

Calcium carbonate nanoparticles as a filler for gelatin-based biofilms: preparation, characterization and properties

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Gelatin-based biofilms filled with calcium carbonate nanoparticles (NPs), synthesized from *Rapana Venosa* shells, were prepared by the solvent casting technique. The content of NPs in the films ranged from 0.5 to 5.0%. The water content, water absorption, solubility in water, tensile properties, and biodegradation were investigated and compared with those of the control gelatin film. Results showed that the addition of 5.0% of calcium carbonate nanofiller reduces the solubility in water and water absorption of the films by 58% and 64%, respectively. In contrast to the initial gelatin film, the incorporation of CaCO₃ NPs into the materials, regardless of the amount, increases the values of the elongation at break. The reinforcing effect of the nanofiller on the gelatin samples was manifested when 5.0% of NPs were added. These materials have a maximum tensile strength and Young's modulus of 7.16 and 70.3 MPa, respectively. It was proven that the NPs make the films more resistant and less susceptible to degradation after exposure to the surface of compost soil for a period of 6 months and could be used to extend the service life of biofilms.

Keywords: calcium carbonate nanoparticles, gelatin, biofilms, solution casting, properties

INTRODUCTION

Gelatin films, as thin-layer biopolymer materials, have attracted significant attention, especially in the fields of food packaging, pharmaceuticals, and biomedical engineering [1–3]. These films exhibit advantageous properties such as biodegradability and biocompatibility, however, pure gelatin films have insufficient mechanical strength, high moisture sensitivity, and limited barrier properties, which restrict their practical applications [4]. To overcome these limitations, researchers incorporate various nanofillers into gelatin matrices to improve their functional properties [5].

Nanocellulose significantly improves the mechanical properties of the gelatin films, enhancing their tensile strength and elasticity [6]. However, its hydrophilic nature can lead to increased water absorption, which is undesirable for applications requiring moisture resistance [7]. The layered structure of nanoclays gives them exceptional barrier properties that significantly reduce the permeability of biopolymer films [8]. The addition of metal and metal oxide nanoparticles into gelatin matrices is primarily due to their antimicrobial and UV-blocking properties [9–11]. They effectively inhibit microbial growth, extending the shelf life of food

products when used in packaging applications. A disadvantage of their use is the concern about potential toxicity and migration into food products [11].

Nano calcium carbonate, extracted from various waste materials, is a sustainable option for incorporation into gelatin matrices. Industrial by-products such as eggshells, mussels, and limestone waste serve as rich sources of calcium carbonate [12–14]. The small particle size and high surface area [13] make it an attractive option for enhancing the mechanical properties of gelatin-based materials. Additionally, nano calcium carbonate has been shown to have antimicrobial properties [15], which could further extend the shelf life of food products when used in packaging.

The aim of the present study is to prepare, characterize and determine the main properties of plasticized gelatin biofilms filled with calcium carbonate NPs. For this purpose, films combining gelatin, calcium carbonate nanofiller in amounts from 0.5 to 5.0% and glycerol as a plasticizer were obtained by the solution casting method. The properties of the biofilms were evaluated in terms of the influence of the additive on them and compared with those of a control film of pure gelatin.

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EXPERIMENTAL

Materials

Animal gelatin powder (type A) was purchased from the local market in Burgas, Bulgaria. Glycerol $C_3H_8O_3$ (molecular weight 92.10 g/mol, density 1.26 g/cm³), used as a plasticizer of the films, was purchased from Marvin Ltd, Dimitrovgrad, without further purification. Biogenic calcium carbonate with a particle size of ~ 40 nm, synthesized from *Rapana Venosa* shells, was provided by the Laboratory of Aquaculture and Biotechnology, Prof. Assen Zlatarov University. Distilled water was used as a solvent for preparing filmogenic solutions.

