Supramolecular approach for an efficient processing of polylactide/starch nanocomposites

Supporting Information

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Experimental section of SI

Preparation of starch nanoparticles (SNPs)

A waxy maize starch (73.45 g, 14.69% Vol$_{acid}$) was mixed with 500 mL of H$_2$SO$_4$ (3.16 M) and continuously stirred for 8 days at 40°C. Then, the suspension was cooled down at room temperature and washed by successive centrifugations in distilled water and redispersed using Ultra Turrax for 5 min at 13,000 rpm to avoid aggregates. The aqueous solution was subjected to diffusion dialysis until reaching neutral pH. SNPs were stored in an aqueous medium at 4°C with several drops of chloroform.

Characterization

SNPs samples morphology were observed using a SEM Hitachi SU8020, with field emission gun with landing energy at 3 kV and SE(UL) detector. $^1$H NMR spectra were collected in CDCl$_3$ solution on a Bruker AMX-500 NMR spectrometer. Purified PDLA-co-PGMA solutions were prepared in CHCl$_3$ (2 mg polymer/mL solvent)

Morphology of SNPs

![SEM micrographs of SNPs from aqueous](image)

**Figure S1**: SEM micrographs of SNPs from aqueous
The first step consists on the preparation of SNPs. The morphologies of SNPs as prepared by hydrolysis of waxy maize starch granules for 8 days with 3.16M H$_2$SO$_4$ at 40°C, were examined by SEM (Figure S1). SEM micrographs were made using a drop of a suspension of the nanocrystals in water.

Nanocrystals with an average size around 35 nm and forming aggregates of 2 µm are visible. This observation is in agreement with previous findings\textsuperscript{37,38}.

**Synthesis of P(D)LA-b-PGMA copolymer**

The Figure S2 represents the $^1$H NMR spectrum of purified P(D)LA-b-PGMA copolymer.

![Figure S2](image)

**Figure S2.** $^1$H-NMR spectrum of P(D)LA-b-PGMA purified product in CDCl$_3$. The black arrows indicate the disappearance of any remaining monomer.
Dispersion and morphological observations of SNPs solutions

The dispersion efficiency of SNPs in different solvents was evaluated by suspension tests carried out in H₂O, acetone, CHCl₃ and DMF. As shown in Figure S3, the suspension of SNPs remained stable in H₂O and DMF while in acetone, SNPs settled down after 10 minutes likely due to formation of aggregates. Similarly, SNPs suspension in CHCl₃ was not homogeneous and differed in appearance from stable aqueous suspension.

Morphological changes of the starch particles during solvent-exchange steps from aqueous solution to acetone, CHCl₃ and DMF were evaluated by TEM and Figure S4 presents the images obtained. As can be seen, SNPs analyzed from aqueous solution are, mainly, regularly circular platelet-like shaped particles with a mean diameter of ∼ 40 nm and a limited degree of aggregation. After the first solvent-exchange to acetone, the same nanoplatelets shape is present but aggregates are more important. When the aqueous solution is exchanged with CHCl₃ SNPs morphology is completely lost and images reveal objects with no specific shape. It is worthy to note that Figure S4C is not representative of all objects seen in TEM for the sample but in no case the common nanoplatelets morphology was observed. In contrast, SNPs observed from DMF solution kept the same morphology than former SNPs in water and very small aggregates are present for the overall sample

Figure S3: Suspension of SNPs in (1) H₂O, (2) C₃H₆O, (3) CHCl₃ and (4) DMF. Pictures recorded (top) immediately after stopping the stirring and (low) after 10 minutes.
Figure S4: TEM micrographs of SNPs (A) from aqueous solution, (B) from Acetone, (C) from CHCl$_3$ solution, (C) from DMF solution

Macroscopic behaviors as well as TEM images clearly indicate that best solvents for keeping a good integrity of SNPs and a good dispersion state are H$_2$O and DMF. The obtained results might be explained with the hydrophilic nature of the SNPs.

Therefore, since water is not a good solvent of PLLA, DMF was selected as the solvent for mixing up SNPs and the block copolymer.