CHEMICAL SYNTHESIS AND CHARACTERIZATION OF BIODEGRADABLE NONTOXIC HYDROGEL FOR CONTROLLED RELEASE OF FRAGRANCE

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Abstract

Hydrogel is a hydrophilic polymer and has the ability to swell on encountering water. The hydrogel can be synthesized from a natural or synthetic polymer, each having merits and demerits. The aim of the present research work is to synthesize biodegradable nontoxic hydrogel from guar gum and sodium alginate that can be tailored to deliver fragrance. The synthesized hydrogel was dried and was further characterized by using Fourier transform infrared spectroscopy [FTIR] analysis, field emission scanning electron microscopy [FESEM], and Ultraviolet-visible (UV-Vis) Spectrophotometer.

In order to overcome the existing problem of odor we have incorporated the lavender essential oil as a fragrance emitting in hydrogel synthesized from guar gum and sodium alginate. These essential oils will gradually release their fragrance in a controlled manner through the process of diffusion from the hydrogel. Hence hydrogel plays a very important role in emitting odor into the environment.

Keywords: Guar Gum, Sodium Alginate, Hydrogel, Lavender, Phosphate Buffer Saline.

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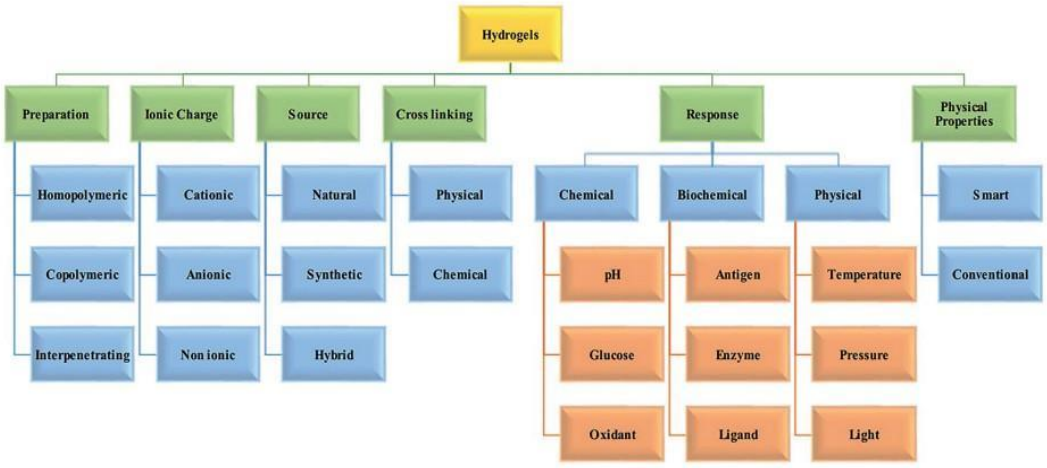
INTRODUCTION

Hydrogels are hydrophilic polymers which can be both homopolymers or copolymers, that tend to absorb water yet maintain their 3D structure.[1] The water-retaining capacity and the permeability are the most unique characteristic features of hydrogel and can absorb 300-400 times water as compared to its dry weight. The raw material used for the synthesis of hydrogel plays a very important role, like the variety of natural and synthetic monomeric and polymeric components, including acrylamide polysaccharides like chitosan, corn starch,[2] cellulose, Alginate, guar gum, and rice husk.[4–7]

Figure 1. Different classifications of hydrogels[3]



The hydrogels are affected by environmental parameters such as temperature, pH, solvent content, and ionic bonding. The synthesized hydrogels have numerous notable properties, like mechanical strength, biocompatible, swelling capacity, biodegradability,[8] hydrophilic nature, absorbance, softness, and fluffiness.

