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Polyphenols/poly(lactic acid) blends – structure, thermal and electret properties

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Poly(lactic acid) (PLA) based functional films incorporated with curcumin, rutin and quercetin were prepared using a solution casting method. The presence of the polyphenols in the polymer matrix was proven by X-ray diffraction analysis. Curcumin was uniformly dispersed in the PLA matrix and showed excellent compatibility with it, as evidenced by the SEM and DSC analysis. The addition of curcumin improved the thermal stability of the PLA film. In contrary, rutin and quercetin were present in micro-sized aggregates in the polymer matrix and showed poor compatibility. All incorporated polyphenols degraded the electret properties of the PLA films.

Keywords: Polyphenols, poly(lactic acid), rutin, curcumin, quercetin, structure, thermal properties

INTRODUCTION

The surge in plastic food packaging waste, largely driven by the fast-food industry, has prompted many countries to urge their packaging manufacturers to enhance food supply chain efficiency [1]. This aims to minimize food spoilage and waste. To tackle this issue, incorporating active agents like antimicrobial and antioxidant compounds into packaging materials has emerged as a promising solution [2]. These 'active' or 'smart' packaging systems can extend food shelf life and reduce food losses, ultimately boosting industry profitability. At the same time, since most plastics are non-biodegradable, their disposal without recycling poses significant environmental challenges [3]. Concerns over these issues, along with the depletion of petrochemical resources, have driven efforts to develop eco-friendly, renewable, and biodegradable biopolymeric materials [4]. Consequently, biodegradable and bioplastic packaging materials derived from renewable resources have garnered significant attention as plastics [5].

Poly(lactic acid) (PLA) is a biodegradable and biocompatible thermoplastic aliphatic polyester derived from renewable resources such as corn starch or sugar beet [6, 7]. It has gained significant attention as a sustainable alternative to traditional petroleum-based plastics due to its environmental friendliness and versatility. While widely used in medicine and some food packaging, PLA suffers from poor mechanical strength and lacks natural antimicrobial properties.

Polyphenols, a class of naturally occurring compounds found in plants, exhibit a wide range of beneficial properties, including antioxidant, anti-inflammatory, and antimicrobial activities. Curcumin, rutin, and quercetin are three prominent polyphenols with potent antioxidant properties [8, 9].

Blending PLA with polyphenols offers a promising approach to address the limitations of PLA while leveraging the advantageous properties of polyphenols. The incorporation of polyphenols into PLA can enhance its mechanical properties, thermal stability, UV resistance, and bioactivity. Additionally, the controlled release of polyphenols from the PLA matrix can provide sustained therapeutic benefits in various biomedical applications [10].

The present research aims to develop new PLA-based multicomponent films with incorporated polyphenols (curcumin, rutin and quercetin) and to examine their morphology, structure, thermal and electret properties.

MATERIALS AND METHODS

Materials

Poly(lactic acid) (PLA), curcumin, quercetin, rutin, and Tween® 20 were purchased from Sigma-Aldrich (Germany) and were used without further characterization or purification. All other chemicals were of analytical grade.

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Preparation of empty and polyphenol loaded PLA films

PLA-based films were prepared by the solvent casting method. First, 2 g of PLA was added to 100 ml of chloroform containing 1.5% Tween® 20, and dissolved for 6 h on a magnetic stirrer. Then 380 mg of polyphenol (curcumin, quercetin or rutin) was slowly added to the PLA solution and dissolved for 1 h at 1000 rpm, followed by homogenization at 12 000 rpm for 5 min. The film-forming solution was cast on levelled glass Petri dishes and dried at a temperature of 30 °C until complete chloroform evaporation. The dry films were stored in a desiccator at a temperature of 25 °C and relative humidity of 20 % for at least 72 h before use. For comparison, neat PLA film without polyphenols was prepared according to the above-described procedure.

The film thickness was measured ten times on each testing sample with a digital micrometer No. 293-5, Mitutoyo, Japan.

Morphology

Scanning electron microscopy (SEM) analysis (ZEISS EVO LS25—EDAX Trident) was applied to investigate the morphology of the materials. For this purpose, part of the sample was directly attached to SEM stubs and subsequently coated with carbon. SEM-EDX was performed at an accelerating voltage of 15 kV.