Film preparation

The gelatin- $CaCO_3$ NPs -based films were obtained by the traditional solution casting technique. Distilled water (40 mL) was mixed with 4 g of gelatin for each film. The resulting solutions were heated at 80°C for 15 min under stirring. 1.5 g of glycerol plasticizer (37.5% by weight of gelatin basis) was added, and the resulting mixtures were stirred for additional 5 min at the same temperature. Then 0.5, 1.0, 2.0, 3.0, and 5.0% of $CaCO_3$ NPs (based on total gelatin in dry state) were added to the mixtures and sonicated using a Branson 8510 ultrasonication bath for 30 min. The film-making solutions containing the indicated amounts of the nanofiller were placed into acrylic mould dishes (diameter: ~130 mm), kept at room temperature for 24 h, and dried in an oven at 40°C for a day to dry up properly. After drying, mould dishes were kept at room temperature for 24 h. Before being characterized, the dried films were removed from the dishes and kept at room temperature for a week. Specimens prepared were designated as control gelatin (G) film, G-0.5 $CaCO_3$, G-1.0 $CaCO_3$, G-2.0 $CaCO_3$, G-3.0 $CaCO_3$, and G-5.0 $CaCO_3$ according to the content of $CaCO_3$ NPs in the biofilms.

Characterization of the gelatin-based biofilms• *Thickness*

A micrometer thickness gauge was used to measure each gelatin biofilm sample's thickness with a 0.0001 mm precision. The average value of the thickness of each film measured at five different locations was taken as the thickness.

• *Water content*

The biofilm samples were cut into 20×20 mm pieces, and their initial weight (W_o , g) was measured. They were then dried in an oven at 70°C for 24 h and reweighed (W_f , g). To calculate the water content (WC , %), expressed as a percentage, the following formula was used:

$$\text{Water content (\%)} = [(W_o - W_f) / W_f] \times 100 \quad (1)$$

• *Water absorption*

Initially, gelatin-biofilm samples were dried in an oven at a temperature of 70°C for a day to get their initial weight (W_o , g). The samples were then immersed in distilled water and kept at room temperature for 210 min. For each measurement, specimens were removed from the water, wiped off, and reweighed (W_f , g) to a precision of 0.0001 g. The following Eq. (2) was used to determine the water absorption (WA , %):

$$\text{Water absorption (\%)} = [(W_f - W_o) / W_o] \times 100 \quad (2)$$

• *Water solubility*

To calculate the water solubility (WS , %) of the gelatin-based biofilms, 20×20 mm sizes of the samples were dried (70°C, 24 h) and weighed (W_o , g). Then each sample was immersed in distilled water and stored at a temperature of 22±3°C for a period of 24 h. The residual insoluble part of the films was removed, dried in an oven for 24 h at 70°C, and weighed again (W_f , g). Eq. (3) was used to calculate the G- $CaCO_3$ NPs biofilm's solubility in water:

$$\text{Water solubility (\%)} = [(W_o - W_f) / W_o] \times 100 \quad (3)$$

• *Tensile properties*

The tensile strength, elongation at break, and Young's modulus of control G film and G- $CaCO_3$ NPs biofilms were determined at room temperature according to EN ISO 50527-1 using a universal testing machine dynamometer INSTRON 4203, England. The grip distance was set at 25 mm, and a crosshead speed of 50 mm/min was applied. The samples' thickness was measured prior to each test.

• *Test for biodegradability*

To assess the biodegradability of gelatin-based films with $CaCO_3$ NPs, from each film samples with dimensions of length 50 mm, width 4 mm, and gauge length 25 mm were cut. Then the samples were weighed (W_o , g) and exposed to the surface of a compost soil for a period of 6 months. The compost soil media used had pH of 5.5 – 6.5 and electrical conductivity of 40 mS/m. After 6 months, the biofilms were removed from the compost soil and cleaned before being again weighed (W_f , g). The biofilms' biodegradability, or percentage weight loss, was calculated using Eq. (4):

$$\text{Weight loss (\%)} = [(W_o - W_f) / W_o] \times 100 \quad (4)$$

• *Visual appearance of the films*

The obtained dried control and gelatin- $CaCO_3$ NPs-based films after removal from the mould dishes were placed on a black base and photographed with a phone camera. To visually monitor the degradation of the samples before and

after exposure in a compost soil environment, the films were photographed again. All the photos taken, with a resolution of 739×1600 pixels, are reported in chronological order during the experiment in the Results and Discussion section.

- *Hardness by Shore*

The Shore A hardness of the resulting gelatin-based biofilms was determined on an apparatus “Stendal”, Germany scale A and ASTM D-2240.

