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OPTIMISATION OF THE APPLICATIVE PROPERTIES OF BIODEGRADABLE CELLULOSE ACETATE-BASED FILMS USING THE PRINCIPLES OF GREEN CHEMISTRY

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ABSTRACT

There is a growing interest in the use of biopolymers for obtaining biodegradable packaging with the addition of green components. The aim of this paper is to develop films based on cellulose acetate and polycaprolactone-diol intended for active packaging by adding biocompatible plasticizers. The films were obtained by solution casting method, and essential oils were used as active components, which showed antimicrobial activity in a low percentage. Biocompatible plasticizers synthesized by esterification and polyesterification reactions were used to improve the flexibility of prepared films. The obtained plasticizers also showed the effect of compatibilizer, improving the miscibility of polymers in the blend. The optical properties of the obtained blends were successfully improved by the addition of a low concentration of newly synthesized azo dye, with the ability to absorb electromagnetic radiation of a certain part of the spectrum.

Keywords: Cellulose acetate, active packaging, azo dye, green chemistry.

INTRODUCTION

The packaging industry is the largest consumer of synthetic, non-biodegradable polymers, with an amount of 40%. Over 50% of plastic waste in the environment comes from food packaging, which generates approximately 90% of waste after one use. It is linked with the increased development of takeaway food meals. Based on the principles of circular economy, materials for food packaging should be biodegradable or recyclable. Therefore, a lot of effort has been invested in order to develop biodegradable packaging able to ensure the protection and prolongation of food product shelf life. An active biodegradable food coating appeared as a mutual answer to these issues. According to the principles of *green* chemistry and sustainable development, in order to obtain biodegradable active packaging, in biopolymer matrix are incorporated antimicrobial compounds from renewable resources such as essential oils. Essential oils are obtained by extraction from different parts of plants. They act antimicrobial in a low concentration serving as natural additives in food products and active compounds in packaging materials. Considering not only the ecological but economic benefits, cellulose derivatives such as cellulose acetate can be used as a biopolymer matrix for the incorporation of essential oil and preparation of active packaging. Cellulose acetate (CA) has various advantages such as solubility in acetone, compatibility with essential oil, good processability, optical properties, and low price. In order to overcome its drawbacks such as fragility, low mechanical and barrier properties, CA is combined with plasticizers and other polymers such as poly(N-vinyl pyrrolidone-co-methyl methacrylate) (Ohno, & Nishio, 2007), vinyl polymers (Miyashita, Suzuki, & Nishio, 2002),

poly(ethylene succinate) (Buchanan et al., 1996), poly (ethylene glycol) (Buchanan et al., 1996), polyaniline (Cerqueira, Valente, Filho, & Burrows, 2009), polyhydroxyalkanoate (Meereboer, Misra, & Mohanty, 2020) in the design of polymer blend films. In order to reduce the glass transition temperature of CA and improved its flexibility, the plasticization of this biopolymer has been achieved using phthalates, citrates, glycerol esters, lactate, and glycerol itself (Hu et al., 2022). As a biocompatible substitution for phthalate, esters of glycerol with acetic and citric acid have been the most researched. In the framework of the development of efficient non-toxic substitution for phthalates, we have synthesized two types of plasticizers using tartaric acid. Tartaric acid was used because of the presence of hydroxyl groups in its structure, as an attempt to improve miscibility between CA and polycaprolactone diol (PCL-diol) blends. Essential oils, as antimicrobials obtained from the plants, were added to film-forming solutions in order to get coatings for active packaging. Using of essential oils in food packaging supports the *green* agenda which implies not only the use of biodegradable polymers and additives but also improvement of process cost-effectiveness and reducing the amount of food waste.

EXPERIMENTAL PART

Materials

Cellulose acetate and polycaprolactone diol was supplied from Sigma Aldrich, USA. Acetone (pro analysis), dimethyl sulfoxide (DMSO), and glycerol were procured from CENTROHEM, Serbia. Bishydroxyethyl terephthalate (BHET) was obtained by polyethylene terephthalate glycolysis. Lemongrass oil was obtained according to the procedure described by Erceg et al, while oregano oil was bought in a pharmacy (Erceg et al., 2022).

