

Covalent grafting effects on the thermal properties of renewable Poly(L-lactide)/cellulose nanocrystal nanocomposites

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Abstract

Poly(L-lactide) (PLLA) is a semicrystalline thermoplastic which belongs to a biocompatible, biodegradable and bioresorbable polymers. PLLA also fulfills many requirements of the traditional non-biodegradable packaging materials and it is therefore considered of great value from an ecological point of view due to its biobased character. Nonetheless, there are several aspects such as its slow crystal growth rate, its marked physical aging when used in ambient conditions and its poor thermal stability which limit the use of PLLA as a commodity plastic [1].

Nanocomposite approach could be viewed as an efficient strategy to overcome the aforementioned drawbacks. In accordance with the 12 Principles of Green Chemistry [2], which underline the basis to develop ecologically friendly materials, in this work fully renewable PLLA nanocomposites have been obtained. Among all the available naturally-occurring nanoreinforcements, the rod-like cellulose nanocrystals (CNC) are of special interest due to their outstanding mechanical properties, low density, low cost and its huge potential for chemical modification. Unfortunately, its strong hydrogen self-association behaviour in nonpolar systems makes CNC difficult to disperse, reducing their efficiency as reinforcing phase. In this sense, *grafting-from* approach has been carried out with the aim of improving the interfacial adhesion and CNC dispersion within the polymer matrix. PLLA chains are initiated from the surface hydroxyl groups of CNC by a surface-initiated ring opening polymerization (SI-ROP) [3].

Results show the crystallization rate is increased by 1.7-5 times in presence cellulose nanocrystals. Additionally, structural relaxation kinetics of PLLA chains has been drastically reduced by 53% and 27% with the addition of neat and grafted CNC respectively. Those results suggest that neat CNC reduce structural relaxation of bulk material to a greater extent than grafted CNC because of the reduction of the available PLLA/CNC interfaces given by SI-ROP process. The thermal degradation activation energy (E) determined from thermogravimetric analysis reveal a reduction on the thermal stability when in presence of CNC-g-PLLA, while raw CNC slightly increases the thermal stability of PLLA. Those results confirm that the presence of residual catalyst in CNC-g-PLLA plays a pivotal role in the thermal degradation behavior of nanocomposites. In this framework, the improvement of the SI-ROP process would be the next important step towards the development of renewable materials with enhanced functional properties.

References

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Figures

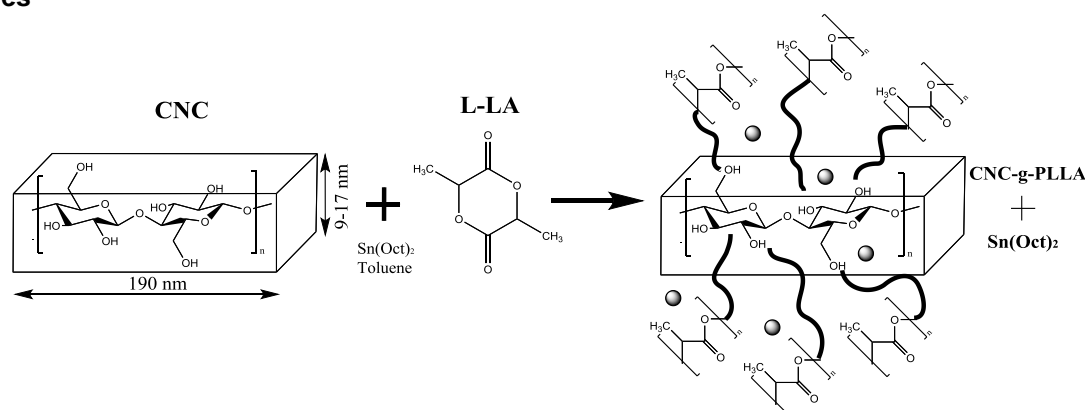


Figure 1. Scheme showing surface-initiated ROP of L-lactide (L-LA) to obtain CNC-g-PLLA+(Sn(Oct)₂).