RESULTS AND DISCUSSION

Visual appearance of gelatin-CaCO₃ NPs biofilms

The films obtained by casting from aqueous solutions of mixtures of gelatin, glycerol (37.5%), and calcium carbonate nanoparticles have good filmogenicity and are easily removed from the casting moulds. They are homogeneous, with a smooth surface and no visible bubbles or air inclusions (see Fig. 1).

As can be seen, the control gelatin film has high transparency and a pale yellow hue due to the gelatin. At a low concentration of NPs (0.5%), the dispersion of particles with a size of ~40 nm is good enough to obtain transparent films. However, the higher the amount of CaCO₃ NPs in the gelatin biofilms, the lower is the transparency of the samples. For example, the transparency of gelatin samples from G-1.0 CaCO₃ is slightly affected, with G-2.0 CaCO₃ being visually more opaque due to the higher concentration of nanoparticles which are

white in color. The use of nano CaCO₃ in higher amounts of 3.0 and 5.0% significantly increases the opacity of films compared to the control G film.

Thickness of gelatin-CaCO₃ NPs biofilms

Detailed data on the change in the thickness of cast gelatin films by the amount of CaCO₃ nanofiller are shown in Table 1. It is known that the thickness of G films is affected and can be increased by increasing the amount of NPs added to them [16, 17]. The data in the table confirm that compared to the control G film (356 μm), the thickness of the filled G film is greater and increases from 358 μm (for G-0.5 CaCO₃) to 382 μm (for G-5.0 CaCO₃). A similar increase in the thickness of gelatin-based biofilms when using CuS or WO₃ nanoparticles has been found by other authors [18, 19].

Water content, water solubility and water absorption of gelatin-CaCO₃ NPs biofilms

Although gelatin films possess sufficiently good mechanical and barrier properties, they are sensitive to the action of moisture. This limits their use, especially in applications where water resistance and water insolubility are required. Therefore, to characterize the biofilms obtained with CaCO₃ NPs, the following indicators; moisture content, water absorption and water solubility were studied and compared with the same for the control film without additive.

