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Development of waterborne polyurethane-ureas added with plant extracts: Study of different incorporation routes and their influence on particle size, thermal, mechanical and antibacterial properties

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ABSTRACT

Polyurethane-ureas are a versatile family of polymers which can be employed in a wide range of applications. Among them, waterborne polyurethane-urea (WBPUU) dispersions are gaining relevance in the field of environmentally-friendly products since their productive process adopts green synthesis routes, avoiding the use of organic solvents. Furthermore, their waterborne character can be exploited to incorporate several water compatible ingredients able to confer functional properties to the final materials. Among them, plant extracts, which are known to have relevant bioactivities, can be viewed as interesting candidates. Therefore, in this work, two extracts known to present antimicrobial activity (*Melissa officinalis* L. and *Salvia officinalis* L.) were obtained by the infusion method and incorporated into the WBPUU (1, 3 and 5 wt%) following different incorporation routes comprising its adding during different phases of the productive process (post-, *in-situ* and pre- methods). Thereafter films were prepared by solvent-casting and characterized from the viewpoint of physicochemical, thermal, mechanical, thermomechanical and antibacterial properties and morphologically. The studied incorporation routes resulted in different intercalation mechanisms that varied from extract positioned among the polyurethane-urea nanoparticles (post-method) to extract partially embedded inside them (*in-situ* and pre-methods), which produced stiffening or flexibilizing effects in the produced films, enhancing in general the antimicrobial characteristics of films after 4 days of incubation comparing with base WBPUU, especially when the extract is embedded.

1. Introduction

In the versatile family of polyurethane-ureas, the use of waterborne polyurethane-urea (WBPUU) dispersions is gaining importance due to the environmentally-friendly character of their synthesis process, reducing, or even eliminate, the use of volatile organic compounds [1]. In this way, low viscosity and high solids content dispersions presenting no flammability are obtained [2]. The incorporation of an internal emulsifier along the polyurethane-urea backbone provides the required hydrophilicity [3], which following an adequate composition ensures stable dispersions for months. From these dispersions, WBPUU films presenting suitable properties such as impact resistance, solvent resistance and adhesion to different substrates can be achieved [4]. Furthermore, WBPUU find a broad range of applications such as paintings, inks, adhesives, coatings and medical uses [5–10].

The waterborne character of these systems enables an easy use of water soluble additives. Among them, the use of vegetal renewable sources to obtain natural additives, through extraction with water (a green solvent), is an interesting approach reinforced by the extensively documented bioactivity of such extracts. In fact, plants are rich sources of bioactive compounds, namely alkaloids, flavonoids, tannins and phenolic compounds. The composition of the obtained extracts vary depending on the plant, growing conditions and used extraction process [11–13], conferring bioactive properties, and among them antibacterial activity.

Examples include *Salvia officinalis* L. (Lamiaceae family), commonly

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known as sage and traditionally used in culinary and medicinal preparations [14], whose chemical composition is associated with effective antibacterial, antioxidant and anti-inflammatory properties [14,15]. *Salvia officinalis* is characterized by presenting mainly terpenoids (such as α- and β-thujone, camphor and 1,8-cineole), and a polyphenolic fraction which includes phenolic acids (rosmarinic, ferulic and caffeic acid), flavonoids (luteolin, apigenin and naringenin) and diterpenes (carnosic acid, carnosol, rosmanol, epirosmanol and isorosmanol) [16,17]. In this way, preparations based on *Salvia officinalis* can be employed in different forms (liquid extracts, essential oils or powder forms) attending to their final application [18]. For example, Bakota and co-workers [19], obtained from this vegetal material an extract rich in polyphenols, demonstrating its antioxidant effect, and suitability to be used in different fields, such as the one of food industry.

Also, *Melissa officinalis* L. (Lamiaceae family) known as Lemon balm due to its flavor and fragrance and traditionally used to treat headache, migraine and nervous tension, is recognized by its antibacterial, anti-inflammatory and antioxidant properties [11,20,21]. *Melissa officinalis* is constituted mainly by eugenol, tannins, flavonoids such as luteolin, apigenin 7-*O*-beta-D-glucopyranoside, terpenes (sesquiterpenes, triterpenes and monoterpene glycosides), hydroxycinnamic acid derivatives, specifically rosmarinic acid, caffeic acid, chlorogenic acid, and metrilic acid [22–24]. Attending to their composition *Melissa officinalis* extracts can be employed in a wide range of applications. For example, Echem and Chukwuike [22] demonstrated the availability of *Melissa officinalis* extracts for inhibiting the corrosion of aluminium in hydrochloric acid medium. In another work Cunha et al. [25] analyzed the efficacy of these extracts against Leishmania and Trypanosoma activity, focusing on biomedical applications.