The hydrogel can be synthesized through two routes namely physical and chemical. Physical gels are formed by the clustering of molecules, which results in the formation of free chain loops that cause heterogeneity and short-lived network imperfections. Hydrogels can be produced through the combination of ionic association, Hydrogen bonding, crystallization, and freeze-thawing. Ionic associations between multivalent cations and hydrophilic associations in polymer chains are examples of physically crosslinked hydrogels that create networks in polymers. When subjected to external stimuli, they become brittle and mechanically weak. Physical hydrogels dissolve in organic solvents.[9,10]

Chemical hydrogels, also called permanent hydrogels, are formed by covalent bonding between the macromolecular chains. Chemically crosslinked hydrogel offers better control over synthesis and its application and which can be utilized to transform the physical properties of hydrogels, including their biodegradability, swelling behavior, and mechanical strength.[11] In comparison to physically crosslinked hydrogels, chemically crosslinked hydrogels offer greater mechanical characteristics and stability. As crosslinking increases, hydrogel's mechanical strength improves, but its capacity for swelling and adsorption is reduced because the polymer chain elasticity is reduced. Therefore, it is important to establish the ideal crosslink while making hydrogels.[12]

Guar gum and sodium alginate as they both are natural polysaccharides that can be used to form hydrogels through chemical crosslinking. These are formed between polymer chains, forming a more stable and durable hydrogel. The crosslinking process can begin by adding a crosslinking agent, glutaraldehyde to a solution of the polymers.

There are numerous applications of hydrogels, it can be used to extract dye from any solution from textile industries, remove heavy metals, in Food packaging, agriculture, and in biomedical engineering for drug delivery to various target organs.[13–18] Biopolymer hydrogel is a boon to medical sciences. They are the perfect material as they can hold water or biological fluids under physiological conditions and have a soft rubbery quality like live tissues. Smart devices like valves; muscles; contact lenses; antibacterial activity; biosensing; wound treatment; tissue engineering;

gel actuators; can be prepared by using hydrogel.[19–21] Hydrogel can also use to emit the aroma that is entrapped in it.

In this paper, we have used lavender essential oil (LEO) to emit aroma. The essential oil is produced from different species of the lavender plant like *Lavandula angustifolia, Lavandula x intermedia, Lavandula latifolia, and Lavandula stoechas.*[22]
Lavandula angustifolia, a flower with a husk-like structure, commonly known as garden lavender; *Lavandula latifolia*, a broad-leaved lavender; *Lavandula x intermedia*, is a hybrid cross between *Lavandula latifolia* and *Lavandula angustifolia*; *Lavandula stoechas*, sometimes known as French lavender. LEO possesses antifungal, anti-depressive, antibacterial, and tranquilizing properties and is effectual for burns and insect bites.[23] LEO is mainly produced by steam distillation from both flower and leaves but chemically it differs, as more treacly and aromatic oils are extracted from its flower.[24]

Guar gum (GG) is an extensively used biodegradable polysaccharide. It is extracted from the seeds of the guar plant (*Cyamopsis tetragonolobus*; family: Leguminosae). This polysaccharide is composed of D-mannopyranose monomer units and has gotten its application in the food industry, pharma industry, and cosmetics.[25] Sodium alginate (SA) is a polysaccharide and it is applied in the food, pharma, and rubber industry, etc. It is used to absorb organic pollutants and heavy metals through physical and chemical changes.[26]
In this paper, we have synthesized hydrogel using biodegradable GG and SA with the incorporation of LEO. The formed hydrogel is characterized by FTIR, FESEM, UV-Vis spectrophotometer and release kinetics evaluated by Krosmeyer-Peppas model. The hydrogel is used to emit aroma in wastewater, ponds, or lakes. LEO oil has been proclaimed to possess a pleasant aroma and antibacterial properties and it has been investigated as a promising agent for odor control in wastewater treatment. It has been found that the incorporation of LEO gradually reduced the intensity of odor in the wastewater. LEO contains compounds such as linalool and linalyl acetate, which have been shown to exhibit antibacterial activity against various strains of bacteria.

EXPERIMENTAL

Material and Methods

Guar Gum (GG) was obtained from Sisco research laboratories Pvt. Ltd. (Maharashtra, India), and Sodium Alginate (SA) was purchased from HiMedia Laboratory Pvt. Ltd (LBS Marg Mumbai, India), Glutaraldehyde was acquired from Loba Chemie (Mumbai, India), Calcium Chloride was procured from Loba Chemie (Mumbai, India), Deionized Water obtained from the laboratory, Lavender Essential oil was purchased from Aromazotika (Pune, Maharashtra).

