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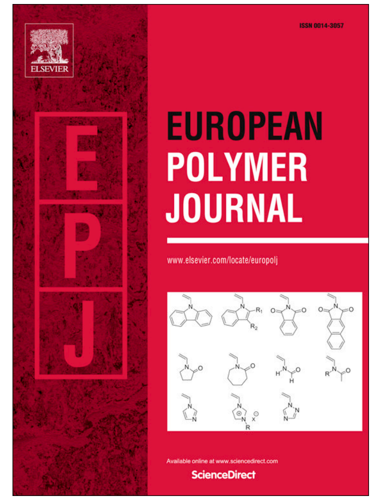

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Polylactide/cellulose nanocrystals: the *in situ* polymerization approach to improved nanocomposites

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The *in situ* polymerization of L-lactide in the presence of various amounts of cellulose nanocrystals (CNC) is described. CNC was prepared efficiently by acidic hydrolysis of cotton linters. Molecular weight, morphology, thermal, mechanical and crystallization properties of the PLA-CNC nanocomposites were evaluated. From size-exclusion chromatography (SEC) analysis, the actual occurrence of chemical bond between CNC and PLA can be assessed. The effect of CNC has been evaluated through differential scanning calorimetry (DSC) analysis, which highlights the probable formation of α' crystals in the obtained materials. More importantly, from thermogravimetric analysis (TGA) a marked improvement in thermal stability of nanocomposites has been demonstrated, with respect to standard PLA and to previously described PLA-CNC blends. Nanocomposites show also an improvement in rheological properties with respect to standard PLA. In particular, storage modulus greatly increases, indicating a reinforcing effect of CNC. The described *in situ* synthetic methodology allows an optimal compatibilization between the two entities (PLA and CNC), facing one of the major problems inherent to the preparation of nanocomposites. It leads furthermore to remarkably improved thermal and rheological properties of the obtained materials.

Introduction

In recent years environmental awareness has been focused onto the replacing of traditional plastics based on petrochemical resources with alternative, more eco-friendly materials. Among them, poly(lactic acid), shortly PLA, is one of the most attractive to researchers and industry,[1] because of its good biodegradability and availability from renewable sources, such as starch and sugar beet.[2] The growing attention towards this thermoplastic polymer comes from both its outstanding properties, such as the good optical and elastic behavior and the excellent melt-processability, and, at the same time, from its cost competitiveness, also with respect to more traditional, not biodegradable polyesters such as PET.[3,4] For all these reasons, nowadays PLA has gained commercial significance and greatly increased its market, especially for what regards packaging and disposables applications.

However, PLA suffers from a lot of drawbacks that strongly limit possibilities for its wide application in many sectors. Indeed, it is endowed with low thermal and mechanical stability upon processing conditions, scarce flexibility and poor barrier properties. All these characteristics place it behind commonly used plastics, for instance for food packaging applications.[5]

Among possible alternatives to overcome some of these limitations, the preparation of nanocomposites has emerged as the most promising suitable solution.[6] In nanocomposites, the surface area/volume ratio of employed reinforcement additives is crucial to the enhancement of material properties. Indeed, as dimensions reach the nanometer level, interactions at phase interfaces become largely improved, bringing nanocomposites to exhibit properties not expected with larger scale particulate reinforcements. A lot of different additives can in principle be used as nanofillers. Among others, carbon nanotubes,[7,8] montmorillonite[9,10] and nanosilica[11,12] have been studied, with satisfactory achievements, in the design of PLA nanocomposites.

Aiming to produce fully organic bionanocomposites, cellulose nanocrystals (CNC) have recently emerged as a kind of biocompatible, biodegradable and renewable additive that could be dispersed into the PLA polymer matrix for the preparation of high performance blends. CNC are acquiring more and more interest