Preparation of plasticizers

The first type of plasticizer (glycerol tritartarate, GTT) was prepared by the bulk reaction of esterification between glycerol and tartaric acid in mass, according to the procedure described by Erceg et al., (Erceg et al., 2022). The second type of plasticizer (BHETTA) was also obtained by reaction of esterification between BHET and tartaric acid, which was performed in DMSO, for 2h, at 105 °C.

Preparation of films

The blends were prepared by dissolving CA and PCL-diol in acetone according to the procedure described by Erceg and al., 2022. A certain amount of plasticizer and essential oils were added to the blend solution in the same amount (7 wt% per blend weight). A series of preliminary tests (mechanical tests, observations) was carried out in order to find the optimal amount of plasticizer in a blend composition, which is 10 wt% for GTT and 30 wt% for BHETTA.

Infrared spectroscopy analysis

The chemical structure of obtained plasticizers was analysed by Infrared spectroscopy with Fourier transformation. Data were collected in the range of 4000-400 cm^{-1}.

Scanning electron microscopy (SEM) analysis

The topography of polymer blends was analysed using the scanning electron microscope (JEOL JSM-6460, Japan).

Mechanical properties analysis

Tensile properties of films were analysed by the Schenck Hydropuls PSB 250 (Germany) universal testing machine, according to the ASTM standard D882-18.

Antimicrobial assessment

Control film (without lemongrass oil) and film with 7 wt% of lemongrass oil were used for grapefruit packaging which was artificially contaminated by *A. brasiliensis* spores (10^4 CFU/mL) (Erceg et al., 2022). Samples were monitored during the 10 days of storage. The other film, with

oregano oil, was used for the wrapping of salad, which was not artificially contaminated, but the presence of *S. aureus* and *Enterobacteriaceae* was monitored during the 10 days. The standardized ISO methods were applied for the determination of S. aureus, and Enterobacteriaceae in food packaged by the film with BHETTA and oregano oil.

RESULTS AND DISCUSSION

FTIR

FTIR spectra of polymer blends are given in Figures 1 and 2. A broad peak with a centre at 3410 and 3460 cm^{-1} in the FTIR spectrum of GTT and BHETTA respectively corresponds to OH stretching (from tartaric acid and BHET). Two small peaks at 2948 and 2890 cm^{-1} (GTT) and 2959 and 2915 (BHETTA, Figure 2) are assigned to -C-H stretching. In the FTIR spectrum of BHETTA appearing of a small peak at 3018 cm^{-1} indicates the presence of an aromatic ring (=C-H stretching). An intense peak at 1704 (GTT) and 1714 cm^{-1} (BHETTA) is attributed to the C=O stretching of the ester bond in the plasticizers.

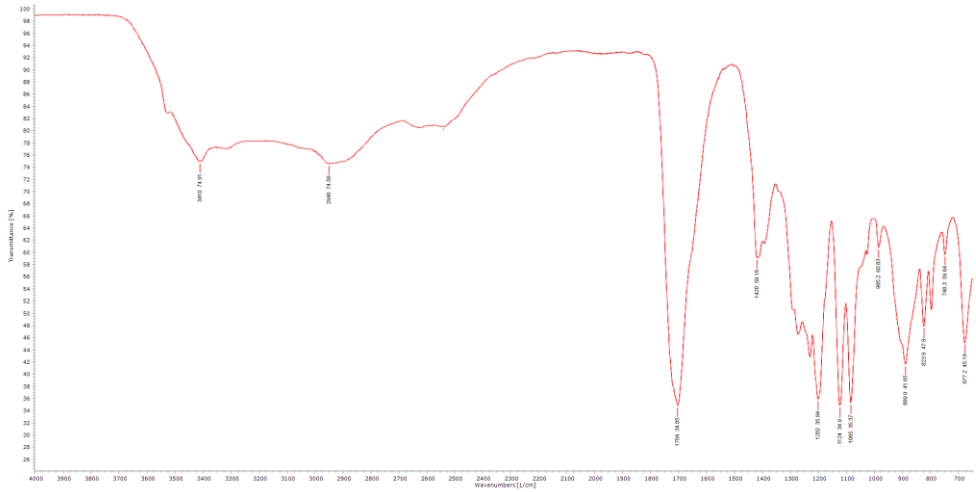


Figure 1. FTIR spectrum of GTT.