Powder X-ray diffraction

Powder X-ray diffraction analysis was conducted using an Empyrean Powder X-ray diffractometer (Malvern Panalytical, Almelo, The Netherlands) equipped with a copper X-ray source (λ = 1.5406 Å) and a PIXcel3D area detector. The diffraction patterns of the compounds PLA, curcumin, rutin, quercetin, PLA-curcumin, PLA-rutin, PLA-quercetin were collected in the 2–50° 2 Theta range using the following operation conditions: 40 kV/30 mA, step size of 0.013°, and rotation speed of 15 rpm. The powder patterns of the bulk microcrystalline products (curcumin, rutin, quercetin) were compared with the powder patterns of the composites, thus confirming the presence of desired/undesired crystalline/amorphous phases. Data Viewer ver. 1.9a software (Malvern Panalytical, Almelo, The Netherlands) was used for visualization of the powder patterns.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on Discovery DSC 50 (TA instruments, New Castle, DE, USA). Samples weighing between 15 and 20 mg were heated in Al_2O_3 pans from 30 to 300 °C (heating rate of 10 °C.min^{-1}) in a dynamic ambient (air) atmosphere (flow rate of 40 mL.min^{-1}).

Differential scanning calorimetry

The melting phenomena and stability of PLA-based films were studied using differential scanning calorimetry (DSC). The DSC 204F1 Phoenix instrument (Netzsch Gerätebau GmbH, Germany) was employed for these investigations. The instrument was calibrated by an indium standard for both heat flow and temperature. The samples were carefully placed in aluminium pans and hermetically sealed, with an identical empty pan serving as a reference. The temperature profile for the DSC analysis included heating from 20 °C to 350 °C at a rate of 10 °C.min^{-1}. The acquired experimental data were analyzed using Netzsch Proteus—Thermal Analysis software (Version 6.1.0B, Germany).

Corona treatment and surface potential measurement

The created composite films were cut into 30 mm samples and charged under corona discharge in normal atmospheric conditions. The charging of the samples in a corona discharge was carried out by means of a conventional corona triode system consisting of a corona electrode (needle), a grounded plate electrode and a grid placed between them. For the charging process, positive 5 kV voltage was applied to the needle electrode and 1 kV of the same polarity was applied to the grid. All films were charged for 1 min. The electret surface potential of the charged samples was determined with the vibrating electrode method with compensation and the estimated error was less than 5%. The normalized surface potentials V/V_0 were calculated, as the value V_0 is the initial surface potential measured about 1 min just after charging the electret.

RESULTS AND DISCUSSION

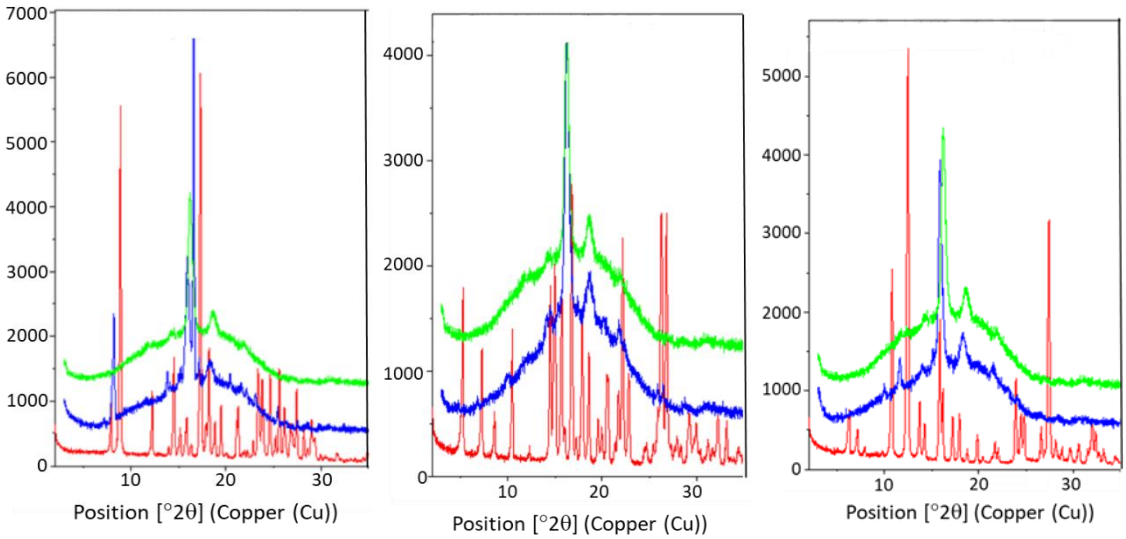
The incorporation of the polyphenols in the PLA matrix and their phase state was confirmed by the X-ray diffraction method. The XRD patterns shown in Figure 1A demonstrate that curcumin was successfully loaded into the PLA matrices (blue graph).