Synthesis of Hydrogel and Bead formation

The hydrogel was prepared by varying concentrations of GG and SA (1:2, 1:3, 1:4, 2:3, 2:5). Both the polymers were mixed in 100 ml distilled water until no lump remains. 5%v/v glutaraldehyde was mixed into the GG/SA solution along with 5%v/v of LEO was added and mixed with glass rode. 3 M Calcium Chloride ($CaCl_2$) was mixed in chilled distilled water and the resulting mixture was slowly added dropwise in Calcium Chloride solution with the help of a dropper which leads to the formation of beads that are oval in shape. After 2h the beads were washed with deionized water and were dried in a hot air oven at 40^0C for 1h- 2h.[27,28]

Swelling percentage

The swelling percentage of hydrogel was calculated using the formula.[29]
Swelling percentage: $\frac{w2-w1}{w1} * 100$
W1- Weight of swelled hydrogel.
W2- Weight of dry hydrogel.

Detection Method

FTIR analysis
The FTIR (Fourier Transform Infrared) spectra of the hydrogel beads were obtained using a diamond ATR (Attenuated Total Reflection) spectrophotometer and the Potassium bromide (KBr) pellet method in the spectral range of 4000-400 cm^{-1}. The FTIR spectra of the mixed film revealed that the free carboxylic group of guar gum had been completely esterified.[30] This confirmed the polymer's strong intermolecular bonding.

FESEM analysis
After coating the sample with a gold film, Field Emission scanning electron microscopy (FESEM) was used to capture images of the hydrogel beads. FESEM revealed the blend ratios and cross-linker-influenced surface morphology.

UV- Visible spectrophotometer:
The delivery investigation of LEO is quantified by UV-visible spectrophotometer and tests were inspected at 270 nm of frequency. The hydrogel is drenched in Phosphate buffer saline (PBS) (pH-

6.94), at various intervals of time, the sample is withdrawn, and a fresh solution of the same volume is added.[31] The release kinetics of LEO is checked by the Krosmeyer-Peppas model, this model is generally used when the release mechanism is unknown or there is more than one strategy for it.[32]

RESULTS AND DISCUSSION

Hydrogel obtained by the synthesis of GG/SA in $CaCl_2$ was oval in nature and pale yellow in color but after drying in hot air oven at 40°C its changes to yellowish in color. However, Hydrogel with LEO was a bit lighter in color and slippery in nature as compared to one without LEO.

Figure 2. Synthesized Hydrogel

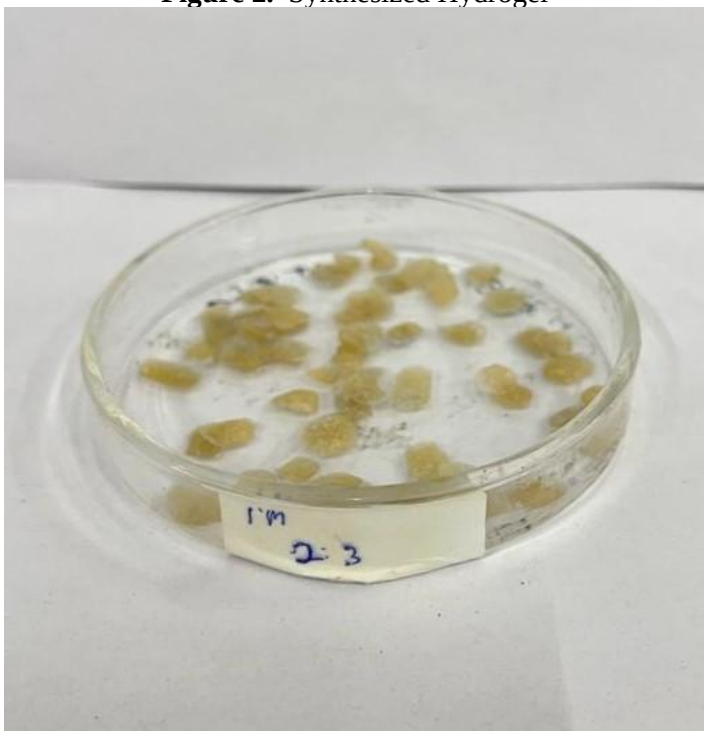
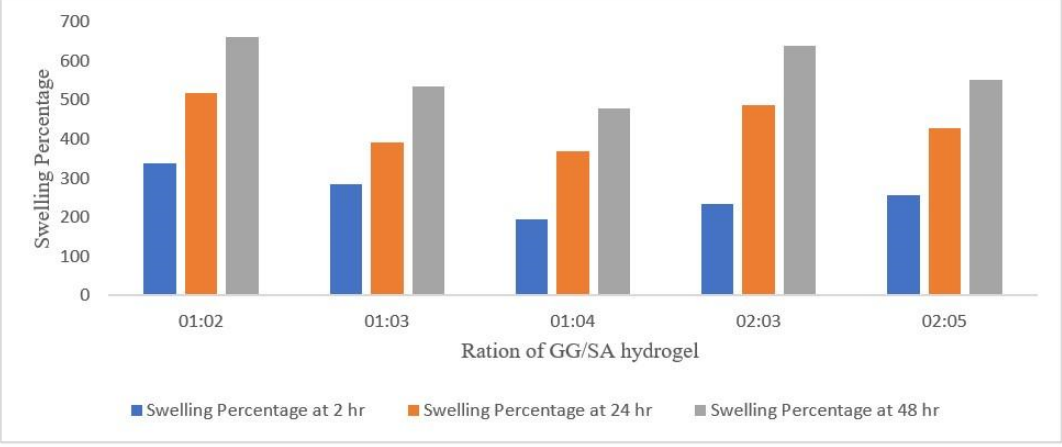


