2. Maximum strength tests.

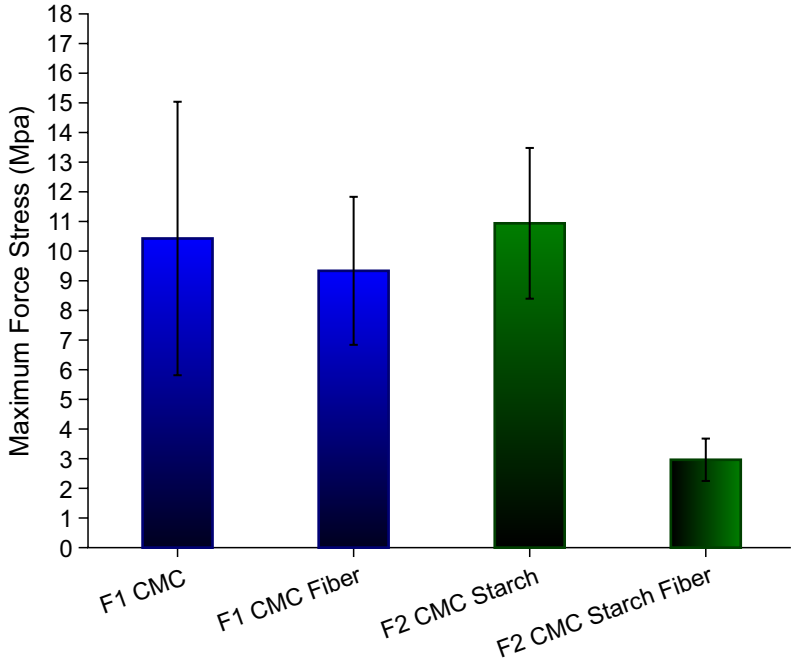


Figure 3. Modulus of elasticity testing.

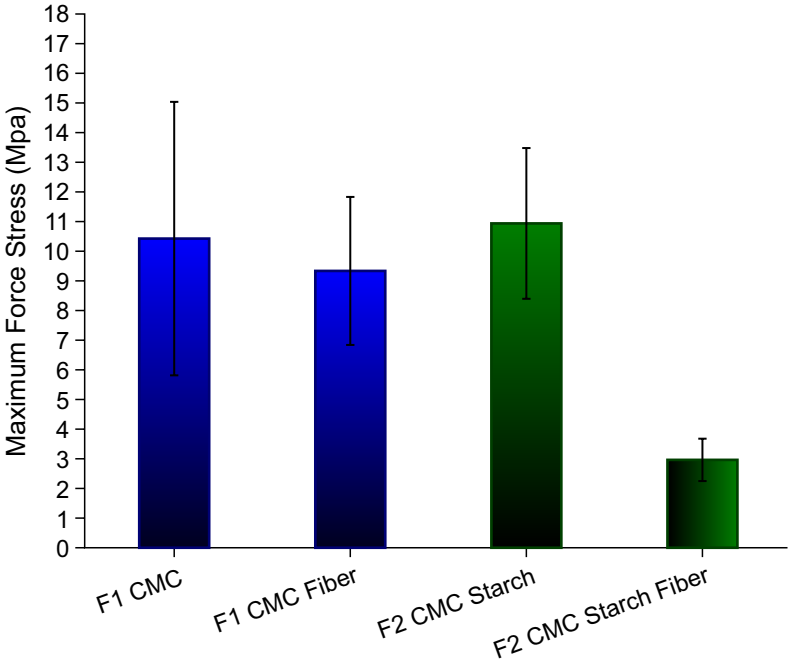


Figure 4. Tests for specific deformation at the break.

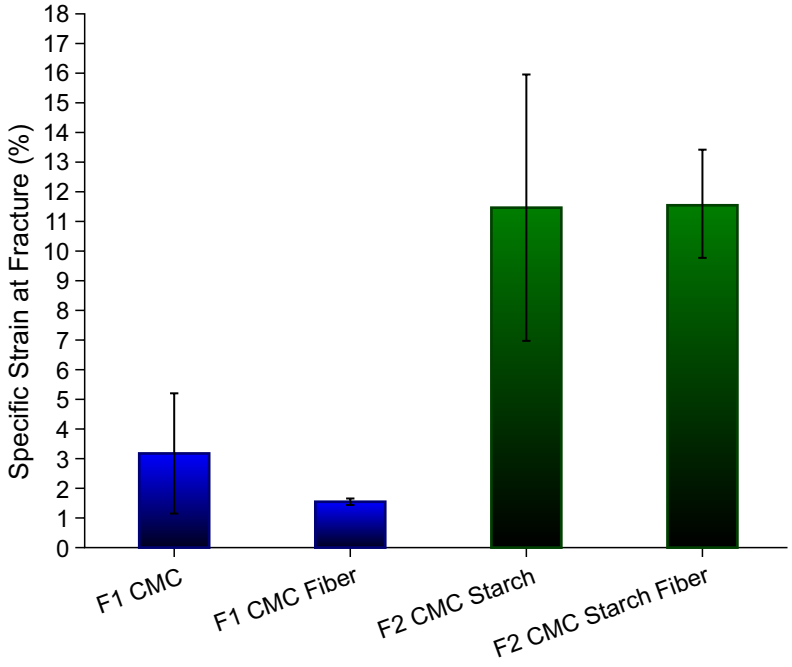


Table 6. Moisture Content on a dry basis.