In the case of PLA-curcumin multicomponent film, the PLA support remains basically unchanged as visualized by XRD and SEM (Figures 2a, 2b). The SEM images show the appearance of "roughness" on the surfaces of the films, though no separate crystallites related to curcumin are visible. This is not the case for rutin and quercetin, where, in

addition to the surface "roughness", aggregates can be observed on the surface (Figures 2c, 2d).

The XRD pattern for the PLA-rutin composite (Figure 1b) demonstrates similar features as the PLA-curcumin. However, the presence of rutin in the PLA matrix is not as clearly displayed as that of curcumin, as the two reflexes associated with the rutin phase possess lower intensity when compared to curcumin.

This may indicate inhomogeneous distribution of rutin as observed on the SEM images (Figure 2c). The situation is similar for the PLA-quercetin case (Figures 1c and 2d). The TGA data (Figure 3) reveal that the PLA matrix loses ~5% surficial water up to 100 °C (in two steps) then melts around 130 °C and decomposes above 250 °C. The thermal behavior of the composites seems to prevent the interaction of PLA with ambient moisture. The PLA-curcumin combination is very stable (only ~1% water losses) and starts to decompose after 275 °C.



A) Curcumin B) Rutin C) Quercetin

Figure 1. XRD patterns of PLA (green), polyphenol powder (red), and PLA-Polyphenol multicomponent film (blue)

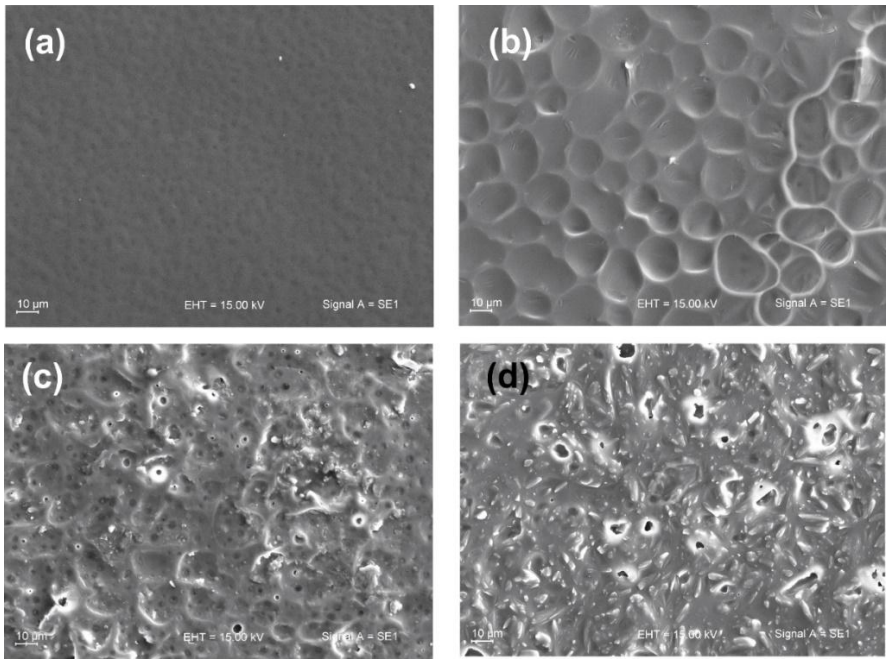


Figure 2. Scanning electron microscopy images of (a) PLA matrix, (b) PLA-curcumin film, (c) PLA-rutin film and (d) PLA-quercetin film.

A similar improvement in thermal stability was reported by Zia *et al.* for an LDPE-curcumin multicomponent film [11]. The thermal comportment of the PLA-rutin also follows this observation, although the losses are a little bit more pronounced (~2% up to 100 °C), and then decomposes above 260 °C. The TGA data for PLA-quercetin differ for the previous two sets. The losses are registered at higher temperatures (130 and 225 °C) and are more pronounced - ~4% in total. The decomposition/melting is registered at values similar to the PLA, rutin and curcumin blended films.