Figure 2 represents the hydrogel synthesized from GG/ SA and then dried in hot air oven at 40°C for 1- 2 hours. The morphology of it appears to be oval in nature with dark yellow color and it was then immersed in water in order to find its swelling percentage.

From Figure 3, it is clear that on increasing the concentration of SA, the swelling percentage of hydrogel decreases whereas on increasing the concentration of GG the selling percentage of hydrogel increases. Further, the ratio of GG/SA of 2:3 hydrogel that has been immersed in water for 48 hours swelled up to 638% as compared to its dry weight. This concludes 2:3 GG/SA is the most stable hydrogel as it is mechanically stable and can absorb the highest percentage of water, which helps in the diffusion of LEO for a longer period of time.

Figure 3. Swelling percentage of GG/SA at different time intervals.



FTIR analysis

FTIR analysis confirmed the crosslinking of GG/SA, and the result is shown in Figure 4. The FTIR spectrum of GG/SA hydrogel was observed to display a distinctive broad absorption band at 3350 cm^{-1}, attributed to N-H stretching vibrations of the polymer and it was observed that the sharp peak substantially reduced with a slight shift towards a longer wavelength,[33] while a peak at 2105 cm^{-1} was linked to CΞC stretching vibrations. The bands at 1632 cm^{-1} and 1426 cm^{-1} were identified as C=C cyclic alkene stretching and C-O stretching vibrations, respectively. Moreover, the absorption band close to 1426 cm^{-1} (C-O bending) was diminished, and the band close to 2105 cm-1 (CΞC) nearly entirely vanished. These results indicate that the crosslinking process had a profound influence on the molecular structure and chemical composition of the hydrogel, causing alterations in the hydrogen bonding and formation of novel chemical bonds between the GG and SA molecules.[34,35]

Figure 4. FTIR analysis of Synthesized Hydrogels.