Samples	Moisture Content (%)
Sample 1 (F4 Starch)	0.9748
Sample 2 (F5 Starch)	0.9756
Sample 3 (F1 CMC)	0.9714
Sample 4 (F2 CMC)	0.8902
Sample 5 (F3 CMC)	0.9022
Sample 6 (F4 CMC)	0.9470
Sample 7 (F3 Coconut fiber)	0.9784
Sample 8 (F4 Coconut fiber)	0.9492

formulations containing the natural polymer had high solubility content values and low moisture content on a dry basis (Table 7).

The study analyzed the ability of formulations that met the research criteria to change color, using triplicates and incorporating pH indicators (bromothymol blue, anthocyanin, and phenolphthalein). Most of the samples showed consistent test results, especially the formulations with bromothymol blue and phenolphthalein, which responded satisfactorily to acid, neutral, and basic pH variations (2, 7, and 9) (Figure 5). Although cellulolytic fungi contaminated some plates (Figure 6), the acid-base indicators effectively detected pH changes in contaminated areas, demonstrating their potential as microbiological markers.

Conclusion

The study used principal component analysis to evaluate films composed of starch and CMC, highlighting higher solubility and lower moisture on a dry basis. Adding green coconut fiber waste increased the strength, reduced the films' flexibility, and decreased the solubility compared to other samples. This waste was combined with natural bioactive compounds to produce biodegradable composites with low toxicity, contributing to the management of organic urban waste. Glycerol improved film formation as a plasticizer, making it an economically viable by-product for producing new products. Colorimetric analysis revealed that the films with phenolphthalein and bromothymol blue effectively detected pH variations, indicating potential for intelligent packaging and as

Table 7. Determination of solubility content.

Samples	Solubility Content (%)
Sample 1 (F4 Starch)	98.4250
Sample 2 (F5 Starch)	94.8920
Sample 3 (F1 CMC)	94.9713
Sample 4 (F2 CMC)	95.4002
Sample 5 (F3 CMC)	95.0424
Sample 6 (F4 CMC)	95.6640
Sample 7 (F3 Coconut fiber)	93.8670
Sample 8 (F4 Coconut fiber)	92.4661

Figure 5. Developed formulations with pH indicators.

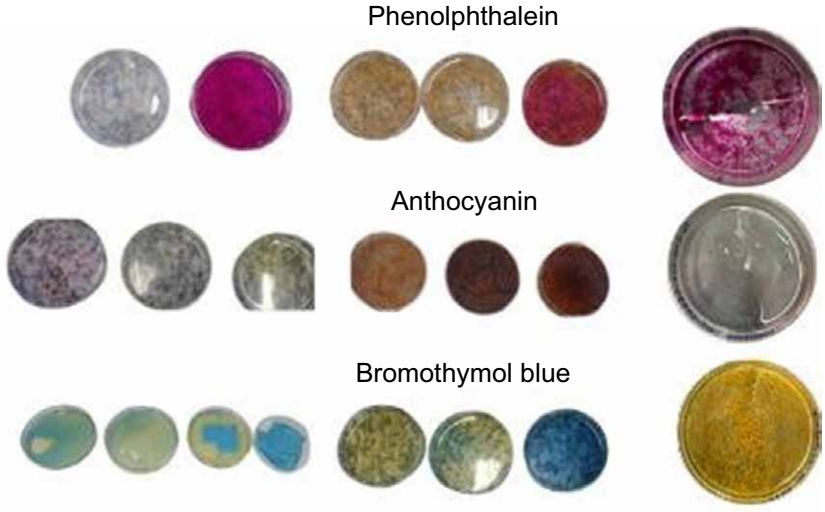
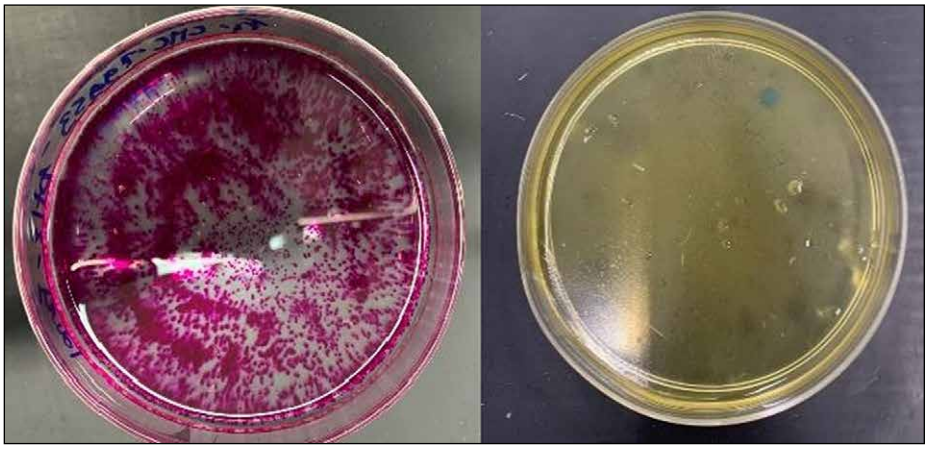


Figure 6. Formulations 1 and 3 (CMC) were contaminated with unknown microorganisms with phenolphthalein and bromothymol blue indicators, respectively.



microbiological markers to monitor contamination during product storage and distribution. These results contribute to the development of new materials using advanced production techniques.

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