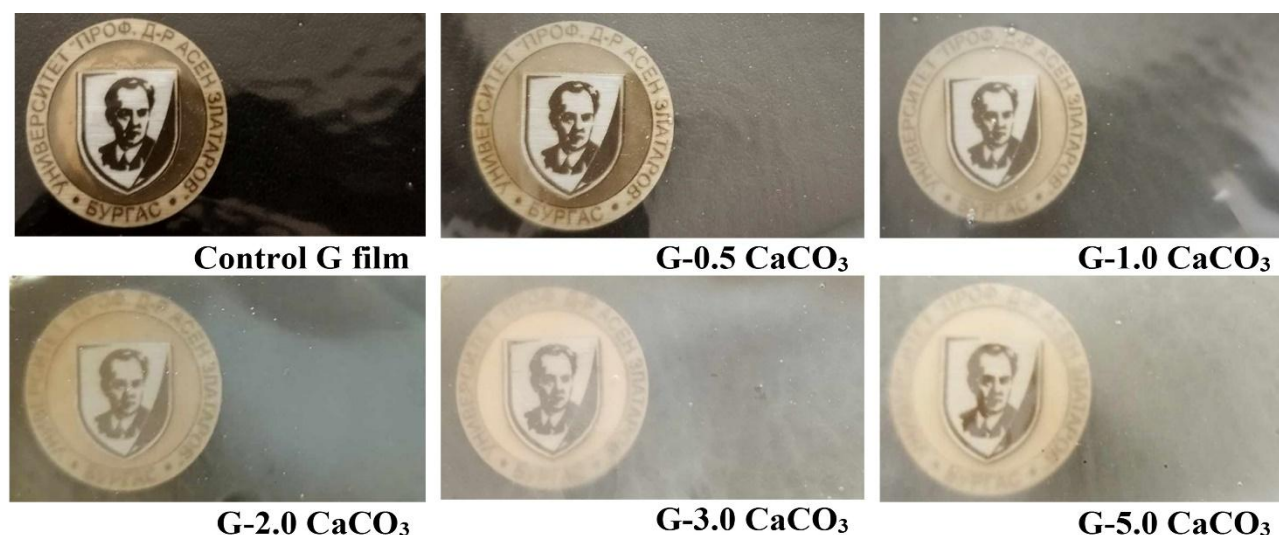


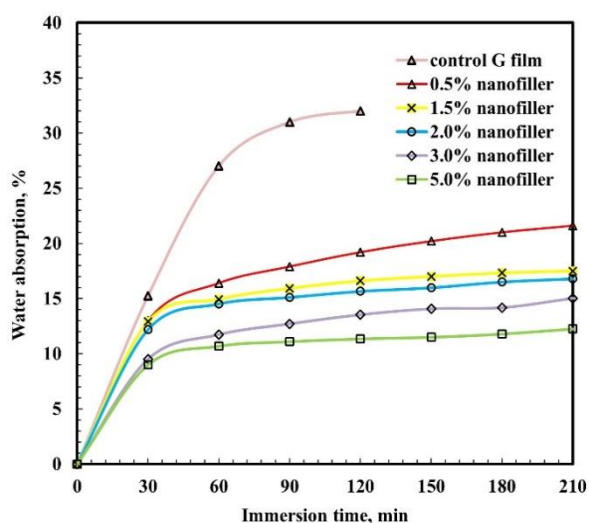
Fig. 1. Photographs of gelatin-based films with different contents of calcium carbonate NPs

Table 1. Thickness, water content, water solubility, Shore hardness and biodegradation of gelatin-based biofilms with calcium carbonate NPs.

Films	Thickness, μm	Water content, %	Water solubility, %	Shore hardness	Biodegradation, %
Control G film	356	0.376	5.697	74.3	8.537
G-0.5 CaCO_3	358	0.353	4.672	74.7	8.402
G-1.0 CaCO_3	361	0.308	4.458	74.5	8.371
G-2.0 CaCO_3	366	0.285	4.354	75.0	8.142
G-3.0 CaCO_3	370	0.245	3.662	74.9	6.564
G-5.0 CaCO_3	382	0.212	2.402	82.0	4.990

Table 1 shows the calculated water content (WC , %) and water solubility (WS , %) of the gelatin films. The trend observed is that both investigated parameters decrease after the addition of CaCO_3 NPs in amounts from 0.5 to 5.0%, the decrease in WC of the biofilms being weaker compared to the decrease in WS . The moisture content of the control G film is 0.376% and decreases to 0.353% and 0.353% for G-0.5 CaCO_3 and G-1.0 CaCO_3 samples, respectively. When using larger amounts of nano calcium carbonate, WC varies between 0.308 – 0.212%. The higher WC values for the control plasticized with glycerol G film are due to its sensitivity to water, due to its hygroscopic and hydrophilic nature [20]. The latter is the reason for the limited application of gelatin-based films in contact with food products with high moisture content [17, 21]. On the other hand, the CaCO_3 nanofiller is able to bind to the free hydroxyl groups by forming bonds with gelatin chains, which reduces their number and therefore lowers the WC and the sensitivity of NPs-based biofilms to water [22].

The water absorption curves of the control film and gelatin biofilms with nano calcium carbonate over time are illustrated in Fig. 2.

**Fig. 2.** Water absorption curves of gelatin-based biofilms on calcium carbonate nanofiller content

The highest water absorption (WA , %) of 32% is displayed by the control G film at a water immersion time of 120 min. With longer immersion, the plasticized gelatin film begins to dissolve in water [23] and it becomes impossible to determine its WA . The inclusion of nanoparticles in amounts up to 5.0% in the composition of the biofilms reduces the water absorption of the samples compared to that of the pure gelatin film. For example, for the control film after 90 min, WA is 31%. With the addition of filler, the water absorption of materials with 0.5, 1.0, 2.0, 3.0 and 5.0% CaCO_3 NPs decreases to 17.9, 15.9, 15.1, 12.7 and 11.1%, respectively. The tendency to decrease WA with increasing NPs concentration is maintained even at longer immersion times, probably due to the excellent barrier properties of these nanoparticles [24]. This means that the nano CaCO_3 synthesized from *Rapana Venosa* shells successfully improves the water resistance and stability of gelatin-based biofilms in a high-humidity environment.