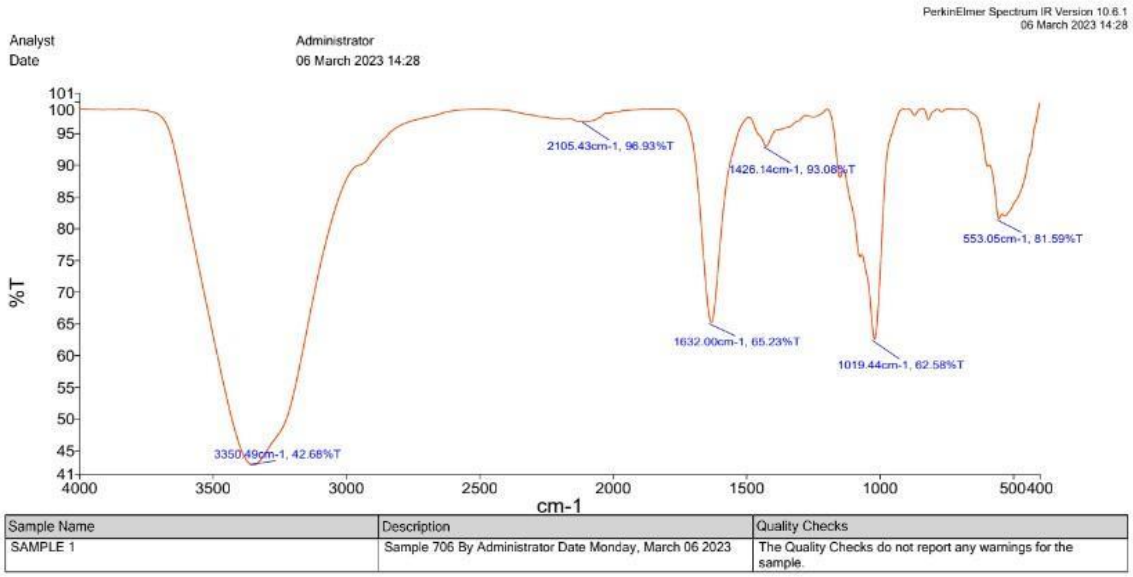
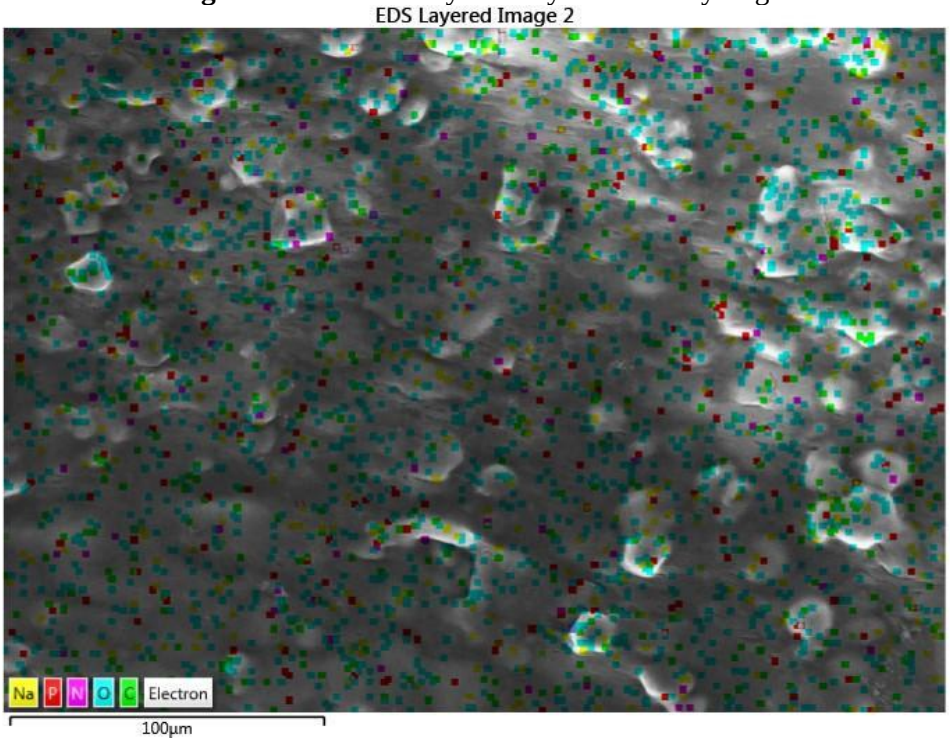


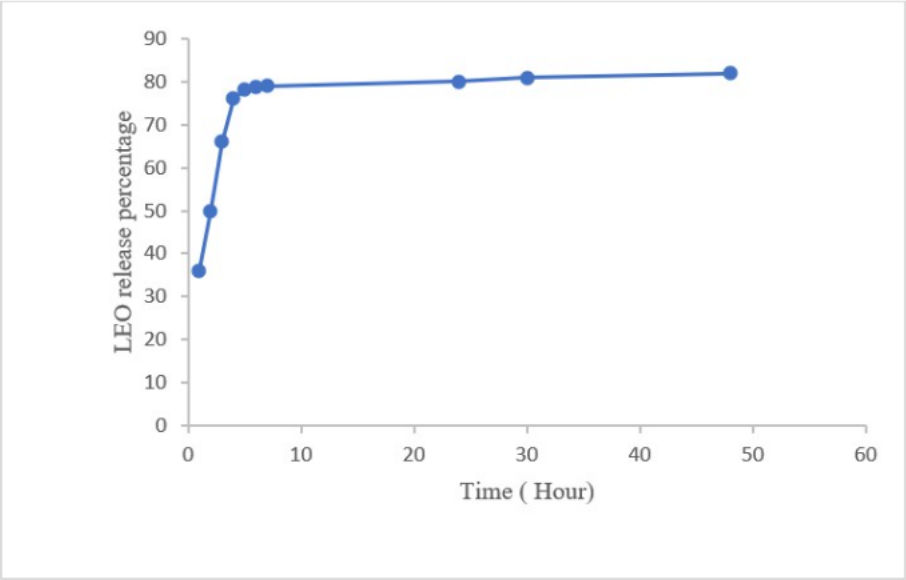
Figure 5. FESEM analysis of Synthesized Hydrogel



