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Polyphenol-containing water-soluble bio-composite films as alternative food packaging materials

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Abstract. Historically, the development of better food preservation techniques has been one of the main factors in the prosperity and health of any human population, and with the exponential rise in food demand leads science in search of eco-friendlier solutions. One such path is the development of water-soluble biodegradable coatings based on easily accessible and abundant natural polymer materials. As a common byproduct of the food industry, corn zein is one of the most promising biopolymers for food packaging, offering excellent barrier properties. Its main drawback – poor mechanical strength – can be mitigated with the addition of other biodegradable polymers that would result in the creation of bio-composite materials with controllable properties. Further improvements of such biopolymer coatings can be achieved with the addition of other materials, such as different polyphenols, that may improve their antioxidant properties. The presented paper investigates water-soluble bio-composite films, created by dissolving equal parts zein and hydroxypropyl methylcellulose in ethanol solution (70:30 ethanol to water ratio). Polyethylene glycol was used as plasticiser in all samples. Two different polyphenols (quercetin and curcumin) were incorporated in the bio-composites at a concentration of 2 mg/cm^2. The mechanical properties of the created films were studied with a use of Universal Testing Machine (Lloyd Instrument). The surface morphology was investigated with scanning electron microscopy and the surface free energy was determined with the use of the sessile drop method. The dependence of the normalized surface potentials on the storage time of the charged substrates was studied. Parameters, important for food preservation, such as water vapor permeability, were investigated.

Key words: food packaging, biopolymer, polyphenols.

Introduction

The development of better food preservation techniques throughout history has been one of the most significant factors that has allowed humanity to spread into every biome and has contributed to the improvement in living standards of many different population groups throughout the globe (Dennis, 2024; Risch, 2009). However, the rapid increase in the demand for better and cheaper food packaging has also led to a significant increase in waste products, whose environmental impact has become a major concern in modern times (Heller et al., 2019; Arfelli et al., 2024). The rapid development and vast utilisation of plastic-based packaging materials in the last century has caused significant damage to of ecosystems, such as the Great Pacific Garbage Patch (Pyrek, 2016; Lebreton et al., 2018) and could also adversely affect the health and well-being of a majority of the global population (Claudio, 2012; Picó & Barceló, 2019; Wu et al., 2017).

The increasing environmental impact of plastic-based packaging is a major concern of the global research community and has led to an increased interest in the research and development of more environmentally friendly alternatives (Ncube et al., 2020; Dilkes-Hoffman et al., 2018). The last couple of decades have seen a vast increase in the research and development of biodegradable materials, based on natural and renewable sources, that can be utilised as a viable alternative to the most common plastic-based packaging applications (Perera et al., 2023; Agarwal et al., 2023). Different biopolymers, such as zein (Plasencia et al., 2025; Corradini et al., 2014) and cellulose (Shanmuga Priya et al., 2014; Athanasopoulou et al., 2025), could be utilised for the creation of completely biodegradable and biocompatible packaging materials, whose environmental impact would be significantly smaller when compared to conventional packaging materials and even some of their more popular alternatives (such as paper-based packaging).

One of the major hurdles preventing the wider spread of these biodegradable alternatives is the poorer properties of these materials when compared to their plastic-based counterparts. Most of the biodegradable alternative materials cannot match the mechanical and barrier properties of the widely used plastics. This factor can be mitigated by the combination of several biopolymer materials, creating bio-composites with tailored properties (Weligama Thuppahige & Karim, 2022; Din et al., 2020). The properties of these bio-composites can be additionally enhanced with the addition of different antimicrobial (Cooksey, 2005) and antioxidant materials, such as different polyphenols (Al-Naymi et al., 2025; Tang et al., 2024). However, more research is required before the proper implementation and wider spread of these biodegradable alternatives within the wider food packaging market. The current research is focused on the investigation of the physical properties of one such biodegradable composite, consisting of zein and hydroxypropyl methylcellulose (HPMC), and containing two different polyphenols (curcumin and quercetin).