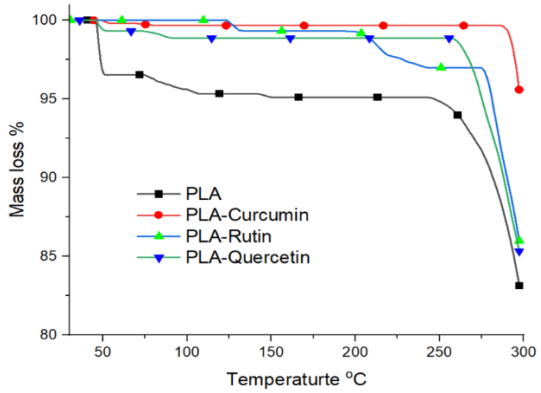


Figure 3. Thermogravimetric analysis (TGA) of PLA, PLA-curcumin film, PLA-rutin film, PLA-quercetin film.

The results from TGA are confirmed by the phase transitions in the PLA-based films, which are examined by differential scanning calorimetry (DSC). The DSC curves of neat PLA film and PLA films loaded with polyphenols, are presented in Figures 4 and 5, respectively. The thermogram of the neat PLA film is characterized by wide endothermic peak between 50 °C and 100 °C which is probably due to evaporation of some moisture content, which was also observed in the TGA curve. A second endothermic peak with a maximum at 155 °C corresponds to the melting phenomena. The increase of the DSC signal at 250 °C is related to thermal decomposition of the material. Similar results for the PLA thermal behavior were demonstrated by Chartarrayawadee and co-workers, who found that the melting temperature of pure PLA is 153.3 °C [12].

No water evaporation is observed in the curcumin-loaded PLA film, suggesting that its water content is very low. It is characterized by two endothermic processes at temperatures of 144.6 °C and 183.7 °C, which can be interpreted as melting of the PLA phase and curcumin crystals, respectively. These data are summarized in Table 1.

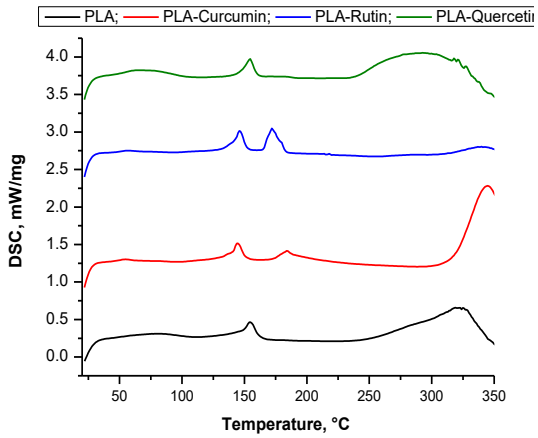


Figure 4. DSC curves of PLA-based films

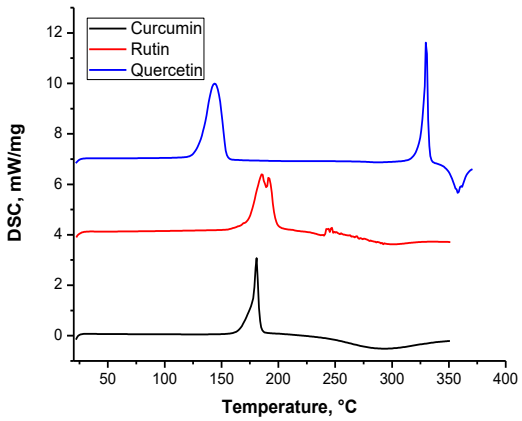


Figure 5. DSC curves of polyphenol powders

Table 1. Melting phenomena in PLA-based films, loaded with polyphenols

Film	Peak 1		Peak 2		
	Temperature, °C	Enthalpy, J/g	Temperature, °C	Enthalpy, J/g	Polyphenol crystallinity, %
PLA	154.6	16.23	–		
PLA - curcumin	144.6	9.829	183.7	6.264	30
PLA – rutin	146.2	11.3	171.8	17.48	42
PL-A - quercetin	154.4	13.6	–		

This film is stable until 300 °C. Taking into account the melting enthalpy of the non-immobilized curcumin and its content in the film, it can be estimated that about 30% of it recrystallized during the curing of the films. The thermal behavior of the PLA–rutin film is very similar. In it, the melting is realized at 146.2 °C and 171.8 °C and the degree of crystallinity of the loaded rutin is 42 %. The DSC data for PLA-quercetin film differ from the previous two sets. In this case no second peak is detected, which could mean that quercetin does not crystallize. The absence of a crystalline structure of the included quercetin is also confirmed by the absence of reflexes in the XRD pattern of the PLA-quercetin film (Figure 1c).