FESEM analysis:
FESEM is used to identify the morphology of the GG/SA hydrogels shown in Figure 5. The prepared hydrogels show a spherically shaped structure and are highly porous in nature.[36] This porous structure is likely to help hydrogel to retains more swelling capacity. FESEM image also reveals the presence of crosslinking points between the polymer chains, indicating successful crosslinking of the hydrogel.

LEO release:
The LEO has liberated from the hydrogel when it assimilates water and expands, further, it diffuses in water. As shown in Figure 6, illustrate the release percentage of LEO, which can be clearly seen to be 76% in the first four hours and 80% after 24 hours. As a result, it has been determined that the percentage of LEO released increases over time. In the beginning, 70% of LEO bursts into the environment, which helps to suppress order. Then, for the next 48 hours, there is a sustained release of LEO, which helps to emit aroma for a longer time.[37]

Figure 6. LEO release percentage with respect to time



Drug release kinetics:
To evaluate the release mechanism, the data is fitted in the Krosmeyer-Peppas model.

$$\frac{M_t}{M_\infty} = kt^n$$

where Mt/M is the fraction of the drug that was released at "t," K is the release rate constant, and n is the release exponent. The Krosmeyer-Peppas model was used to evaluate the involved LEO release mechanism using the initial 60% LEO release data. The transport mechanism is described by the release exponent “n,” where n=0.5 indicates that the drug is released via Fickian diffusion, with a rapid initial release followed by a slower rate over time. If n>0.5 suggests non-Fickian transport, the release rate is initially rapid but slower than Fickian Diffusion. The release mechanism is diffusion and swelling, which is a combination of both that is diffusion and erosion control release, and n=1 describes the non-Fickian case II (zero order) transport, which means it is independent of time.

The sample showed good linearity, where N = 0.62, R2= 0.963. For our tested results, n>0.5 indicates that developed films followed non-Fickian kinetics, implying that drug release is mediated by both diffusion and erosion. LEO is released in the matrix system through PBS penetration, which involves several steps: first, the hydrogel is submerged in PBS, causing it to swell, then LEO diffusion and degradation, resulting in LEO release. The non-Fickian drug release from films has been described by a number of authors. These outcomes reinforce our swelling studies, in which we observed slight film erosion.[32]

CONCLUSION

Today there are numerous methods for the synthesis of hydrogel for different applications. This study provides information about the use of biodegradable non-toxic GG/SA-based hydrogels for fragrance release which is an environmentally sustainable approach. FTIR analysis revealed the presence of characteristic functional groups of GG and SA. FESEM images showed the porous

microstructure of the hydrogel, which can facilitate the diffusion of the fragrance molecules. UV-Visible spectrophotometry can measure the absorbance of light through a sample containing lavender essential oil and with the help of the Krosmeyer-Peppas model, the release kinetics of LEO is evaluated. The hydrogel's-controlled release properties allow for a sustained and long-lasting fragrance effect, while the biodegradable nature of the GG/SA ensures that the hydrogel will degrade and not persist in the environment. The hydrogel also demonstrated good stability and compatibility with fragrance oils. Thus, this study highlights the potential for the development of biodegradable hydrogels as effective delivery systems for fragrances and other active ingredients. Further research is needed to optimize the formulation and explore the potential applications of these hydrogels in various fields, including personal care, household products, and air fresheners. Overall, this study provides valuable insights into the formulation and characterization of biodegradable hydrogels for fragrance release applications and highlights the potential of such hydrogels for various other applications in the future.

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