Materials and methods

Materials

Both biopolymers (zein and hydroxypropyl methylcellulose) as well as both polyphenols (curcumin and quercetin) were purchased from Sigma – Aldrich (Merck KGaA, Darmstadt, Germany) and were used as delivered. All other chemicals were of analytical grade.

Film Creation

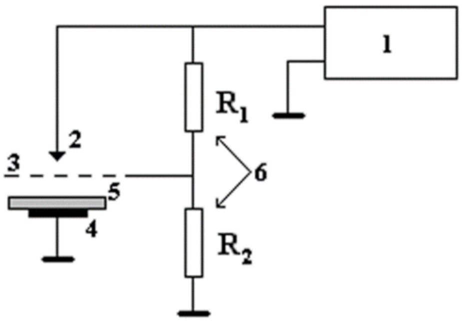
The water-soluble biodegradable films were created using the following procedure: A mixture of the two biopolymers (at a ratio of 1:1, 0.5 g of each polymer) is dissolved in a 30 ml mixture of water and ethanol at a ratio of 70:30. A set amount (0.5075 g) of plasticiser (PEG 400) is also added. Two different polyphenols (curcumin and quercetin) are also separately incorporated in the mixture at a set concentration, so that the final concentration of polyphenol in the films is 2 mg/cm^2. The resulting solution is stirred on a magnetic stirrer for 1 hour at 70°C. The mixture is then poured into a plastic petri dish and dried in an incubator at 60°C for 1 hour, after which it is placed on a level surface at room temperature and dried for 24 hours until the complete evaporation of the solvent. The resulting films are kept in a dry desiccator at room temperature until further use.

Corona charging

The surface modification of the samples was carried out under corona discharge at room temperature with the use of a tri-electrode system, consisting of a corona electrode (needle), a grounded plate electrode and a metal grid (controlling electrode) placed between the other two (Fig. 1). The sample (placed on a thin metal disc) (5) is positioned on the grounded electrode (4). Set voltage is then supplied to both the corona electrode (2) and the metal grid (3). The voltage supplied to the metal grid determines the size of the surface potential created on the surface of the samples. The voltage supplied to the corona electrode was set to 5 kV, and the voltage of the grid was set to 1 kV for 1 minute. Both voltages were of positive or negative polarity.

Scanning electron microscopy (SEM)

The morphology of the created biodegradable composite films was determined with the use of scanning electron microscopy (SEM) (Prisma E SEM, Thermo Scientific, Waltham, MA, USA). Two milligrams of each of the tested samples was attached to an aluminum holder and subsequently coated with carbon and gold, with the use of a turbomolecular pumped sputter coater system Quorum Q150T Plus (Quorum Technologies, West Sussex, UK). The resulting images were captured with the use of a back scattered electron detector (Prisma E SEM, Thermo Scientific, Waltham, MA, USA) at an accelerating voltage of 15 kV at different magnifications.



1 – high voltage source, 2 – corona electrode, 3 – metal grid, 4 – grounded plate electrode 5 – sample on metal disc, 6 – voltage splitter.

Fig. 1. Tri-electrode schematic for the creation of electrets under corona discharge (Grigorov et al., 2025).

Sessile drop method

Investigation of the hydrophobic properties of the investigated composite films was carried out in standard conditions (room temperature and normal atmospheric pressure) with the use of two different liquids (water and diiodomethane CH_2I_2). Small droplets (2 µl) of each of the liquids were carefully deposited on the surface of the films with the use of a precise 10 µl micro syringe (Innovative Labor System GmbH, Germany). A total of 6 drops of each liquid were deposited on the surface of the films, after which the collected results were averaged and utilized for the determination of the hydrophobic properties of each sample. The contact angles were determined by measuring the angle created by the tangent of the drop profile and the surface of the films from images captured with the use of a high-resolution camera. ImageJ software was used for the analysis of the captured images.