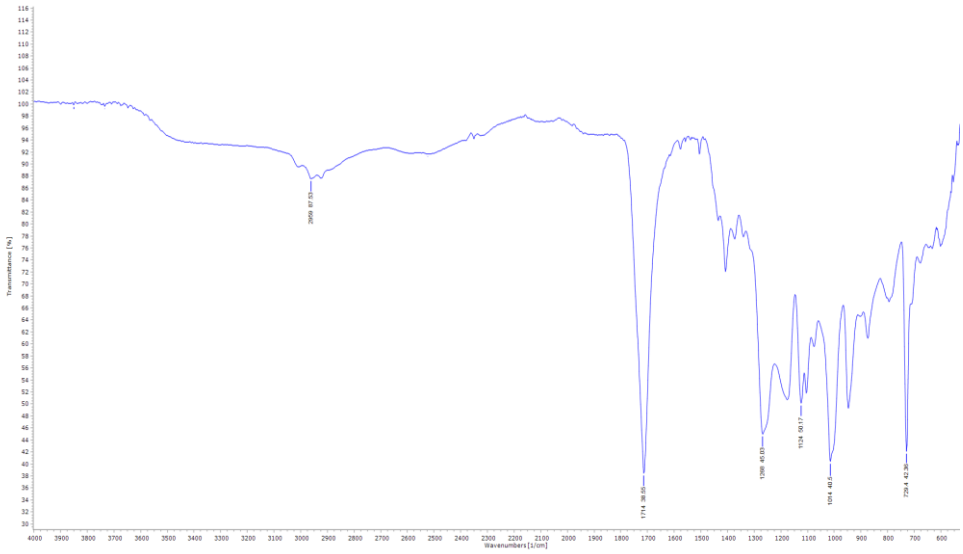
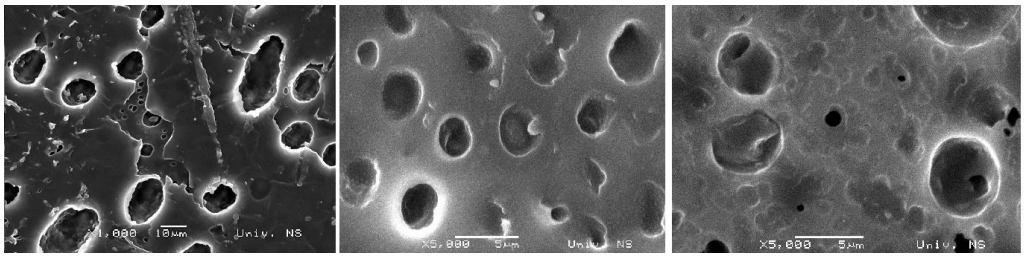


Figure 2. FTIR spectrum of BHETTA.

SEM

Figure 3a shows the SEM image of the blend without the addition of any plasticizer, while Figure 3b and 3c show the topography of the blend with the optimal amount of GTT (10 wt%), and BHETTA (30 wt%). The incorporation of plasticizer leads to a decrease in the depth and diameter of the pores, implying the compatibilization of polymers in a blend.



a. b. c.

Figure 3. SEM images of: a) CA/PCL diol, b) CA/PCL diol-10% GTT, c) CA/PCL diol – 30% BHETTA.

Mechanical properties

The addition of plasticizers in optimal amounts leads to significant improvement of tensile properties. Plasticizer BHETTA in the amount of 30 wt% gives a film with significantly improved elongation at break (EB), above 29% and tensile strength (TS), above 46 MPa . Less improvements in values of EB and TS were observed for GTT in the optimal amount (7.21% and 24.82 MPa) (Table 1).

Table 1. Tensile properties for CA/PCL-diol samples with and without added plasticizer.

Sample	TS (MPa)	EB (%)
CA/PCL-diol	19.77	4.21
CA/PCL-diol-10% GTT	24.82	7.21
CA/PCL-diol-30% BHETTA	46.35	29.87

Antimicrobial properties

The shelf life of grapefruit packaged in the investigated film with lemongrass oil was prolonged more than 2 times, in comparison to the film without the addition of lemongrass oil. In salad packaged by control film, the critical level of *S. aureus* was achieved after three days, while in salad wrapped by active film, during the whole storage period (10 days), the critical level was not achieved; Enterobacteriaceae were not detected in a salad with active film, while in control salad they made for critical value the last day of storage period.

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