It was found that the addition of nanofiller also reduces the water solubility (WS , %) of the obtained plasticized films. Increasing the amount of CaCO_3 NPs from 0.5 to 3.0% gradually reduces WS and it is in the range from 4.672 to 3.662% (Table 1). The main reason for this is that CaCO_3 NPs make the structure of the G film more compact and thus limit the access of water molecules to the matrix [22, 25] and prevent its interaction with them [26]. That is why the smallest WS value of 2.402% is displayed by the G-5.0 CaCO_3 samples, which is almost 2.5 times lower compared to the control biofilm without nanofiller.

Tensile properties of gelatin- CaCO_3 NPs biofilms

To preserve the properties of biofilms during their use and eventual application, they should have appropriate strength and elasticity. Therefore, the tensile properties of the obtained biofilms were determined, namely, the tensile strength (Fig. 3), the

elongation at break (Fig. 4), and the modulus of elasticity (Fig. 5).

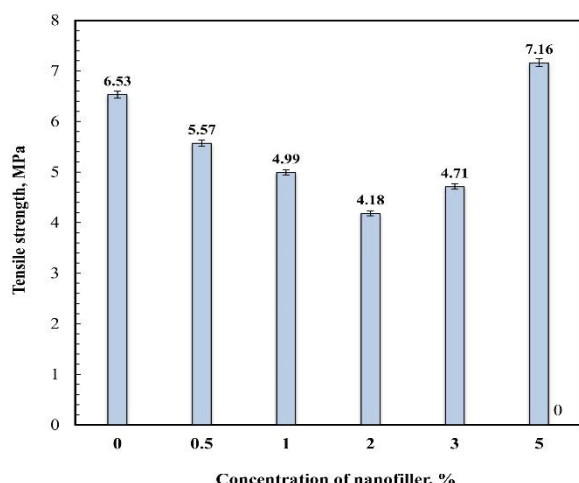


Fig. 3. Dependence of the tensile strength of gelatin-based biofilms on calcium carbonate nanofiller content

Fig. 3 shows the dependence of the tensile strength of gelatin films on the concentration of CaCO_3 NPs added. With an increase in the introduced calcium carbonate NPs to 2.0%, a decrease in the strength of the biofilms is observed. The reduced tensile strength of the films compared to the control G film can be due to the influence of NPs on the interactions in the gelatin matrix and the weakening of intermolecular bonds. Above the indicated amount, the strength slightly increases to 4.71 MPa but is still less than that of the initial biofilm without the additive. A similar decrease in strength for gelatin-based films when the concentration of incorporated ZnO NPs was increased has also been found by Sahraee *et al.* [27]. The reinforcing effect of nanofiller on the gelatin samples is realized in the G-5.0 CaCO_3 film. A maximum tensile strength of 7.16 MPa was determined for it. The probable reason for this is that filling with 5.0% of nanoparticles reduces the mobility of G chains and enhances the interaction between them, resulting in an increase in the tensile strength of biofilms at this concentration of NPs.

The opposite tendency was seen in elongation at break of the obtained biofilms. With increasing NPs concentration from 0.5 to 1.0%, the elongation at break of the films (Fig. 4) increased from 124.6 for control G film to 205.1% for G-1.0 CaCO_3 . When using larger amounts of the filler, the studied indicator decreased to 141.6% for G-5.0 CaCO_3 samples. However, all films, regardless of the amount of added biogenic nano calcium carbonate, showed higher values of elongation compared to the initial gelatin film without an additive.

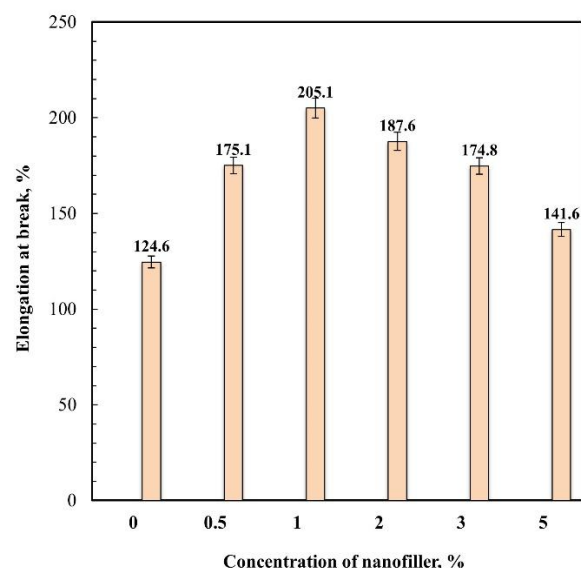


Fig. 4. Dependence of the elongation at break of gelatin-based biofilms on calcium carbonate nanofiller content

An increase in elongation at break over that of control G film by the addition of NPs was also found by other authors [28].