Results and Discussion

Electret properties

The electret properties of the created composite films were investigated. Time dependences of the normalized surface potential of HPMC+zein, HPMC+zein with curcumin (HPMC+zein+C) and HPMC+zein with quercetin (HPMC+zein+Q) electrets, possessing either positive or negative charges, were investigated during 30 days. The values of the surface potential were first collected each day for the first 5 days, due to the more rapid decrease of the surface potential in that period, after which the samples were measured less frequently (every 3-4 days). Six samples of each type of composite films were used for the determination of the surface potential by averaging the values of the normalised surface potential at each time interval. The statistical error of the averaged values (which was determined to be lower than 5%) was also calculated. Time dependences of the normalised surface potential for all investigated films are presented in Fig. 2a – positive corona and Fig. 2b - negative corona.

The results presented in Fig. 2 show that the normalised surface potential values were decaying exponentially for the first 15 days. After this, the rate of decay decreased and was practically stabilised within 30 days. These results demonstrate the existence of different surface states that were localised on the surface of the sample and that contain entrapped charges within them. The initial exponential decrease can be attributed to the release of weakly captured charges from any shallow energy states. After this period, the potential became stable at a steady state value, which can be due to the remaining tightly entrapped charges in deeper traps. Similarly, exponential decay with subsequent slow linear reduction of the electrets' charge was observed by Sessler (2001) and Viraneva et al. (2025).

It was established that the normalised surface potential for positively charged films is higher than that of the negatively charged ones, regardless of the type of polyphenol included. This can be explained by the theory that during the corona discharge in air, at atmospheric pressure, different types of ions are deposited on the sample, since the charging in a corona discharge depends on the corona polarity. In the case of a positive corona, the ions are mainly $H^+(H_2O)n$ and the ones for a negative corona - CO_3^- (Giacometti et al., 1999). These ions are bound in traps of various depths and their release depends on the surrounding conditions.

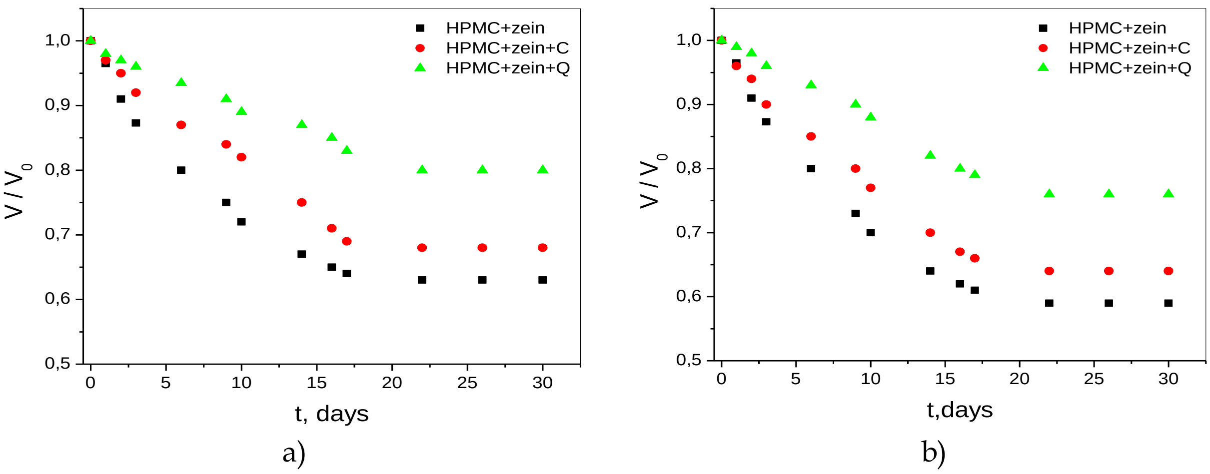


Fig. 2. Time dependences of the normalised surface potential for PDLA composite films charged a) in a positive corona and b) in a negative corona.

It was also observed that the values of the normalised surface potential were the smallest for pure HPMC+zein electrets and increased when the different polyphenols were included. The highest values of the normalised surface potential were observed for the HPMC films with quercetin charged in a positive corona. This is probably due to the structure of the films and their conductivity. The conductivity of all investigated composite films is presented in Fig. 3.