Therefore, in this work a base WBPUU dispersion was synthesized and incorporated with aqueous extracts of *Salvia officinalis* L. and *Melissa officinalis* L. having in view the obtainment of products with improved antimicrobial activity. Three incorporation pathways were designed, where the extracts were added at three different contents (1, 3 and 5 wt%). The incorporation routes were defined taking into account key points of the productive process. In brief, extracts were always added dissolved in water as follows: (i) in the first route, post-method, the extract was added once WBPUU dispersion was synthesized, thus after the formation of the WBPUU particles; (ii) in the second via, *in-situ* method, the extract was gradually added during the phase inversion step, *i.e.* simultaneously with the WBPUU nanoparticles formation; (iii) in the third alternative, pre-method, the extract was added in the beginning of the phase inversion step, *i.e.* before nanoparticles formation. The obtained dispersions were characterized in terms of pH, viscosity and particle size, and the prepared films analyzed in what concerns morphology and physicochemical, thermal, mechanical and thermomechanical properties. Moreover, antibacterial properties of the films were analyzed against Gram positive *Staphylococcus aureus* (*S. aureus*), and Gram negative *Escherichia coli* (*E. coli*) and *Pseudomonas aeruginosa* (*P. aeruginosa*) which are microorganisms responsible for many infections and common pathogens with difficult treatment [26].

2. Experimental

2.1. Materials

WBPUU dispersions were synthesized using poly(ε-caprolactone) diol (PCL) ($\overline{M_w}$ = 2000 g mol^{-1}) provided by Solvay as soft segment. Isophorone diisocyanate (IPDI), purchased from Bayer and ethylenediamine (EDA) supplied by Panreac were used as the isocyanate and as the chain extender components, respectively. 2,2-Bis(hydroxymethyl) propionic acid (DMPA), purchased from Fluka, was selected as the internal emulsifier. Triethylamine (TEA), provided by Fluka, was used to neutralize the ionic groups of DMPA. PCL and DMPA were dried under vacuum at 50 °C during 4 h previously to the synthesis process. Dry acetone, purchased from Panreac was employed as viscosity modulator, and dibutyltin dilaurate (DBTDL), supplied by Fluka, was used as catalyst.

Salvia officinalis L. from Raizes da Natureza and *Melissa officinalis* L. from Tetley were acquired in a local herbalist.

2.2. Obtainment of Salvia and Melissa extracts

Extracts of *Salvia officinalis* L. and *Melissa officinalis* L. were obtained by the infusion method from dry plant material according to the procedure described in the work of Isabel C.F.R. Ferreira and co-workers [14]. The extracts were selected due to their recognized antimicrobial activity, as described in literature [11,14,20]. Briefly, 20 g of grinding plant was added to 800 mL of boiling distilled water and maintained for 5 min. Then, the resultant suspension was filtered and lyophilized to obtain the extract in powder form. For each plant, the extraction yield was calculated according to Eq. (1):

$$yield\,(\%) = \frac{W_i - W_f}{W_i} \cdot 100 \quad (1)$$

Where W_i refers to the used plant weight and W_f to the obtained extract weight. Yields of 13 ± 1% and 17 ± 2% were obtained for Salvia and Melissa extracts, respectively.

2.3. Synthesis of waterborne polyurethane-urea

Waterborne polyurethane-urea dispersions were synthesized following a two-step polymerization process using a NCO/OH ratio of 1.67 and 5 wt% of DMPA in the prepolymer synthesis step, resulting in a hard segment (HS) content around 32 wt%. The reaction was carried out in a 500 mL four neck jacketed reactor equipped with an intracooler, a thermocouple and a mechanical stirrer and controlled from a computer during the synthesis process.

The synthesis was carried out under nitrogen atmosphere and the reaction progress followed by the dibutylamine back titration method, according to ASTM D 2572-97. PCL, IPDI and DBTDL (0.037 wt%) were mixed in the reactor and allowed to react at 80 °C until the theoretical NCO value was reached. Afterwards, the mixture was cooled to 50 °C and the previously neutralized DMPA (with TEA), dissolved in a small amount of acetone, incorporated. The final NCO terminated prepolymer was cooled to 25 °C and distilled water was added dropwise under vigorous stirring. The obtained dispersion was heated to 35 °C previously to chain extension with EDA. For that EDA added dissolved in 20 mL of distilled water at a flow rate of 0.3 mL min^{-1}. The needed amount of EDA was calculated based on a chain extension degree of 40%. Finally, acetone was removed in a rotary evaporator at 40 °C and 350 mbar, thus obtaining a dispersion with a solids content of around 35–40 wt%.

2.4. Salvia- and Melissa-based WBPUU dispersions and films preparation

Extracts were incorporate at contents of 1, 3 and 5% (wt, prepolymer-basis). Three alternative incorporation routes were designed for the preparation of the Salvia- and Melissa-based WBPUU:

Post-method: in this method, the required amount of extract was dissolved in distilled water and incorporated dropwise to the synthesized WBPUU under mechanical stirring. This procedure was done previously to the corresponding film preparation. For that 10 mL of dispersion were mixed with 10 mL of the extract solution using the required amount of extract.

In-situ method: according to this method the extract was dissolved in the distilled water used in the phase inversion step. In this way, the extract was incorporated progressively during the phase inversion step, *i.e.* during the WBPUU nanoparticles formation.

Pre-method: in this method, the extract was dissolved in a small amount of distilled water (15 mL) and incorporated, in one portion, to