Similar to the tensile strength, the dependence of Young's modulus of biofilms on the addition of NPs of calcium carbonate follows the same course (see Fig. 5).

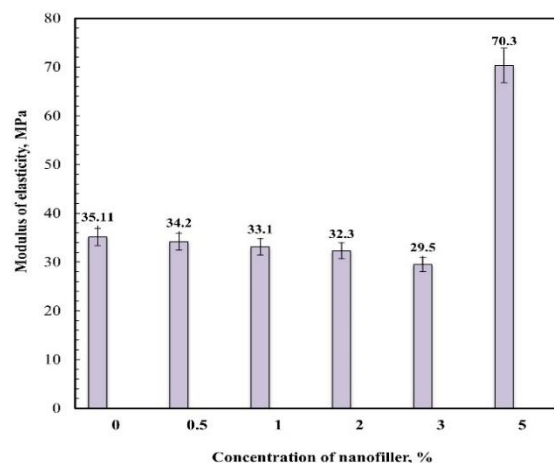


Fig. 5. Dependence of Young's modulus of gelatin-based biofilms on calcium carbonate nanofiller content.

When the amount of nanofiller is lower (up to 3.0%), the modulus smoothly decreases from 35.11 to 29.5 MPa for control G film and G-3.0 CaCO_3 , respectively. With a further increase in the amount of the additive in the samples to 5.0%, its influence becomes apparent, and the Young's modulus has a maximum value of 70.3 MPa. The high modulus found for cast G-5.0 CaCO_3 films is associated with the higher tensile strength (Fig. 3) and hardness (Table 1).

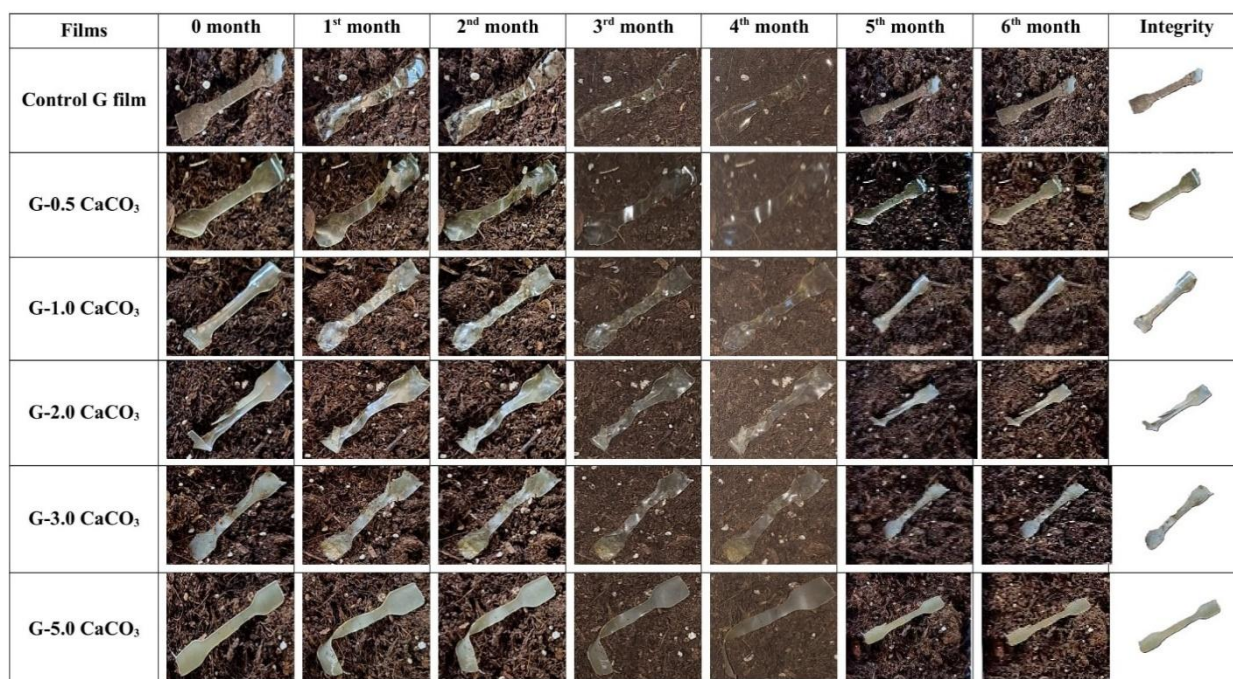


Fig. 6. Changes in the appearance of gelatin films before and after 6 months of exposure to compost soil surface