The results presented in Fig. 3 show, that the highest values of the conductivity were observed for the pure composite films. The inclusion of different polyphenols in the HPMC+zein matrix leads to a decrease in conductivity independently of the applied voltage. As the applied voltage increases, the conductivity of the investigated composite films decreases, independently of the type of polyphenol included.

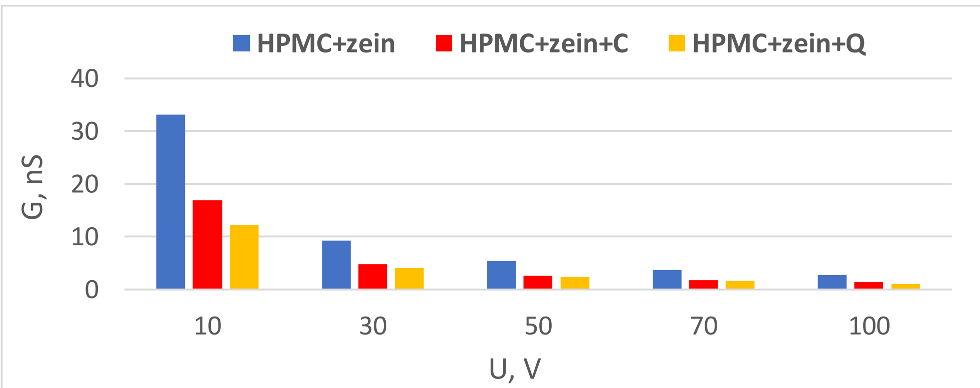


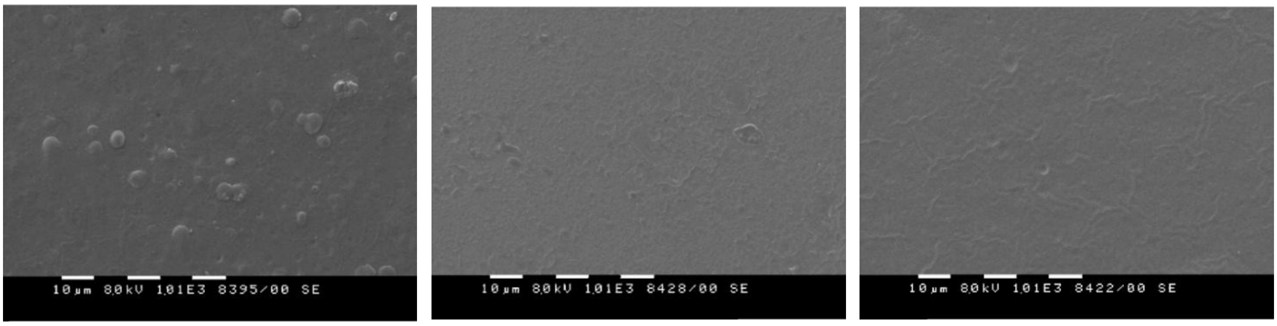
Fig. 3. Conductivity of all investigated composite films.

Scanning electron microscopy (SEM)

SEM is an intuitive technique for observing the morphology of samples, which was performed to provide some information about the physical structures of three types of investigated composite films: pure films (HPMC+zein), films containing curcumin (HPMC+zein+C) and films containing quercetin (HPMC+zein+Q).

Zein is a hydrophobic polymer that tends to aggregate and form particles in the presence of water, and when used in combination with a water-soluble polymer as HPMC, gaps are observed, as seen in the current images (Tian et al., 2024). This tendency of zein was confirmed and manifested in the preparation of a composite film based on equal mass ratios between it and HPMC.

The images obtained for the HPMC+zein films show the formation of spherical and oval particles with an average diameter of about 3 µm (Fig. 4a), which can be attributed to undissolved zein clusters migrating to the surface of the film. The rest of the SEM images (Fig. 4b and 4c) show that the inclusion of the polyphenols in the structure of the composite films increased their surface roughness. The inclusion of curcumin and quercetin in the structure led to a significant increase in the surface roughness, which was possibly due to the higher content of hydroxyl groups in the two polyphenols, leading to the easier interaction with zein (Liu et al., 2021).



a) b) c)

Fig. 4. SEM images of a) HPMC+zein, b) HPMC+zein+C and c) HPMC+zein+Q.