Analyzing the DSC curves of the multicomponent films, two general trends are observed: both the melting temperature of PLA and the enthalpy of the phase transition decrease. The decrease is most noticeable for the PLA-curcumin films, while almost no decrease is registered in the PLA-quercetin system. Such behavior may be related to the compatibility and homogeneity of the polyphenol distribution in the PLA matrix. The PLA–rutin film is the most homogeneous one, as confirmed by SEM analysis. Roy and Rhim also reported compatibility between PLA and curcumin, demonstrated by DSC analysis [13].

An important feature for food packaging are their electret properties [14]. They enable the material to retain a stable electrostatic charge, which can help prevent contamination by attracting and trapping dust, microorganisms, and other fine particles. This enhances the cleanliness and safety of the packaged food, extending shelf life and maintaining quality. Additionally, electret materials can offer antimicrobial benefits and improve barrier properties without relying on additives or external energy sources.

Time dependences of the normalized surface potential for positively charged PLA samples and PLA samples with different polyphenols were measured for 360 min. During the first half hour measurements were taken every 5 min due to the rapid decrease of the surface potential, after which measurements were taken less frequently, due to the decrease of the rate of decay. The measurement was continued until the determination of the steady state values (at 360 min) of each sample. Time dependences of the normalized surface potential of all investigated samples are presented in Figure 6. The data show the averaged value of 6 samples, with standard deviation less than 5% from the mean at 95 % confidence level.

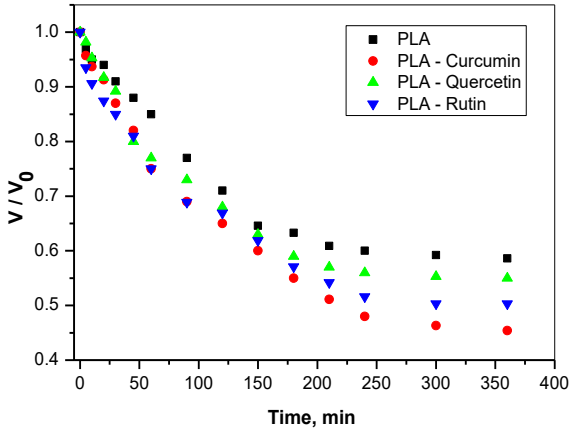


Figure 6. Time dependences of the normalized surface potential for PLA composite films charged in a positive corona.

The obtained experimental results demonstrate that the decay of the normalized surface potential for the first 120 min of the study is exponential, after which the normalized surface potential decreases and it is practically stabilized within 360 min. These results demonstrate the existence of different surface states that are localized on the surface of the sample and that contain entrapped charges within them. The initial exponential decay can be accredited to the release of weakly captured charges from the shallow energy states. After this period of time the normalized surface potential becomes stable at a set value, which can be attributed to the remaining tightly entrapped charges in deeper traps. Similar behavior has been observed earlier in [15, 16]. It was also observed that the normalized surface potential values decrease with the addition of different polyphenols. The results demonstrate that electrets created from PLA possess the highest values of the normalized surface potential when compared to all other types. This can be explained with the differing crystallinity degrees that were determined with the use of the DSC method (see DSC analyses) and the chemical structure of the polyphenols.

CONCLUSION

This study demonstrates the successful incorporation of three polyphenols – curcumin, rutin and quercetin in a poly(lactic acid) matrix. The PLA-curcumin film is characterized as homogeneous, while micro-sized aggregates are found in PLA-rutin and PLA-quercetin films. The appearance of inhomogeneities in the films containing rutin and quercetin is most likely caused by aggregation, which is due to the poor solubility of these two polyphenols in chloroform. To reduce the number and size of aggregates, it is necessary to increase the solubility, for example, by adding appropriate

co-solutes. Loading of curcumin improves the thermal stability of the PLA matrix. In all studied multicomponent films, the presence of polyphenol reduces the surface potential and degrades the electret properties of the films. Considering the analyses performed and their results, it can be assumed that the most suitable polyphenol included in the polylactic acid matrix is curcumin. This type of film could be used for packaging of rapidly oxidizing food products.

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