For all gelatin-based samples, both those without and those with NPs the measured hardness (from 74 to 82) is in full accordance with the results observed for the tensile strength and modulus of biofilms. This, according to the Shore A hardness scale, places the biofilms casted as medium hard.

Biodegradability of gelatin- CaCO_3 NPs biofilms

The visual change that gelatin films undergo is one of the first signs of the degradation process [29]. Already in the first month, the samples changed their original shape, and after the third month, the changes in the color and appearance of the biofilms with CaCO_3 NPs are obvious (see Fig. 6). With increasing the amount of NPs from the fourth month onwards, the opacity of the biofilms increases, especially for those with over 1.0% nanofiller. At the 6th month of the experiment, the films still show no signs of disintegration, but only changes at the edges of the samples and traces of degradation. The G-5.0 CaCO_3 film retained its shape and dimensions to a greater extent, despite the change in color and transparency after a period of 6 months on the surface of compost soil. This is probably due to structural changes occurring in the samples, which is the reason for the decrease in biodegradability, estimated by weight loss (Table 1). When comparing the biodegradability of the control G film to the biodegradability of those with the additive, it is seen that the addition of CaCO_3 NPs in the films in amounts from 0.5 to 5.0% slows down the degradation process (Table 1). The determined weight loss of the control G film is

8.537% after exposure to the surface of compost soil for 6 months. The weight loss of the biofilms with a nanofiller content of up to 2.0% is close to that of the gelatin film without the additive – from 8.402 to 8.142%. When increasing the amount of CaCO_3 NPs to 3.0%, a slowdown in the degradation process is observed. The G-5.0 CaCO_3 film undergoes the least degradation (4.990%) after 6 months of exposure to the surface of compost soil. It is assumed that the inclusion of nanoparticles in the matrix stabilizes the structure and reduces the degree of biodegradation due to an increase in the crystallinity of the biofilms [17]. Furthermore, the reduced water absorption of the nano calcium carbonate materials (Fig. 2) also hinders degradation, as the presence of water in the gelatin films is crucial to accelerate the process. The above is an evidence that the used additive of CaCO_3 NPs in the gelatin films makes them more resistant and less susceptible to degradation after exposure to the surface of a compost soil for a period of 6 months and therefore can increase the service life of biofilms.

CONCLUSIONS

Films combining gelatin, calcium carbonate nanofiller in amounts from 0.5 to 5.0% and glycerol as a plasticizer were obtained by the solution casting method, and their main properties were determined. The results for the properties of the plasticized gelatin biofilms filled with nanoparticles were monitored in terms of the influence of the additive on them and compared with those of a control film of pure gelatin. It was found that the nano calcium

carbonate used reduces the water solubility and water absorption of the films, increases the thickness and the elongation at break, and the films with 5.0% of the filler have the best tensile strength and modulus of elasticity. It has been proven that calcium carbonate nanofiller successfully slows down the biodegradation process of gelatin-based biofilms, and after exposure to the surface of compost soil for 6 months, they retain their integrity.