Surface free energy of the investigated composite films

Surface hydrophobicity is related to the ability of a liquid to preserve contact with a surface of a solid, which shows the magnitude of the intermolecular interactions of a system. For this reason, the surface hydrophobicity of pure HPMC + zein films and HPMC + zein with different polyphenols films was determined by surface contact angle measurements with the use of the sessile drop method. Following the theory of Owens & Wendt (1969), the total surface free energy of all investigated composite films was calculated. The obtained results are presented in Fig. 5.

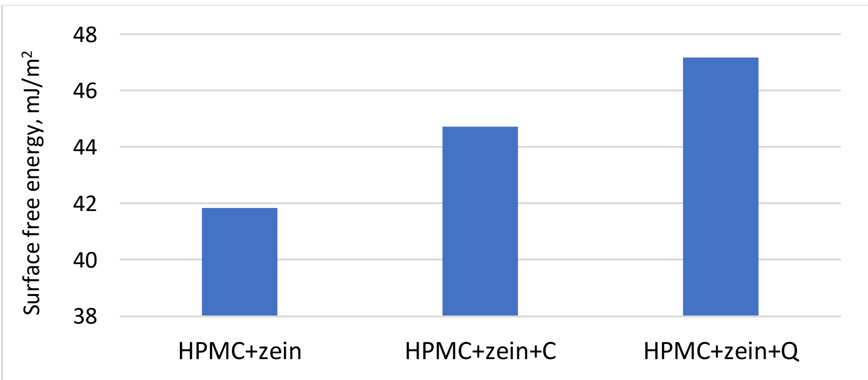


Fig. 5. Surface free energy of all investigated composite films.

The results presented in Fig. 5 show that the surface free energy increases when different polyphenols (curcumin and quercetin) are included. With the addition of polyphenols, the surface free energy of the created films increased from 41.9 mJ/m^2 (HPMC + zein) to 44.7 mJ/m^2 (HPMC + zein + C) and 47.2 mJ/m^2 (HPMC + zein + Q). Therefore, the hydrophilicity of composite films increased after the incorporation of the investigated polyphenols. The reason may be that, with their hydrophilic groups, polyphenols can cause an increase in the interaction between the film surface and water, resulting in a decrease in contact angle and an increase in surface energy. The presence of zein in the investigated films may also affect hydrophilicity. It was established by Yang et al. (2025) that zein has poor hydrophilicity due to its high content of hydrophobic amino acids.

Although zein is considered to be a water-insoluble protein, it has a contact angle of less than 90°, which may be caused by the fact that zein still contains a portion of hydrophilic amino acids such as glutamic acid. This may be related to the disruption of hydrogen bonding in the molecular chain of zein, resulting in an increase of free amino or hydroxyl groups in the zein matrix. As shown in Xu et al. (2022), the hydrogen of control samples of zein is the highest, and the hydrogen of all zein–polyphenol films decreases, which reveals that the surface of modified zein becomes more hydrophilic. The hydrogen of protein is related to the location as well as the number of non-polar groups, and the introduction of hydrophilic hydroxyl groups in polyphenols may contribute to the decline of hydrogen. The increase of polarity around tyrosine residues could be another reason. The combination of polyphenols with the hydrophobic sites of zein changed the folding pattern of the protein. Therefore, the aromatic heterocyclic hydrophobic groups in the tyrosine residues of zein were buried, which resulted in an increase of the hydrophilicity of zein–polyphenol films.

Conclusions

The results presented in this paper demonstrate the potential of the water-soluble biocomposite polymer materials as alternative food packaging materials. The increase in the surface potential with the inclusion of the polyphenols shows that their addition can further improve the properties of the biofilms, thus additionally increasing their viability. This, combined with the improved electret properties and increased surface roughness, could allow any packaged food products to last longer and maintain its desirable properties for longer.

Acknowledgments

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