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Tuesday 12TH September 2017
Session 4. Auditorium 500. Chairperson Ramani Narayan
09.00-09.40. Invited Lecture. **Filip Du Prez** (Ghent University, Belgium). "Rigid polyurethanes, polyesters, polycarbonates and polyamides from novel renewable building blocks"
09.40-10.10. Keynote Lecture-3. **Luc Avérous** (University of Strasbourg, France). "From biomass to innovative renewable polyurethanes. Our overview"
10.10-10.30. Oral Communication-15. **José María Lagarón** (IATA-CSIC, Valencia, Spain). "Electrospun biopolyesters to provide functional properties to food packaging materials"
10.30-10.50. Oral Communication-16. **Armando J.D. Silvestre** (University of Aveiro, Portugal). "Deep eutectic solvents as efficient media for the extraction of hemicelluloses and lignins in biorefinery processes"
Session 4. Auditorium 200. Chairperson Sandra Domenek
10.10-10.30. Oral Communication-17. Arantzazu Santamaría (University of the Basque Country, San Sebastián, Spain). "Different environmentally-friendly strategies for loading waterbone polyurethane and polyurethane-urea dispersions"
10.30-10.50. Oral Communication-18. **Carolin Menzel** (KTH, Royal Institute of Technology, Stockholm, Sweden). "Starch carbamate films"
10.50-11.40. Coffee Break and Poster session-2

DIFFERENT ENVIRONMENTALLY-FRIENDLY STRATEGIES FOR LOADING WATERBORNE POLYURETHANE AND POLYURETHANE-UREA DISPERSIONS

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Introduction

The environmental awareness has increased the research and development of eco-friendly green synthesis routes for many different applications, such as the waterborne polymer systems. Among others, waterborne polyurethanes (WBPU) and waterborne polyurethane-ureas (WBPUU) have gained attention due to their versatility in terms of composition and properties, making them suitable in a wide range of applications [1]. WBPU and WBPUU synthesis process is based on the incorporation of internal emulsifiers covalently bonded to the polymer obtaining stable water dispersions over months. Furthermore, the waterborne character of the dispersions provides the opportunity of incorporating water dispersible nanoentities and water soluble additives, enhancing or even providing additional properties. In this context, the use of renewable derivatives opens the possibility of enhancing the environmentally-friendly character. Among them, cellulose nanocrystals (CNC) are presented as a suitable candidate for the preparation of nanocomposites, considering their unique properties in the nanoscale dimension, provided by their high length/diameter aspect ratio and high specific mechanical properties [2]. Otherwise, the incorporation of natural water soluble additives has focused attention on extracts obtained from plants, consisting in biologically active compounds [3], whose antimicrobial character can determine the antimicrobial behavior of the WBPU and WBPUU. Therefore, in this work, different strategies have been analyzed for the preparation of WBPU-CNC nanocomposites and WBPUU-plant extracts varying their content as well as their incorporation route.

Experimental

Different WBPU and WBPUU were synthesized varying molar ratio of poly(ε-caprolactone) diol (PCL) (M_w = 2000 g mol^{-1}), isophorone diisocyanate (IPDI), 2,2-bis(hydroxymethyl) propionic acid (DMPA), and 1,4-butanediol (BD) or ethylendiamine (EDA) in order to synthesize WBPU or WBPUU, respectively. **WBPU** (IPDI/PCL/DMPA/BD of 3.15/0.5/0.5/2) and **WBPU1.2** (IPDI/PCL/DMPA/BD of 3.6/0.5/0.5/2) presenting isocyanate/hydroxyl (NCO/OH) groups' ratio of 1.05 and 1.2, respectively, were synthesized. In the case of **WBPUU** NCO/OH of 1.67 and 5 wt% of DMPA was employed. Once the prepolymer was formed, in the case of WBPU, BD chain extension was carried out and then, phase dispersion step was performed obtaining the dispersion. Instead, in the case of the WBPUU, first phase inversion step was carried out and after that, EDA chain extension was conducted. Furthermore, renewable derivatives were prepared. CNC were isolated via acid hydrolysis from microcrystalline cellulose and bioactive extract was obtained from *Melissa officinalis* plant by infusion method. Regarding WBPU-CNC nanocomposites, 1, 3 and 5 wt% of CNC were incorporated via *ex-situ*, mixing by sonication in both WBPU and WBPU1.2. Furthermore, nanocomposites containing 1 and 3 wt% of CNC were prepared via *in-situ* for WBPU matrix. In the case of WBPUU-extract, 1, 3 and 5 wt% of the extract were incorporated by 3 different routes: post (mixing with the already synthesized WBPUU dispersion dissolved in water), *in-situ* (adding during the phase inversion dissolved in the water) and pre (adding prior to the phase inversion dissolved in a

small amount of water). The designed routes are shown in **Figure 1** and films were prepared by casting.