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REFERENCES

1. S. Hajji, H. Kchaou, I. Bkhairia, R. Ben Slama-Ben Salem, S. Boufi, F. Debeaufort, M. Nasri, *Food Hydrocoll.*, **116**, 106639 (2021).
2. S. Al-Nimry, A. A. Dayah, I. Hasan, R. Daghmash, *Mar. Drugs*, **19**, 145 (2021).
3. I. Zulkiflee, M. B. Fauzi, *Biomedicines*, **9**, 979 (2021).
4. A.A. Tyuftin, J.P. Kerry, *Food Packag. Shelf Life*, **29**, 100688 (2021).
5. Z. Yang, S. Chaieb, Y. Hemar, *Polym. Rev.*, **61**, 765 (2021).
6. P.O. Onyeaka, H. Dai, X. Feng, H. Wang, Y. Fu, Y. Yu, H. Zhu, H. Chen, L. Ma, Y. Zhang, *Food Hydrocoll.*, **144**, 108972 (2023).
7. I. Surya, C. M. Hazwan, H. P. S. Abdul Khalil, E. B. Yahya, A. B. Suriani, M. Danish, A. Mohamed, *Polymers*, **14**, 4147 (2022).
8. P. Trigueiro, J. P. D. L. Pereira, M. G. Ferreira, L. B. Silva, L. Neves, R. R. Peña-Garcia, *Minerals*, **14**, 613 (2024).
9. D. Lin, Y. Yang, J. Wang, W. Yan, Z. Wu, H. Chen, Q. Zhang, D. Wu, W. Qin, Z. Tu, *Int. J. Biol. Macromol.*, **154**, 123 (2020).
10. M. Abbas, M. Buntinx, W. Deforne, R. Peeters, *Nanomaterials*, **9**, 1494. (2019).
11. W. Zhang, J. W. Rhim, *Food Packag. Shelf Life*, **31**, 100806 (2022).
12. N.S. Ahmed, F.H. Kamil, A.A. Hasso, A.N. Abduljawaad, T.F. Saleh, S.K. Mahmood, *J. Mech. Behav. Mater.*, **31**, 1 (2022).
13. A.I. Hussein, Z. Ab-Ghani, A. N. Che Mat, N. A. Ab Ghani, A. Husein, I. Rahman, *Appl. Sci.*, **10**, 7170 (2020).
14. S. El-Sherbiny, S. El-Sheikh, A. Barhoum, *Powder Technol.*, **279**, 290 (2015).
15. P. Fadia, S. Tyagi, S. Bhagat, A. Nair, P. Panchal, H. Dave, S. Dang, S. Singh, *Biotech.*, **11**, 457 (2021).
16. S. Kundu, A. Das, A. Basu, M. F. Abdullah, A. Mukherjee, *Carbohydr. Polym.*, **170**, 89 (2017).
17. M.R. Khan, M.B. Sadiq, *Polymer Bulletin*, **78**, 4047 (2021).
18. S. Roy, J-W. Rhim, *Appl. Sci.*, **11**, 6307 (2021).
19. K. Rubini, A. Menichetti, M. C. Cassani, M. Montalti, A. Bigi, E. Boanini, *Gels*, **21**, 354 (2024).
20. P.V. Pulla-Huillca, A. Gomes, A.M.Q.B. Bittante, R.V. Lourenco, P.J. do Amaral Sobral, *J. Food Eng.*, **297**, 110480 (2021).
21. P. Bergo, I.C.F. Moraes, P.J.D.A. Sobral, *Food Hydrocoll.*, **32**, 412 (2013).
22. R. Huang, A. Yao, Y. Yan, J. Wang, Q. Li, K. Li, Y. Tian, S. Wang, J. Wu, *eFood*, **5**, e179 (2024).
23. M.I.J. Ibrahim, S.M. Sapuan, E.S. Zainudin, M.Y.M. Zuhri, A. Edhirej, in: Advanced Processing, Properties, and Applications of Starch and Other Bio-Based Polymers, Faris M. Al-Oqla, S.M. Sapuan (eds.), Elsevier, 2020, p. 35.
24. H. He, J. Yang, W. Huang, M. Cheng, *Adv. Polym. Tech.*, **37**, 1022 (2016).
25. J. Chen, L. Luo, C. Cen, Y. Liu, H. Li, Y. Wang, *Int. J. Biol. Macromol.*, **220**, 462 (2022).
26. Y. Wang, A. Liu, R. Ye, X. Li, Y. Han, C. Liu, *Int. J. Food Prop.*, **18**, 2442 (2015).
27. S. Sahraee, B. Ghanbarzadeh, J.M. Milani, H. Hamishehkar, *Food Bioprocess Technol.*, **10**, 1441 (2017).
28. P. Soo, N.M. Sarbon, *Food Packag. Shelf Life*, **15**, 1 (2018).
29. S.H. Othman, N.D.A. Ronzi, R.A. Shapi'i, M. Dun, S.H. Ariffin, M.A.P. Mohammed, *Coatings*, **13**, 777 (2023).