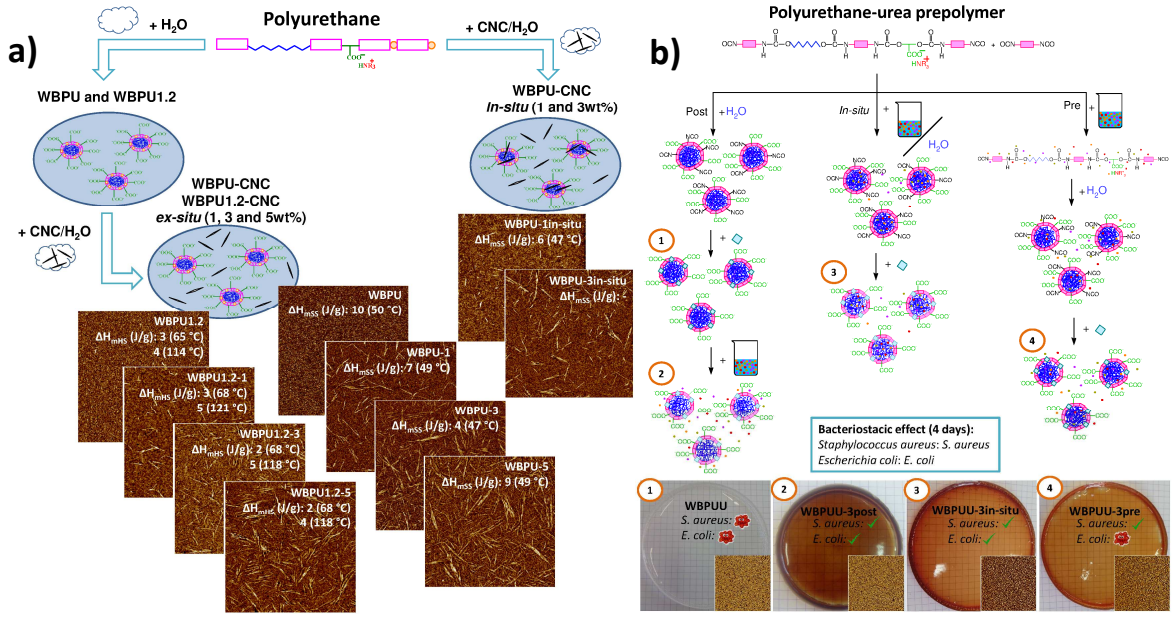

Figure 1 - a) WBPU-CNC nanocomposites and b) bioactive WBPUU-extract systems preparation routes and AFM phase images of spin coated films (3x3 μm^2)

Results and discussion

Regarding CNC based nanocomposites, **Figure 1a**, WBPU matrix presented an enthalpy attributed to the soft segment (SS), whereas in WBPU1.2 two endothermic transitions related with the hard segment (HS) were observed. In this way, CNC matrix showed different modulating effects depending on the matrix. In the case of WBPU, CNC acted as crystals growth inhibitor, being the effect more discernible in the case of incorporating by *in-situ* route. However, in WBPU1.2 nanocomposites, CNC presented a nucleating agent effect, favoring the ordering of HS. The antibacterial effect of WBPUU-extract films, shown in **Figure 1b**, against Gram positive bacteria *Staphylococcus aureus* ATCC 19213 and Gram negative *Escherichia coli* ATCC 10536 was analyzed after 4 days of incubation at 37 ºC. The base WBPUU film did not presented antibacterial effect. However, the incorporation of bioactive extracts promoted the bacteriostatic effect of the films against both bacteria, except in the case of pre-method (3 wt%) for *E. coli* bacteria. This fact could be related with the intercalation mechanism of the extract and the polyurethane-urea nanoparticles, considering also the greater resistance in general of Gram – bacteria comparing with Gram+ [4].

Conclusion

Different strategies were designed for the incorporation of renewable CNC and bioactive extract in water to WBPU and WBPUU resulting in environmentally-friendly materials. The incorporation of CNC and extract modulated the properties of the matrix, thus opening their applicability field.

Acknowledgments

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